

Functionalization and Analysis of Hard Carbon Surfaces for Sodium-Ion Batteries

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“Now then, it's this sodium that I extract from salt water and with which I compose my electric cells.”

– Jules Verne, *Twenty Thousand Leagues Under the Sea* (1870)

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Felix Bauer

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Abstract

Every day, we rely on batteries: Whether they are in our mobile phones, laptops or electric vehicles, the use of electrochemical energy storage solutions has become a permanent part of our daily lives. As part in the diversification of energy storage technologies, the development of sodium-ion batteries (SIBs) is playing an increasingly important role to complement and relieve lithium-ion battery (LIB) markets, especially regarding resource availability. Promising developments in SIB research over the last decade successfully facilitated the transition from the laboratory to consumer technology.

However, the loss of cyclable sodium during the first cycle represents a critical bottleneck in SIB development, which is commonly quantified by the Initial Coulombic Efficiency (ICE). A low ICE directly reflects irreversible sodium consumption and leads to an irretrievably reduced cell capacity. A major origin of this irreversible sodium consumption is attributed to the formation of a solid electrolyte interphase (SEI) on the anode surface. While the SEI is essential for cell operation, its formation irreversibly consumes a substantial portion of the already limited sodium inventory. These losses have been partly attributed to surface reactions involving oxygen functional groups (OFGs) present on hard carbon, the most widely used anode material for SIBs. Although the exact role of OFGs in SEI formation and their impact on ICE remains under debate, the controlled tuning and chemical modification of OFGs have emerged as promising strategies to mitigate irreversible sodium loss and improve ICE.

In this thesis, the surface properties of hard carbon with regard to the oxygen functionalization with its influence on SEI formation and irreversible losses in the first cycles are investigated. Spherical hard carbon with a low oxygen content was synthesized from furfuryl alcohol and served as a model substrate for subsequent functionalization approaches. Adsorption of functional pyrenes was performed to decorate the surface with a single OFG species. Findings evidence that oxygen functionalization on the surface plays a pivotal role during SEI formation, but is not a decisive factor for the coulombic losses observed in the first cycle. Pyrenes with OFGs displayed an impeded reversible capacity due to reduced accessibility of internal pores, as evidenced by increased slope-to-plateau capacity ratios.

Ozone was employed as an oxidative treatment leading to either the functionalization or structural degradation of the hard carbon, depending on the temperature. While room temperature treatment leads predominantly to functionalization, higher temperatures promote structural degradation and erosion of the carbon framework. Supported by experiments on model carbon substrates and spectroscopic evidence, a mechanistic model is proposed to rationalize the interaction of ozone with hard carbon at different temperatures. Against widespread believe that a high degree of oxygen functionalization inevitably leads to a low ICE, it is demonstrated that rather the structural degradation of hard carbon and modification

of its internal pore environment drives the loss of charge during the first cycles and leads to low reversible capacities.

Finally, this thesis addresses the challenges and limitations of X-ray photoelectron spectroscopy in analyzing OFGs on hard carbon. The methodology developed in this work enables reliable differentiation and quantification of these functionalities despite their intrinsic spectral overlap, which has previously hindered systematic analysis of hard carbon surfaces. The results demonstrate that pristine hard carbon contains only a negligible concentration of electrolyte-accessible hydroxyl and carboxyl functionalities (< 1 at.%), while ozone treatment significantly increases their abundance, thereby providing direct experimental validation and spectroscopic evidence of the proposed ozone functionalization mechanism.

Zusammenfassung

Jeden Tag verlassen wir uns auf Batterien: Ob in Mobiltelefonen, Laptops oder elektrischen Fahrzeugen, die Nutzung elektrochemischer Energiespeicher hat festen Einzug in unseren Alltag gefunden. Im Zuge der Diversifikation von Energiespeichersystemen spielt die Entwicklung von Natrium-Ionen Batterien (SIBs) eine zunehmend wichtigere Rolle um bestehende Märkte von Lithium-Ionen Batterien (LIBs) zu ergänzen und zu entlasten, insbesondere im Hinblick auf die Ressourcenverfügbarkeit. Vielversprechende Entwicklungen in der Forschung an SIBs im letzten Jahrzehnt haben den Übergang von der Labor- zur Verbrauchertechnik erfolgreich vorangetrieben.

Jedoch stellt der Verlust an zyklierbarem Natrium während des ersten Zyklus eine erhebliche Einschränkung in der Entwicklung von SIBs dar, welcher häufig durch die Initiale Coulomb Effizienz (ICE) beziffert wird. Eine geringe ICE spiegelt direkt einen irreversiblen Verbrauch an Natrium wider und führt zu einer unwiederbringlich reduzierten Kapazität der Zelle. Ein Großteil des irreversiblen Natriumverlustes wird der Ausbildung einer Festelektrolytphase (engl. Solid Electrolyte Interphase, SEI) auf der Anode zugeschrieben. Während die SEI essentiell für die Funktionalität einer Zelle ist, verbraucht ihre Ausbildung einen nicht unerheblichen Teil des bereits limitierten Natriumvorrats. Zugerechnet werden diese Verluste teilweise dem Vorhandensein von funktionellen Sauerstoffgruppen (engl. oxygen functional groups, OFGs) auf der Oberfläche von Hartkohlenstoffen (engl. hard carbon), den meistgenutzten Anodenmaterialien für SIBs. Obwohl die exakte Rolle von OFGs auf die Ausbildung der SEI kontrovers diskutiert wird, haben sich die gezielte Einstellung und chemische Modifikation von OFGs als vielversprechende Strategien herausgestellt, um irreversible Natriumverluste zu vermindern und die ICE zu verbessern.

Daher konzentriert sich diese Arbeit auf die Oberflächeneigenschaften von Hartkohlenstoff im Hinblick auf ihre Sauerstofffunktionalisierung und darauf, wie diese die Bildung der Festelektrolytphase beeinflussen und irreversible Ladungsverluste im ersten Zyklus verursachen. Sphärischer Hartkohlenstoff mit einem geringem Sauerstoffanteil wurde aus Furfurylalkohol synthetisiert, welcher als Modellsystem für nachfolgende Funktionalisierungsansätze diente.

Zur Modifikation der Oberfläche mit Sauerstoffgruppen wurde die Adsorption von funktionellen Pyrenen durchgeführt. Die Ergebnisse zeigen, dass die Sauerstofffunktionalisierung an der Oberfläche zwar eine ausschlaggebende Rolle bei der SEI-Bildung spielt, jedoch kein entscheidender Faktor für die im ersten Zyklus beobachteten Ladungsverluste ist. Pyrene mit Sauerstofffunktionsgruppen zeigten eine beeinträchtigte reversible Kapazität auf, welche auf eine eingeschränkte Zugänglichkeit der inneren Porosität zurückzuführen ist, wie durch erhöhte Verhältnisse von Neigungs- zu Plateaukapazität belegt wird.

Ozon wurde als oxidative Behandlung eingesetzt, um entweder eine Funktionalisierung oder den strukturellen Abbau des Hartkohlenstoffs temperaturabhängig herbeizuführen. Es konnte gezeigt werden, dass eine Behandlung bei Raumtemperatur vorwiegend zu einer Funktionalisierung des Hartkohlenstoffs führt, während höhere Temperaturen die strukturelle Degradation und Erosion des Kohlenstoffgerüsts begünstigen. Gestützt durch Experimente an Modell-Kohlenstoffsubstraten und spektroskopischer Messungen wird ein mechanistisches Modell vorgeschlagen, um die Wechselwirkung von Ozon mit Hartkohlenstoff bei verschiedenen Temperaturen zu erklären. Entgegen der weit verbreiteten Annahme, dass ein hoher Grad an Sauerstofffunktionalisierung unweigerlich zu einer geringen anfänglichen Coulomb-Effizienz führt, wird gezeigt, dass der strukturelle Abbau und eine modifizierte Porenumgebung im Partikel den Ladungsverlust während der ersten Zyklen sowie die geringen reversiblen Kapazitäten verursacht.

Abschließend befasst sich diese Arbeit mit den Herausforderungen und Grenzen der Röntgen-Photoelektronenspektroskopie bei der Analyse von funktionellen Sauerstoffgruppen auf Hartkohlenstoff. Es wurde ein Derivatisierungsprotokoll entwickelt und anhand von Polymer-Modellsubstraten validiert. Diese Methode ermöglicht eine zuverlässige Unterscheidung von Sauerstofffunktionsgruppen und etabliert sich damit als ergänzendes Werkzeug für die Oberflächenanalyse. Es gelang, die inhärente spektrale Überlappung verschiedener Sauerstofffunktionalitäten zu überwinden und die individuellen Beiträge von Hydroxyl- und Carboxylgruppen zu quantifizieren. Es konnte ferner gezeigt werden, dass Hartkohlenstoff nur eine geringe Konzentration an Elektrolytzugänglichen Hydroxyl- und Carboxylfunktionalitäten aufweist (<1 at.%). Es wurde auch nachgewiesen, dass die Ozonbehandlung die Konzentration an Hydroxyl- und Carboxylfunktionalitäten signifikant erhöht, was das vorgeschlagene mechanistische Modell stützt.

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Abbreviations

General

ad.C	Adventitious carbon
CV	Cyclic voltammetry
DSC	Dynamic scanning calorimetry
ESB	Energy selective backscattering
FWHM	Full-width at half maximum
GCE	Glassy carbon electrode
GCPL	Galvanostatic cycling with potential limitation
GIC	Graphite intercalation compound
HC	Hard carbon
HOMO	Highest occupied molecular orbital
HOPG	Highly ordered pyrolytic graphite
ICE	Initial coulombic efficiency
IMFP	Inelastic mean free path
LIB	Lithium-ion battery
LUMO	Lowest unoccupied molecular orbital
NHE	Normal hydrogen electrode
OFG	Oxygen functional group
PAH	Polycyclic aromatic hydrocarbon
EIS	Electrochemical impedance spectroscopy
SEI	Solid electrolyte interphase
SEM	Scanning electron microscope
SIB	Sodium-ion battery
SLP	Single-layer pouch cell
TGA	Thermogravimetric analysis
XPS	X-Ray Photoelectron Spectroscopy
XRD	X-Ray diffraction

Chemicals

CMC	Carboxymethyl cellulose
DTBCD	N,N'-Di-tert.-butylcarbodiimide
EC	Ethylene carbonate
FA	Furfuryl alcohol
FEC	Fluoroethylene carbonate
PAA	Poly(acrylic acid)
PC	Propylene carbonate
PEEK	Polyether ether ketone
PEG	Polyethylene glycole
PVA	Poly(vinyl alcohol)

PVAc	Poly(vinyl acetate)
PVMK	Poly(vinyl methyl ketone)
SBR	Styrene-butadiene rubber
TFAA	Trifluoroacetic anhydride
TFE	2,2,2-Trifluoroethanol
TFEH	Trifluoroethyl hydrazine

Units

°C	Centigrade
μm	Micrometer
a.u.	Arbitrary units
at. %	Atom percent
cm	Centimeter
cps	Counts per second
eV	Electron Volt
g	Gram
h	Hour
Hz	Hertz
K	Kelvin
kHz	Kilohertz
kV	Kilovolt
l	Liter
M	Molar
mA	Milliampere
mAh	Milliampere hours
mg	Milligram
mHz	Millihertz
min	Minute
mL	Milliliter
mm	Millimeter
mM	Milli molar
mV	Millivolt
nm	Nanometer
rpm	Rotations per minute
s	Second
V	Volt
vol. %	Volume percent
wt. %	Weight percent

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1 Fundamentals and Concepts

1.1 Role of the Sodium-Ion Battery

Sodium-ion batteries (SIBs) have long been considered a key technology to gap an inevitable lithium scarcity due to the rapid increase of lithium-ion batteries (LIBs). Forecasts based on annual growth rates of mined lithium exceeding 5% suggested that global demand could surpass mineable reserves by 2050.^[1] These concerns were fueled by a sharp increase and high volatility in prices for lithium carbonate in 2022/23.^[2,3] Currently, global market prices of lithium have settled at a moderate level and recycling of used batteries has been identified as an alternative source of lithium.^[4] However, LIB production is still relying on fragile supply chains from countries with geopolitical insecurities. Moreover, a full circular battery economy has not yet been achieved, especially regarding the recovery of graphite from spent LIBs.^[4,5] Therefore, a transition from geographically concentrated mining sites of critical elements towards widespread available resources could ensure long-term security of supply.^[6] Figure 1 illustrates the development of prices for battery grade lithium and sodium carbonate over the last 14 years and their mineable reserves on earth.

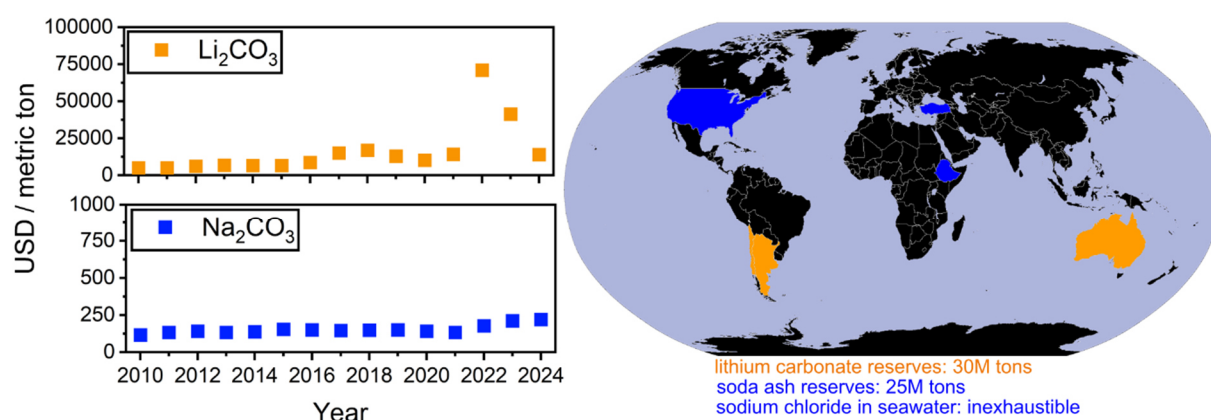


Figure 1. Prices of lithium and sodium carbonate of the last 14 years (left). Distribution of estimated reserves of lithium carbonate and soda ash (right). The reserves of sodium in seawater are declared as inexhaustible. World map adapted from public domain image (Wikimedia Commons).

In this context, the relevance of SIBs should be re-evaluated and assessed from a broader, more holistic perspective. Sodium, the charge carrier in SIBs, is abundantly available in Earth's crust and seawater, and is not subject to resource shortages.^[7] Additionally, SIB cathode chemistries do not rely on cobalt, a critical and expensive element commonly used in LIBs. This not only reduces material costs but also avoids ethical and geopolitical concerns associated with cobalt mining.^[8] This opens the opportunity to establish a stable and resilient supply of energy storage systems. Another advantage of SIBs lies in their technical feasibility: structure, cell-architecture and manufacturing are analogous to LIBs, which enables the use of pre-existing infrastructure. This so-called “drop-in” capability of SIB technology further reduces transition costs and facilitates industrial scale-up of processes.^[9] If the performance

of SIBs experiences the same dynamic development as LIBs in recent decades, they can represent an economically and technologically competitive supplementation in the medium and long term.^[10]

In terms of sustainability SIBs also offer interesting perspectives. When comparing the negative electrodes, herein referred to as anodes of LIBs and SIBs, the mining of natural graphite and production of synthetic graphite for LIB anodes are energy-intensive and thus impose a significant carbon footprint on the battery production process. Additionally, recycling of graphite from LIBs is currently not economically feasible. In contrast, the most promising anode material for SIBs, hard carbon (HC), can be sourced from bio-based precursors and thus has a noteworthy smaller carbon footprint. The use of naturally derived HC further opens the opportunity of binding carbon in the long term, which could also become relevant in context of mitigating causes of climate change.^[10]

Taken together, SIBs should not be viewed as a successor or even competitor technology to LIBs, but rather as a complementary solution that addresses specific limitations of current LIB systems. Their strategic implementation within the existing energy storage landscape could contribute to the diversification of raw material sources, the decarbonization of battery production, and the development of more sustainable and resilient energy storage systems.

Although sodium-ion batteries typically exhibit lower volumetric and gravimetric energy densities than LIBs and experience stronger irreversible capacity losses in the first cycle, they provide advantages in applications where energy density is not the primary requirement. In particular, their cost-effectiveness, resource availability, and environmental benefits make them well-suited for stationary energy storage systems. This complementary role allows LIBs to remain the preferred choice for high-end mobile applications such as electric vehicles and portable electronics, while SIBs can serve as a sustainable and scalable solution for grid-level storage and related applications.^[6]

Despite their advantages, SIBs are still limited by comparatively high irreversible capacity losses during the first cycle, which reduce the overall efficiency of the system. Addressing these initial losses is therefore essential for improving their practical applicability and enabling their effective integration into the energy storage landscape. The following chapters will examine the fundamental origins of these losses and critically evaluate strategies reported in the literature to mitigate their impact.

1.2 Components and Working Principle of SIBs

SIBs operate based on the reversible insertion and extraction of sodium-ions between two electrodes, which are immersed in an electrolyte and separated by a porous membrane (Figure 2). Against electrochemical conventions, the electrodes are always referred to as cathode and anode, depending on their polarity during discharge. The cathode typically consists of a sodium-rich compound, while the anode is made of a material capable of accommodating sodium-ions within its structure at potentials close to elemental sodium ($E_0(\text{Na}^+/\text{Na}) = -2.71 \text{ V vs. NHE}$). By applying an external current, sodium-ions are extracted from the cathode active material and migrate through the electrolyte towards the anode, where they are inserted. Simultaneously, the electrons flowing through the external circuit maintain charge balance. During discharge, the process is reversed: sodium-ions move back from the anode to the cathode, while electrons travel through the external circuit to power a consumer. Electrode reactions of a typical HC anode and polyanionic sodium vanadium phosphate cathode are depicted on the right in Figure 2.

The electrolyte serves as an ionic conductor and electronic insulator between the electrodes. It comprises a sodium salt, such as sodium hexafluorophosphate (NaPF_6), sodium perchlorate (NaClO_4) or sodium bis(trifluoromethylsulfonyl)imide (NaTFSI), which are selected for their weakly coordinating nature, thereby minimizing ion-ion interactions and promoting efficient ionic dissociation. They are dissolved in an aprotic organic solvent to prevent hydrogen evolution driven by the low redox potential of sodium.^[11] Most commonly, cyclic and linear carbonates are employed, but also ethers are frequently used.^[12,13] The separator prevents direct contact between the electrodes, thereby avoiding short circuits, while allowing fast ionic transport through its porous structure. Therefore, a separator must exhibit excellent chemical stability and mechanical strength, while also possessing good wettability and appropriate porosity, and should be as thin as possible.^[14]

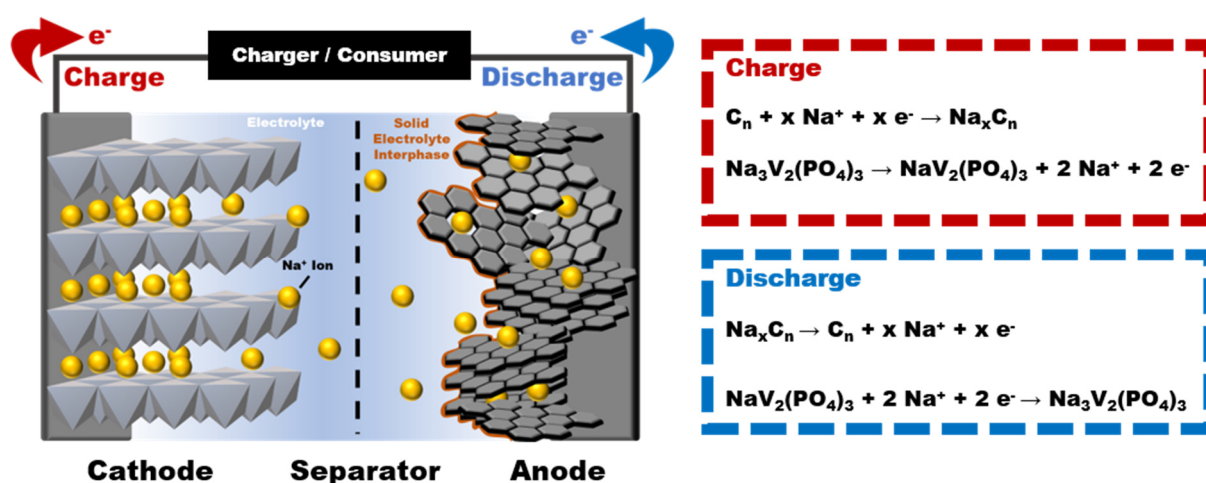


Figure 2. Working principle of a sodium-ion battery (left) and chemical reactions during charge and discharge (right). Adapted from reference [15].

A critical limitation in SIBs is the finite sodium inventory available within the cell, which is determined by the cathode chemistry. During the first cycle, irreversible sodium losses occur, which are quantified by the Initial Coulombic Efficiency (ICE), defined as the ratio of charge extracted during the first discharge to the charge inserted during the initial charge.^[16] These initial coulombic losses originate primarily from parasitic side reactions, most notably the formation of a solid electrolyte interphase (SEI) on the anode surface. The SEI is an essential passivation layer spontaneously formed by electrolyte decomposition at low potentials. However, its formation irreversibly consumes sodium-ions, which reduces the amount of cyclable sodium in the cell. Because the sodium inventory is fixed by the cathode in full-cells, any loss during the first cycle leads to a permanent reduction in accessible capacity and thus diminished energy density.^[16] Consequently, achieving a high ICE is crucial for maximizing cell capacity. Literature reported ICE values in SIBs cover a wide range from 30 to 90% depending on the materials and cell types.^[17]

To achieve a high specific capacity, the cathode must provide a high sodium content, and the anode offer sufficient sites for sodium storage. Among cathode active materials, three classes have emerged as promising candidates: Prussian blue analogues, layered transition metal oxides and polyanionic compounds. While all three candidates offer individual favorable electrochemical properties, it remains uncertain which one will become dominant in large-scale applications. Similar to the development of LIBs, it is likely that different cathode chemistries will be optimized for specific use cases, depending on factors such as cost, voltage range, stability, and scalability.

On the anode side, metallic sodium or a zero-excess blank electrode would appear to be an ideal choice due to their high theoretical capacities. However, sodium's tendency to form dendritic structures during plating poses a significant safety risk, as these dendrites can penetrate the separator and cause short circuits. Despite the existence of mitigation strategies, the safety requirements for practical battery systems do not tolerate any residual risk associated with dendrite formation.^[18]

Graphite, the standard anode material in LIBs, is unsuitable for SIBs due to several fundamental limitations, which are discussed in detail in the following chapter. Conversion materials (e.g. tin, antimony or lead) offer high theoretical capacities by formation of intermetallic compounds, but are impeded by their large volume expansion of up to 420% during charging, making them subject to self-pulverization and rapid degradation already after few cycles.^[19] Among all available options for the anode, HC stands out with its favorable balance between capacity and cycling stability, leaving the ICE as one of the remaining key parameters to be optimized to enable SIBs to become a viable complementation to LIBs.

1.3 Hard Carbon as Anode Material in Sodium-Ion Batteries

HC has become the anode material of choice for SIBs because graphite exhibits extremely limited sodium storage capability. The low sodium storage capacity of graphite at room temperature (12 mAh g^{-1} , corresponding to NaC_{128})^[20] appears counterintuitive when compared to its homologues lithium (372 mAh g^{-1} , LiC_6)^[21] and potassium (278 mAh g^{-1} , KC_8)^[22]. Sodium-rich graphite intercalation compounds (GICs) are thermodynamically unstable, a fact that is often mistakenly attributed to the ionic radius of sodium.^[23,24] This explanation is inconsistent with the fact that potassium, rubidium, and cesium, all of which have larger ionic radii, can form stable graphite intercalation compounds.^[25,26] In reality, lithium is the anomaly amongst the alkali metals. The stability of Li-GICs arises from a significant covalent contribution to the Li–C bond, which is absent in sodium and potassium analogues. This covalent interaction compensates for lithium’s weaker ionic binding, making Li-GICs more stable than Na-GICs despite the smaller ionic radius. Without contributions from covalent Li–C bonding, Li-GICs would be even less stable than Na-GICs.^[25]

The unfavorable interlayer spacing of graphite and the positive intercalation enthalpy of sodium hinder the formation of stable, sodium-rich GICs.^[27] Theoretical studies by Cao *et al.* have shown that the intercalation energy barrier strongly depends on the interlayer distance. For graphite with an interlayer spacing of 0.335 nm, Li-ion insertion requires only 0.03 eV, whereas Na-ion insertion demands 0.12 eV.^[28] Therefore, redox potentials below 0 V vs. Na^+/Na would theoretically be required to form sodium-rich GICs, but under these conditions, sodium plating occurs on the graphite surface instead.^[20] To overcome the intrinsic limitations of sodium intercalation in graphite, two major strategies have been pursued over the last years. Co-intercalation of sodium-ions with solvent molecules enables reversible intercalation with notably higher capacities, while increasing the interlayer spacing of graphite (expanded graphite) further reduces the energetic barrier for sodium insertion.^[29]

The latter approach led to the use of non-graphitizable carbons *i.e.* HC, which inherently exhibit larger interlayer distances and offer additional advantages such as structural disorder and accessible porosity, making them suitable for sodium-ion storage. While graphite is a crystalline material with a defined interlayer distance, HC exhibits only short-range order, with its microstructure consisting of curved, misaligned, and randomly oriented graphene plane fragments (Figure 3).^[30] Some curved graphene sheets can locally stack to form graphitic-like nanodomains with multiple layers.^[31,32] On the atomic scale, individual layers are composed of sp^2 -hybridized carbon atoms arranged in a honeycomb lattice, which incorporates structural defects such as vacancies, edges (zig-zag, armchair), dangling bonds, non-hexagonal rings, bridging sp^3 carbon atoms and oxygen functional groups (Figure 3).^[33,34] Curvature within the graphene lattice is attributed to the incorporation of five- and seven-membered rings, which

disrupt the planar geometry and induce local strain.^[31,33] The random orientation and curvature of graphene sheet fragments prevents dense packing and results in pores of various sizes.^[31] These pores can be classified as either open, which are accessible to the electrolyte, or closed, meaning they are trapped within the particle.^[35]

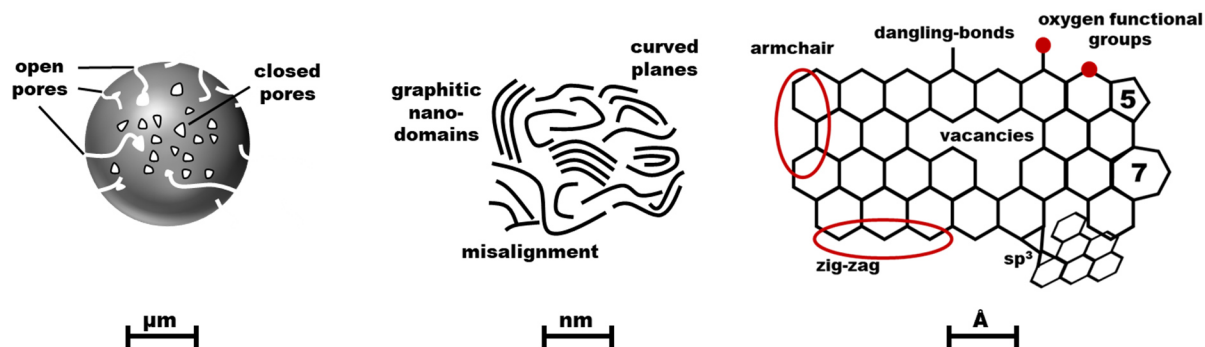


Figure 3. Morphological and structural features of hard carbon at different scales. Primary particles are in the micrometer scale (left), microstructural components in the nanometer scale (middle) and characteristic atomic motifs are on the Å scale. Adapted from reference [33] and [35].

The structure of HC is often summarized by the “falling-cards” model, which is also able to explain the storage of sodium-ions in the structure.^[36,37] This is typically reflected in the potential vs. capacity curve of HC, which shows a characteristic division into a sloping region (>0.1 V) and a low-potential plateau (<0.1 V). Four mechanisms have been identified to contribute to the capacity:^[38]

1. Adsorption at surface and open pores

Sodium-ions can be adsorbed at the surface and within the open porosity of hard carbon, where they interact with heteroatoms and defect sites.^[39] Computational studies conducted by Olsson *et al.* suggest based on energetical considerations, vacancy defects are more likely to be found at the (near) surface because of their lower defect formation energy.^[40] In contrast to closed pores, open pores are accessible to the electrolyte and thus contribute to the active surface area.

2. Storage at defects and heteroatoms

Sodium-ions can also be stored in the bulk of the material at defects and heteroatoms. This sodium-ion storage capacity can be further enhanced by targeted introduction of heteroatoms, which either serve directly as reversible storage sites for sodium-ions or indirectly by increasing the interlayer distance between the graphene fragments allowing pseudo-intercalation.^[41] Numerous publications have already reported on the doping of HC with elements such as phosphorus, nitrogen, boron, and sulfur.^[41,42] Oxygen is usually considered unique among the heteroatoms, since it is an inherent and abundant component of many precursor materials and is partly conserved after pyrolysis.

3. Pseudo-intercalation and insertion between layers

Nanocrystalline graphite-like domains are found to varying extends in the structure of HC.^[43] Sodium-ions can either be intercalated stepwise leading to the formation of sodium-rich GIC-like domains, or be inserted between the layers in a random manner with a broad energy distribution.^[23,37]

4. Pore filling

Restructuring of graphene planes and the release of gas molecules during pyrolysis of HC precursors generates internal porosity, which can serve as an additional contributor for sodium storage, contributing to the low-potential plateau capacity. This is attributed to the formation of (pseudo-)metallic sodium clusters within closed pores in HC and has been validated by *ex-situ* NMR studies.^[39,44,45] This clustering is increasingly understood as an underpotential deposition (UPD)-like process, in which sodium deposition within carbon nanopores is thermodynamically favored over bulk sodium plating.^[45–47] Initial adsorption of Na^+ at defect sites and pore surfaces facilitates partial charge transfer and subsequent sodium clustering, resulting in quasi-metallic species whose formation is strongly influenced by pore size and their surface chemistry. Elevated carbonization temperatures reduce defects and interlayer spacing, while simultaneously increasing the volume of closed pores.^[34]

Several models have been developed to interpret the potential-capacity profile of HC, each based on two or more of the four proposed sodium storage mechanisms. Although these models are logically derived from specific experimental observations, they are often system-specific and not universally applicable. Moreover, some of these models present contradicting interpretations of the underlying storage mechanisms, reflecting the structural and chemical heterogeneity inherent to HC materials.

The Insertion-Adsorption model was proposed by Stevens and Dahn alongside their “house of cards” structure model in 2000.^[37] The sloping capacity is attributed to the insertion of sodium between layers and the decreasing potential is explained by the procedural insertion of metal atoms between the layers (Figure 4a). Furthermore, the turbostratic structure of HC gives rise to a broad distribution of insertion sites with different potentials. The plateau capacity is defined by the insertion of metal into nanopores in a process analogously to adsorption. The quasi-metallic deposition succeeds at sites with a potential close to 0V.

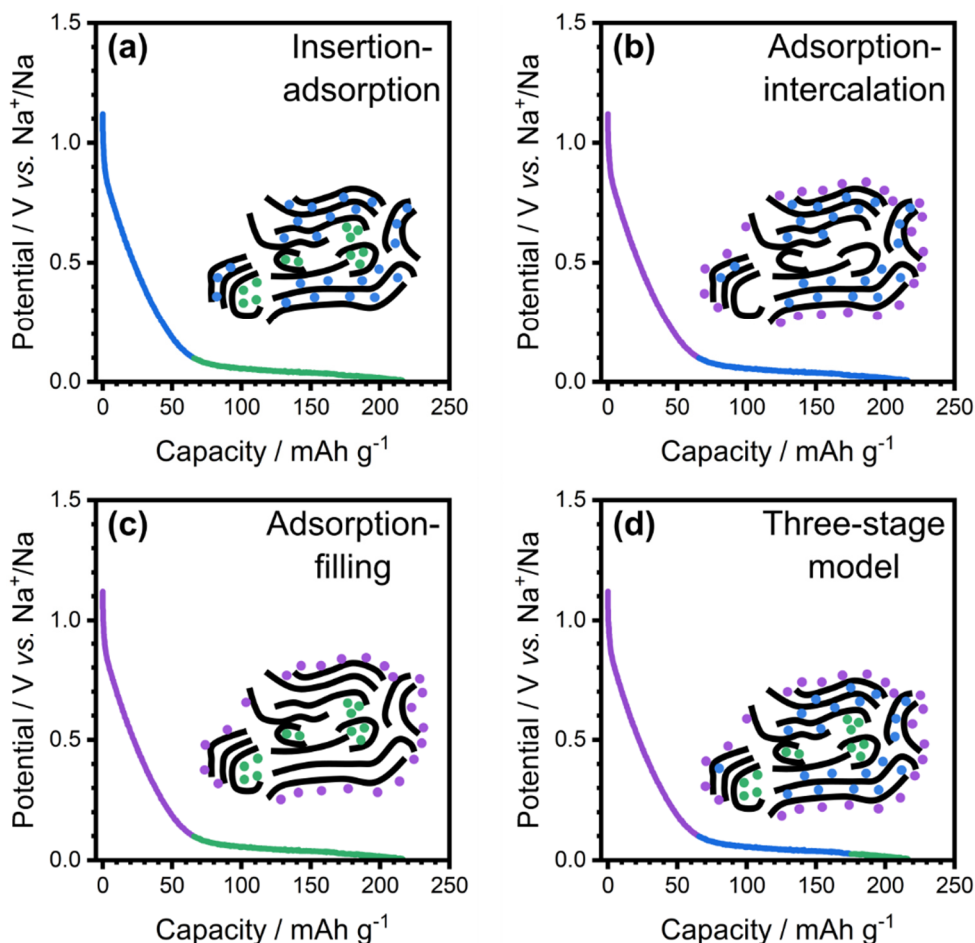


Figure 4. Four different models explaining the sodium storage mechanisms in HC. The insertion-adsorption (a), adsorption-intercalation (b), adsorption-filling (c) and the three-stage model (d). Adapted from reference [38].

Cao *et al.* later proposed the Adsorption–Intercalation mechanism, assigning the sloping capacity to charge-transfer reactions at the surface of small graphitic clusters, while the plateau capacity arises from sodium intercalation between graphitic microcrystallites (Figure 4b).^[28] The adsorption-filling model describes the slope capacity as the addition of sodium to carbon at the surface and ascribes the plateau capacity strictly to filling of micropores. Stratford *et al.* observed no intercalation, as their pair distribution function measurements revealed no change in C–C bond length, which would be observable, if sodium was intercalated into the graphitic domains (Figure 4c).^[39]

Bommier *et al.* proposed a three-stage model, linking the sloping capacity to sodium storage at defect sites.^[48] They observed a direct correlation between defect concentration and sloping capacity, suggesting that each defect type has a distinct sodiation potential. The plateau region is subdivided into two stages, *i.e.* initial insertion between pseudographitic layers followed by micropore filling. This subdivision is supported by a variation in diffusion coefficients, which peak around 50 mV, indicating a transition in the sodiation mechanism near the end of the plateau (Figure 4d).

1.4 Surface Properties of Hard Carbons and Characterization Methods

The surface chemistry of HC and in particular the presence of surface OFGs is debated to play a crucial role on the extend of irreversible sodium losses ascribed to SEI formation in the first cycle. Understanding the origin and reactivity of surface OFGs is therefore of central importance to decipher their impact on the ICE.

For sodium-ions to migrate into the particle, a balanced interaction with the surface is required, because insufficient surface-to-ion affinity impedes diffusion, whereas excessively strong binding can result in ion immobilization and thus irreversible depletion of sodium inventory.^[49,50] A pristine basal plane exhibits only limited affinity for sodium, as calculated adsorption energies are low, ranging from -0.52 to -0.62 eV depending on the sodium configuration relative to the lattice, reflecting weak adsorption and correspondingly low energy barriers for surface diffusion.^[49]

In addition to the fundamental structural motifs of basal planes and edge sites, various OFGs persist even after high-temperature pyrolysis of carbon materials (Figure 5).^[32,51–55] OFGs can be categorized based on their acidity: Carboxyl and anhydride groups exhibit acidic character, whereas phenols, ether, and epoxy functionalities are neutral or weakly acidic.^[52] In contrast, quinone, carbonyl, and ketone groups are considered basic.^[56] The acidity of hydroxyl and carboxyl functionalities remains a subject of debate, as studies report that hydroxyl groups can exhibit stronger Brønsted acidity than carboxyl groups.^[57] This pronounced acidity of phenolic species is attributed to the ability of their conjugate base to delocalize the negative charge across the sp^2 -hybridized carbon network, whereas in carboxyl groups the charge is primarily delocalized between the two oxygen atoms.

Density functional theory calculations performed to probe the interaction of Na^+ on different OFG groups showed that weak adsorption energies occur for hydroxy and epoxy groups, while strong adsorption energies are present for ether, carbonyl, and carboxyl groups, whereas quinone groups exhibit the highest adsorption energy, ascribing their presence to irreversible losses.^[50]

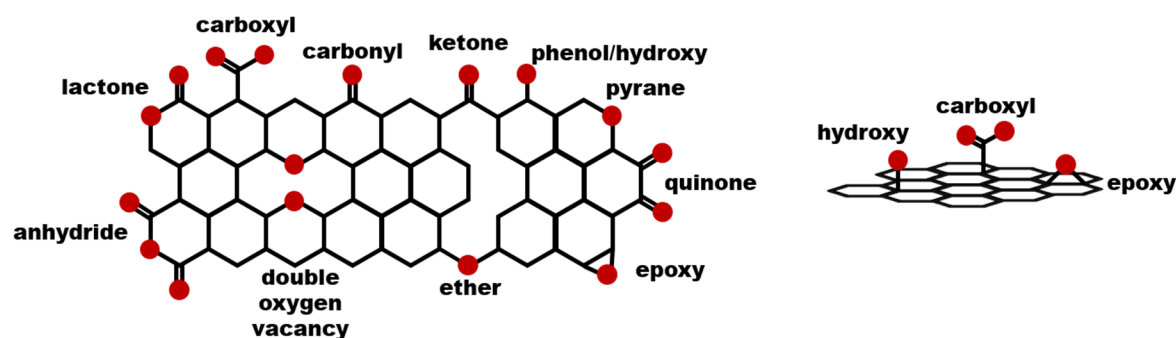


Figure 5. Oxygen functional groups present on the hard carbon on the edges and defects (left) and on the basal plane (right).^[52,58,59]

OFGs are predominantly located at the edge sites of the basal planes due to distortions they would impose on the basal plane because of poor orbital overlap.^[53,60] A comparison of computational derived defect formation energies E_F for hydroxy, carboxyl, and carbonyl groups corroborate that functionalization at edge sites is energetically more favorable than on the basal plane: For hydroxy groups, E_F is -0.95 eV on the basal plane and -4.48 eV at edge sites, while carboxyl groups exhibit -0.27 eV on the basal plane and -4.31 eV at the edge. The only configuration found to be stable on the basal plane involves oxygen in a bridging arrangement, as observed in epoxy functionalities with an E_F of -2.43 eV.^[60] Density functional theory calculations come to a similar conclusion, indicating that OFG functionalization is prevalent at edge and defect sites. Cyclic OFG configurations such as anhydrides, quinones and lactones exhibit greater stability than ketones, carboxy, and hydroxy functions.^[61] Although the surface of HC is generally considered inert under standard conditions, studies have shown that prolonged exposure to air in a humid environment can lead to gradual rise in surface OFGs.^[62]

Identification and differentiation of individual surface OFGs proves to be experimentally difficult because their chemical and structural properties are closely related. Various in-plane OFG substitution vacancies can be resolved by scanning transmission electron microscopy, whereby oxygen pair configurations were found most frequently.^[59] Such double oxygen vacancies are believed to be beneficial for Na^+ adsorption and simultaneously innocuous for ion diffusion.^[49]

Fourier-transformed infrared spectroscopy suffers from the opacity of carbon materials, absorbing a majority of IR photons.^[57] Raman spectroscopy of carbon materials is highly sensitive to structural disorder, which is introduced by OFGs, yet it cannot differentiate individual species.^[63] The interpretation of Raman spectra is complex, as there are no set rules to distinguish between different defect types. The D-band in Raman spectroscopy does not directly represent defects but rather the graphitic lattice vibrations influenced by them, making it inappropriate to attribute a specific OFG or defect to this band. Moreover, Raman spectroscopy probes both surface and bulk regions, therefore subtle surface modifications are most likely not detectable.^[63]

X-ray photoelectron spectroscopy (XPS) is commonly used for quantitative surface analysis, enabling determination of the elemental composition. Monochromatic X-rays induce the emission of core level photoelectrons from atoms in the sample. By measuring the kinetic energy of these photoelectrons, the corresponding binding energies can be determined, which are element-specific and sensitive to the oxidation state. Higher oxidation states of carbon (e.g. C–O, C=O, O–C–O) cause a shift toward higher binding energies, as the reduced electron density resulting from covalent bonding to a more electronegative atom increases the effective nuclear attraction on the core-level electrons. Although the formal oxidation state of carbon in carbonyl and O–C–O groups are identical, their chemical reactivity can differ significantly.

Similarly, carbon in O=C–O environments can occur in cyclic structures such as lactones and anhydrides or as free carboxyl functionalities with a proton. This spectral overlap of different OFGs limits precise assignment to distinct functionalities.^[57,64]

Nonetheless, these limitations are often overlooked in literature, where XPS spectra are frequently interpreted superficially without adequate consideration of underlying physical constraints.^[65] Chemical derivatization methods have been developed to address the intrinsic spectral overlap between different OFGs in XPS analysis. This approach exploits the selective reactivity of a specific OFG with a marker molecule containing a distinguishable element (e.g. fluorine), which is not present in the pristine carbon. Quantification of the marker element in the XP spectrum enables indirect determination of the concentration of the targeted functional group.^[66] While this derivatization approach has previously been applied to elucidate the surface OFG composition of carbon fibers^[66], biochars^[67] and functionalized HOPG^[68], this work reports its first application to HC for SIBs and establishes a direct link between the surface OFG composition and electrochemical parameters such as ICE and physicochemical phenomena like SEI formation.

The inelastic mean free path (IMFP) of photoelectrons extends several nanometers into the material, the detected signal represents an average over multiple atomic layers in carbon-based materials, thereby raising questions about the surface sensitivity of the technique. Detailed information on XPS fitting procedures and derivatization technique used in this work are described in the experimental details section.

The variation in thermal stability of OFGs allows their indirect analysis by temperature programmed desorption, which is often coupled to a mass spectrometer (TPD-MS). OFGs decompose over characteristic temperature ranges, releasing gases such as CO, CO₂, and in some cases H₂O and H₂.^[56] The combination of gas type, quantity, and decomposition range provides valuable insights into the nature of the functional groups present. CO₂ is typically evolved from carboxylic groups at 200–450 °C and from lactones at 550–700 °C, whereas anhydrides release both CO and CO₂ between 450–650 °C. CO formation can originate from phenolic groups (600–750 °C), carbonyls or quinones (700–950 °C), and ethers at temperatures above 1000 °C.^[69–71]

Ghimbeu *et al.* reported that HC prepared from cellulose at 1000 °C exhibited the presence of anhydrides, phenols, ethers, and quinones, as indicated by an intense CO desorption peak between 400 and 950 °C. In contrast, CO₂ evolution was considerably lower, suggesting a reduced abundance of carboxyl groups.^[56] Beda *et al.* reported similar findings for HC pyrolyzed from a phenolic resin precursor at 1300–1600 °C, where predominant CO desorption indicates the presence of thermally stable OFGs.^[71] Nita *et al.* observed unique gas desorption profiles for walnut, coconut, and corn silk derived HC pyrolyzed at 1300 °C, indicating

variations in surface OFG composition. They report a strong dependence of surface oxygen chemistry on precursor type. Notably, HC from walnut exhibited higher concentrations of carboxyl and anhydride groups following oxygen treatment.^[72]

Boehm titration is a method to distinguish OFGs on carbon materials based on their relative acidity in aqueous solution by titration with NaOH, Na₂CO₃ and NaHCO₃.^[73] However, when OFGs exhibit similar pK_a values, the method becomes less reliable. Moreover, aprotic acidic groups that hydrolyze into hydroxyl or carboxyl functionalities in water cannot be differentiated from native hydroxyl or carboxyl groups.^[57]

Taken together, the simultaneous presence, structural similarity, and complex reactivity of multiple OFGs on HC surfaces severely hinder their unambiguous identification and quantification using conventional analytical techniques.^[53] These limitations do not only complicate the interpretation of experimental data, but also obscure the fundamental understanding of their role in SEI formation and irreversible sodium losses. Therefore, the development of advanced and selective characterization strategies is essential to reliably differentiate individual functional groups and to establish a direct correlation between surface chemistry and electrochemical performance.

1.5 Solid Electrolyte Interphase

The formation of a SEI film on the anode is widely recognized as the primary origin of irreversible sodium loss during the first cycle in SIBs and thus represents a key factor governing the ICE. In this context, it is crucial to elucidate why the SEI forms, how sodium is incorporated within its structure, and how interfacial properties of the anode with regard to its oxygen functionalization affect its composition, structure, and growth. This chapter therefore provides an overview of the fundamental processes governing SEI formation, the nature of its inorganic and organic components, and the role of surface chemistry in directing interfacial reactions.

During charging, sodium-ions need to get rid of their solvation shell and diffuse into the HC particle. As the potential of the anode approaches that of elemental sodium, electrolyte components undergo reduction at the surface of the anode. This occurs, when the chemical potential of the anode μ_A rises above the energy level of the lowest unoccupied molecular orbital (LUMO) of e.g. a solvent molecule. One or more electrons are transferred to the molecule, which is equivalent to a chemical reduction.^[74,75] At the other electrode, the oxidative stability of an electrolyte is determined by the energy of its highest occupied molecular orbital (HOMO). The energy gap between the HOMO and the lowest unoccupied molecular orbital (LUMO) of the electrolyte components determines the theoretical electrochemical stability window.^[12] Experimentally, deviations from the theoretical HOMO–LUMO stability window

have been observed due to interactions between electrolyte components and surface-electrolyte interfaces.^[76]

The SEI is a pure cationic conductor, nonuniform and usually only a few nanometers (< 30 nm) thick.^[74] It prevents continuous electrolyte degradation by formation of an electronically insulating electrolyte-electrode film, while remaining conductive to sodium-ions.^[77,78] The SEI is considered a dynamic interphase, as it is initially formed during the first charge cycle, develops gradually and is subject to aging mechanisms like dissolution or growth.^[79–81]

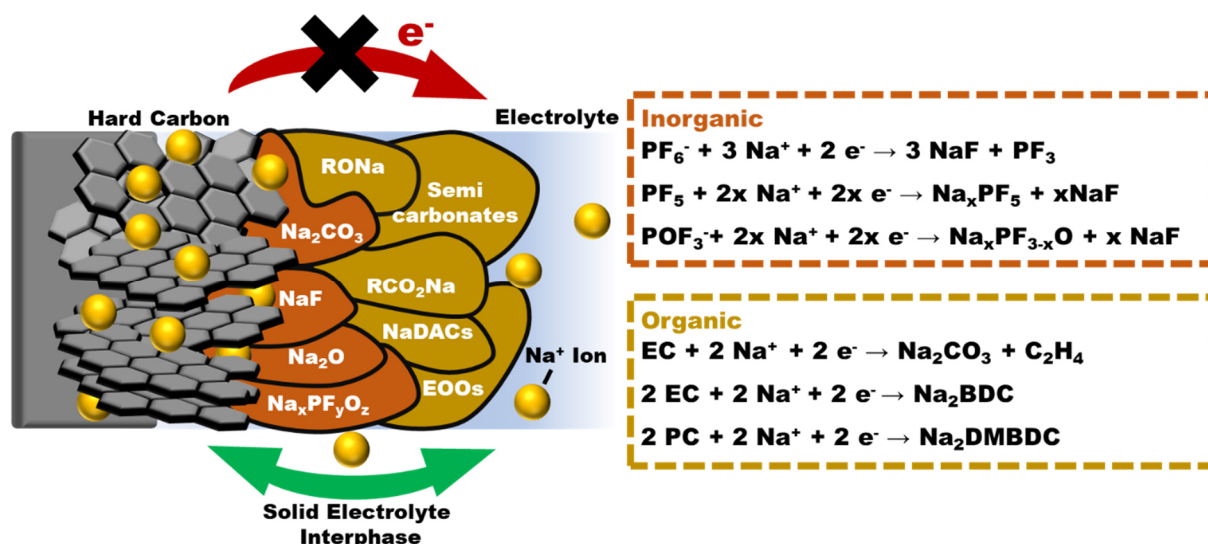


Figure 6. Mosaic model of SEI formation on hard carbon (left) and proposed reactions of electrolyte components forming the SEI (right).^[82–87]

Although various models have been proposed to describe the SEI, the mosaic model currently enjoys broad acceptance.^[88] Originally proposed by Peled *et al.* for graphite anodes in LIBs, this model has since been adopted for SIBs as well (Figure 6).^[88] It conceptualizes the SEI as a “mosaic of microphases,” comprising heterogeneously distributed inorganic and organic components. The composition of the inorganic SEI components is strongly influenced by the salt anion and typically includes sodium fluoride (NaF), sodium carbonate (Na₂CO₃), sodium oxide (Na₂O) or mixed compounds including Na_xPF_yO_z.^[76,81,83,89–91] In the presence of protic impurities, particularly trace amounts of H₂O, hydrofluoric acid (HF) can form and subsequently react with basic SEI constituents like Na₂CO₃ leading to dissolution and continuous reformation of the SEI.^[83] To prevent such degradation beforehand, it is important to store and handle electrolytes in moisture-free environments including gloveboxes or dry-rooms. Solvent molecules including ethylene carbonate (EC) and propylene carbonate (PC) may decompose to form a variety of products. These include ethene (C₂H₄), sodium alkoxides (NaOR), semi-carbonates (NaCO₂R), sodium dialkyl carbonates (NaDACs) and ethylene oxide oligomers (EOOs).^[83,84,87,92] Inorganic components are more likely to be found in the inner part of the SEI, as PF₆⁻ anions are less stable at reducing potentials.^[82,83,90] PC reduction can commence either *via* a one electron ring opening reduction to NaPC and subsequent dimerization to 2,3-

dimethylsodiumbutylene dicarbonate (Na_2DMBDC) or through a two electron reduction to Na_2CO_3 and propylene.^[53,93] Figure 6 gives an overview over the reported SEI formation reactions.

In addition to thermodynamic considerations, structural properties such as defects or OFGs on the surface play an important role in the reaction pathways of the electrolyte components to SEI formation. Alptekin *et al.* demonstrated in computational calculations that the PF_6^- anion has no tendency to adsorb on the basal plane of carbon domains ($E_{\text{ads}} = +1.68$ eV) but anion fragments can adsorb more easily, functionalizing the basal plane with fluorine ($E_{\text{ads,F}} = -3.54$ eV).^[89] When subsequently sodium ions are adsorbed, the strong binding energy of the Na-F bond drives the formation of sodium fluoride (NaF), although its surface affinity is lower ($E_{\text{ads,NaF}} = -2.08$ eV). The gradual decomposition of PF_6^- at the carbon surface results in the formation of a thin and stable SEI, with the presence of NaF being associated with beneficial interfacial properties and thus improved cycling stability.^[89]

Liu *et al.* report a strong interaction of epoxy and quinone groups with NaPF_6 . However, they also state strong binding tendencies of those groups with EC, rendering it prone to reduction.^[90] In *ab-initio* molecular dynamics simulations performed by Olsson *et al.* it was found that EC has a low adsorption energy (-0.46 eV) on the basal plane of a graphene surface.^[85] A repulsive interaction is observed for vacancy defects (+1.02 eV) and oxygen substitutional defects with adjacent carbon vacancy (+0.77 eV). Contrary, if double substitutional oxygen defects (e.g. carboxyl groups) are present, EC can strongly bond to the defect site (-1.39 eV). EC breakdown is reported to commence either into ethylene and a carbonate fragment or into sodium butylene carbonate (Na_2BDC) by an anionic radical reaction described by the equation in Figure 6.^[85–87] Epoxy groups on the surface are believed to suppress EC decomposition by increasing activation barriers and the energy required for the initial bond-cleavage step.^[86]

In summary, SEI film formation is a highly complex and interdependent process that is strongly influenced by the surface properties of HC. To date, the influence of OFGs on SEI formation has been primarily described based on theoretical considerations. The following chapter therefore explores experimental approaches to selectively modify the surface chemistry of HC, enabling a systematic investigation of the role of OFGs in SEI formation and electrochemical performance.

1.6 Review of Surface Modification Methods for Hard Carbon

The relevance of HC surface properties for SEI formation and ICE has been established in previous chapters. However, a controlled modification of OFGs on the surface would be essential to understand their influence during the first cycles. There are several guiding principles that any modification method should follow. First, some approaches may alter HC morphology, such as porosity or surface area, which can also influence ICE. Ideally, methods

should adjust the surface OFG composition without introducing additional structural changes, extra porosity, or increasing the surface area. Second, the introduced OFGs must be thoroughly characterized, *e.g.* by XPS. Introducing a single type of OFG would provide the clearest insight into its individual effect, although it is experimentally complicated and possible synergistic interactions between multiple OFGs should also be considered. Finally, electrochemical characterization should be performed in appropriately designed cell systems. Herein, only post-treatment methods are critically evaluated, as they modify the surface of HC particles while preserving the bulk structure.

1.6.1 Post oxidation and reduction

Immersion of HC in aqueous media containing oxidizing agents such as nitric acid^[50,56,94] (HNO_3), sulfuric acid^[95] (H_2SO_4) or hydrogen peroxide^[55] (H_2O_2) are straightforward methods to introduce OFGs to the surface of HC. Zhao *et al.* reported that the oxygen content of glucose derived HC could be increased from 7.1 to 22.1 at.% by stirring in concentrated H_2SO_4 and potassium permanganate for 12 hours.^[95] They conclude that the abundant OFGs introduced disrupt the π -system, which leads to a reduction in electronic conductivity and an increase in charge-transfer resistance. Nevertheless, they report an increase of the ICE from ~37% to 55%, which they attribute to the formation of a thinner SEI due to increased OFG surface content.

HC from potassium citrate, which was treated under hydrothermal conditions with dilute HNO_3 , exhibited an oxygen increase from 8.4 up to 20.2 at.% after 12 hours.^[94] Simultaneously, the authors report a decrease in surface area from over 1000 to 685 m^2g^{-1} , which they attribute to a microstructural breakdown of mesopores caused by etching of the acid. This concurrent change in surface area and composition limits the informative value of their electrochemical data, as the treatment may exhibit opposing tendencies on the SEI formation and thus the ICE. While an increase of the ICE is reported from 45.6 to 81.5%, it comes at the cost of a capacity reduction.

In both cases discussed, the reported improvements in ICE are accompanied by trade-offs that complicate interpretation. The unselective introduction of OFGs together with structural changes suggests that both materials deviate from typical HC behavior and instead exhibit capacitor-like characteristics rather than insertion or pore-filling dominated storage. Conversely, other studies employing similar oxidative treatments report only marginal improvements or even detrimental effects on ICE.

Ghimbeu *et al.* investigated cellulose-derived HC subjected to concentrated HNO_3 at 60°C for two hours. TPD-MS profiles of acid-treated HC revealed increased evolution of CO_x , H_2O and H_2 compared to pristine HC.^[56] However, no XPS analysis was performed to quantify the surface oxygen content. Following the acid treatment, the ICE decreased markedly from 82.7

to 55.9% indicating a negative contribution from the additional OFGs. Subsequent annealing in a reducing hydrogen atmosphere removed these functionalities again, but further lowered the ICE to 48.2%. The active surface area, determined by CO₂ adsorption, increased from 40 to 163 m² g⁻¹ after acid treatment and to 221 m² g⁻¹ after hydrogen treatment. Once again, the inherent coupling of functionalization with morphological change limits the ability to disentangle their respective contributions to electrochemical performance.

High-energy ball-milling HC with dry ice represents a mechanochemical approach to introduce OFGs to the carbon surface.^[50,96] In this process, dry ice provides a CO₂-rich atmosphere, while repeated impacts of the milling balls with the container walls can amorphize the HC structure. This leads to generation of reactive sites, which can subsequently react with CO₂ molecules to form carboxyl-rich HC. Wang *et al.* report an increase in oxygen from 4.8 to 20.1 at.% for HC derived from anthracite attributing it to the formation of carboxyl groups at the edge sites of the graphene planes.^[50] However, peak broadening in C 1s spectra together with the claimed amorphization may also indicate incorporation of carboxyl groups at newly generated sp³ centers. Alongside functionalization, the ICE decreases from ~66 to 47.7% with irreversible losses attributed to the introduced porosity by the mechanochemical treatment. Subsequent annealing in hydrogen atmosphere reduces the oxygen content back to 5.7 at.%, but further lowers the ICE to 32.5%, indicating that the surface OFGs are not decisive for a high ICE. In contrast, their HC subjected to acid treatment in a H₂SO₄/HNO₃ mixture exhibited 17.6 at.% of oxygen and an ICE of 71.4%, supporting their assumption that OFGs may not solely affect the ICE. These findings were confirmed through comparable studies by other research groups.^[96]

Oxygen plasma can be produced by microwave discharge, giving rise to reactive oxygen species capable of reacting with carbon surfaces.^[97,98] Xie *et al.* treated sucrose-derived HC in an oxygen plasma cleaner, increasing the oxygen content from 6.0 to 15.6 at.% while preserving particle morphology.^[98] This treatment also raised the ICE from 51.4% to 65.9%. Based on XPS analysis, the authors report an increase in C=O functionalities accompanied by a decrease in sp³ carbon, which they attribute to reactions between reactive oxygen species and sp³ sites. However, these conclusions warrant caution, as the C 1s peak fitting neglects the inherent asymmetry of the sp² component, a common source of OFG overestimation.^[64]

The heterogeneity in carbon sources for HC, functionalization approaches, and electrochemical protocols makes it challenging to isolate specific contributions of OFGs from other variables influencing SEI formation and ICE. An overview of the discussed and additional post-treatment approaches, including oxidative and reductive methods together with corresponding oxygen contents, ICEs, and cycling performance, is provided in Table 1.

Table 1. Overview of different oxidative and reductive functionalization approaches.

Precursor @T _{carbonization}	Treatment	O-content by XPS at. %	ICE / %	Cycling performance capacity / mAh g ⁻¹ cycles @current / mA g ⁻¹	Electrolyte	Reference
Glucose @900°C	conc. H ₂ SO ₄ + KMnO ₄	Pristine 7.1 HC-O 22.1	Pristine 37 HC-O 55	322 1000 @50	1M NaClO ₄ EC:PC:FEC	[95]
Potassium citrate @750°C	Hydrothermal HNO ₃	Pristine 8.4 1.5h 16.2 3h 17.5 6h 19.8 12h 20.2	Pristine 45.6 12h 81.5	225 1000 @2000	1M NaClO ₄ EC:PC	[94]
Sucrose @800°C	H ₂ O ₂	Pristine 3.4 25% 6.6 50% 8.6 75% 10.0 100% 11.7	Pristine: n/A 75% 20	218 4000 @2000	1M NaClO ₄ EC:PC:FEC	[55]
Coconut shell @1300°C	KOH	n/A	Pristine 57.5 3h 69.8	~290 100 @100	1M NaPF ₆ EC:DMC	[99]
Glucose @700°C	Quantitative Air, 700°C, 2h	Pristine 5.1 0.2 ratio 13.3	Pristine 41.6 0.2 ratio 47.3	149 100 @1000	1M NaClO ₄ EC:DEC:FE C	[100]
Cellulose @1400°C	1. conc. HNO ₃ 2. H ₂ 900°C	n/A	Prist. 82.7 Ox 55.9 Ox-red 48.2	n/A	1M NaPF ₆ EC:DMC	[56]
Anthracite @1600°C	1. dry ice + ball milling (M) 2. (M) in H ₂ (M- R) 3. H ₂ SO ₄ and HNO ₃ (AT)	Pristine 4.8 M 20.1 M-R 5.7 AT 17.6	Pristine ~66% M 47.7 M-R 32.5 AT 71.4	141 2000 @1500 (M)	1M NaClO ₄ EC:PC:FEC	[50]
Sucrose @1300°C	HNO ₃	Pristine 5.4 HNO ₃ 16.0	Pristine 85 HNO ₃ 30	287 ~110	0.8M NaPF ₆ EC:DMC	[101]
Cellulose @1000°C	1. dry ice + ball milling (CO ₂) 2. (CO ₂) in H ₂	Pristine 12.1 CO ₂ 19.3 CO ₂ -H ₂ 3.9	Pristine 34.3 CO ₂ 39.5 CO ₂ -H ₂ 21.9	80 2000 @1000 (CO ₂)	1M NaClO ₄ EC:DEC	[96]
Sucrose @1300°C	Oxygen plasma	Pristine 6.0 O ₂ 15.6	Pristine 51.4 O ₂ 65.9	72.5 600 @500	1M NaClO ₄ EC:PC	[98]
Commercial HC	Oxygen plasma	Pristine 3.7 1h 5.6 2h 10.0 3h 10.5	Pristine 60.6 1h 69.7 2h 80.9 3h 69.8	n/A	1M NaPF ₆ Diglyme	[97]
Litchi wood @1400	Oxygen plasma	n/A	Pristine 87.8 OHC 90.4	n/A	1M NaPF ₆ DEGDME	[102]
Apricot shells @900°C	2h H ₂ @800°C	Pristine 6.7 H ₂ 4.6	Pristine 66 H ₂ 73	~290 300 @0.4 C	1M NaClO ₄ EC DEC	[103]

1.6.2 Surface engineering

To overcome the limitations of conventional oxidative or reductive chemical treatments, surface engineering methods provide versatile strategies for controlled modification of HC surfaces. In contrast to conventional post-treatment methods, which frequently couple functionalization with structural changes, surface engineering approaches aim to selectively tailor surface chemistry while preserving the underlying carbon structure.

Sun *et al.* adopted an *in-situ* surface engineering strategy by exposing HC samples to cyclohexane or ethanol vapors at 1300 °C.^[101] Under these conditions, the molecules decompose into highly reactive fragments that can react with defect sites or OFGs, promoting the removal of the latter and active curing of structural defects. For cyclohexane vapor treatment, the oxygen concentration decreased to 1.2 at.% compared to 5.4 at.% in the pristine material, whereas ethanol vapors resulted in a less pronounced reduction, yielding 4.4 at.% oxygen. XPS analysis indicated an increase in the sp^2/sp^3 ratio in C 1s spectra, but the evaluation once again neglects the asymmetry of the sp^2 peak, limiting the informative value of the peak fit. High-resolution transmission electron microscopy images revealed the deposition of a graphitic-like layer on particle boundaries, suggesting that the process resembles a chemical vapor deposition-like coating rather than pure defect healing. Nevertheless, the ICE improved from 70 % to 85 % after cyclohexane treatment, implying that carbon coatings can be beneficial for SEI development, which is supported by similar results from other studies.^[104,105]

Grafting of OFGs onto the native surface of HC involves the covalent attachment of oxygen-containing functional groups to existing sites on the carbon framework, providing a controlled route to tailor surface chemistry without extensive structural disruption. Liu *et al.* followed a surface-functionality-reconstruction strategy by the reaction of caffeic acid with the surface of xylose-derived HC.^[90] Caffeic acid reacts with native hydroxy groups of the HC in a dehydration condensation reaction, and the introduction of abundant C=O functionalities by the caffeic acid acts as reversible storage sites for Na^+ ions as well as nucleation sites for SEI development. The authors report a decrease in surface area from 63.9 to 11.5 m² g⁻¹, which they attribute to the blocking of micropores. Additionally, a rise in oxygen levels is observed from 3.7 to 10.0 at.% was determined by XPS. However, high resolution XP spectra of C 1s may also overestimate oxygen functionalization for the same reasons discussed before. A high ICE of 93.2 % was achieved for HC functionalized with caffeic acid compared to the moderate 69 % observed for pristine HC. *Post-mortem* SEI analysis by XPS revealed that the SEI on functionalized HC contained a higher proportion of inorganic components, whereas the SEI on the pristine material exhibited a greater fraction of organic species, suggesting predominant decomposition of solvent molecules.

An overview of the discussed and additional surface-engineering methods with corresponding oxygen contents, ICEs, and cycling performance, is provided in Table 2.

Table 2. Overview of different surface engineering methods.

Precursor @T _{carbonization}	Treatment	O content by XPS / at. %	ICE / %	Cycling performance capacity / mAh g ⁻¹ cycles @current / mA g ⁻¹	Electrolyte	Referenc e
Sucrose @1300°C	In-situ engineering cyclohexane / Ethanol vapor @1300°C	Pristine 5.4 C-HC 1.2 E-HC 4.4	Pristine 70 79 85	287 100 @20	0.8M NaPF ₆ EC:DMC	[101]
Sucrose @1100°C	Physical vapor deposition of carbon	n/A	Pristine ~55 ^a C-coated ~70 ^a	n/A	1M NaPF ₆ EC:PC	[104]
Sucrose @ 1000	Pyrolysis in Toluene vapor + Ar	n/A	Pristine 54 CVD 83	222 100 @60	1M NaClO ₄ EC:DEC	[105]
Xylose @1200	Grafting of caffeic acid	Prist. 3.7 Caff.-HC 10.0	Pristine 69 Caff.-HC 93.2	380 10 000 @5000	1M NaPF ₆ EC:DEC	[90]
Grapefruit peels @600	1. NaOH + citric acid 2. Urea (GPC-U) or melamine (GPC-M)	Pristine 14.3 GPC-U 9.8 GPC-M 9.9	Pristine ~30 ^a GPC-U ~29 ^a GPC-M ~43 ^a	n/A	1M NaPF ₆ EC:PC:DMC	[106]
Sucrose @1200	In-situ polymerization of DEBA	n/A	Pristine 65.2 DEBA-1 73.0 DEBA-3 77.2 DEBA-5 75.4 DEBA-10 72.3	~90 2000 @1000	1M NaPF ₆ EC:DEC	[107]
Cellulose @1000°C	Solvothermal HF	Pristine 10.2 CDC-F 5.7	Pristine 37.3 CDC-F 55.4	372 1000 @100	1M NaClO ₄ EC:EMC:DE C	[108]
Commercial HC	Grafting of trifluoroacetyl- benzoic acid	n/A	Pristine 71.8 FB-HC 90.0	359 5000 @2000	1M NaPF ₆ diglyme	[109]

^a calculated from galvanostatic cycling plots

Overall, the many studies on post-treatment and surface engineering approaches highlight the strong influence of surface properties on SEI formation and ICE. However, these studies sometimes fail to clearly distinguish between the effects of chemical functionalization and concurrent changes in morphology, porosity, or surface area, which limits a mechanistic interpretation of the results. In addition, the reporting of surface oxygen contents is frequently incomplete or inconsistent, further complicating comparison across studies.

1.7 Experimental Methods

This chapter outlines the fundamental principles of the main characterization techniques used in this work, whereas details on procedures and experimental conditions are provided in the Experimental Details section in chapter 3.

1.7.1 Electrochemical Characterization

Since the phenomenological operating principle of SIBs has already been described in Chapter 1.2, this section focuses on the experimental principles of the electrochemical characterization methods employed in this work.

Electrochemical measurements are often performed in half-cells using a three-electrode configuration with a current-free reference electrode in order to minimize polarization effects and allow monitoring of individual electrode potentials (Figure S1a).^[110] Consequently, the applied current flows between the working electrode (HC) and the counter electrode, as depicted in Figure S1c. Elemental sodium is used in half-cell experiments as both counter and reference electrode and serves as a quasi-infinite sodium reservoir.

Galvanostatic Cycling with Potential Limitation (GCPL)

The specific capacity of HC can be determined by galvanostatic cycling, during which a constant current is applied while the electrode potential is continuously recorded. Once the potential reaches a predefined cut-off value (e.g. 5 mV vs. Na⁺/Na), the charging step is terminated and the subsequent discharge step is initiated by reversing the current direction. The specific capacity can be calculated by the following equation:

$$C = \frac{I \cdot t}{m} \quad (\text{I})$$

where C is the capacity in mAh g⁻¹, I the applied current in mA, t the time in h and m the mass of active material in g. The coulombic efficiency (CE) is a measure of the reversibility of an electrochemical cell. It is defined as the ratio of the charge extracted during discharge to the charge inserted during charge and can be calculated according to the following equation:

$$\text{CE} = Q_{\text{discharge}} / Q_{\text{charge}} \quad (\text{II})$$

In contrast to lithium intercalation in graphite, where lithium ions are inserted into a host lattice with a fixed stoichiometry, sodium storage in HC does not exhibit a well-defined theoretical capacity.^[21] This is primarily due to the internal porosity of HC, where sodium storage involves multiple mechanisms, including adsorption and filling of micropores, which do not follow a fixed stoichiometric relationship.^[28,37,41,48] Consequently, the maximum electrochemically achievable storage capacity strongly depends on the microstructural properties of the HC material. For this reason, the applied current is commonly normalized to the mass of the HC electrode in

order to enable meaningful comparison between different materials and electrodes, and is reported in units of mA g^{-1} . By modulation of the applied current over successive cycles, the rate capability of the electrode can be evaluated, which is particularly relevant for fast-charging applications but can also allow conclusions on diffusion constraints.

For HC materials, a differentiation between the sloping (>0.1 V) and plateau (<0.1 V) attributed capacities is a frequently used approach to evaluate and rationalize the effects of material structure and sodium storage mechanisms. This distinction reflects the fundamentally different kinetic and thermodynamic characteristics of surface-controlled storage processes and pore-filling phenomena according to the widely accepted adsorption-filling model.

Differential capacity plots are obtained from the derivative of potential–capacity curves and offer detailed insights into potential-dependent electrochemical processes. This representation is especially valuable for analyzing reversible and irreversible redox reactions, such as SEI formation, and for identifying changes in the underlying storage mechanisms during cycling.

Cyclic Voltammetry (CV)

Cyclic voltammetry measures the current response of an electrochemical cell during a cyclic, linear sweep of the applied potential within a defined potential window. This technique enables the identification of potential-dependent redox processes, which appear as characteristic current peaks.

For reversible electrochemical reactions, a negative peak current is observed during the cathodic scan (e.g. $2\text{ V} \rightarrow 5\text{ mV}$ vs. Na^+/Na), followed by a positive peak current during the subsequent anodic back-scan. The positions and separation between the anodic and cathodic peak potentials provides insight into overpotentials, diffusion constraints, and resistive contributions of the system. In contrast, the peak current magnitude is directly related to the reaction kinetics and transport properties of the electrode. Irreversible reactions like SEI film formation lead to cathodic peaks, without a corresponding anodic peak.

Electrochemical Impedance Spectroscopy (EIS)

In EIS, the electrochemical cell is subjected to a small sinusoidal modulation of the applied potential, while the resulting current response is measured. From the amplitude and phase shift of the current response relative to the potential perturbation, the impedance of the system can be determined. Due to the phase shift between the applied potential and the resulting current response, the frequency-dependent impedance is represented as a complex number and is often visualized in Nyquist-plots. Since different electrochemical processes within the cell, such as charge-transfer reactions, ion transport across the SEI and diffusion are

characterized by distinct time constants, modulation over a wide frequency range allows these processes to be separated.

The interpretation of impedance spectra is commonly accompanied by modeling the electrochemical response with equivalent electrical circuits and fitting the parameters to the experimental data. In this approach, electrochemical processes are represented by corresponding electrical components. This allows individual contributions, such as electrolyte resistances, interfacial processes, and charge-transfer kinetics to be quantified and compared in a physically meaningful manner.

Galvanostatic Intermittent Titration Technique (GITT)

GITT is a routinely used electrochemical method to study diffusion-controlled ion transport in battery electrodes by combining small current perturbations with relaxation periods to probe quasi-equilibrium behavior. A quantitative description of diffusion-controlled transport based on GITT measurements was first established by Weppner and Huggins, who derived an analytical expression relating the potential response during a current pulse to the apparent chemical diffusion coefficient under the assumption of semi-infinite diffusion.^[111] The apparent diffusion coefficients in this work are calculated using the formulation established by Bommier *et al.*, which is frequently employed for HC electrode systems (Equation III).^[48]

$$\tilde{D} = \frac{4}{\pi \tau} \left(\frac{m_b V_M}{M_B S} \right)^2 \left(\frac{\Delta E_S}{\Delta E_t} \right)^2 \quad \left(t \ll \left(\frac{L^2}{\tilde{D}} \right) \right) \quad (\text{III})$$

where $\tilde{D}$ is the calculated apparent diffusivity, τ is the current pulse time in s, m_b the sample mass in g, V_M the molar volume in $\text{cm}^3 \text{mol}^{-1}$, M_B the molar mass in g mol^{-1} and S the contact surface area in cm^2 . Figure S2a,b present a typical GITT measurement curve and an individual pulse phase with subsequent potential relaxation. The applicability of the GITT diffusion model proposed above is only valid if the potential follows a linear relationship with the square root of the time during the pulse (Figure S2c).

1.7.2 X-Ray Photoelectron Spectroscopy

In X-ray photoelectron spectroscopy, monochromatic X-rays eject core-level electrons of a material. The photoemission process of electrons can be described by

$$h\nu = E_{\text{binding}} + E_{\text{kin.}} + E_{\text{spectrometer}} \quad (\text{IV})$$

where h is Planck's constant, ν the frequency of the photon, E_{binding} the binding energy of the nucleus to the photoelectron, $E_{\text{kin.}}$ the kinetic energy of the photoelectron and $E_{\text{spectrometer}}$ the instrument specific contribution to the work function of the photoemission process. The

measurement is performed in an ultra-high vacuum because unspecific interactions of photoelectrons with gas molecules would reduce signal intensity and energy resolution.

If $E_{\text{spectrometer}}$ is known, the binding energy can be calculated by measurement of the kinetic energy of the photoelectrons. Because binding energies of core-level electrons are element specific, XPS allows the discrimination and quantification different elements, as long as there is no overlap from different photoemission processes. The IMFP of electrons in condensed matter is in the range of nanometers, which renders XPS a surface sensitive technique.

For carbon materials, XPS is frequently used to distinguish between different oxidation states, as the binding energy of the C 1s core-level electron depends on the chemical environment of the carbon atom. More electronegative substituents (e.g. oxygen or fluorine) draw electron density in covalent bonds, which leads to an increase of the effective charge of the nucleus on the C 1s electron and thus increases its binding energy. Deconvolution of spectra is done by peak-fitting procedures, where mixed Gaussian (spectrometer-derived) and Lorentzian (core-hole lifetime) profiles are approximated to resemble individual chemical states in spectra.

Relaxation from valence electrons to core-hole states emits X-rays, which can induce the emission of valence electrons called Auger electrons. C KLL Auger electrons are more surface-sensitive than C 1s photoelectrons due to their shorter IMFPs and thus provide a complementary insight on the surface chemistry. The degree of surface graphitization for example can be assessed using the C KLL Auger D-parameter, which represents the energy difference between extrema in the first derivative of the carbon KLL transition. This semi-empirical metric ranges from ~13 eV for sp^3 -rich carbons to ~22.5 eV for purely sp^2 carbon.^[64]

1.7.3 Scanning Electron Microscopy

Particle morphologies and surface texture are regularly assessed by scanning electron microscopy (SEM). A focused beam of primary electrons is raster-scanned over the sample, leading to the emission of secondary electrons, from which an image of the sample is constructed. Secondary electrons generated directly by inelastic interactions of the primary beam are referred to as SE1, whereas emission of additional secondary electrons (SE2) is induced indirectly by backscattered electrons that excite further electrons within the sample.

1.7.4 Raman Spectroscopy

The Raman effect describes the inelastic scattering of photons at molecular or lattice vibrational modes by monochromatic irradiation. While most photons of the incident beam are scattered elastically (Rayleigh-scattering), some either lose (Stokes-Shift) or gain energy (Anti-Stokes-Shift). The intensities of the vibrational modes are plotted as a function of the frequency shift relative to the incident beam, from which structural information can be derived.

For carbon materials, Raman spectroscopy is a widely used tool to study the structural disorder and defect concentrations, because their sp^2 planes give rise to several molecular vibrations capable of being excited. The in-plane stretching mode of sp^2 planes is observed at $\sim 1580\text{ cm}^{-1}$ and is often denoted as G-band, whereas deviations from the sp^2 crystal symmetry and defects lead to the emergence of peaks at $\sim 1330\text{ cm}^{-1}$ (D-band), $\sim 1620\text{ cm}^{-1}$ (D'-band), $\sim 1550\text{ cm}^{-1}$ (D''-band) and $\sim 1230\text{ cm}^{-1}$ (D*-band). The intensity ratio of the D and G bands is frequently employed as a descriptor to assess relative defect contributions in carbon materials.

2 Scope of This Work

The previous chapters outlined the atomistic structure of HC and the role of surface OFGs in interactions with electrolytes and Na^+ ions, which affect SEI development and thus the ICE, a key parameter determining the energy density of SIBs. However, literature remains inconclusive due to conflicting reports regarding the effect of oxygen surface functionalization. Therefore, this work aims to establish minimally invasive oxygen functionalization strategies for hard carbon that selectively modify surface chemistry while retaining structural integrity, but can be systematically driven towards structural degradation by adjusting treatment parameters. This enables direct investigation of the interplay between surface functionalization, carbon framework stability, and their impact on electrochemical properties.

Spherical HC was synthesized from furfuryl alcohol, which serves as an experimental framework for covalent and non-covalent post-treatment methods. Building on the guiding principles outlined at the beginning of Chapter 1.6, two different surface functionalization strategies were designed to achieve a controlled surface modification whilst minimizing structural disruption and preservation of electrochemical integrity. In addition, a derivatization approach of surface OFGs was pursued to identify the native surface composition and dissect their contributions beyond the resolving power of conventional XPS methods.

2.1 Pyrene Functionalization

Pyrenes are polycyclic aromatic compounds that can be functionalized with OFGs. Owing to their strong π - π stacking interactions with graphene and graphitic domains, they adsorb efficiently onto sp^2 carbon surfaces, enabling surface coverage.^[112] This approach enables precise decoration of the carbon surface with a single, well-defined functional group without altering particle morphology. Although pyrene and its derivatives have been extensively studied in the context of catalysis for redox-flow batteries,^[113,114] in supercapacitors^[115] and graphite anodes for LIBs,^[116] the functionalization of HC with pyrene-based species remains unexplored. Addressing this gap could provide valuable insights into the effect of selectively introducing surface OFGs to HC, thereby advancing the current understanding of their role in SEI evolution.

2.2 Ozone assisted Functionalization

In contrast to modification by pyrene adsorption, ozone (O_3) offers a versatile tool for controlled covalent functionalization of carbon surfaces. Owing to its high oxidative potential (2.07 V) and high reactivity toward carbon-carbon bonds, ozone enables selective oxidation of surface sites.^[117] Importantly, the extent of reaction can be tuned *via* treatment conditions, allowing a transition from surface-limited functionalization to progressive structural degradation. This

provides a unique opportunity to systematically investigate the boundary between chemical surface modification and structural degradation of the carbon framework.

In this work, the oxidative potential of ozone is utilized to modify the surface of HC. While ozone has previously been used to functionalize graphene^[118], graphite^[119], and carbon nanotubes^[120], its application to hard carbon, particularly with respect to controlled surface modification and its impact on SEI formation and ICE, has not yet been systematically investigated.

2.3 Derivatization of OFGs

To complement the surface functionalization strategies, selective chemical derivatization of OFGs was employed as an advanced analytical method. As discussed in Chapter 1.4, the complex and overlapping chemical signatures of OFGs limit their identification by conventional techniques such as XPS. Conventional surface analysis techniques like XPS lack the ability to discriminate between different OFGs with carbon atoms that share the same oxidation state (e.g. C=O and O-C-O).

For the first time, selective chemical derivatization of hydroxyl, carbonyl, and carboxyl groups on hard carbon using fluorinated markers enables the indirect quantification of these OFGs by XPS. A dedicated derivatization protocol was developed, and its selectivity as well as its reaction stoichiometry were thoroughly validated using five different model polymers, each containing a single functional group in a defined stoichiometric ratio.

3 Experimental Details

3.1 Hard Carbon Synthesis and Materials

Hard carbons were synthesized *via* cationic polymerization of furfuryl alcohol (Sigma-Aldrich) within micelles formed by the surfactant Pluronic F127 (Sigma-Aldrich) at a 6:1 (wt.%) ratio in an ethanol–water mixture (3:1 vol.%) according to Yao *et al.* Polymerization was initiated by adding concentrated hydrochloric acid (4.0 vol.%) and allowing the mixture to stir overnight.^[121] Cross-linking was induced by the addition of 5 M sulfuric acid (31 vol.%) and heating the mixture to 100 °C until a brown paste formed. The resulting material was purified by three cycles of water washing and centrifugation, followed by drying at 80 °C and subsequent grinding into a powder.

Pyrolysis was conducted in argon flow (0.5 L min⁻¹) by first heating the precursor to 200 °C for 2 h (pre-carbonization), and then ramping at 1 K min⁻¹ to 850 °C (or 1200 °C) for a 5 h dwell time. After cooling to room temperature, the resulting HC powder was obtained, ground into a fine powder and used without further purification.

Highly ordered pyrolytic graphite (HOPG) was purchased from SPI Supplies and glassy carbon electrodes (GCE) from Redoxme AB.

3.2 Surface Modification Methods

3.2.1 Pyrene Adsorption

Stock solutions (100 mL, 5 mM) of pyrene derivatives were prepared in ethanol, including 1-pyrenecarboxylic acid, 1-hydroxypyrene, 1-pyrenebutyric acid, 1-pyrenebutanol, and pyrene (all purchased from Sigma-Aldrich, ≥99% purity). For each modification, 2.00 g of HC was dispersed in 50 mL of the respective 5 mM pyrene solution. The suspension was stirred for 24 h at room temperature to allow adsorption of the pyrene molecules onto the carbon surface.

Following the adsorption period, the solution was separated from the HC by centrifugation for five minutes at 8000 rpm and subsequently collected with a filter syringe (0.45 µm). The modified carbon powders were then separated by vacuum filtration, thoroughly washed with demineralized water to remove unbound molecules, and dried at 80 °C overnight. The resulting functionalized powders were used as obtained for further characterization and electrode preparation.

3.2.2 Ozone Assisted Surface Oxidation

HC (1.00 g) was finely ground and evenly distributed in an alumina crucible before being subjected to a 3 h ozone treatment in a glass tube furnace at 25, 60 or 100 °C. Ozone was generated using a Woodland WOZ 3 ozonator operated at full power with an oxygen flow rate of 0.5 L min⁻¹. A reference sample was treated under identical conditions at 100 °C but without

ozone exposure. Glassy carbon and HOPG samples were processed under the same ozone conditions. Washing of the 100 °C O₃ treated HC was performed by three consecutive cycles of dispersing the material in water, centrifugation, and decanting the supernatant.

3.3 Surface Derivatization

3.3.1 Polymer reference samples

Polyvinyl alcohol (PVA), polyacrylic acid (PAA), polyvinyl methyl ketone (PVMK), and polyvinyl acetate (PVAc) were obtained from Sigma-Aldrich, and polyethylene glycol (PEG) was purchased from Merck. PVMK and PVAc were dissolved in acetone, whereas PEG was dissolved in methanol. PAA and PVA were used directly in their as-received powder form.

3.3.2 Derivatization Protocols

Derivatization reactions were carried out by immersion of the samples in the respective derivatization mixtures. For HC powders, electrodes and polymer powder samples, 50 mg of material were immersed in 200 µL of the derivatization reagent for 12 h in an argon-filled glovebox (MBraun), with oxygen and water levels below 0.1 ppm. All derivatization reagents were obtained from Sigma-Aldrich and used as received.

For polymers, solutions were drop-cast onto silicon wafers and dried under ambient conditions prior to derivatization. Following the reaction, all samples were dried under vacuum at 80 °C for 4 h and subsequently transferred directly to the X-ray photoelectron spectrometer for surface chemical analysis. Hydroxyl functionalities were derivatized using anhydrous trifluoroacetic anhydride (TFAA). Carboxyl groups were derivatized by reaction with anhydrous 2,2,2-trifluoroethanol (TFE), pyridine (stored over molecular sieve) and N,N'-Di-tert-butylcarbodiimide in a 100:45:36 ratio. Carbonyl functionalities were derivatized using 2,2,2-trifluoroethyl hydrazine (TFEH, 70% aqueous solution).

3.4 Electrode Preparation

A blend of active material (93 wt.%) and carbon black (1.4 wt.%, TIMCAL Super C65) was ground and dispersed in ultrapure water, after which homogenization was conducted using a THINKY speedmixer at 1500 rpm for 10 min. Carboxymethyl cellulose (1.87 wt.%, added as a 2 wt.% aqueous solution) and styrene-butadiene rubber (3.73 wt.%, added as a 39.8 wt.% dispersion) were subsequently added, followed by mixing at 800 rpm for 10 min.^[122] The slurry was then cast onto aluminum foil by blade coating with a gap of 200 µm. The coating was dried sequentially at room temperature for 12 h, at 80 °C for 12 h, and finally for 12 h at 120 °C in vacuum. Typical electrode loadings were in the range of 4-5.3 mg cm⁻².

3.5 Cell Assembly

All cells were assembled inside argon-filled gloveboxes (MBraun or KIYON) with oxygen and water levels below 0.1 ppm. Unless otherwise stated, the electrolyte consisted of 1 M NaPF₆ dissolved in a 50:50 wt.% mixture of ethylene carbonate (EC) and propylene carbonate (PC) supplied by E-Lyte. Fluoroethylene carbonate (99%, Sigma-Aldrich) was added as an electrolyte additive where specified (5 wt.%). Whatman GF/D glass-fiber separators were used in all cell configurations.

Three-electrode half-cells

Three-electrode half-cells were assembled using custom-built polyether etherketone (PEEK) housings.^[123] A HC working electrode (ø12 mm) and a sodium metal disk (ø12 mm) counter electrode were separated by two ø13 mm GF/D separators (Figure S1b). A sodium reference electrode was positioned perpendicular to the working and counter electrode. The electrolyte contained 5 wt.% fluoroethylene carbonate (99%, Sigma-Aldrich) as an additive.

Three-electrode full-cells

Three-electrode full-cells were assembled in PEEK housings similar to the three-electrode half-cells using a HC anode (ø12 mm) but a NVP/C composite cathode (ø12 mm), separated by a ø13 mm GF/D separator. A sodium reference electrode was positioned perpendicular to the working and counter electrode.

CR2032 coin-cells

CR2032 coin-cells were assembled using a HC anode (ø14 mm) and a NVP/C composite cathode (ø14 mm), separated by a ø16 mm GF/D separator. 150 µL of electrolyte was added to each cell.

Single-layer pouch-cells (SLPs)

Single-layer pouch-cells were prepared using a 32×45 mm NVP/C composite cathode (14.40 cm²) and a 33×46 mm HC anode (15.18 cm²), separated by a 35×50 mm GF/D separator. 1 mL of electrolyte was added prior to evacuating the pouch for 15 s and subsequent hot sealing.

3.6 Electrochemical Measurements

Electrochemical testing was conducted at 25 °C using BioLogic VMP3 potentiostats. Cells were rested at open-circuit potential for 8 h prior to testing. Half-cell measurements were performed in a potential window of 2.0 V to 5 mV vs. Na⁺/Na with current densities normalized to the mass loading of the HC electrode unless stated otherwise. Full-cells were cycled within a voltage window of 2.3–3.9 V using currents normalized to the theoretical capacity of the cathode, where C-rates (C/X) correspond to a full (dis)charge within X hours.

3.6.1 Half-Cell Measurements

Rate Capability Tests and Long-term Cycling

Rate capability tests were conducted on individual cells with five cycles at each current density (50, 100, 200, 500, and 1000 mA g⁻¹), followed by 20 cycles at 50 mA g⁻¹ to assess reversibility.

Long-term cycling was performed at 50 mA g⁻¹.

Cyclic Voltammetry (CV)

CV measurements were carried out at scan rates of 0.1 mV s⁻¹, with five cycles recorded at each scan rate.

Galvanostatic Intermittent Titration Technique (GITT)

Sodium-ion diffusion kinetics were evaluated using GITT after five cycles at 50 mA g⁻¹. Current pulses of 20 mA g⁻¹ were applied for 1800 s, followed by relaxation periods of 2 h. Apparent diffusion coefficients were calculated using the Weppner–Huggins method based on the potential response during relaxation.

Electrochemical Impedance Spectroscopy

EIS measurements were conducted after five formation cycles at 50 mA g⁻¹ over a frequency range from 200 kHz to 10 mHz with a 10 mV perturbation amplitude and 9 points per decade.

3.6.2 Full-Cell Measurements

Galvanostatic Cycling

Cells were subjected to four formation cycles at C/20, followed by cycling at C/2 until 100 cycles were reached.

Rate Capability Test

Rate capability tests of SLPs were performed on individual cells at C/20, C/10, C/5, C/2, and 1C, followed by 20 cycles at C/10 to evaluate reversibility and capacity retention.

3.7 X-Ray Photoelectron Spectroscopy (XPS)

XPS was carried out using a Thermo Scientific K-Alpha+ spectrometer equipped with a monochromated Al K α source (1486.6 eV, 400 μ m spot size) and a concentric hemispherical analyzer (pass energies: 200 eV for survey scans and 50 eV for high-resolution scans). Samples were mounted on silicon wafers using conductive carbon tape. Charging of samples was compensated by employing the spectrometer's dual-beam charge compensation system employing 8 eV electrons in combination with low-energy Ar⁺ ions.

Spectra were analyzed using the Thermo Advantage software package. A Shirley background was subtracted and spectra were referenced to the C1s sp² peak at 284.4 eV for carbon materials or sp³ (CC/CH) at 285.0 eV for polymers. The sp² peak asymmetry was attributed by using a tail mix of 70–90%, tail exponent 0.04–0.06, and full-width at half maximum (FWHM) of 0.8–1.3 eV. Other C1s components were fitted using mixed Gaussian–Lorentzian profiles (FWHM: 1.3–1.6 eV), and O1s components with FWHM of 1.6–2.3 eV. Elemental compositions were quantified using Scofield sensitivity factors.^[124]

The C KLL Auger D-parameter was used to assess surface sp²/sp³ hybridization. Carbon KLL spectra were therefore smoothed using a Gaussian filter (FWHM: 2 eV) and numerically differentiated by a width of 2.10 eV.

3.8 Scanning Electron Microscopy

Particle morphology was assessed by a thermal field emission scanning electron microscope (FE-SEM) from Carl Zeiss SMT AG using an acceleration voltage of 6 kV. Samples were mounted on a steel sample holder with adhesive carbon tape.

3.9 Thermogravimetric Analysis coupled Infrared Spectroscopy (TGA-IR)

To monitor the pyrolysis procedure in hindsight to mass loss and decomposition of OFGs, thermogravimetric analysis with dynamic scanning calorimetry and coupled with infrared spectroscopy was carried out on a Netzsch STA 449C Jupiter and a Bruker Alpha-p Tensor II instrument equipped with an external gas flow cell analyzer.

Samples were analyzed in argon by heating from 30 °C to 1200 °C at a ramp of 5 K min⁻¹. Infrared spectra were simultaneously recorded from 700 to 3000 cm⁻¹.

3.10 Raman Spectroscopy

Raman spectra were recorded using a LabRAM HR Evolution spectrometer (HORIBA Scientific) with a HeNe laser (632.8 nm), 600 g mm⁻¹ grating, and 50 $\times$ objective. At least three spectra were collected per sample from different regions. Data were processed using the CasaXPS software package. A cubic spline background subtraction was applied to all spectra.

D and G bands were fitted with absolute Lorentzian profiles, while residual features were fitted using mixed Gaussian–Lorentzian functions.

3.11 Ultraviolet–Visible Spectrophotometry (UV-VIS)

UV-VIS spectroscopy was carried out using a Cary 5000 UV-Vis-NIR spectrophotometer (Agilent). Spectra were recorded between 200 and 500 nm. A reference dilution series of pyrene and its derivatives (5 to 1 mM) was prepared from the stock solutions for comparison with the supernatant solution. All solutions were further diluted by a factor of 100 right before spectroscopic characterization.

3.12 X-ray diffraction (XRD)

XRD measurements were conducted using a Stadi P powder diffractometer from Stoe in transmission mode with Mo-K α 1 radiation. Diffraction patterns were measured from 5 and 45° in 0.015° steps.

4 Results and Discussion

4.1 Baseline Synthesis and Characterization of Hard Carbon

Understanding the synthesis of the baseline HC used in this work and evaluating the structural and surface properties of the pristine material is fundamental to the discussion of surface functionalization and characterization methods in the subsequent chapters.

4.1.1 Hard Carbon Synthesis and Characterization

The HC precursor is synthesized by the cationic polymerization of furfuryl alcohol inside micelles formed by a non-ionic surfactant in an ethanol/water mixture as described in the experimental details in chapter 3.1. The development of a cross-linked structure in the precursor is critical to ensure that the material behaves as a thermoset rather than a thermoplastic during pyrolysis. A highly cross-linked structure can preserve the precursor morphology and prevent structural collapse during pyrolysis.^[125] The resulting pore structure is of particular importance for sodium-ion storage because appropriately sized micropores can facilitate adsorption and clustering of sodium.^[44,126,127] Cross-linking within micelles can further trap residual solvent, which can later serve as a pore-forming phase.^[128] Upon addition of hydrochloric acid, initial polymerization begins, and linear oligomeric furfuryl alcohol condensates are formed through methylene or ether bridge formation (Figure 7a).^[129] As the reaction proceeds, the solution changes color from transparent pale yellow to opaque dark brown. This visual change reflects the growth of conjugated polymer chains, because increasing electron delocalization shifts the electronic transitions to lower excitation energies.^[130] During polymer chain growth, cross-linking reactions can occur as side reactions. One plausible pathway is a Diels-Alder type ring condensation between neighboring polymer chains (Figure 7b) or through ring-opening of furan moieties (Figure 7c).^[129] This ring-opening generates ketones and enoles, which can subsequently react with adjacent chains. The degree of cross linkage is increased further upon addition of sulfuric acid and heating by the formation of methylenium-ions (CH_2^+) through dehydration by the increasing concentration of H^+ ions in the sulfuric acid (Figure 7d).^[121]

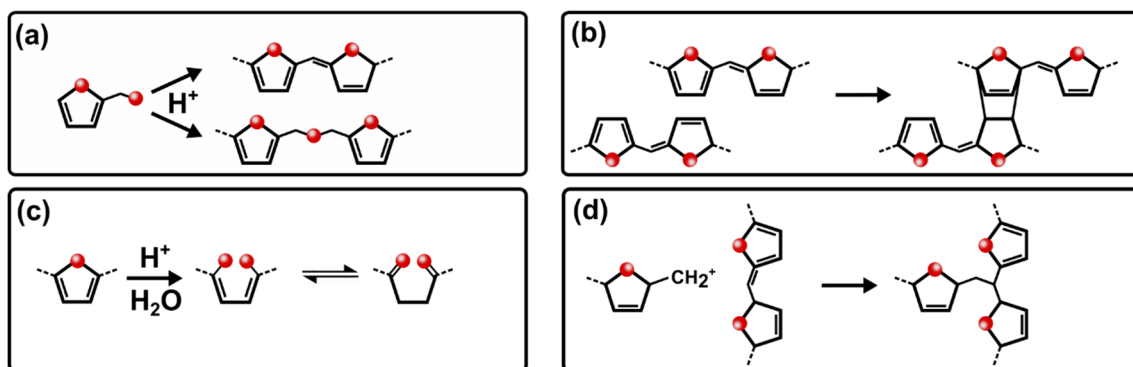


Figure 7. Cationic polymerization reaction pathways of furfuryl alcohol (a). Diels-Alder cross-linking mechanism (b). Hydrolysis of polyfurfuryl alcohol chains (c). Methylenium-ion mediated cross linking (d).

During pyrolysis, chemical and structural rearrangements occur as thermally unstable OFGs are cleaved and the resulting dangling bonds reorganize to form a turbostratic, amorphous carbon matrix. Figure 8a shows the TGA-DSC profile of the HC precursor from 30 to 1500°C. Between 100 and 200°C, a substantial endothermic mass loss of nearly 50% is observed, which is attributed to desorption of residual solvent, moisture and removal of volatile organic compounds. Subsequent mass loss is associated with the cleavage of OFGs, mainly carboxylic acids, lactones, and anhydrides, which decompose to CO and CO₂ between 300 and 700°C.^[69] Phenolic groups, carbonyls, and quinones may decompose between 600 and 900°C.^[71] The DSC signal shows a strong increase in exothermic reactions at the same temperature, consistent with the evolution of CO and CO₂. At temperatures above 600°C, mass loss slows and the DSC profile approaches zero. This behavior results from carbon rearrangement into nanoscopic sp² domains, which requires energy, while the most stable OFGs, such as ethers or pyrans, are cleaved. As pyrolysis temperature increases further, the rearrangement and growth of sp² domains intensifies, although the intricate carbon network prevents full graphitization.

Figure 8b shows a heatmap of inline recorded IR spectra of the pyrolysis gases as a function of temperature. The initial mass loss between 100 and 200°C is confirmed to arise from evaporation of water and volatile organic species. In this temperature range, several spectral features appear in the fingerprint region between 700 and 1500 cm⁻¹, which are indicative of oxygen functionalized volatile organic species.^[70] During the second substantial mass loss between 300 and 700°C, a strong signal at ~2400 cm⁻¹ is observed, indicative of CO₂ evolution from the decomposition of OFGs. At temperatures higher than 800°C, only a faint CO₂ signal is observed, ascribed to the cleavage of the most stable OFGs.

XPS provides insight to the surface properties of carbon materials and was used to compare the carbon environments before and after pyrolysis (Figure 8c). The precursor exhibits a dominant peak at 285.0 eV, ascribed to sp³ and CC/CH carbon with three shoulders at higher binding energies, resembling the increasing oxidation states of carbon, *i.e.* C–O (286.6 eV), C=O and O–C–O (288.0 eV) and O=C–O (289.0 eV).^[131] After pyrolysis, the main spectral feature shifts to 284.4 eV and the peak shape changes to a tailing towards higher binding energies, due to quantum coupling of core electrons with conduction electrons.^[132] Higher oxidation states of carbon like C–O or O=C–O nearly vanish, because these groups are removed predominantly as CO₂ during pyrolysis. While the precursor contains 23.6 at.% oxygen, the pyrolyzed product contains as little as ~4 at.%.

The morphology and surface texture of HC particles were examined by SEM. Figure 8d shows SEM images of the spherical precursor and the pyrolyzed HC. The spherical morphology is preserved during synthesis, sulfuric acid hardening, and pyrolysis, implying that the precursor

is a stable, cross-linked thermoset polymer. The sphere size distribution ranges from ~500 nm to 2 μm , likely due to insufficient micelle stabilization caused by inhomogeneous agitation and turbulent flow in the reaction vessel.

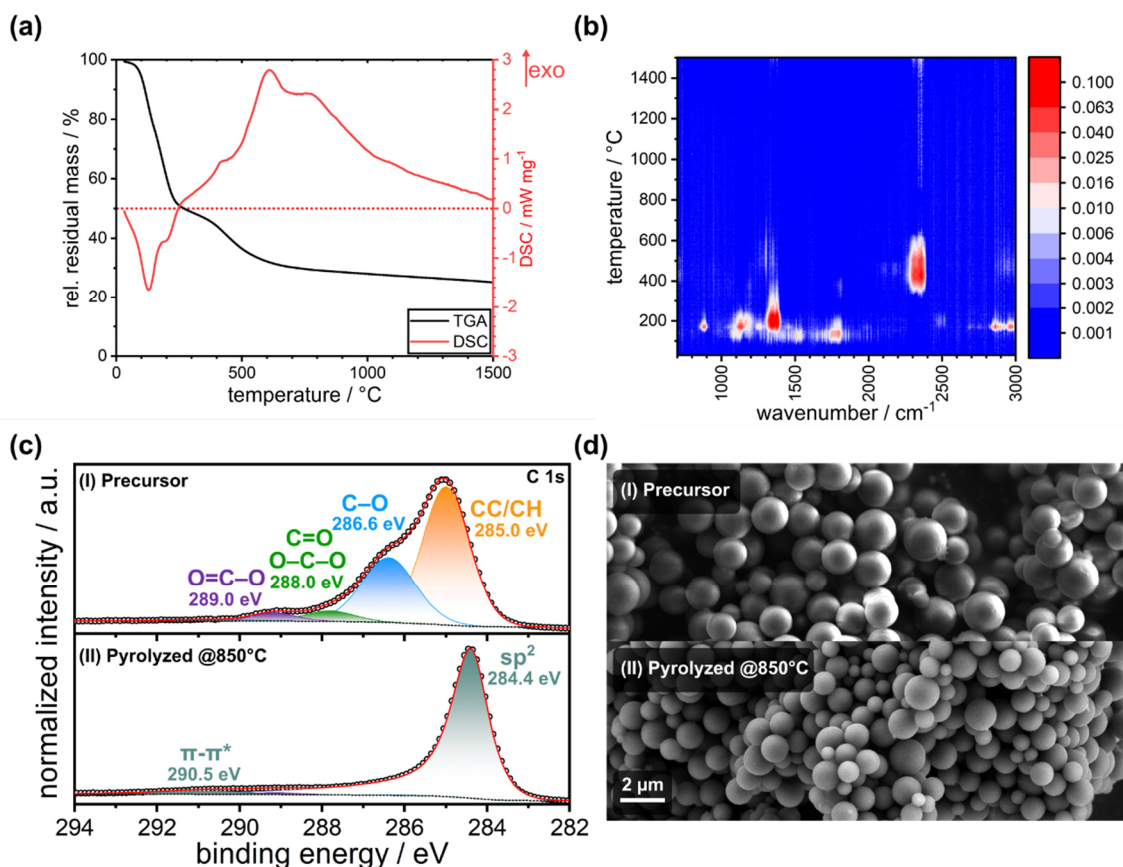


Figure 8. Thermogravimetric and differential scanning calorimetry profile of the HC precursor pyrolysis (a) with infrared spectroscopy analysis of the evolving gases (b). XPS C 1s detail (c) and SEM images (d) of the precursor and the pyrolyzed HC.

4.1.2 Hard Carbon vs. Sodium Half-Cells

To investigate the sodium storage behavior of HC and associated irreversible losses of sodium inventory, three-electrode half-cell experiments were conducted. Unlike two-electrode full-cell configurations, half-cells enable the isolated view on the active material by providing an effectively unlimited sodium reservoir and decoupling electrode processes. Therefore, HC electrodes were tested using sodium metal as both the counter and reference electrode. The use of a current-free reference electrode enables the monitoring of individual electrode potentials, in contrast to two-electrode systems where only the cell voltage is measured.^[110,133]

Figure 9a shows the measured electrode potential from the first five cycles of HC, plotted against the specific capacity. The potential curve can be divided into two characteristic contributions: a sloping region between 1 and 0.1 V, where the potential decreases monotonously, and a plateau region below 0.1 V, where the decrease is significantly slower with increasing state of charge, consistent with postulated adsorption-filling models.^[39] The first cycle reaches higher charging capacities than subsequent cycles, which is attributed to

irreversible reactions such as SEI formation and sodium trapping within the particle. For the pristine HC, an ICE of 77% is recorded, which lies in the upper mid-range of values reported in the literature for HC materials.^[50,56,101,107,109] Small variations in reversible capacity and ICE were observed between different batches of HC. To minimize the impact of batch-to-batch variability, the synthesis was scaled up from ~2 g to 30 g yield, allowing each experimental series to be conducted using material from a single batch. While minor absolute differences between batches may still persist, the trends observed within individual series are considered robust and transferable.

Long-term cycling at 50 mA g⁻¹ was performed for 300 cycles to evaluate the capacity retention of the HC over extended operation (Figure 9b). Although the average CE is 99.0%, rapid capacity fading is observed, with only ~80% of the initial capacity retained after 100 cycles and 57% after 300 cycles (132 mAh g⁻¹ after 300 cycles vs. 230 mAh g⁻¹ initial).

A major contribution to the observed capacity decay is attributed to the instability of the sodium metal reference- and counter electrodes leading to continuous electrolyte degradation.^[134,135] Due to the reducing potential of metallic sodium, a passivation layer is spontaneously formed on the surface and the repeated dissolution and re-deposition of dendritic sodium during cycling leads to the recurring formation of fresh SEI-like passivation layers. This continuous SEI growth consumes electrolyte while simultaneously increasing the internal cell resistance. Compared to lithium-based systems, many sodium SEI components exhibit higher solubility in common ester-based electrolyte solvents.^[136] As a result of electrolyte consumption and SEI dissolution, ohmic overpotentials rise over extended cycling, causing the cut-off potentials (5 mV and 2 V vs. Na⁺/Na) to be reached earlier and thus leading to an apparent progressive loss of accessible capacity.

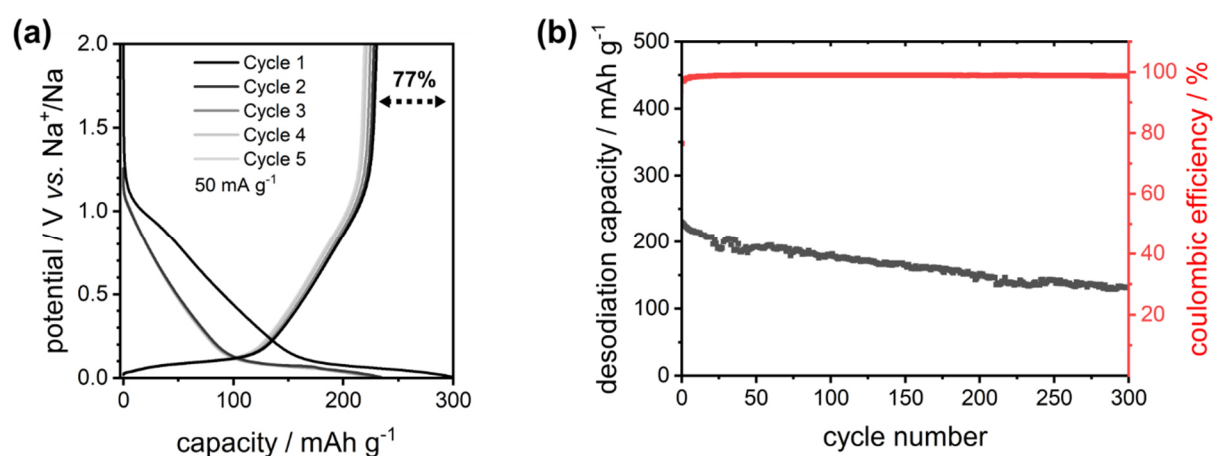


Figure 9. Charge-discharge potential vs. capacity plot of the first cycle of HC (a). Long-term cycling over 300 cycles at 50 mA g⁻¹ (b).

Despite the limitations described above, three-electrode half-cell measurements provide a well-controlled platform to investigate the intrinsic sodium storage mechanisms of HC in early-stage material development. The decoupling of anode processes from complex interactions in full-cells as well as allowing independent monitoring of electrode potentials highlight the importance of three-electrode half-cells as model system for fundamental studies of electrochemical processes. Consequently, three-electrode half-cells serve as a powerful proxy for fundamental studies of electrochemical processes, particularly for elucidating irreversible capacity losses and SEI formation during the first cycles. However, to assess the transferability of these findings under more application-relevant conditions, HC vs. NVP/C full-cells in different cell formats were assembled and electrochemically characterized, which is discussed in the following.

4.1.3 Hard Carbon vs. NVP/C full-cells

A key question is, whether fundamental phenomena observable in half-cells such as irreversible capacity losses during the first cycle are also observed in full-cell configurations and the findings therefore transferable. To bridge the gap between the model system and application-relevant conditions, HC was paired with a $\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ (NVP/C) cathode and investigated across three different cell formats depicted in Figure 10a. Three-electrode full-cells allow monitoring of individual electrode potentials, CR2032-format coin-cells serve as a standard lab-scale validation, and 12 mAh single-layer pouch cells (SLPs) were prototyped as an application-relevant system. A slightly modified cycling protocol was applied for full-cells, comprising four formation cycles at C/20 followed by cycling at C/2 for up to 100 cycles.

Figure 10b shows the cell potential vs. capacity profile of the three-electrode full-cell. A voltage plateau at ~ 3.4 V is expected, corresponding to the reaction of $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ to $\text{NaV}_2(\text{PO}_4)_3$.^[133] In the present case, the plateau is only weakly developed, which is likely due to an overbalanced anode. Accurate capacity balancing of anodes and cathodes is essential in full-cell systems to prevent sodium plating, yet it remains challenging for HC materials, as sodium storage in HC does not follow well-defined stoichiometric reactions as lithium does in graphite.^[21,28,48] The cell exhibits an initial charge capacity of 105 mAh g^{-1} , slightly below the theoretical maximum capacity of $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ (113 mAh g^{-1}). Upon discharge, a reversible capacity of 77 mAh g^{-1} is obtained, corresponding to an ICE of 73.3%, which is in good agreement with those obtained from half-cell measurements. During subsequent cycling at C/2, a pronounced capacity fade is observed. This behavior is not solely attributed to the active material but is strongly influenced by limitations of the three-electrode full-cell configuration.^[137] In the three-electrode PEEK cell housing used here, the contact pressure between the electrodes cannot be well assessed, which can lead to increased cell resistance.^[138] Although the employed sodium metal reference electrode is current-free, parasitic reactions associated with metallic sodium may still contribute to electrolyte consumption, as discussed in the

previous chapter.^[137] However, the relatively large electrolyte volume (~300 μL) should mask electrolyte depletion effects, highlighting that the mere presence of metallic sodium still exerts a significant influence on the electrochemical behavior of the cell. The pronounced capacity decay is reflected in the lower average CE of 98.5% between cycle 2 and 100, indicating ongoing side reactions and increasing internal resistance during cycling.

CR2032 coin-cells are a widely used two-electrode lab-scale system to validate the performance of electrode materials in full-cell configurations (Figure 10b).^[137,137,138] Contrary to the three-electrode setup, a cell voltage is measured and no individual electrode potentials can be assessed. The tested coin-cells reach an initial charge capacity of 99 mAh g^{-1} , but retain a capacity of 77 mAh g^{-1} , which translates to an ICE of 78% and is therefore in good agreement with the three-electrode full- and half-cells (Table 3). The capacity plots reveal highly reversible cycling at C/20 with nearly identical potential profiles. During the subsequent C/2 cycling phase, a high reversible capacity of 69.5 mAh g^{-1} is maintained with an outstanding retention of 94.8% after reaching 100 cycles and an average CE of 99.3% (Figure 10b,c).

The superior performance compared to the three-electrode configuration is likely related to more homogeneous compression of the electrode stack, resulting in improved interfacial contact and reduced resistance.^[138] In addition, the absence of metallic sodium prevents sodium-driven electrolyte decomposition. This also enables operation at a lower electrolyte-to-electrode ratio, which can positively influence cycling stability.

The promising results obtained in coin-cell experiments motivated the transition toward a more application-relevant system in the SLP format.^[137,139] The significantly larger electrode area (15.18 cm^2 vs. 1.54 cm^2) provides a more representative average of electrode properties, reducing the influence of local variations inherent to smaller electrodes. Compared to coin-cells, the voltage plateau is more pronounced in SLPs, which exhibit an initial charge capacity of 102 mAh g^{-1} and a discharge capacity of 76 mAh g^{-1} , corresponding to an ICE of 74.9%. Although slightly lower than the values obtained in coin-cells, the results remain within a comparable range. During the C/2 cycling phase, an average CE of 99.2% is observed. The specific capacity decreases from 62 mAh g^{-1} in the initial C/2 cycle to 51 mAh g^{-1} after 100 cycles. Rate capability tests were carried out on a separate set of cells. A high relative capacity is retained even at high currents, with 75% of the capacity obtained at C/20 maintained at a charging rate of 1C (Figure 10d). Finally, a prototyped SLP was implemented in a small self-built demonstration system, where it successfully powered a microcontroller with an OLED display (Figure 10f).

To contextualize the performance of the pouch cells, a comparison with literature data on comparable SLPs was conducted.^[137] The ICE obtained in this work (~75%) is slightly higher than reported values (~70%), indicating comparable initial processes. However, differences

become apparent in terms of reversible capacity and long-term stability, with lower capacities ($\sim 76 \text{ mAh g}^{-1}$ vs. $\sim 90 \text{ mAh g}^{-1}$) and capacity retention ($\sim 85\%$ vs. $97.5\text{--}98.7\%$ after 100 cycles), while the average coulombic efficiency remains similar ($\sim 99.2\text{--}99.3\%$). This suggests that the fundamental electrochemical mechanisms are consistent across both, whereas the observed discrepancies primarily arise from differences at the cell-system level.

In particular, the presence of a slight electrode overhang in the cells presented here may reduce the effective utilization of the active material. Furthermore, differences in separator type and electrolyte volume influence interfacial processes and ion transport, thereby affecting capacity and stability. The use of a CC/CV protocol in the comparative study likely contributes to a more complete utilization of the cathode capacity, whereas a constant-current protocol was applied here. Overall, these differences can be attributed to variations in cell design and testing methodology rather than intrinsic material properties.

Importantly, the observed electrochemical trends are consistent across all investigated cell formats, indicating that key features like the ICE identified in three-electrode half-cell measurements are comparable to full-cell systems. This further demonstrates that the herein investigated HC material exhibits stable cycling behavior independent of cell configuration and is therefore well suited for targeted modification studies. In this context, three-electrode half-cells represent an effective model system for isolating material-specific effects without interference from full-cell level complexities. Consequently, insights obtained in half-cells obtained in this work can be reasonably extrapolated to full-cell configurations.

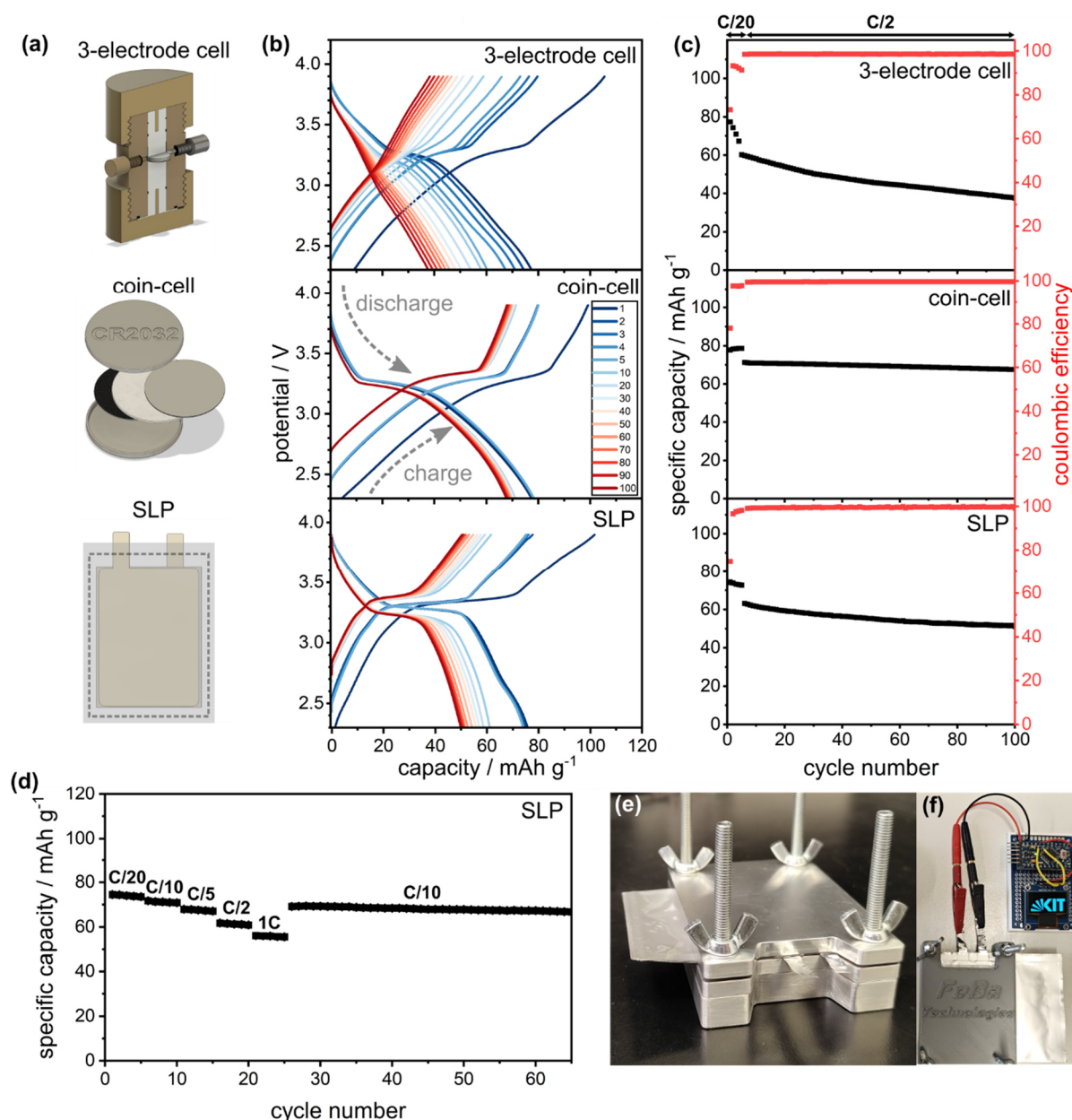


Figure 10. Illustrations of different cell formats: PEEK 3-electrode cell, CR2032 coin-cell and single-layer pouch cell (a). Cell potential vs. capacity plots (b) and long-term cycling over 100 cycles. Rate capability test of a single-layer pouch cell (d) and photograph of an assembled pouch cell inside the clamping rig (d). A cell powering a microcontroller with a small OLED display (e).

Table 3. Comparison of HC vs. NVP/C full-cells in different cell formats.

	anode electrode area	Electrolyte volume	ICE	Reversible Capacity @C/20	Average CE @C/2	Capacity Retention cycle 6-100
	/ cm ²	/ μ L	/ %	/ mAh g ⁻¹	/ %	/ %
3-electrode cell	1.13	~300	73.3	72.6	98.5	62.4
coin-cell	1.54	150	78.1	78.4	99.3	94.8
SLP	15.18	1000	74.9	73.4	99.2	81.0

4.2 Adsorption of Pyrenes for non-covalent Oxygen Functionalization

4.2.1 Methodology and Preliminary Characterizations

The surface of HC plays a pivotal role in the initial cycles of SIBs, as it governs the formation of the SEI and thus likely influences the extent of irreversible reactions. Consequently, precise tuning of surface properties enables a systematic investigation of their influence on the irreversible reactions during the first charge. Polycyclic aromatic hydrocarbons (PAHs), *e.g.* pyrene and its oxygen functionalized derivatives, can adsorb on the basal plane of sp^2 carbon through non-covalent π - π interactions and thus selectively introduce OFGs.^[112] To investigate the individual influence of surface OFGs on the SEI formation, five different pyrenes were chosen as surface model adsorbents for HC pyrolyzed at 1200°C. The high pyrolysis temperature was chosen to minimize the presence of native functional surface groups on HC. This approach provides a model system in which specific oxygen functionalities can be introduced at the carbon surface without altering the underlying carbon framework, thereby enabling decoupling of chemical surface effects from structural contributions.

For clarity, the functionalized pyrenes are referred to as carboxy (1-pyrenecarboxylic acid), hydroxy (1-hydroxypyrene), butylcarboxy (1-pyrenebutyric acid), and butylhydroxy (1-pyrenebutanol), as shown in Figure 11a. The pristine HC powder was functionalized by stirring in ethanol solutions containing the dissolved pyrenes. After adsorption, the powders were filtered, washed with water to remove excess pyrenes, and used for electrode preparation (Figure 11b).

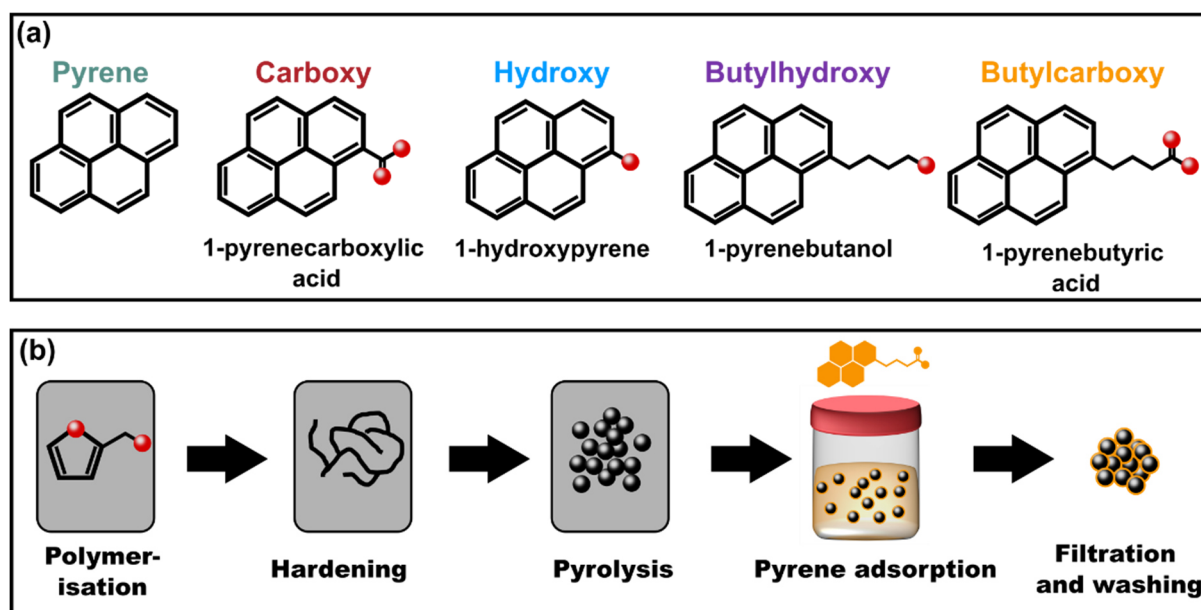


Figure 11. Pyrene and its oxygen functionalized derivatives (a) and the surface functionalization approach (b).

Figure 12 compares SEM images of the pristine HC with the pyrene-modified powders. It should be noted that, for the pyrene functionalization study, a larger batch of HC was synthesized, which may result in minor morphological differences compared to the material presented in the previous chapter. These differences are likely related to altered stirring conditions during scale-up of the synthesis which affects micelle formation and stability during precursor synthesis. As it can be seen in SEM images in Figure 12a, the spherical morphology is conserved during hardening and pyrolysis. Large primary particles are surrounded by smaller secondary particles. The observed bimodal particle size distribution likely stems from insufficient stabilization of smaller micelles or accelerated polymerization, leading to their aggregation into larger particles.^[121] However, this variation in morphology and particle size distribution is not expected to significantly influence the surface chemistry of the HCs.

The pyrene-modified HCs (Figure 12b-f) exhibit the same morphological appearance as the pristine particles. Unlike many other surface modification techniques, this adsorption method preserves the morphology of the HC particles, allowing for an isolated and unambiguous evaluation of surface chemical effects independent of morphological or structural variations. Consequently, differences in electrochemical behavior can be directly attributed to the chemical nature of the introduced functional groups.

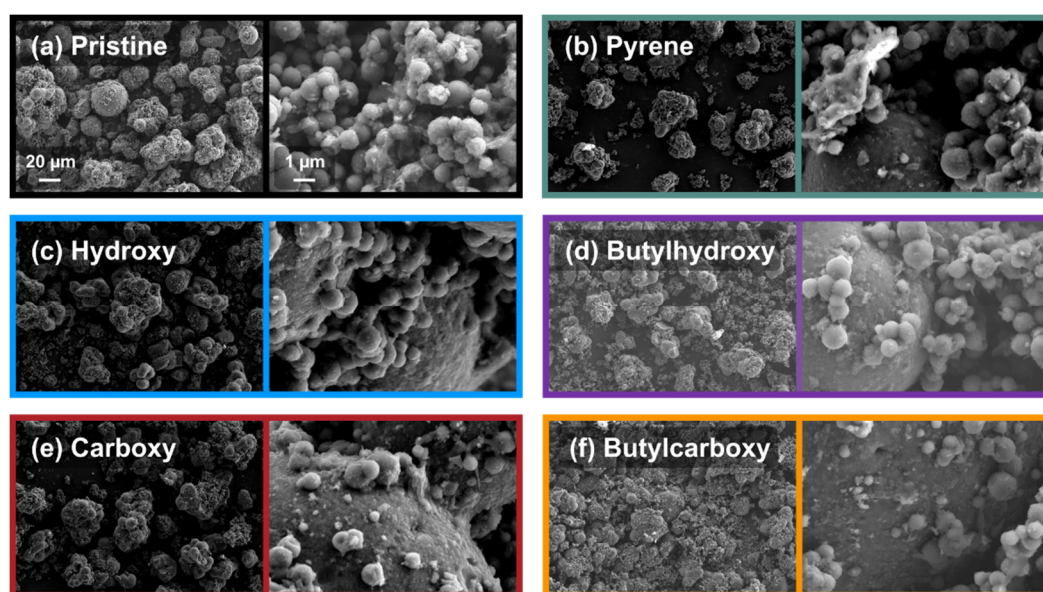


Figure 12. SEM morphology analysis of the pristine and pyrene functionalized HC powders (a-f).

CV measurements in aqueous electrolyte were used to confirm pyrene adsorption and probe the electrochemical activity of the modified surfaces.^[113,116] As shown in Figure 13a, pristine HC does not exhibit redox features, whereas all pyrene-modified samples display distinct redox peaks, confirming the presence and electrochemical activity of adsorbed pyrenes and their electronic coupling to the carbon matrix. These results are consistent with earlier studies on pyrene interactions with graphitic surfaces.^[116] Pyrenes adsorbed to carbon surfaces are also reported to increase the double-layer capacitance in supercapacitors.^[140]

During the first cycle of the CV scan, pristine HC powder does neither exhibit any redox activity during the first cycle and subsequent cycle. In contrast, hydroxy-modified HC exhibits a redox peak at 0.71 V in the first cycle, which shifts to 0.38 V upon subsequent cycling (Figure 13b,c). This behavior is attributed to electrochemically induced homocoupling of surface-bound pyrene molecules, forming dimers or oligomers that alter the electronic structure and redox properties of the adsorbed layer.^[141] This observation indicates that the adsorbed pyrene layer is not static but can undergo electrochemical transformations, potentially altering its interfacial properties during cycling.

To quantify the amount of adsorbed pyrene, UV–VIS spectroscopy of the supernatant solutions was employed.^[142] Comparison with calibration curves reveals an adsorbed amount of ~0.2 mmol for hydroxy, whereas pyrene exhibits significantly higher adsorption of ~0.88 mmol (Figure 13d). The significantly higher adsorption of pristine pyrene can be attributed to its ability to adopt an optimal parallel, offset-stacked configuration on the graphitic domains of HC (Figure 13g).^[143,144] This geometry maximizes π – π interactions and represents the most energetically favorable adsorption mode for aromatic systems.

In contrast, the introduction of functional groups alters both steric and electronic properties of the molecule, limiting the ability to maintain this parallel adsorption geometry.^[143] As illustrated in Figure 13h, steric constraints could force the adsorbed molecules into tilted or perpendicular configurations (T-shaped or Y-shaped), which significantly reduces the effective π – π overlap with the carbon surface. This effect explains the generally lower adsorption observed for all functionalized pyrenes compared to pristine pyrene. For hydroxy- (0.20 mmol) and carboxy-functionalized pyrene (0.22 mmol), the relatively small substituents still allow partially parallel alignment, albeit with reduced surface contact, resulting in moderate adsorption. Additionally, electron-withdrawing or electron-donating heteroatom substituents are known to modulate the π -electron density of the aromatic system, thereby influencing the strength of π – π interactions and contributing to the overall adsorption behavior.^[143]

A more pronounced effect on adsorption is observed upon introduction of a butyl spacer, which increases the distance between the pyrene and the carbon surface due to steric hindrance. This destabilizes parallel adsorption and may promote tilted or perpendicular configurations (Figure 13h). Consequently, π – π interactions are significantly weakened. This geometrical constraint is most evident for butylcarboxy pyrene, which exhibits the lowest adsorption (0.06 mmol). In this case, steric hindrance combined with strong solvation of the carboxyl group in the solvent shifts the equilibrium towards the dissolved state, thereby disfavoring adsorption and limiting effective surface interaction. In contrast, butylhydroxy pyrene (0.33 mmol) shows the highest adsorption among the functionalized pyrenes despite similar steric constraints. This behavior suggests that the solvation energy of butylhydroxy in ethanol is lower, thereby

allowing the molecule to retain a greater fraction of π - π interaction compared to the carboxy-terminated analogue.

Overall, the observed adsorption behaviors are governed by the ability of the molecules to adopt favorable parallel π - π stacking configurations, which can be hindered by steric effects and functional group-induced solvation, leading to a shift towards less favorable adsorption geometries. Consequently, the nature, density, and orientation of the adsorbed pyrene species are expected to directly influence the interfacial reactions with the electrolyte and thus the formation and properties of the SEI.

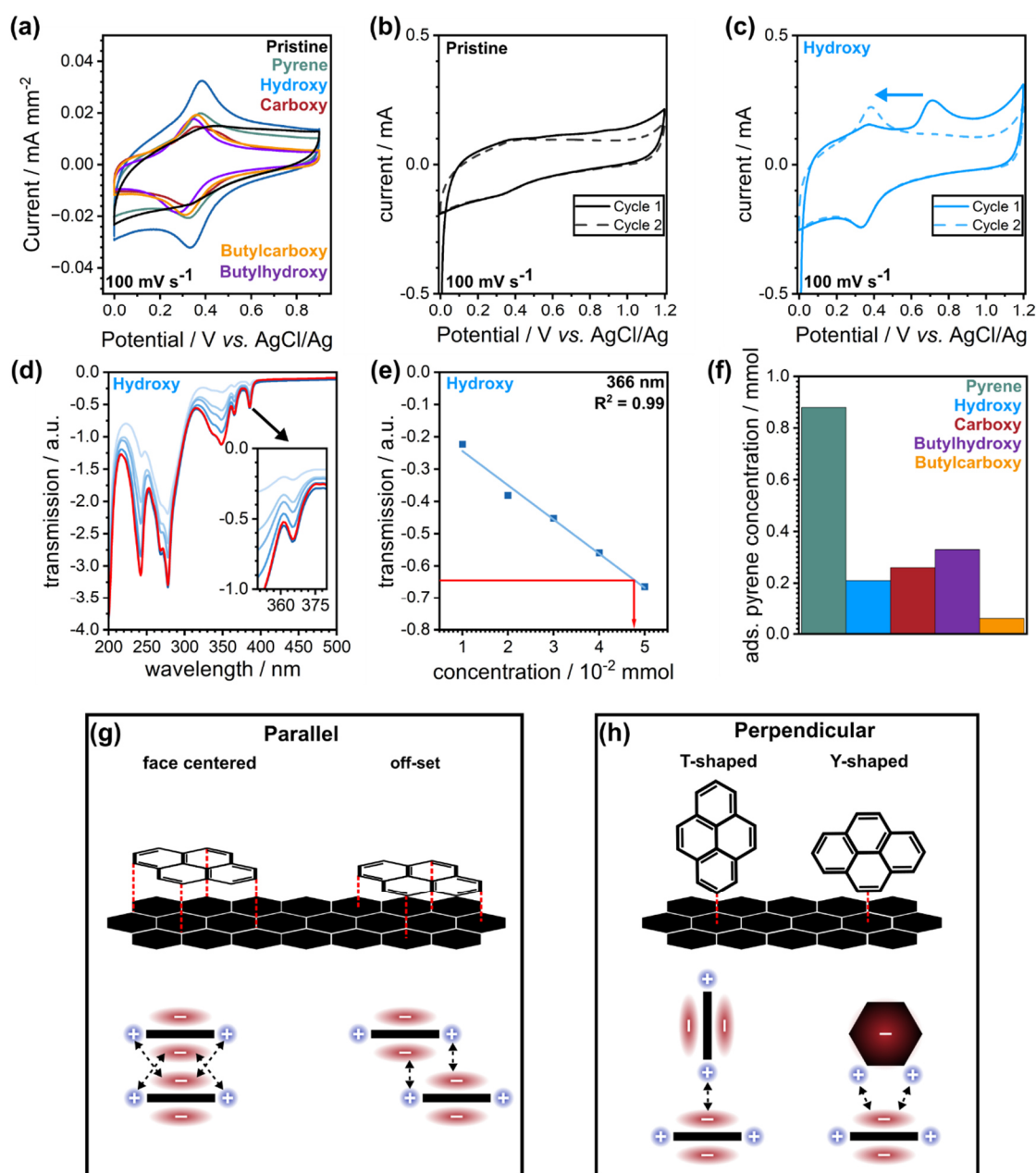


Figure 13. CV scans of pristine and pyrene-modified HC powders in H₂SO₄ (a). First two cycles of pristine (b) and hydroxy (c) modified HC. UV-VIS spectra of 1-5 mM calibration solutions (blue curves) and the supernatant solution after adsorption (red curve) (d). Lambert-Beer plot of hydroxy modified HC powder (e). Concentrations of adsorbed pyrene and its derivatives on HC (f). Schematic representation of possible adsorption geometries of pyrene derivatives on graphitic carbon surfaces: parallel (face-centered and offset) (g) and perpendicular (T- and Y-shaped) configurations (h). Panel (g) and (h) are adapted from reference [144].

4.2.2 XPS Surface Analysis

XPS provides valuable insights into the surface composition and chemical states of elements in carbon materials. C 1s detail spectra show a dominant peak at 284.4 eV corresponding to sp^2 carbon with a broad satellite peak located at 290.5 eV, resembling the $\pi-\pi^*$ shakeup feature in aromatic carbon compounds (Figure 14a).^[131] Reflecting the shift of higher oxidation states toward higher binding energies, small C–O and O=C–O peaks are observed at 286.4 eV and 289.0 eV, respectively. Although XPS is generally considered a surface-sensitive technique, the IMFP of electrons in carbon materials translates to a sampling depth of several nanometers, providing information averaged over approximately 20 atomic layers. Therefore, consistent with expectations, no change in the C 1s spectra could be observed following adsorption of oxygen functionalized pyrenes. For instance, the contribution of a carboxyl carbon (O=C–O) in 1-pyrenecarboxylic acid accounts for only 5.3 at.% of the molecule and when distributed over about 20 layers, the additional signal from surface-adsorbed pyrene becomes negligibly small.

In contrast, O 1s spectra show pronounced changes in peak shape after treatment with oxygen-functionalized pyrenes (Figure 14b). These changes are clearly visible in O 1s spectra because the intrinsic oxygen content of the HC is relatively low (~4.5 at.%), so additional surface oxygen groups noticeably modify the O 1s peak shape. In the C 1s region, such changes are not detectable because the signal is dominated by the large sp^2 carbon framework of the HC, which masks the small carbon contribution from the adsorbed pyrene derivatives. While unmodified pyrene preserves the relative intensities of the O–C and O=C components, functionalization with a hydroxy group results in an increased O–C peak, whereas carboxy-functionalized pyrenes lead to a pronounced O=C signal (Figure 14d).

In agreement with observations from UV-VIS spectrophotometry and CV measurements in sulfuric acids, XPS findings corroborate that the pyrenes are present and electrochemically active on the surface of HC.

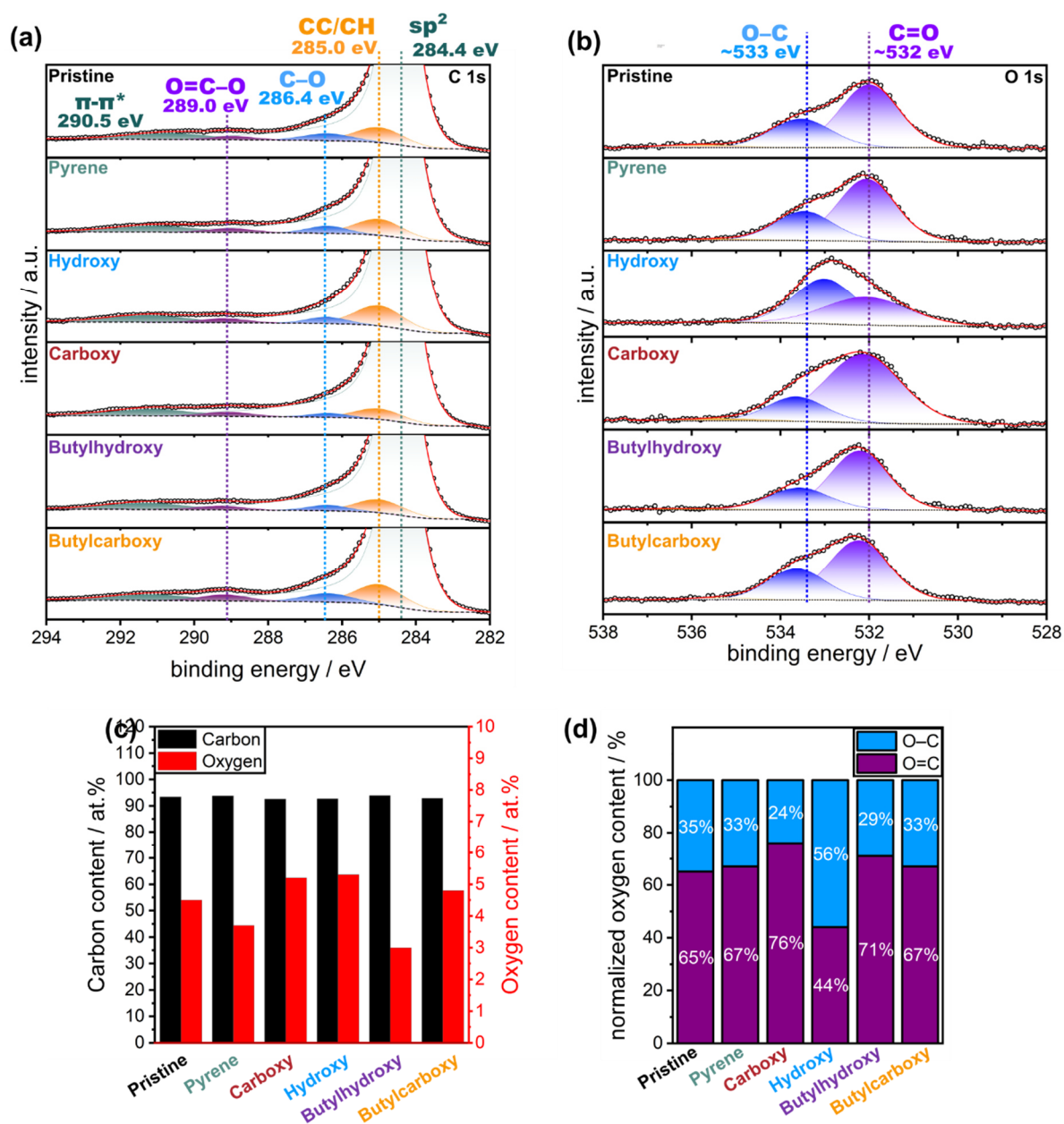


Figure 14. C 1s (a) and O 1s (b) spectra of pristine and pyrene functionalized samples. Relative composition of carbon and oxygen ratio (c) and oxygen species from O 1s spectra (d).

4.2.3 Electrochemical Characterization

Cyclic voltammetry enables the identification of potential-dependent reactions such as SEI formation, which typically appear as cathodic features during the first cycle and are absent in subsequent scans. Accordingly, HC was tested in three-electrode half-cells with the first five CV cycles of pristine and pyrene-modified electrodes shown in Figure 15. All samples exhibit a cathodic feature at ~ 1.0 V vs. Na^+/Na with varying intensity, which is attributed to SEI formation and initial electrolyte decomposition at the carbon surface.^[103] Notably, the position and intensity of this feature varies depending on the surface modification, reflecting differences in the chemical nature and coverage of the surface-modifying species, while being consistent with literature reports on functionalized carbon surfaces.^[96,98] In comparison to pristine HC, the pyrene-modified electrode shows more pronounced (de-)insertion currents in the low potential regime, which is ascribed to the storage of sodium-ions in micropores. This behavior is more likely related to modifications of the interfacial chemistry, where the adsorbed pyrene layer alters SEI formation, leading to a more favorable interphase for sodium-ion transport at low potentials. In contrast, the carboxy-modified HC shows reduced (de)insertion currents, likely due to stronger interactions between sodium ions and polar carboxyl functionalities, which modify interfacial charge-transfer processes and increase polarization.^[50] Both the butylhydroxy and hydroxy-modified electrodes exhibit a cathodic feature at ~ 0.4 V, similar to the pyrene functionalized sample, which can be attributed to additional electrolyte reduction processes facilitated by the redox-active pyrene layer.

These electronic effects are expected to influence the redox activity of the adsorbed layer and thereby modify the onset and pathway of electrolyte decomposition. For example, the oxygen substitution in the hydroxypyrene molecule draws electron density from the pyrene π -system ($-I$ effect), whereas the lone pairs of oxygen can donate electron density through a mesomeric effect ($+M$ effect).^[116] A similar outcome can be observed for the butylhydroxy electrode, where an inductive $+I$ effect of the butyl substitution donates electron density. For butylcarboxy, this effect is less pronounced, as the carboxyl functionality also draws electron density due to its high electronegativity. For carboxy electrodes, the effect is least pronounced, which is in line with a $-M$ and $-I$ effect of the direct carboxyl functionalization that draws electron density from the pyrene π -system through resonance and inductive effects.

Overall, these observations demonstrate that the electrochemical behavior is governed not solely by the presence of OFGs, but by the specific interfacial environment created by the adsorbed pyrene species, including their spatial distribution, surface coverage, and electronic properties. Importantly, these results further highlight that identical functional groups can lead to different electrochemical behavior depending on how they are introduced and distributed at the carbon interface.

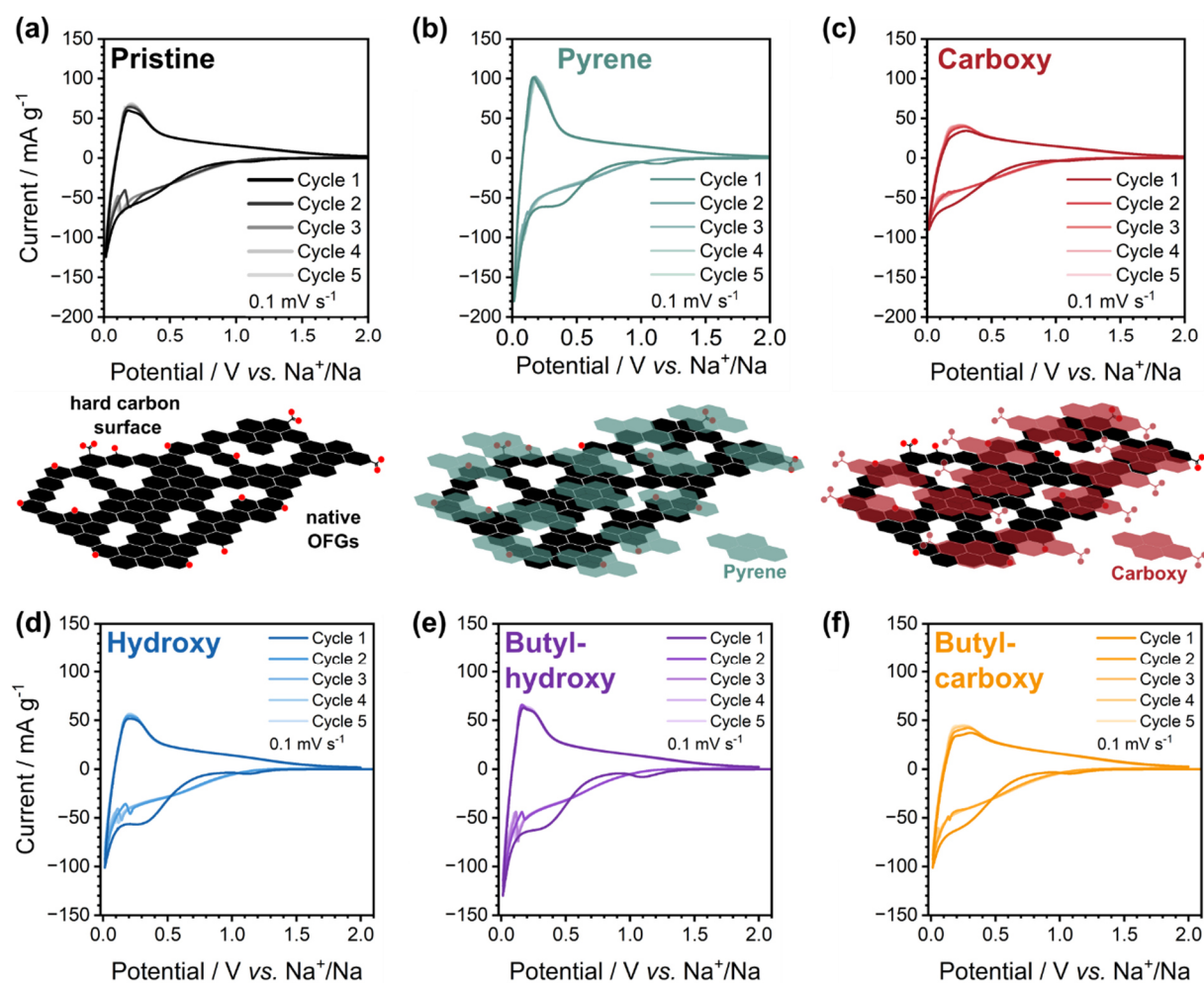


Figure 15. CV scans of pristine (a), pyrene (b) and carboxy (c) modified HCs with expected surface functionalization chemistries below. CV scans of hydroxy (d), butylhydroxy (e) and butylcarboxy (f) electrodes.

Cycling under galvanostatic conditions in three-electrode half-cells was used to evaluate the performance of HC. The reversible capacity was determined as the average of the first five cycles obtained from two independent cells. The capacity recorded above 0.1 V was assigned to the sloping region, while contributions below 0.1 V were attributed to the plateau capacity. ICEs were calculated as the average of the ratios of first-cycle charge to discharge capacity of the two cells (Table 4). Figure 16a depicts exemplary first charge-discharge profile of pristine and pyrene-modified HC electrodes. In agreement with results from CV, all pyrene-modified samples show capacity shoulders at ~1 V in varying intensities, reflecting interfacial reactions associated with the adsorbed pyrene species, consistent with SEI formation observed in CV.

Differential capacities (dQ/dV) were calculated for the first cycle and plotted as a function of potential (Figure 16c). These plots complement CV data by highlighting potential-dependent processes under galvanostatic conditions and are thus able to reveal subtle redox features. As in the CV measurements, interactions between pyrene groups and the electrolyte primarily occur near 1 V vs. Na^+/Na . This is further confirmed in the inset of Figure 16b, where modified electrodes display distinctive features in this potential region, indicative of irreversible processes associated with SEI formation. This observation supports the conclusions drawn

from the CV measurements, suggesting a pronounced interaction of the surface functional groups with the electrolyte during early stages of cycling.

ICE values for pristine and pyrene-modified HC, presented in Table 4, further illustrate the influence of surface chemistry during the first cycle. Pyrene and butylhydroxy substitution show no significant effect on the ICE, with values around fluctuating at ~82%. In contrast, carboxy and butylcarboxy substituted pyrenes reduce the ICE to 77.1 and 77.8% implying that strongly polar functional groups like carboxyl species promote pronounced electrolyte decomposition during the first cycle. Even at low surface coverage, carboxyl functional groups can act as highly reactive sites, promoting electrolyte decomposition and unstable SEI formation, which disproportionately affects the electrochemical performance. While hydroxy-functionalized pyrene exhibits a comparable reduction in ICE, its effect differs from carboxyl groups, suggesting that not only the extent but also the nature of interfacial reactions is modified. Importantly, the effects of oxygen-modified pyrene adsorption are not solely determined by the presence of OFGs, but by the local chemical environment and interaction of the adsorbed species with the electrolyte.

Rate tests were conducted at currents ranging from 50 to 1000 mA g⁻¹ to evaluate sodium-storage performance under increasing current loads (Figure 16c). At low currents of 50 mA g⁻¹, pristine HC exhibits an average reversible capacity of 187 mAh g⁻¹, whereas pyrene-modified HC exhibits slightly higher capacities of 194 mAh g⁻¹. The slightly increased capacity of pyrene-modified HC at low current is attributed to improved interfacial conditions and more favorable SEI formation rather than structural changes in the pore system. The pronounced decrease in plateau capacity for oxygen-functionalized pyrenes indicates that sodium storage in micropores is strongly affected by the interfacial conditions governing sodium insertion. This suggests that unfavorable SEI formation can hinder efficient pore filling, even when the pore structure itself remains unchanged.^[78]

At higher current densities, the electrochemical response becomes increasingly dominated by kinetic limitations, including diffusion constraints and polarization effects. These limitations are more pronounced for oxygen-functionalized pyrene systems due to less favorable interfacial properties, which lead to increased polarization and reduced accessible capacity already at moderate current densities.

This behavior is reflected in the significantly reduced reversible capacities of oxygen-modified pyrenes (~100 mAh g⁻¹) and the pronounced decrease in plateau capacity, resulting in a shift toward slope-dominated storage. This effect is particularly evident for hydroxy-functionalized pyrene, which exhibits the highest slope-to-plateau ratio (1.50), highlighting its strong impact on interfacial conditions governing sodium insertion into micropores.

The increased polarization accelerates the approach to the cut-off potential (5 mV vs. Na^+/Na), thereby artificially limiting the accessible capacity even at 50 mA g^{-1} . At higher current densities, these interfacial differences become less distinguishable, as the electrochemical response of all samples converges and is dominated by transport limitations within the electrode.

To further evaluate the intrinsic sodium storage capability independent of kinetic limitations, additional measurements were conducted at low current densities ($\sim 7\text{--}11 \text{ mA g}^{-1}$). The applied current of the first five cycles corresponds to C/20 based on a theoretical full-cell pairing with an NVP/C cathode delivering a capacity of 1.2 mAh. The resulting variation in current density arises from differences in anode active material loading and should not significantly affect the electrochemical response at these low rates.

Under these low-current conditions, all samples exhibit reversible capacities well over 200 mAh g^{-1} , indicating that the intrinsic sodium storage capability of the HC is preserved regardless of pyrene modification (Figure 16d). In particular, the plateau region, which is strongly suppressed at higher currents for oxygen-functionalized pyrenes, is fully accessible, demonstrating that the pore structure and attributed sodium storage itself remains unchanged.

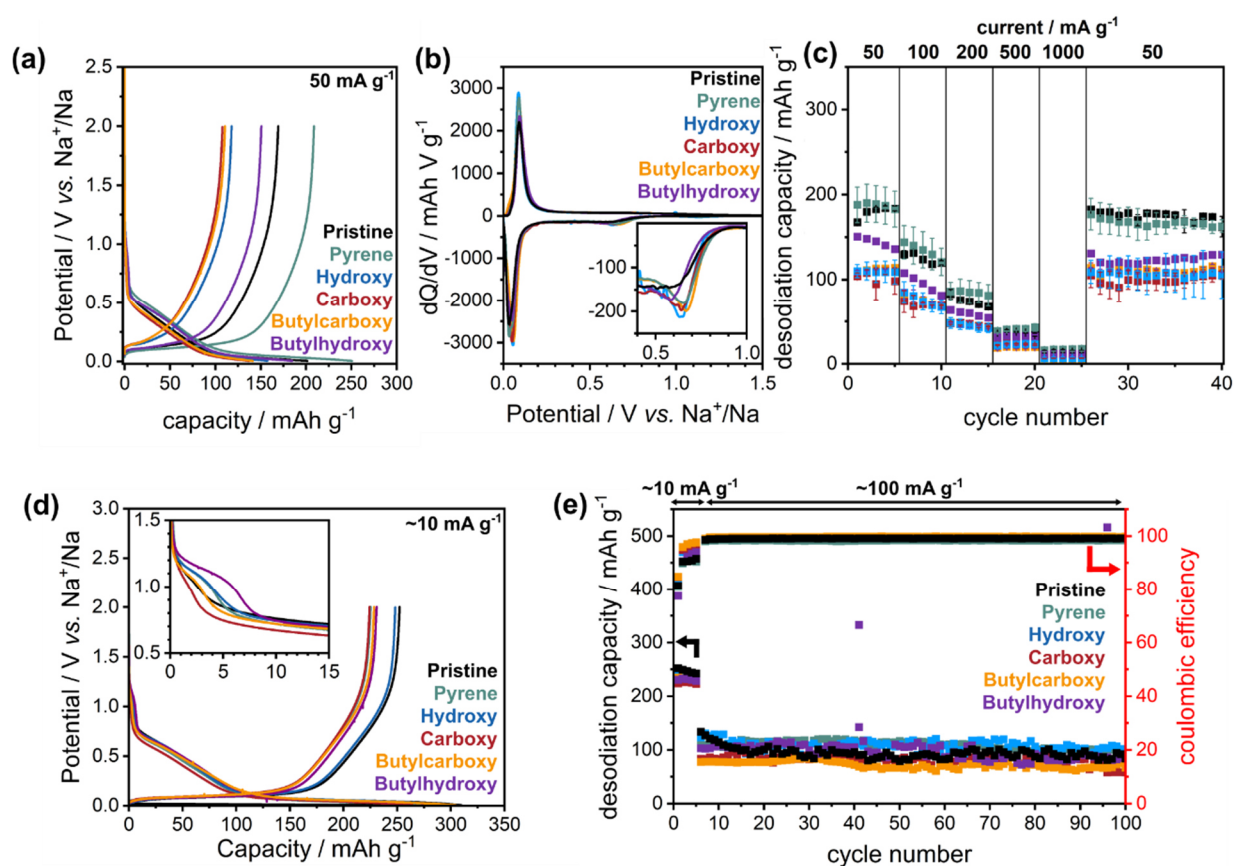


Figure 16. First cycle of galvanostatic charge-discharge potential vs. capacity profiles of pristine and pyrene functionalized HC samples (a). Corresponding differential capacity plots (b). Rate tests (c). Lower current density (d). Long-Term cycling (e).

Table 4. Overview of pristine HC and pyrene functionalized samples with their reversible capacities, slope- and plateau capacities, and initial coulomb efficiencies (mean $\pm$ standard deviation).

	reversible capacity at 50 mA g⁻¹	slope capacity	plateau capacity	slope / plateau ratio	ICE
	/ mAh g ⁻¹	/ mAh g ⁻¹	/ mAh g ⁻¹		/ %
Pristine	187 $\pm$ 3	71 $\pm$ 1	116 $\pm$ 2	0.62	83.4 $\pm$ 0.4
Pyrene	194 $\pm$ 24	75 $\pm$ 2	118 $\pm$ 22	0.65	82.3 $\pm$ 0.9
Hydroxy	113 $\pm$ 14	66 $\pm$ 2	47 $\pm$ 12	1.50	76.3 $\pm$ 1.4
Carboxy	113 $\pm$ 3	59 $\pm$ 3	54 $\pm$ 1	1.10	77.1 $\pm$ 1.6
Butylcarboxy	115 $\pm$ 1	61 $\pm$ 2	54 $\pm$ 1	1.12	77.8 $\pm$ 0.6
Butylhydroxy	135 $\pm$ 17	68 $\pm$ 1	67 $\pm$ 17	1.12	81.6 $\pm$ 0.0

After five cycles at C/20, the current was increased to C/2 to assess whether a collapse of the reversible capacity occurs for the pyrene-modified samples under higher-rate conditions. It should be noted that the applied current densities during C/2 cycling vary between 70 and 110 mA g⁻¹ due to differences in electrode loading arising from the full-cell balancing approach. While such variations are expected to influence polarization behavior, the observed performance trends do not correlate with the applied current density (Figure 16e). For instance, samples with lower effective current densities (e.g. butylcarboxy) still exhibit significantly reduced capacities, whereas pyrene-modified electrodes maintain comparatively higher capacities despite being cycled at higher current densities. This lack of correlation indicates that the electrochemical behavior is not governed by differences in applied current, but rather by interfacial effects related to the chemical nature of the adsorbed species. This demonstrates that the interfacial properties established during the first cycle are not transient, but also define the long-term electrochemical behavior.

The absence of improved performance for both pristine and pyrene-modified electrodes during C/2 cycling suggests that SEI formation differs from that at higher current densities, thereby influencing the accessible reversible capacity.^[78] Furthermore, hydroxy-functionalized pyrene exhibits the highest reversible capacities during prolonged cycling despite reduced ICE in rate-tests, suggesting the formation of a more favorable interphase formation at lower currents. In contrast, carboxyl-functionalized systems maintain lower ICEs, indicating persistent limitations in interfacial charge transfer and increased polarization.

These findings confirm that the performance differences observed at higher current densities do not originate from structural variations in the pore system, but rather from interfacial effects that govern the kinetic accessibility of sodium storage sites. In this context, the increased SEI resistance and polarization induced by oxygen-functionalized pyrenes limit sodium insertion into micropores under practical cycling conditions, while the total storage capacity remains fundamentally unaffected.

4.2.4 Conclusion

Although pyrene adsorption on HC could be clearly confirmed by CV, UV–Vis spectrophotometry, and XPS, the results demonstrate that the electrochemical impact of OFGs is highly complex and cannot be understood solely by their chemical identity alone. Instead, their influence is governed by the specific interfacial environment created by the adsorbed species, including their spatial distribution, surface coverage, and electronic properties.

While pyrene-derived oxygen functionalities significantly influence SEI formation and exhibit distinct electrochemical activity, their impact on ICE is less pronounced than expected. Despite the introduction of well-defined surface functionalities, no substantial changes in ICE were observed. This may be attributed to a comparatively low effective concentration of introduced OFGs at the surface by pyrene adsorption, as well as a potential partial desorption of the species in the electrolyte during cycling.

Instead, the most notable effect is a reduction in reversible capacity, which is attributed to modifications of the interfacial layer. These findings suggest that OFGs primarily influence the nature of the SEI and the resulting interfacial transport properties, thereby limiting the accessibility of sodium storage sites rather than altering the intrinsic storage capability of the carbon.

This is further evidenced by the suppression of plateau capacity observed for oxygen-functionalized pyrenes under increasing current loads highlights that efficient sodium storage in micropores is not solely determined by the pore structure itself, but critically depends on the interfacial conditions that govern sodium insertion during SEI formation. These findings demonstrate that initial electrochemical behavior is dominated by surface chemistry, whereas rate capability is dominated by the efficient accessibility and utilization of the internal pore network.

Importantly, this model system reveals that identical oxygen functionalities can lead to fundamentally different electrochemical behavior depending on how they are introduced. In the present case, adsorption of functionalized pyrenes creates chemically distinct interfacial environments. As will be shown in the following chapter, oxygen functionalities introduced directly into the carbon framework *via* ozone treatment can exhibit markedly different effects, highlighting the critical role of the mode of incorporation in determining electrochemical performance.

4.3 Ozone treatment as a covalent Functionalization Method

To address the limitations identified for non-covalent surface modification by adsorption of functionalized pyrenes, this chapter investigates ozone as a controlled oxidative treatment capable of directly functionalizing the HC surface or structurally degrade the carbon framework.

The subchapters 4.3.1 to 4.3.6 are extracted from the submitted manuscript “Ozone-Induced Surface Functionalization of Hard Carbon for Sodium-Ion Batteries: Mechanism, Composition, and Electrochemical Impact”.

4.3.1 Preliminary Characterization of Hard Carbon

Oxygen surface functionalization of HC was achieved by subjecting the HC, which was pyrolyzed at 850°C, to a stream of ozone at different temperatures. To maintain consistent nomenclature, samples are denoted as HC–X–T, where X describes the atmosphere of the treatment (O₃ or O₂) and T the treatment temperature in °C.

Particle morphology and surface texture were examined by SEM. Figure 17 presents the spherical morphology of pristine HC which has an average particle size of 3.9 µm. A quantitative particle size distribution derived from SEM image analysis is provided in Figure S3. HC–O₃–25 exhibits no morphological differences compared to HC and also the average diameter is comparable. In contrast, HC–O₃–60 and HC–O₃–100 yield smaller average diameters of 3.4 and 3.2 µm, respectively. In addition, spheres display pronounced surface roughening. This can be attributed to the increased oxidative reactivity of ozone at elevated temperatures that leads to carbon surface erosion, which would also cause the loss of near-surface carbon mass and structural degradation. This interpretation is supported by the observed mass loss (17.8%) for HC–O₃–100 (Table 5). Given the open porosity of HC, the observed structural degradation at elevated ozone-treatment temperatures is not limited to the external particle surface but likely also propagates into the particle.

Treatment in oxygen at 100°C was also tested to isolate the role of ozone in the functionalization process resulting in the sample HC–O₂–100 (Figure 17e). In comparison with the other samples, morphology of the spheres closely resembles pristine HC and lacks the ozone-induced surface features, confirming that ozone and not oxygen alone drives the observed morphological changes.

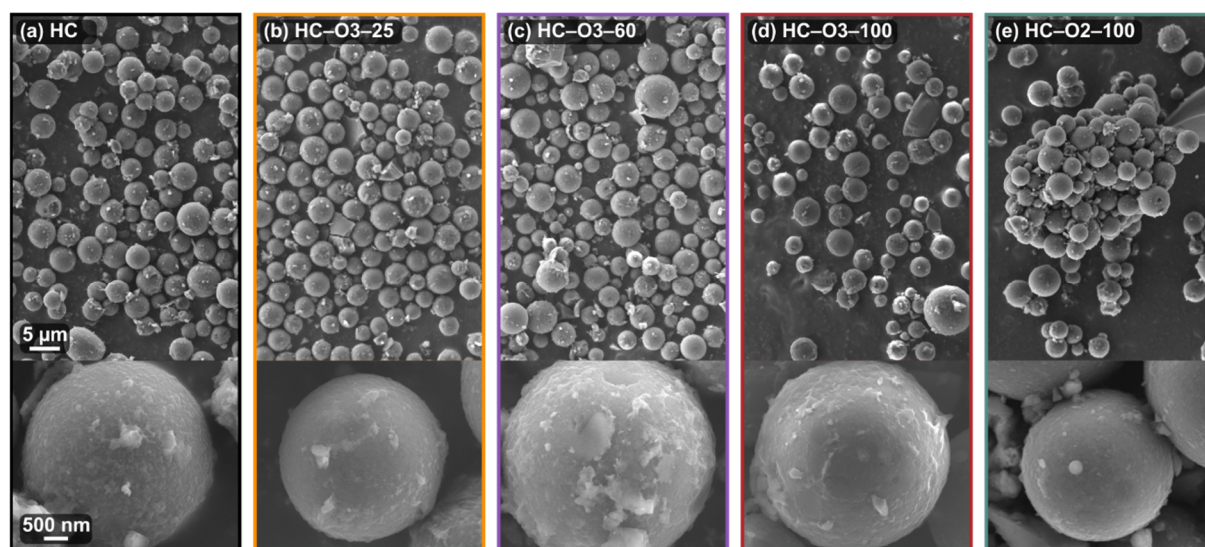


Figure 17. HC morphologies at different magnifications. a) Pristine hard carbon. b)-d) HC powder treated in O₃ at room temperature, 60°C and 100°C for 3 hours. d) HC powder treated in O₂ at 100°C for 3 hours.

Table 5. Residual masses of HC after ozone or oxygen treatment and average sphere diameter from particle size distribution analysis.

Sample	Residual mass after treatment / %	Average sphere diameter / μm
HC	-	3.9
HC-O3-25	105.5	3.7
HC-O3-60	98.2	3.4
HC-O3-100	82.2	3.2
HC-O2-100	95.4	3.6

HC-O3-100 was immersed in water to determine whether low-molecular highly-oxidized compounds (LOCs) were formed, which would be indicative of carbon erosion resulting in the sample denoted as HC-O3-100W. After separation of the carbon from the liquid phase by centrifugation, the supernatant formed a dark, non-sedimenting dispersion, which accounted for ~15% of the sample mass after drying (Figure S4a), suggesting the presence of LOCs. SEM imaging of the dried dispersion showed a non-conductive, brittle film (Figure S4b), which aligns with the expectations of low-molecular, highly oxidized carbonaceous fragments. The morphology and surface texture of HC-O3-100W spheres differ markedly from the other samples, exhibiting a much smoother surface, which suggests that the particles are also encapsulated by LOCs. Despite three consecutive washing steps, the LOC film could not be visibly removed, suggesting that for HC-O3-100 also the surface reacts with the LOCs, thereby anchoring them on the surface. Nonetheless, the LOC film on the surface is very small, as no notable increase in the average particle size could be detected (Figure S4c-e).

The reactivity of the HC-O3-100 surface is further corroborated by observations made during electrode fabrication, as agglomeration of the slurry occurred upon the addition of the aqueous SBR-CMC binder mixture. The agglomeration can plausibly be explained by a pH shift due to potentially introduced acidic surface groups by the ozone treatment, which affect the CMC binder. On the other hand, SBR contains unsaturated double bonds that are susceptible to

radical-initiated reactions, and ozone in aqueous environments can generate hydroxyl radicals ($\cdot\text{OH}$) capable of attacking such moieties.^[145,146] In the presence of reactive oxygen species, radical-mediated crosslinking of SBR may explain the observed agglomeration.

4.3.2 Surface Chemistry of Ozone treated Hard Carbon

XPS analysis was employed to determine the surface elemental composition and carbon/oxygen chemical environments, enabling detailed analysis of oxidation and bonding states in HC. High-resolution C 1s spectra (Figure 18a) of HC are dominated by an asymmetric sp^2 C–C peak at 284.4 eV with a π – π^* shake-up feature at ~290.5 eV, characteristic of sp^2 domains.^[132] Weak higher binding energy contributions correspond to C–O (~286.6 eV) and O=C–O (~289.0 eV) species, associated with hydroxyl/ether and carboxyl-type functionalities, respectively. Ozone treatment markedly increases the oxygen content, which rises from 5.9 at.% for HC to 21.0 at.% for HC–O3–25 (Figure 18d). Notably, oxygen uptake is non-monotonic with temperature, decreasing slightly from 30.5 at.% for HC–O3–60 to 27.9 at.% for HC–O3–100. The reduced oxygen content at 100 °C likely reflects the temperature-accelerated oxidation rate that promotes OFG cleavage and CO_2 release, consistent with Arrhenius-type kinetics.

HC–O3–25 exhibits strongly increased C–O and O=C–O contributions, confirming effective surface oxidation. Additional features appear at ~288.0 eV, assigned to O–C–O and C=O species, and at ~285.0 eV, attributed to sp^3 carbon and carbon adjacent to oxygenated sites.^[147] With increasing treatment temperature, oxygen-related peaks broaden and intensify, indicating higher OFG concentrations and increased chemical heterogeneity. Simultaneously, the relative intensity of the sp^2 peak decreases, while its FWHM increases from 1.1 to 1.3 eV, indicating increased structural disorder. The O=C–O peak at ~289.0 eV becomes the dominant oxidized-carbon feature, identifying carboxyl-type species as major oxidation products. HC–O3–100W demonstrates a slight increase in the sp^2 carbon contribution compared to HC–O3–100 (Figure S5a), reinforcing the plausible presence of LOCs on the surface. In contrast, the intensities of oxidized-carbon spectral components (C–O, C=O, O=C–O) remain unchanged, indicating that the dominant surface functionalities persist after washing. Only O–C–O and C=O contributions decrease, suggesting that these groups undergo hydrolysis upon contact with water.

Analysis of the washed supernatant confirms this interpretation: peaks and intensities in C 1s spectra closely match those of HC–O3–100, but lack O–C–O, C=O and sp^2 peaks (Figure S5b). IR spectroscopy of the centrifugate corroborates the high concentration of OFGs in LOCs (Figure S5c). Washing thus removes the LOCs only partly and promotes encapsulation of the spheres with a surface layer.

O 1s spectra (Figure 18b) offer complementary information, however interpretation is impeded by overlapping binding energies, which prevents unambiguous determination. Spectra were deconvoluted into three components: single-bonded O–C (~ 533 eV), double-bonded O=C (~ 532 eV), and a high-binding-energy component at ~ 535.5 eV attributed to adsorbed water.^[148] Figure 18e shows that the O=C–O contribution in the C 1s spectra increases steadily with higher ozone-treatment temperatures. In contrast, the sp^3 -carbon fraction remains constant at approximately 30 at.%, suggesting that a steady-state composition is reached at high temperatures. This interpretation is supported by the observation that the intensities of the C–O and C=O/O–C–O components do not continue to rise, identifying them as intermediate reaction products. Figure 18f depicts the distribution of oxygen species in O 1s spectra. HC–O3–25 and HC–O2–100 show an increased proportion of O=C-type contributions. In contrast, treatments conducted with ozone at elevated temperatures result in spectra in which O–C species become slightly more dominant.

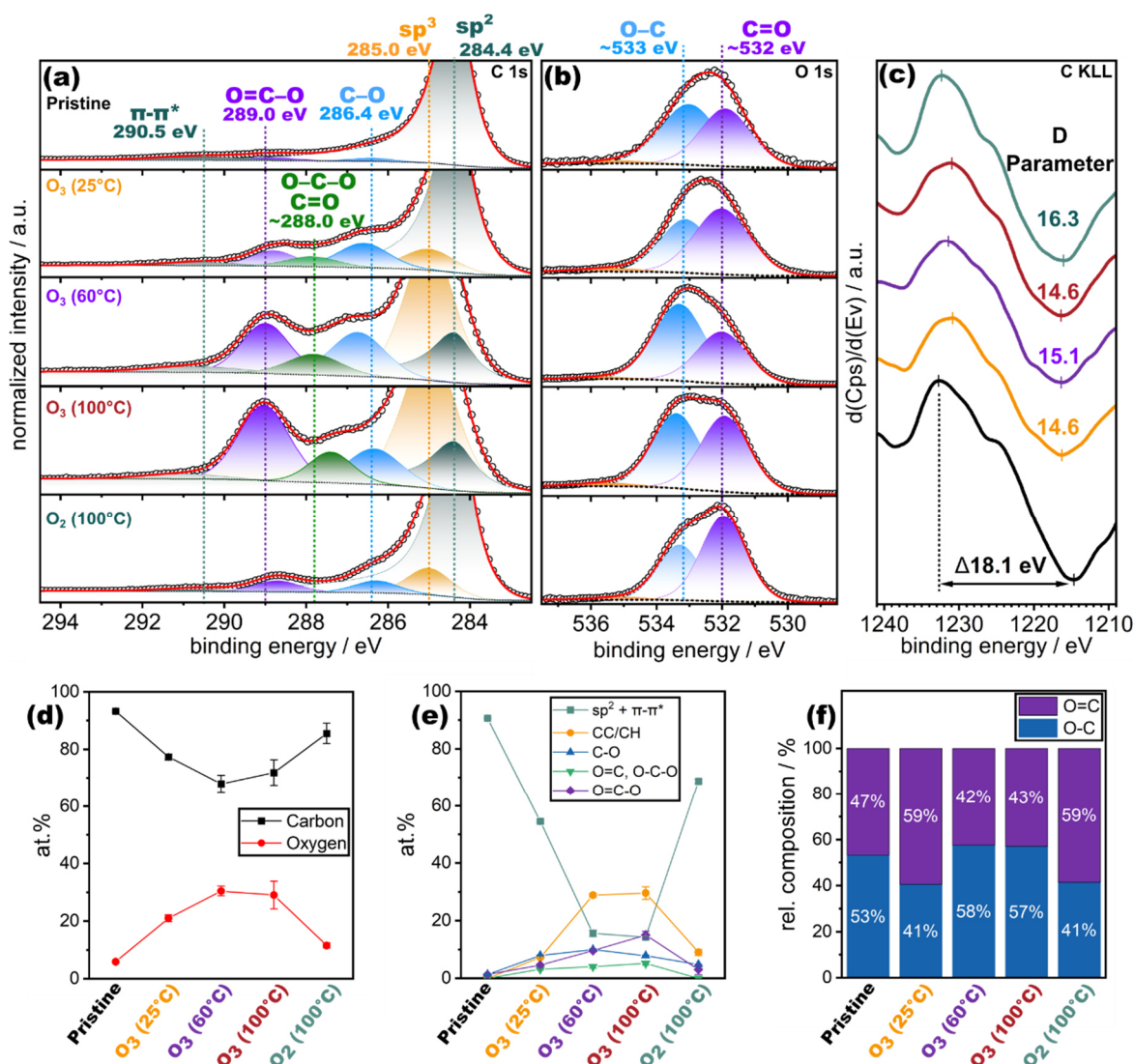


Figure 18. C 1s (a) and O 1s (b) spectra of pristine and functionalized HC samples. Relative carbon and oxygen concentrations (c) and individual component contributions in C 1s (d) and O 1s (e) spectra.

To further resolve the depth dependence of ozone-induced oxidation, carbon KLL Auger peaks were evaluated for a complementary, highly surface-sensitive analysis (Figure 18c). In contrast to C 1s and O 1s photoelectrons, which probe several nanometers into the carbon matrix, the three-electron process of C KLL Auger emission generates electrons with low kinetic energy and thus a significantly reduced IMFP. Consequently, the detected signal originates almost exclusively from the outermost surface, enabling a more differentiated assessment of surface-confined vs. subsurface oxidation when combined with C 1s spectra results.

Surface graphitization was quantified using the D-parameter, which is defined as the energy separation between the extrema in the first derivative of the C KLL Auger transition. This semi-empirical descriptor varies from approximately 13 eV for sp^3 -rich carbon to about 22.5 eV for purely sp^2 -hybridized graphite-like materials.^[64] HC exhibits a D-parameter of 18.1 eV, corresponding to a sp^2 fraction of approximately 34%, which is characteristic of amorphous carbon materials.

Independent of the applied treatment temperature, ozone exposure leads to a pronounced reduction of the D-parameter to values between 14.6 and 15.1 eV, indicating a surface sp^2 contribution below 10%. In contrast, HC–O2–100 lowers the D-Parameter only to 16.3, which underscores the reactivity of ozone compared to oxygen. In conjunction with C 1s and O 1s spectra probing deeper regions of the material, these results reveal distinct oxidation depths. For HC–O3–25, oxidation is largely confined to the outermost surface layer, whereas ozone treatments at elevated temperatures induce oxidation extending into subsurface regions.

This distinction is of critical relevance for electrochemical performance. While surface OFGs directly influence SEI formation and interfacial charge transfer, subsurface oxidation may promote additional irreversible capacity losses by trapping sodium ions within the carbon matrix. The combined analysis of photoelectrons and Auger electrons therefore emphasizes that not only the amount, but also the spatial distribution of oxygen functionalities should be considered during electrochemical testing.

4.3.3 Proposed Model for Ozone Surface Functionalization of HC

A mechanistic framework inspired by classical Criegee-type ozonolysis is proposed to explain the formation of OFGs on HC surfaces. In its original formulation, ozonolysis involves the reaction of ozone with aliphatic C=C bonds through reactive intermediates.^[117] Although originally postulated for organic molecules, this concept has been adapted to describe reactions occurring on carbonaceous materials.^[119,149–151]

Figure 19 outlines the proposed reaction sequence for carbon edge sites:

(I) Initial ozone exposure:

Ozone first adds to carbon edge sites *via* a concerted 1,3-dipolar cycloaddition. This step is driven by HOMO–LUMO interactions between the electron-rich C=C sites and the electrophilic O₃ molecule (Figure S6).

(II) Formation of a molozonide:

The cycloaddition yields a short-lived, unstable molozonide intermediate.

(III) Fragmentation to a Criegee intermediate:

The molozonide rapidly decomposes and rearranges to produce a carbonyl oxide species, referred to as a “Criegee intermediate”.

(IV) Cyclization to a trioxolane:

Intramolecular ring closure of the Criegee intermediate leads to formation of a trioxolane.

(V) Hydrolysis and further oxidation:

Upon contact with water, molecular oxygen, or excess ozone, the trioxolane undergoes hydrolysis or oxidative cleavage, ultimately generating carboxyl, carbonyl, and hydroxyl surface functionalities on the HC structure.

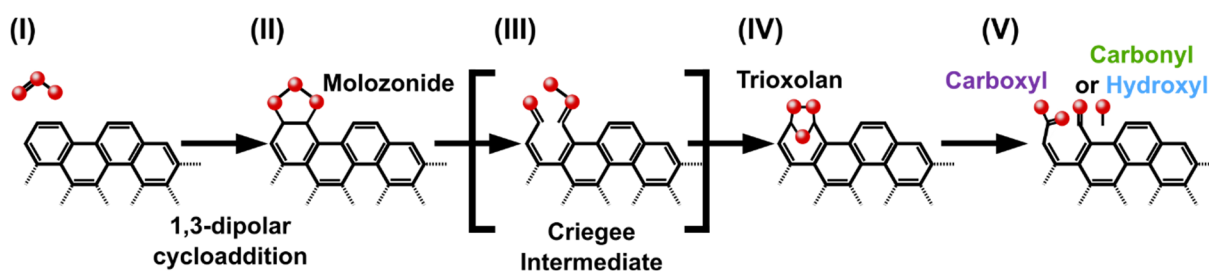


Figure 19. Proposed reaction mechanism of ozone with HC.

The relation between this mechanistic sequence and the carbon oxidation states probed by XPS is illustrated in Figure 20. Pristine HC is dominated by sp²-hybridized carbon (284.4 eV) with minimal contributions from oxidized species, consistent with an essentially intact graphitic lattice (I). Upon initial ozone exposure, C–O-type species begin to form at edge and defect sites, reflected by the growth of the peak at ~286.6 eV. Rearrangement to trioxolane-like intermediates corresponds to the appearance of an O–C–O signal near 288 eV (II).

With ongoing hydrolysis or oxidation, carboxyl-type groups arise, indicated by the intensification of the O=C–O peak at ~ 289.0 eV (III). At this stage, the coexistence of several oxidation states reflects the sequential multistep reaction mechanism. Extended ozone treatment further increases the abundance of oxidized species while reducing contributions from sp^2 carbon, revealing progressive functionalization of the graphitic structure and a higher degree of surface oxidation.

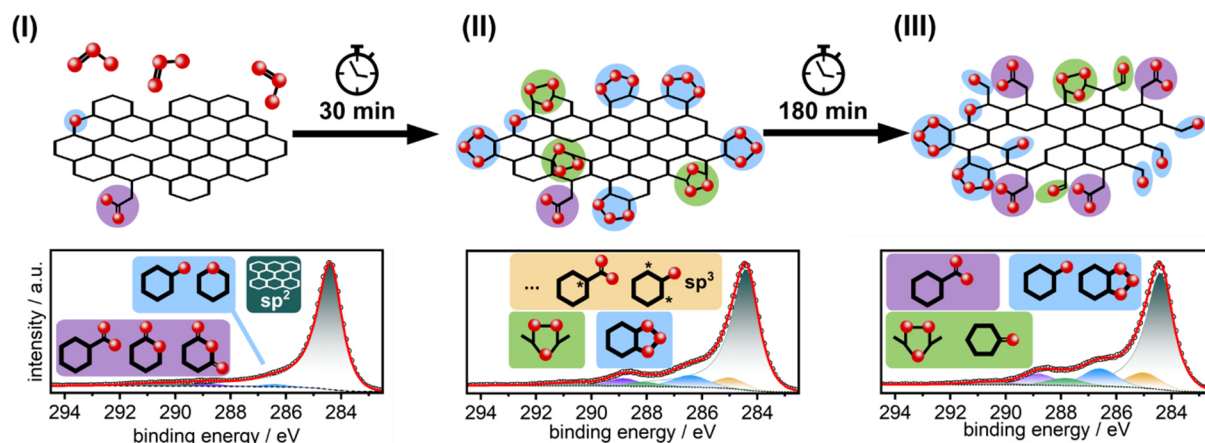


Figure 20. Proposed functionalization mechanism of the HC surface with corresponding C 1s detail spectra of the involved functional groups.

However, this model alone cannot explain the generation of LOCs which are clearly observed for HC treated in ozone at higher temperatures. Therefore, the model was expanded to account for the LOC generation (Figure 21). The pristine HC features an intact sp^2 domain with a low amount of native OFGs present after pyrolysis (I). At 25 °C ozone treatment temperature, reaction kinetics are slow and ozone molecules mainly functionalize edge and defect sites, which does not lead to significant LOC generation (II). Based on activation energies for oxidative and surface-bound reactions, increasing the temperature from 25 °C to 60 °C accelerates the reaction by approximately one order of magnitude, corresponding to a significant accelerated reaction rate, which accounts for the increased LOC formation (III). Ozone molecules do not only functionalize edges, but also act as a "molecular scissor" and excise LOCs out of the HC sp^2 planes. Because ozone can diffuse through the intrinsic open porosity of HC, LOC formation is expected to occur not only at the external surface but also within the particle. However, the thermal energy at 60 °C remains insufficient to promote significant conversion of these fragments into CO_2 , which agrees with the observed low mass loss of HC–O3–60. The highest reaction rate is thus expected for HC–O3–100 and at this temperature, it is also plausible that LOCs further degrade to CO_2 explaining the significant mass loss (IV).

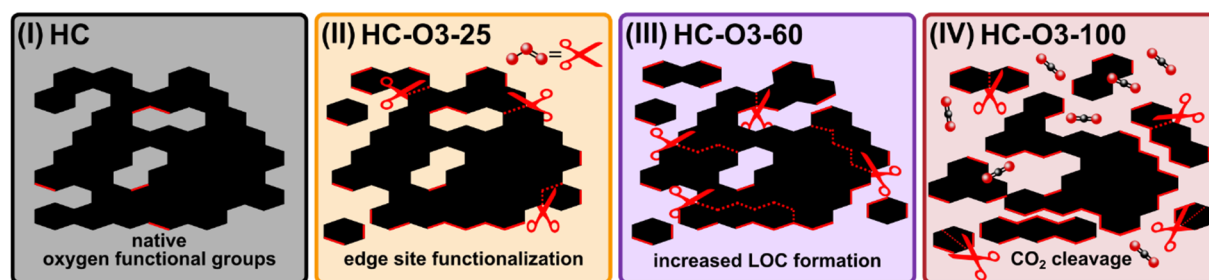


Figure 21. Proposed functionalization mechanism and generation of LOCs on the hard carbon with ozone at different temperatures.

Overall, the proposed ozonolysis model provides a coherent explanation for both the evolution of OFGs on HC observed by XPS and the appearance of LOCs for treatment at higher temperatures.

4.3.4 Validation of the Ozonolysis Mechanism using Model Carbon Substrates

To further elucidate ozone reactivity on carbon materials and evaluate the proposed mechanism, glassy carbon electrodes (GCE) and highly ordered pyrolytic graphite (HOPG) were subjected to identical ozone treatments at 25 °C and 100 °C. Glassy carbon can be considered as a dense form of HC synthesized by high-temperature pyrolysis (~3000 °C), which removes intrinsic oxygen and leads to very low porosity. Because sodium does not significantly insert into GCEs, its electrochemical response is dominated by surface processes. XPS depth profiling proves that oxygen signals of pristine GCEs disappear after ~60 s of Ar⁺ sputtering (Figure 22a). Upon treatment in ozone, the oxygen content significantly increases to 6.8 at 25°C and 40.3 at.% at 100°C and is accompanied by significant decrease in the D-Parameter from 22.4 to 15.2 (Figure 22b,c).

A visual change upon treatment in ozone could only be seen for the 100°C sample, which exhibited an altered visual appearance under the microscope, where the GCE was exposed in the O₃ stream (Figure 22d). SEM images reveal that pristine GCE possess a smooth and featureless surface, which is conserved during treatment in ozone at 25°C. In contrast, the GCE subjected to ozone at 100 °C exhibits a pronounced microstructured, fractal ridge-like surface morphology. This observation suggests that ozone preferentially attacks defects and edge sites, which are progressively degraded at elevated temperatures as the reaction advances deeper into the carbon matrix.

The morphological changes observed by SEM are further corroborated by XPS analysis of C 1s and O 1s detail spectra. Although no pronounced differences are observed in C 1s spectra between the pristine and 25°C treated GCE, O 1s spectra reveal an increased contribution of O–C species, which is in agreement to C 1s spectra from HC (Figure 22e). This indicates that functionalization is largely restricted to the outermost surface layer, since the C 1s signal also includes contributions from subsurface carbon, whereas the oxygen signal can exclusively originate from surface-bound species (Figure 22f). Consistent with the strong

structural degradation observed by SEM, GCEs treated at 100 °C exhibit a high abundance of oxidized carbon species in the C 1s region as well as a prominent oxygen signal in O 1s spectra.

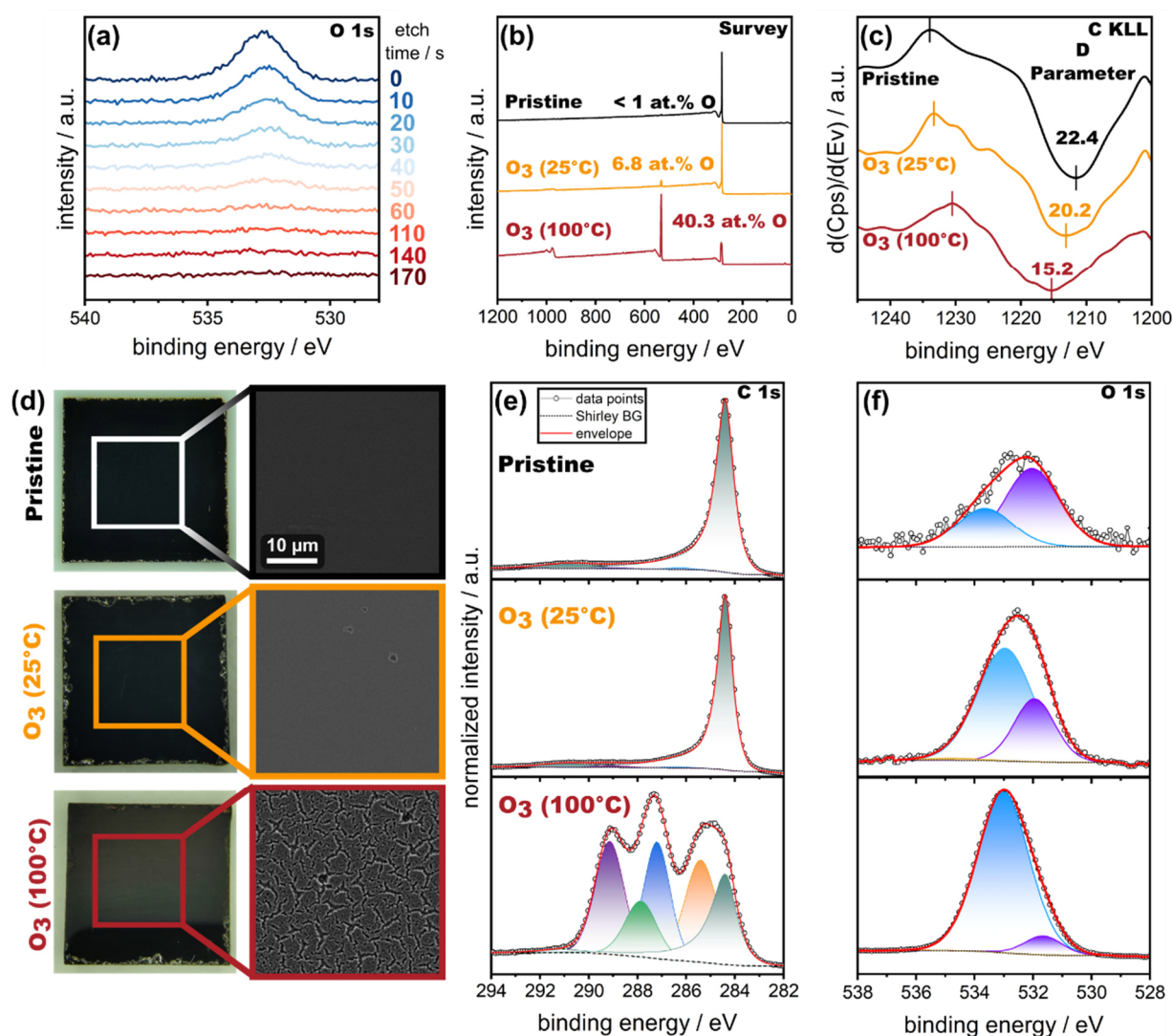


Figure 22. O 1s depth profile of a pristine GCE electrode (a), survey spectra of pristine and ozone treated GCEs (b) and KLL Auger peak analysis (c). Optical microscope and SEM images of pristine and ozone treated GCEs (d). Stacked C 1s spectra of the GCEs (e) and corresponding O 1s spectra (f).

HOPG was used as a model substrate for a low-defect, basal-plane dominated model substrate. Because the lateral size of basal-plane sp^2 domains in HOPG exceeds the geometric contribution of edge sites by several orders of magnitude, both ozone interaction and XPS analysis predominantly probe basal-plane carbon, with edge sites contributing less than ~1 % to the detected signal.

Freshly cleaved HOPG shows no detectable oxygen signal (Figure 23a). Here, ozone treatment at 25°C introduces a small oxygen fraction (2.5 at. %), consistent with limited basal-plane reactivity reported in literature.^[151] This indicates that also the basal plane is functionalized by ozone, but the effect is far less pronounced than on edge sites. When ozone

treatment is conducted at 100 °C, the total oxygen content remains essentially unchanged (2.1 at.%), suggesting that no significant additional basal-plane oxidation occurs under these conditions.

In contrast, a HOPG surface that was intentionally mechanically damaged (roughened) prior to ozone exposure at 100 °C exhibits a markedly higher oxygen content of 4.4 at.%. As the entire XPS analysis area was located on a mechanically roughened region of HOPG, an edge-rich, defect-dominated surface was observed. This pronounced increase in oxygen concentration provides further evidence that defects and edge sites constitute the primary attack sites for ozone on graphitic carbon, whereas the basal plane remains comparatively inert. Surface textures of pristine and roughened electrodes were assessed by SEM (Figure 23b).

The pristine HOPG crystal does not feature any visible surface structures whereas the surface of a roughened surface shows a highly delaminated graphitic structure with torn, stacked, and irregularly uplifted lamellar flakes. Compared to untreated scratched HOPG, the 100 °C O₃ treated surface shows smoother, more rounded lamellar edges, fewer large delamination features, more compact and less uplifted sheet structures, as well as small bright particulate deposits that likely originate from oxidation-induced surface residues.

Taken together, the experiments on GCE and HOPG demonstrate that ozone functionalization predominantly occurs at defect and edge sites, while the basal plane of sp² is mostly unreactive to ozone. Furthermore, the treatment temperature governs the transition from selective surface functionalization to pronounced structural degradation.

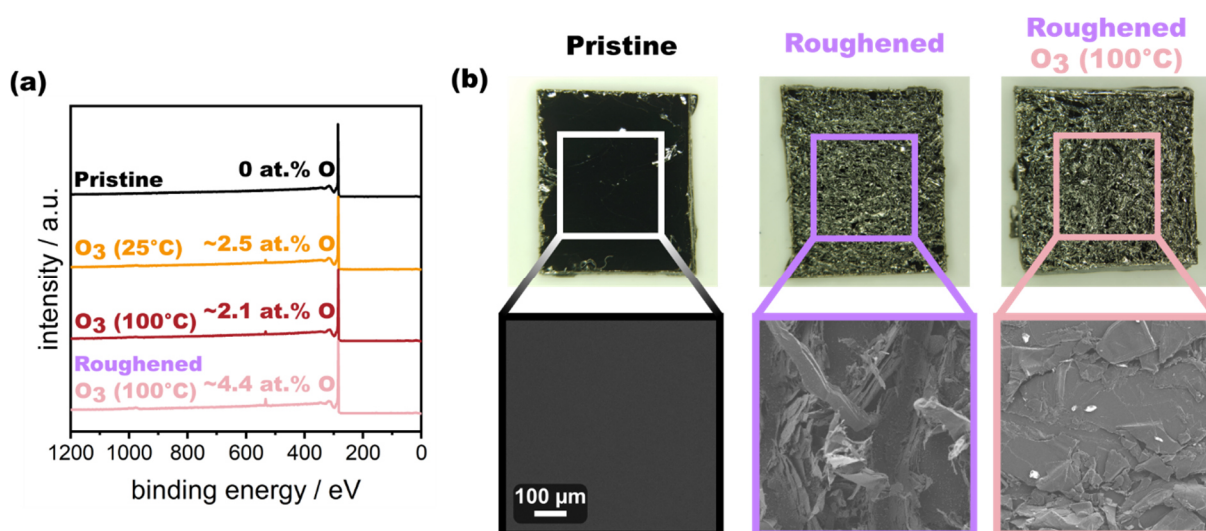


Figure 23. Survey spectra of pristine and ozone treated HOPG crystals (a) with corresponding microscope and SEM images (b).

4.3.5 Structural and Thermogravimetric Characterization

To discriminate surface functionalization from possible bulk structural modifications, Raman spectroscopy was employed. In Raman spectroscopy, photons are inelastically scattered at molecular vibrations, whereby they either lose (Stokes-shift) or gain energy (Anti-Stokes-shift). The corresponding frequency shifts are measured. For carbon materials, the Raman spectrum is highly sensitive to disorder: the D band ($\sim 1338\text{ cm}^{-1}$) arises from defect-activated breathing modes of sp^2 carbon units, whereas the G band ($\sim 1586\text{ cm}^{-1}$) corresponds to in-plane stretching of sp^2 C–C bonds.^[152] The intensity ratio I_D/I_G is therefore commonly used as a qualitative descriptor of structural disorder.

Significant graphitization is not expected, as the pyrolysis temperature of $850\text{ }^\circ\text{C}$ is low compared with other reported HCs.^[50,98,99,102] The quasi-graphitic domains are thus very small, and the Raman response is dominated by molecular-scale structural motifs inherited from the precursor.^[153] X-ray diffraction confirms the high amorphicity, showing only broad reflections for both pristine and ozone-treated samples (Figure 24b). The lateral crystallite size L_a is therefore estimated to be below 2 nm , a regime in which the Tuinstra–Koenig relation is not applicable.^[153,154] Furthermore, the D band represents the combined contribution of disorder-activated vibrations rather than specific defect types, meaning Raman spectroscopy cannot resolve individual OFGs or distinguish defect chemistries in HC.

Despite these limitations, Raman analysis still provides comparative insight. Deconvoluted spectra of pristine and ozone-treated samples show broad, overlapping bands typical of amorphous carbons (Figure 24a).^[50] The reduced I_D/I_G ratio is attributed to preferential oxidation and removal of highly defective carbon regions, which are abundant in HC and particularly susceptible to ozone attack.^[151] Conversion of these domains into volatile products effectively etches the most disordered regions, enriching the remaining framework in relatively more ordered sp^2 domains. This results in a lower I_D/I_G ratio and a slight D-band red shift, while the G-band position remains largely unchanged. At higher treatment temperatures, I_D/I_G increases slightly, consistent with progressive carbon framework erosion that increases the relative contribution of edge sites despite continued removal of defective regions (Table 6). This interpretation aligns with SEM observations of increasingly roughened particle surfaces for samples treated at $60\text{ }^\circ\text{C}$ and $100\text{ }^\circ\text{C}$.

Analysis of the $I_D/I_{D'}$ ratio can provide further information on the defect character. Ratios of ~ 3 , observed for pristine and high-temperature-treated samples, indicate predominately edge-type defects, whereas higher ratios (~ 7) are associated with vacancy-like defects.^[155] The $25\text{ }^\circ\text{C}$ ozone-treated sample exhibits an increased $I_D/I_{D'}$ ratio (4.21), suggesting vacancy formation under slow reaction kinetics. At elevated temperatures, secondary oxidation of initial vacancies likely generates additional edge sites, reducing the ratio again.

Thermogravimetric analysis was employed to assess the thermal stability and desorption behavior of OFGs (Figure 24c). HC shows an initial mass loss of ~4% at 100°C due to desorption of adsorbed moisture, followed by a near constant mass up to ~800°C and a gradual decline at higher temperatures, consistent with desorption of residual oxygen functionalities. OFGs in carbon materials decompose over characteristic temperature ranges: aldehydes/ketones (200–400°C, CO), carboxylic acids/anhydrides (400–650°C, CO₂), ethers/phenols (600–800°C, CO), quinones/carbonyls (750–1000°C, CO₂), and cyclic species such as lactones or pyrans (600–800°C, CO₂).^[63,141] As pyrolysis was performed at 850°C, the remaining mass loss is attributed primarily to thermally stable cyclic oxygen groups.

HC–O3–25 exhibits a TGA profile similar to the pristine material but with pronounced mass loss at 100 °C, ascribed to increased surface polarity and moisture uptake. In contrast, HC–O3–60 and HC–O3–100 show substantially different profiles. LOCs in the particle start to decompose which accounts for the mass loss until 700°C, where the slope of the mass loss for all samples is the same. Residual masses of ~65% (HC–O3–60) and ~60% (HC–O3–100) support the removal of LOCs during heating. Given the ~30 at.% oxygen content determined by XPS, the observed mass losses are quantitatively reasonable (Table 6).

Taken together, Raman spectroscopy and TGA demonstrate that ozone treatment can alter both the structural disorder and thermal stability of HC, with the extent of these changes depending on the treatment temperature. Raman data reveal shifts in defect character and overall disorder, while TGA confirms substantial oxygen incorporation and complex thermal desorption behavior. These observations are consistent with XPS results and support the conclusion that ozone enables controlled surface and subsurface functionalization.

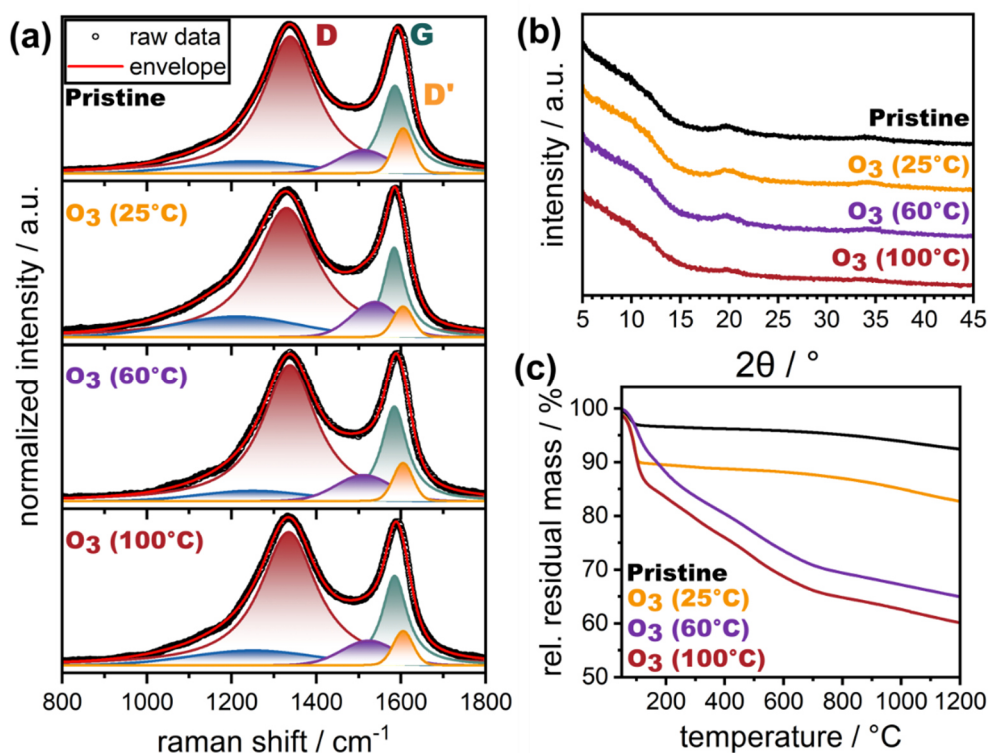


Figure 24. Deconvoluted Raman spectra (a), X-ray diffraction patterns (b) and thermogravimetric profiles (c) of pristine and ozone treated HC.

Table 6. Parameters for Raman spectroscopy and thermogravimetric analysis.

sample	Raman spectroscopy						TGA
	I_D/I_G	$I_D/I_{D'}$	D-Band Position / cm^{-1}	D-Band FWHM	G-Band Position / cm^{-1}	G-Band FWHM	mass loss /rel. %
HC	1.56	3.04	1338	157	1586	79	8
HC-O3-25	1.44	4.21	1329	179	1584	62	17
HC-O3-60	1.45	3.59	1338	156	1584	73	35
HC-O3-100	1.49	3.88	1335	162	1585	71	40

4.3.6 Electrochemical Characterization

Cyclic voltammetry was used to correlate the oxygen functionalization with the electrochemical response of ozone treated HCs, providing insights into potential-dependent electrolyte decomposition, SEI film formation and sodium-storage processes during initial cycling.

Figure 25 presents the first five CV cycles of pristine and ozone-treated HC electrodes at 0.1 mV s^{-1} . HC exhibits a cathodic onset near $\sim 1 \text{ V}$ vs. Na^+/Na , commonly attributed to sodium adsorption at defect sites and OFGs.^[50] Given the low oxygen content of HC (5.9 at.%), the density of reactive SEI-forming sites is limited. The redox peak at 0.1 V reflects sodium insertion and pore filling, while the reverse scan shows a broad anodic feature corresponding to sodium extraction.^[90,99] The progressive increase of the peak-current over successive cycles indicates gradual accessibility of pore storage sites, whereas strong overlap of CV curves between 0.1 and 1.0 V demonstrates high reversibility in the sloping-potential region.

For HC–O3–25, higher insertion currents at low potentials imply facilitated interfacial kinetics despite increased OFG density as confirmed by XPS. This behavior is consistent with formation of a more ion-conductive SEI and enhanced charge-transfer kinetics promoted by surface functionalization, particularly at edge or defect sites.^[50,96]

In contrast, HC–O3–60 shows strongly diminished insertion currents in the first cycle and negligible activity in subsequent cycles (Figure 25c), indicating the suppression of reversible sodium storage at low potentials. A reason for this suppressed insertion is the presence of LOCs inside the particle, which block the internal porosity being responsible for the storage of sodium at low potentials. HC–O3–100 exhibits a broad first-cycle cathodic currents below ~ 0.5 V vs. Na^+/Na , attributed to pronounced electrolyte decomposition and SEI formation (Figure 25d). After treatment at 100°C , LOCs are extensively fragmented and, in some regions, oxidized to such an extent that they have been released as CO_2 , as evidenced by the observed mass loss. In HC–O3–60, however, LOCs remain immobilized within the particle. Moreover, in HC–O3–100, the severe oxidation and substantial material loss likely opened additional diffusion pathways, again enabling sodium storage within the porosity. HC–O3–100W closely resembles the profile of HC–O3–60, which agrees with the fact that the LOCs may block the porosity, leading to diminished insertion currents (Figure S7).

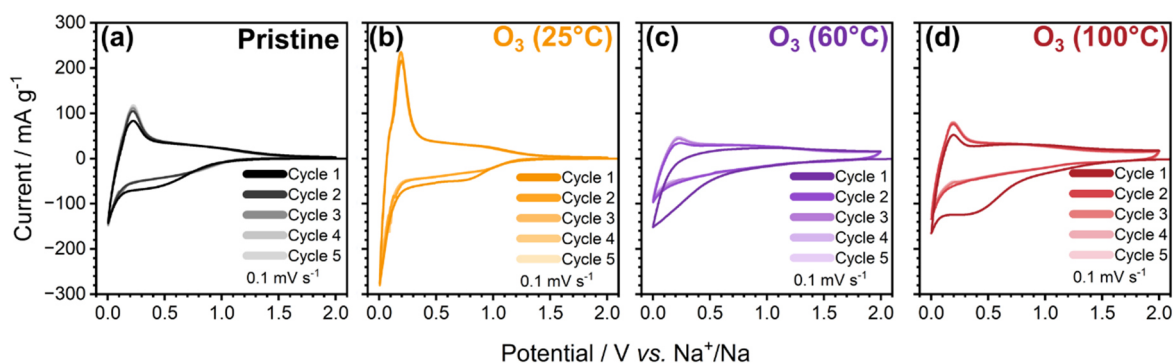


Figure 25. CV curves of the first five cycles of the HC samples at a scan speed of 0.1 mV s^{-1} .

To distinguish surface from bulk-controlled storage processes, GCE and HOPG were employed as model substrates. First-cycle CVs of pristine and ozone-treated GCE are shown in Figure 26a. The pristine electrode exhibits overall low current densities and features a weak cathodic current response at ~ 1 V. After ozone treatment at 25°C , the cathodic onset shifts to ~ 2.0 V, reflecting earlier interfacial reactions with OFGs. A cathodic feature at ~ 0.2 V appears exclusively for the 25°C O_3 treated GCE and is assigned to SEI formation. Ozone treatment increases the surface reactivity of GCEs and may also expose new diffusion pathways into the bulk. This could arise from OFG functionalization and mild etching at edges and defects, which would facilitate sodium transport and account for the higher de-insertion currents.

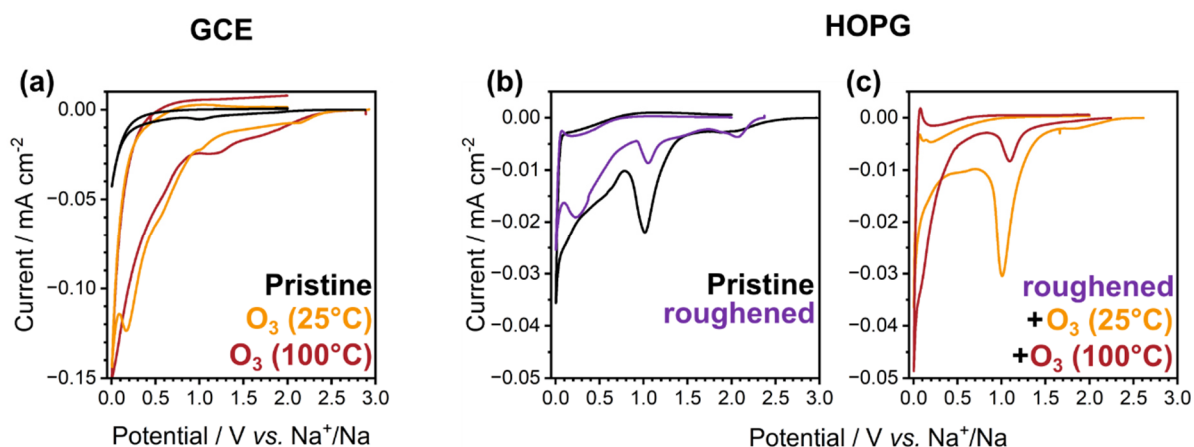


Figure 26. First cycle CV scans at 0.1 mV s⁻¹ of GCEs (a) and HOPG crystals (b,c).

Pristine HOPG shows a prominent first-cycle cathodic peak at ~1.2 V characteristic of irreversible electrolyte decomposition on basal-plane carbon and formation of a NaF-rich SEI (Figure 26b).^[89] Edge site exposed, roughened HOPG exhibits two additional reduction peaks at ~2.1 V and ~0.4 V, while the ~1.2 V feature becomes less pronounced, reflecting different reactivity of defect-rich regions relative to intact basal planes.

As discussed previously, ozone treatment of a roughened HOPG crystal at 100°C leads to a smoother surface with fewer delamination features and less uplifted sheet structures, which agrees with the first cycle CV scan (Figure 26c). The reduction features exclusively observed for the roughened HOPG crystal at ~0.4 and ~2.1 V are no longer present, whereas the intensity of the ~1.2 V SEI formation peak remains essentially unchanged. Contrary, functionalization of a roughened HOPG crystal with ozone at 25°C leads to a pronounced SEI formation peak at 1.2 V, indicating that functionalized carbon edge sites also contribute to the a high-potential SEI formation.

EIS was performed after five formation cycles to probe SEI conductivity and interfacial properties. The Nyquist plot of pristine HC comprises a high frequency-intercept corresponding to electrolyte resistivity ($R_{\text{electrolyte}}$), a small high-frequency assigned to SEI resistance (R_{SEI}), a mid-frequency semicircle associated with charge-transfer resistivity (R_{CT}) and a low frequency Warburg-type increase, reflecting sodium-diffusion in the porous carbon matrix. A simplified contact-Randles-film equivalent circuit was used to model the impedance spectra and to extract the relevant electrochemical parameters.^[156] The nested structure of the equivalent circuit is well suited to approximate the impedance response of multi-particle electrodes and can be interpreted as a low-level analogue of a transmission line model.

HC-O3-25 decreases R_{SEI} from 31 Ω to 24 Ω , indicating that the SEI is more ion-conductive and corroborating potential beneficial influence of OFGs on SEI formation. A stronger effect is observed for R_{CT} , which decreases from 138 Ω to 33 Ω , due to facilitated Na⁺ desolvation and interfacial transfer due to increased surface polarity and enhanced sodium-ion affinity of

OFGs.^[44] In contrast, HC–O3–60 and HC–O3–100 display an additional low-frequency, ascribed to an extra electrochemical process with a distinct time constant semicircle (Figure 27b). To account for the LOCs generated by the ozone treatment, R_{LOC} was incorporated into the equivalent circuit as an additional RC element representing an ion-transport barrier. LOCs drastically increase the resistivity for HC–O3–60 adding R_{LOC} of 835 Ω . R_{SEI} (33 Ω) and R_{CT} (110 Ω) of HC–O3–100 are comparable to values from HC, while the resistivity of R_{LOC} contributes an additional ~ 360 Ω , offsetting the beneficial effects observed for HC–O3–25. HC–O3–100W on the other hand shows a reduced R_{LOC} resistance of 159 Ω , further corroborating the negative impact of LOCs on the hard carbon. Overall, the EIS-derived reductions in R_{SEI} and R_{CT} for HC–O3–100 directly correlate with the enhanced insertion currents observed by CV, indicating improved interfacial kinetics. Conversely, the additional low-frequency process for HC–O3–60 and HC–O3–100 coincide with suppressed insertion behavior, reflecting kinetically hindered sodium transport due to LOCs (Figure S8).

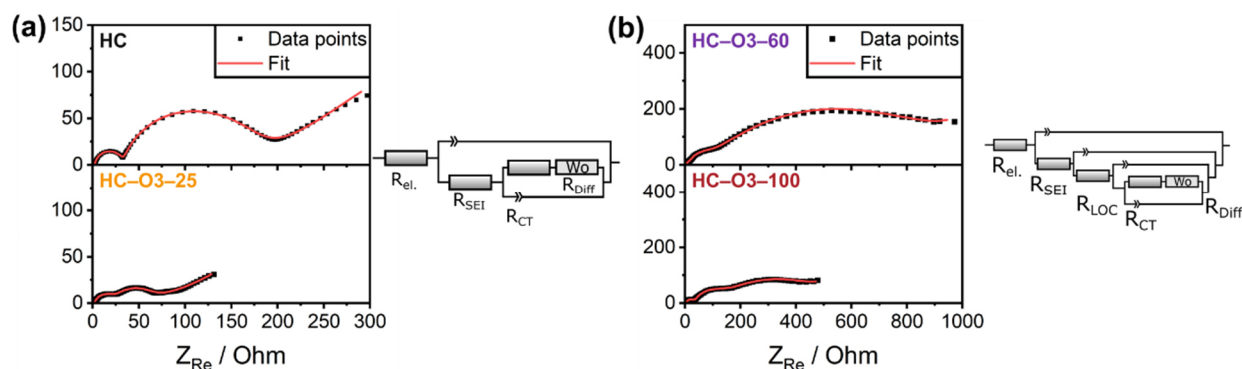


Figure 27. Nyquist plots of HC and HC–O3–25 with equivalent circuit (a). HC–O3–60 and HC–O3–100 with corresponding equivalent circuits (b).

Table 7. Overview of samples and their calculated resistivities from charge transfer, SEI and LOCs

Sample	R_{CT}	R_{SEI}	R_{LOC}
	/ Ω	/ Ω	/ Ω
HC	114	31	
HC–O3–25	33	24	
HC–O3–60	60	33	835
HC–O3–100	110	33	360
HC–O3–100W	135	42	159
HC–O2–100	104	20	

Galvanostatic cycling provides a complementary perspective on the sodium-storage behavior of pristine and ozone-treated HC, enabling quantitative assessment of capacity, reversibility, and cycling stability. Rate performance is summarized in Figure 28a. HC delivers an initial discharge capacity of ~ 190 mAh g^{-1} , which increases slightly during the first cycles. As observed for CV measurements, where insertion currents increase successively over the first five cycles, an electrochemical activation likely takes place, attributed to progressive access to previously inactive regions potentially enabled by microcrack formation from local volume

changes during sodiation.^[157] In ozone-treated samples, this activation is absent, because of ozone-induced pore opening and enhanced electrolyte accessibility already in the initial state.

In agreement with CV and EIS data, HC–O3–25 demonstrates a small increase in capacity at low (50 mA g⁻¹) and intermediate (100–200 mA g⁻¹) current densities, whereas HC–O3–60 and HC–O3–100 exhibit a decrease in capacity. At high current densities (500 and 1000 mA g⁻¹), all samples except HC–O3–60 converge to a capacity of ~40mAh g⁻¹, indicating that the applied current exceeds the effective sodium diffusion through the bulk and SEI. Resistivity from charge-transfer processes originates from the SEI-carbon interface and is governed primarily by ion desolvation energetics rather than SEI thickness, as established for Li-ion systems and can therefore reasonably assumed for Na-ion systems.^[158] In contrast, increased SEI thickness mainly raises ionic transport resistance across the interphase.

This distinction is particularly relevant in the low-potential plateau region of HC (<0.1 V vs. Na⁺/Na), where sodium storage is governed by a pore-filling mechanism involving the formation of quasi-metallic sodium species within nanoconfined carbon pores.^[44,45] This process is increasingly understood as an underpotential deposition like phenomenon, in which sodium accumulation at pore walls is thermodynamically favored compared to bulk sodium plating, leading to deposition potentials slightly above 0 V.^[45–47,159] Mechanistically, initial Na⁺ adsorption at defect sites and pore surfaces in the sloping region provides the prerequisite for subsequent sodium clustering, as partial charge transfer (Na⁺→Na^{δ+}, δ < 1) reduces electrostatic repulsion and enables aggregation.^[127] The resulting sodium species exhibit quasi-metallic character, as evidenced by spectroscopic studies, and their formation is strongly dependent on pore size, surface chemistry, and accessibility.^[44] While deposition preferentially occurs on pore walls near oxygen-containing defect sites due to stronger binding energies, continued sodium uptake proceeds into the pore interior in the form of mono and bi-layers, with energetics approaching metallic sodium for larger pores.^[47] Under these conditions, sodium insertion becomes highly diffusion-limited, as transport through narrow pore channels and across the SEI governs accessibility to active storage sites. Consequently, even minor increases in interfacial or pore transport resistivity can significantly restrict the extent of sodium clustering, thereby reducing the accessible plateau capacity. This diffusion-limited UPD-like pore filling mechanism explains the impeded capacity and rate capability of HC–O3–60, as internal LOC formation blocks porosity and disrupts effective diffusion pathways.

In addition to pore blocking by LOCs, ozone treatment at 100 °C is accompanied by measurable material loss, indicating partial carbon etching and a likely enlargement of internal pore structures. Such pore widening has important consequences for the thermodynamics of sodium storage. With increasing pore size, the interaction strength between sodium species and the carbon host decreases, causing the potential of the UPD-like sodium deposition

process to progressively approach that of bulk sodium plating (0 V vs. Na^+/Na).^[46,47] As a result, enlarged pores shift the potentials for sodium UPD below the applied cut-off voltage (5 mV), rendering this capacity electrochemically inaccessible under the chosen cycling conditions. This effect provides an additional explanation for the reduced plateau capacity observed for HC–O3–60 and HC–O3–100.

First-cycle potential profiles (Figure 28b) show the characteristic sloping region (1–0.1 V) followed by a low-potential plateau (<0.1 V) for HC, yielding an ICE of 74.9%. Ozone treatment at 25 °C shifts the onset of the sloping region to higher potentials, evidencing earlier SEI formation, consistent with reports on functionalized HC.^[50,160] The slope-to-plateau capacity ratio increases markedly for HC–O3–60 and HC–O3–100 (Table 8), which agrees with internal pore-blocking caused by LOCs and pore enlargement. Because the blocked pores cannot contribute to the capacity at low potentials, the plateau-capacity is significantly reduced. Furthermore, ICE drops to 44.7% (HC–O3–60) and 48.8% (HC–O3–100), reflecting extensive irreversible reactions with OFGs and LOCs. HC–O2–100 shows a profile similar to HC but with slightly reduced capacity and ICE (72.5%).

First-cycle differential capacity plots (Figure 28c) further resolve potential-dependent processes complementary to CV. HC exhibits a sharp sodiation peak at ~0.03 V, corresponding to sodium storage in pores, in agreement with CV data. HC–O3–25 introduces an additional reduction peak at ~0.84 V, assigned to SEI formation, and enhances the low-potential peak near ~0.1 V, indicating more efficient pore filling. HC–O3–60 shows multiple reduction features (~0.7 V and ~0.48 V), evidencing sequential SEI formation and reactions with LOCs, while HC–O3–100 displays a broader feature centered near ~0.7 V. These trends demonstrate that both the onset potential and complexity of SEI formation strongly depend on the nature and abundance of surface oxygen species and presence of LOCs.

Sodium-ion diffusion kinetics were analyzed by GITT following the principle of Weppner and Huggins and the apparent diffusion coefficients were calculated using the equation reported by Bommier *et al.*^[48,111] HC–O3–25 exhibits significantly increased apparent diffusion coefficients at low potentials, indicating facilitated ion transport not only across the SEI but also within the particle. This supports the presence of functionalization within accessible internal porosity. This enhancement is particularly relevant for the plateau region, where sufficient ion transport is required to sustain the UPD-like sodium deposition and subsequent cluster growth inside pores.^[44] In contrast, HC–O3–60 and HC–O3–100 markedly reduces apparent diffusivity at low potentials, consistent with over-functionalization and increased diffusion barriers due to LOCs blocking the internal porosity.

Cycling stability over 150 cycles at 50 mA g⁻¹ is shown in Figure 28e. HC requires ~5 cycles for activation and remains stable until ~20 cycles, after which increased scatter appears, likely

due to degradation of the sodium counter/reference electrode. Because the plateau region contributes substantially to the capacity, small potential fluctuations near the cut-off criteria of 5 mV can cause large apparent capacity variations. HC–O3–25 exhibits stable capacity from the first cycle and converges rapidly to the pristine capacity, with similar scatter emerging after ~20 cycles. In contrast, the HC–O3–60 exhibits a persistently reduced reversible capacity, attributed to excessive SEI formation, sodium trapping and blocked intrinsic porosity by LOCs.

Coulombic efficiencies over the first 50 cycles (Figure 28f) further differentiate the samples. HC, HC–O3–25, HC–O3–60 and HC–O2–100 stabilize near ~99%. However, HC–O3–25 reaches the ~99% efficiency faster than the other electrodes, indicating advantageous interphase formation. HC–O3–100 performs worst, with efficiencies stagnating near ~97%, evidencing ongoing irreversible processes, *e.g.* electrolyte decomposition.

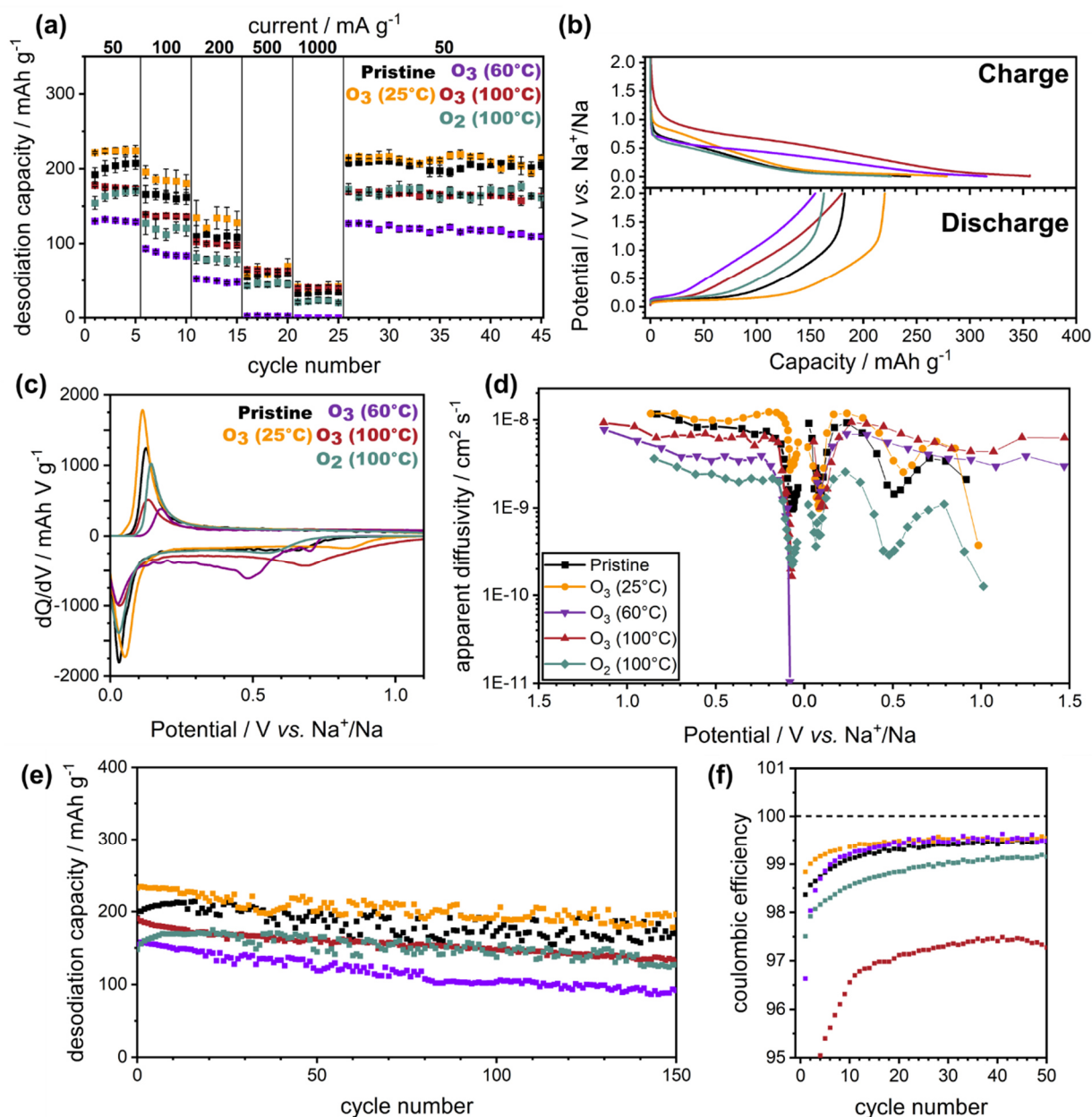


Figure 28. Rate test of pristine and functionalized samples (a), first-cycle charge-discharge profiles (b) and corresponding differential capacity plots (c). Apparent diffusivities calculated from GITT measurements (d). Long-term cycling of pristine and functionalized samples (e) with coulombic efficiencies of the first 50 cycles (f).

Table 8. Overview of pristine HC and ozone treated samples with their reversible capacities, slope- and plateau capacities, and initial coulomb efficiencies (mean $\pm$ standard deviation).

	reversible capacity at 50 mA g ⁻¹	slope capacity	plateau capacity	slope / plateau ratio	ICE
	/ mAh g ⁻¹	/ mAh g ⁻¹	/ mAh g ⁻¹		/ %
HC	208 $\pm$ 8	96 $\pm$ 1	112 $\pm$ 7	0.86	74.9 $\pm$ 0.7
HC-O3-25	229 $\pm$ 6	105 $\pm$ 1	124 $\pm$ 6	0.85	79.1 $\pm$ 0.4
HC-O3-60	144 $\pm$ 11	101 $\pm$ 6	43 $\pm$ 6	2.35	44.7 $\pm$ 1.9
HC-O3-100	185 $\pm$ 9	120 $\pm$ 3	65 $\pm$ 6	1.84	48.8 $\pm$ 0.9
HC-O2-100	176 $\pm$ 11	88 $\pm$ 3	88 $\pm$ 9	1.00	72.5 $\pm$ 1.2

4.3.7 Hydrogen Annealing to modify OFGs of Functionalized Hard Carbon

To further rationalize the effect of oxygen functionalization, a series of hydrogen treatments at elevated temperatures after ozone functionalization at 25°C were investigated. In a reducing hydrogen atmosphere at elevated temperatures, OFGs on carbon materials can either be transformed (e.g. $\text{O}=\text{C}-\text{O}$ to $\text{C}=\text{O}$) by cleavage of water, or reduced entirely to create hydrogen terminated edge sites.^[161] SEM images in Figure 29a–e reveal no change in particle texture or morphology upon ozone treatment and, importantly, no change after subsequent hydrogen annealing, confirming that no substantial morphological changes occur during either treatment.

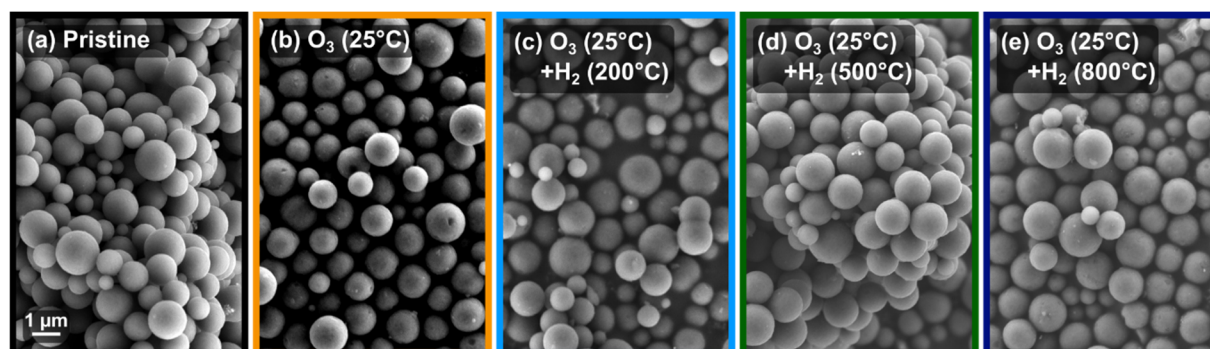


Figure 29. SEM images of pristine (a), O₃ (25°C) (b) treated HC and hydrogen annealed samples (c-e).

The degree of surface functionalization was again evaluated by XPS. Deconvoluted C 1s high resolution spectra reveal that ozone treatment at 25°C introduces expected C–O, O–C–O/C=O and O=C–O components to C 1s spectra for pristine HC (Figure 30a). In agreement with these observations, O 1s spectra exhibit pronounced O–C and O=C related peaks (Figure 30b). Carbon KLL Auger peak analysis corroborates that the surface of HC is effectively functionalized, as the D-Parameter significantly decreases from 18.3 to 15.6 eV, which translates to a reduction in sp² surface carbon from ~50% to ~20% (Figure 30c).^[64] Elemental quantification further demonstrates that ozone functionalization at 25°C introduces 20 at.% of surface oxygen, while subsequent hydrogen treatment at 200 °C keeps the overall oxygen content essentially unchanged (Figure 30c).

Annealing of the ozone functionalized sample in hydrogen at 500 and 800 °C however leads to a monotonic decrease in oxygen concentration suggesting that OFGs are primarily reduced at 200 °C, while higher temperatures promote their cleavage. Nonetheless, even after treatment at 800°C, oxygen surface concentration is still higher than in the pristine sample, implying that the formed oxygen species by ozone treatment are very stable. This interpretation is supported by the deconvolution of carbon oxidation states shown in Figure 30e. Hydrogen treatment at 200 °C increases the contributions of C–O and CC/CH components, while the O=C–O species remains constant. At the same time, C=O and O–C–O constituents decrease and convert into C–O functionalities, which is in accordance with the chemical reduction of these groups. In contrast, O=C–O groups remain mostly unaffected. At 800°C, contributions

of all oxygen-containing species decline, supporting that functional groups are cleaved. This is further accompanied by an increase in the D-Parameter to 16.9 corresponding to ~30% sp^2 surface carbon which concurs with the onset of a surface healing process from reaction of small organic molecules with defect sites.^[101]

In summary, XPS results demonstrate that hydrogen annealing at 200°C causes a transformation of OFGs, whereas higher temperatures (500 and 800°C) lead to cleavage and hydrogen terminated edges on HC surfaces. However, temperatures as high as 800°C in a reducing atmosphere are not sufficient to completely reduce the surface oxygen content to original values, indicating that introduced oxygen by the ozone treatment generates OFGs likely also in cyclic arrangements, because they can persist up to temperatures of 1000°C.^[69–71] Additionally, XPS analysis suggests that C=O and O–C–O components can be reduced to C–O functionalities, whereas O=C–O are rather eliminated as CO₂ than reduced to lower oxidation states.

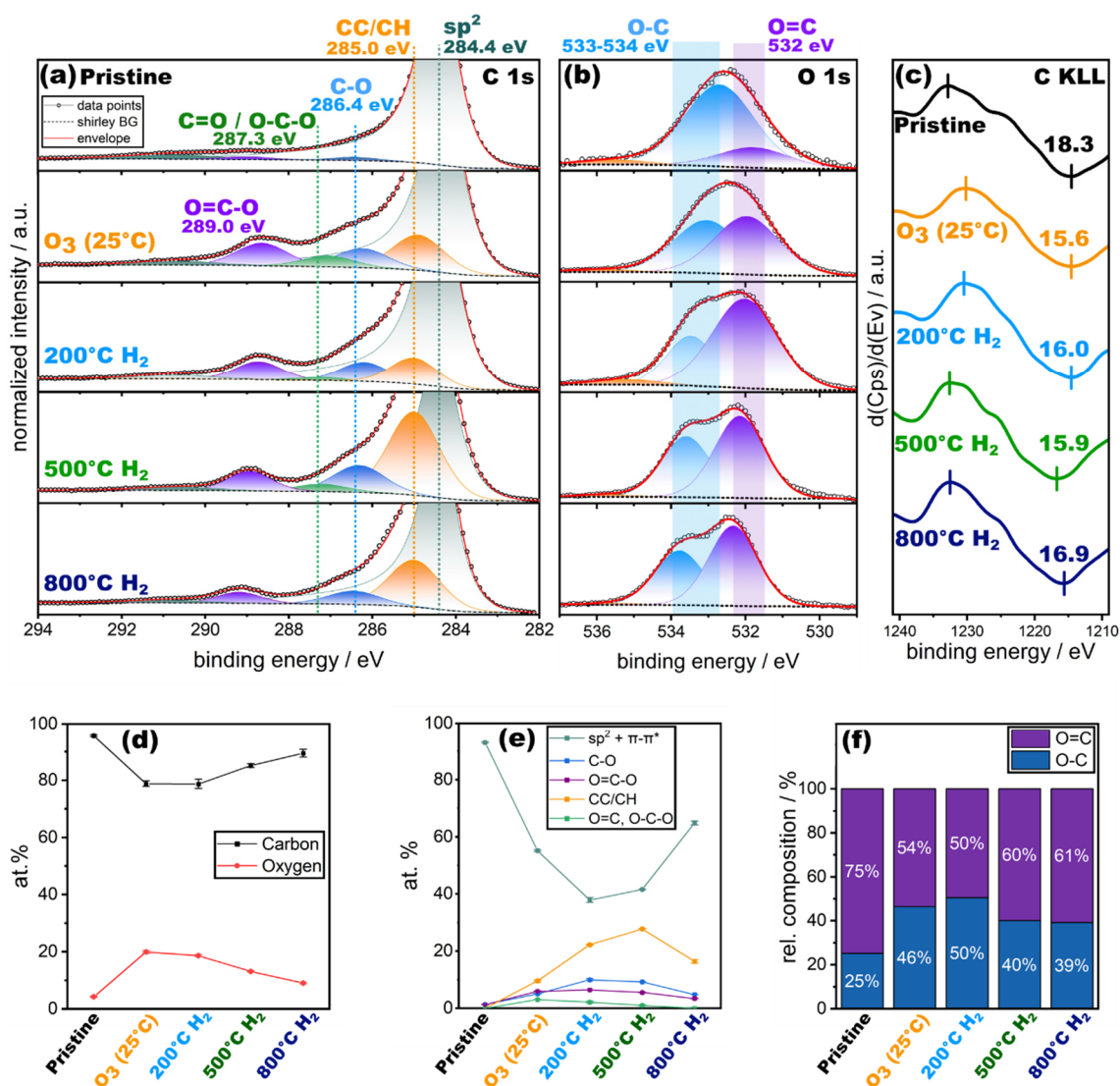


Figure 30. C 1s (a), O 1s (b) spectra and C KLL Auger peak analysis (c) of pristine, ozone treated and hydrogen annealed samples. Carbon and oxygen composition of HC powders (d) and the relative composition of C 1s (e) and O 1s components (f).

First-cycle CV scans of ozone functionalized and subsequently hydrogen annealed samples are shown in Figure 31a-d. Whilst treatment at 200°C in hydrogen does not alter the CV profile, higher temperatures (500 and 800°C) shift SEI formation from ~1.1 V to a strong and broad feature at ~0.3 V, accompanied by reduced de-insertion currents at low potentials. These observations suggest that both interfacial processes and Na-storage mechanisms are fundamentally changed by hydrogen annealing above 200°C.

As a result, it can be concluded that treatment at 200°C H₂ changes the chemical composition of the surface, but does not induce any structural change, whereas higher temperatures again promote structural modification of the HC. The preserved structural integrity but altered chemical composition of the 200°C H₂ treated sample is further supported by TGA-DSC profiles in Figure 31e in addition to XPS. The mass loss profile during heating closely resembles that of the ozone-treated sample. However, the corresponding DSC curve shows an earlier and more pronounced onset of exothermic reactions, indicating that although a comparable mass loss occurs, the underlying reactions are energetically different and involve more reactive, thermally unstable OFGs.

A substantially different thermal behavior is observed for the 500°C treated sample, which exhibits a pronounced mass loss at 100°C from adsorbed moisture due to a potentially enlarged surface area from OFG cleavage. Furthermore, decomposition of OFGs at 500 °C likely also increases the internal pore volume, which could exceed the narrow pore size regime required for sodium cluster formation, explaining the reduced de-insertion currents.^[44] At 800°C, the mass loss of the sample is significantly lower, which may lead to partial restoration of sp² domains and concomitant restructuring of the pore network, potentially reducing pore volume again and thus increasing the accessible sodium storage compared to the 500 °C-treated sample.^[44]

Figure 31f depicts the extended model for hydrogen treatment of ozone functionalized HC:

- (I) Ozone functionalization at 25°C leads to a high degree of oxygen functionalization.
- (II) Treatment at 200°C hydrogen atmosphere partly transforms the OFGs (blue edges) and reduces some OFGs to water.
- (III) At 500°C hydrogen treatment temperature, the functional groups disintegrate and disrupt the carbon network leading to LOC-like fragments which can partially block internal pores while simultaneously inducing local pore widening due to carbon removal.
- (IV) The behavior observed at 800 °C can be attributed to the onset of partial defect healing, as evidenced by the increase in the D-parameter as well as the pronounced changes in the CC/CH peak.

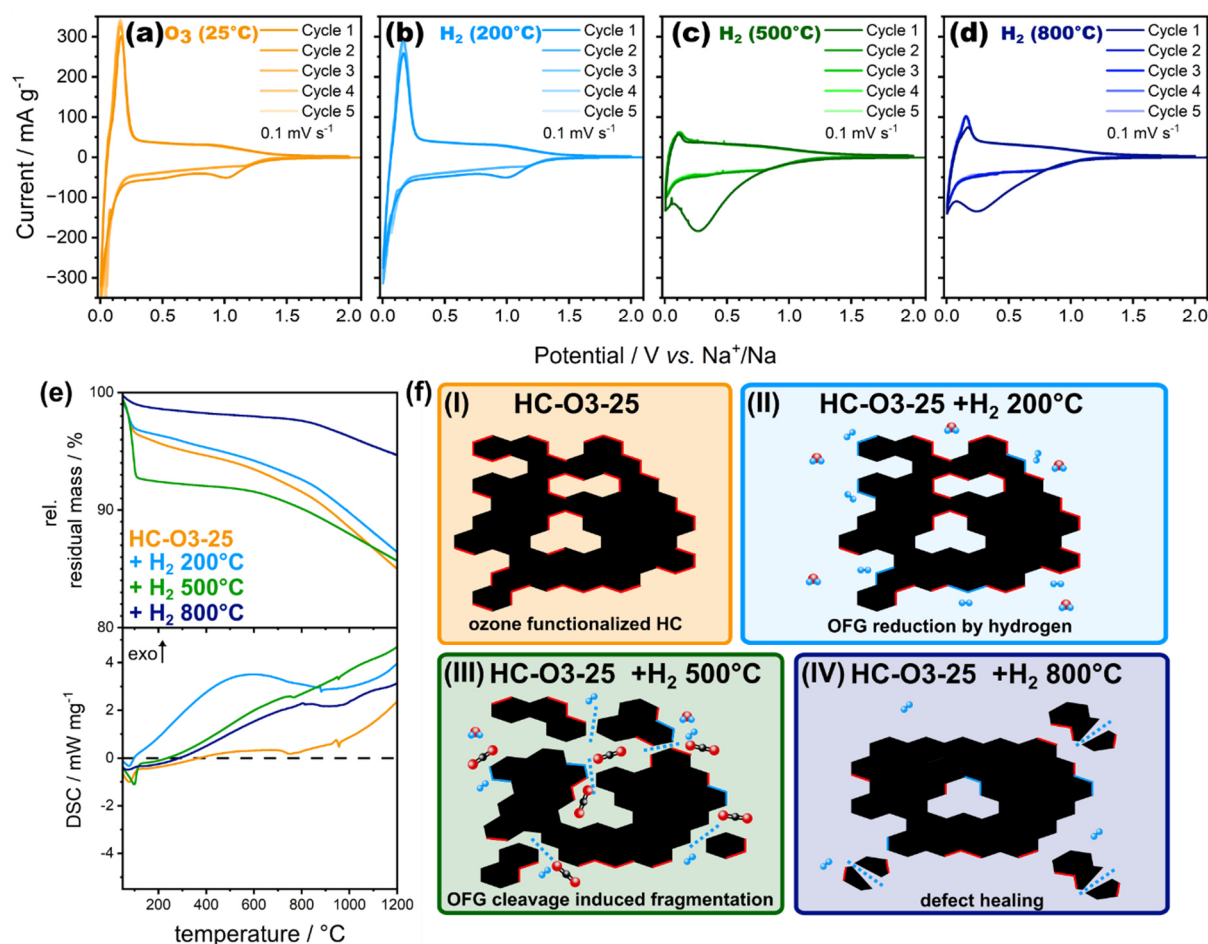


Figure 31. First five CV scans of ozone functionalized (a) and hydrogen annealed samples (b-d). TGA and DSC profiles of the samples (e) and proposed interaction of hydrogen treatment of HC-O3-25 at different temperatures (f).

To further validate the proposed hypothesis of beneficial OFG functionalization vs. structural degradation, galvanostatic cycling was performed. Rate tests of hydrogen annealed ozone samples in Figure 32a reflect the trends from CV experiments: pristine HC exhibits an initial discharge capacity of $\sim 200 \text{ mAh g}^{-1}$ and ozone treatment at 25°C slightly improves both the reversible capacity and rate capability. Annealing the ozone treated sample in H_2 atmosphere at 200°C further increases the reversible capacity and rate capability. However, H_2 treatment temperatures of 500°C and 800°C lead to impeded reversible capacities of 103 and 132 mAh g^{-1} , respectively (Table 9).

Comparison of the first-cycle potential vs. capacity curves reveals the origin of the reduced reversible capacity (Figure 32b): high temperature annealing at 500 and 800°C leads to a reduction of the plateau capacity, whereas the sloping regime of the samples is less affected resulting in a higher slope-to-plateau capacity ratio (Table 9). This indicates that pore-based sodium storage is predominantly impaired, while surface-driven storage remains comparatively preserved.

Differential capacity plots of the samples reproduce the trends observed from CV measurements further confirming the altered SEI formation and inhibited pore-attributed sodium storage at low potentials.

Apparent diffusivities were calculated from GITT measurements and demonstrate that reducing the oxygen functionalization by H₂ treatment leads to higher diffusion rates of Na⁺ for ozone treated HC and the hydrogen annealed sample at 200°C (Figure 32d). Interestingly, the 500°C hydrogen annealed sample shows higher diffusivities than the 200°C sample, which demonstrates that sodium-ion diffusivity is not reduced for the high-temperature treated samples, corroborating that the observed capacity loss cannot be attributed to diffusion limitations. Instead, these results suggest that SEI formation and structural changes affecting the accessibility and suitability of pore environments dominate the electrochemical behavior. The reduced reversible capacity is therefore attributed to the loss of suitable pore environments required for sodium storage at low potentials, limiting sodium storage to surface-dominated mechanisms.

Long-term cycling of the cells over 200 cycles was conducted to evaluate the stability and reversible capacity (Figure 32e). In agreement with the expectations, the ozone treated and subsequently 200°C hydrogen annealed sample exhibits the highest reversible capacity. Contrary, higher hydrogen treatment temperatures of 500 and 800°C lead to low but stable reversible average capacities of ~90 and 107 mAh g⁻¹ over the 200 cycles predominantly attributed to storage of Na⁺ at OFGs and defect sites, as the capacity stems mostly from the sloping part as seen by high slope-to-plateau ratios (Table 9). The low reversible capacity is likely derived from the absence of the pore-attributed storage of Na⁺, which limits sodium storage to sloping-capacity attributed mechanisms.

Hydrogen annealing of ozone-functionalized HC highlights again the complex interplay of surface chemistry and structural properties. While the lowest hydrogen treatment temperature (200 °C) allows slight modification of the OFG composition, higher temperatures (500 and 800°C) simultaneously reduce surface oxygen content and induce structural changes, demonstrating that functionalization and structural modification cannot be fully decoupled under such conditions. Future work could therefore explore alternative reduction strategies, such as milder chemical reductants (e.g. NaBH₄), which may enable a more selective modification of OFGs while minimizing structural alterations of the carbon framework.

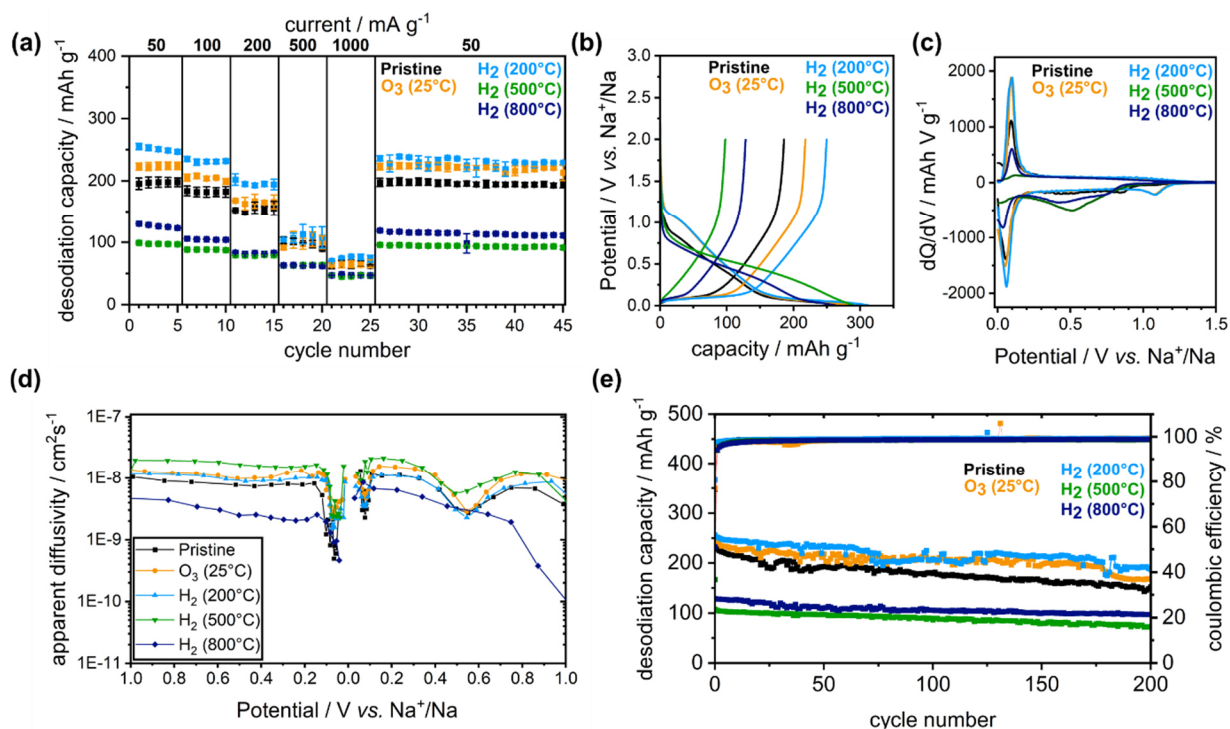


Figure 32. Rate test (a), first cycle galvanostatic charge-discharge profiles (b) and differential capacity plots (c) of pristine, ozone treated and hydrogen annealed HC samples. Apparent diffusivities calculated from GITT profiles (d) and long-term cycling results at 50 mA g⁻¹ (e).

Table 9. Overview of pristine HC, after ozone treatment at 25°C and subsequent hydrogen annealed samples with their reversible capacities, slope- and plateau capacities, and initial coulomb efficiencies (mean ± standard deviation).

	reversible capacity at 50 mA g ⁻¹	slope capacity	plateau capacity	slope / plateau ratio	ICE
	/ mAh g ⁻¹	/ mAh g ⁻¹	/ mAh g ⁻¹		/ %
HC	205 ± 10	103 ± 3	101 ± 7	1.02	71.5 ± 1.5
HC-O ₃ -25	228 ± 5	119 ± 2	109 ± 4	1.10	77.2 ± 1.3
+ H ₂ (200°C)	255 ± 5	127 ± 2	128 ± 3	1.00	80.2 ± 0.3
+ H ₂ (500°C)	103 ± 2	82 ± 2	21 ± 1	3.88	34.0 ± 0.5
+ H ₂ (800°C)	132 ± 3	83 ± 2	49 ± 3	1.72	48.9 ± 0.0

4.3.8 Conclusion

Ozone treatment exerts fundamentally different effects on HC depending on the applied temperature. At 25°C, ozone predominantly leads to functionalization of the surface and pores, whereas at elevated temperatures it acts as a molecular scissor, excising LOCs from the carbon framework. Ozone treatment at 25 °C was able to increase the oxygen content by ~15 at.% without evidence of structural degradation, while higher treatment temperatures lead to oxygen contents of up to ~30 at.% with simultaneous excessive carbon erosion extending in the particle.

To rationalize these findings, a mechanistic framework based on a Criegee-type ozonolysis adapted to carbonaceous materials is proposed. Supported by spectroscopic evidence and experiments on carbon model substrates, defects and edge sites are identified as preferential reaction centers, whereas the basal plane of sp² carbon is mostly inert. It could further be demonstrated how treatment conditions control both the nature and distribution of OFGs as well as the extent of structural degradation. Therefore, this ozone based functionalization framework provides a consistent basis for linking ozone exposure conditions to surface chemistry and to the formation of LOCs.

Importantly, the results refute the common assumption that a high surface oxygen content inherently leads to poor ICE. Instead, both ICE and reversible capacity are governed primarily by both the accessibility and structure of the internal porosity. While ozone functionalization at 25 °C enhances ion-transport kinetics, as evidenced by reduced charge-transfer resistance, high-temperature ozone treatment promotes structural degradation and the formation of LOCs that obstruct internal pore networks, thereby reducing the reversible capacity of HC.

Overall, these findings identify mild ozone treatment as a facile functionalization strategy to introduce OFGs to the surface of HC. Future work should therefore focus on the selective introduction of specific OFGs to further optimize SEI formation and sodium-ion transport. This effort should be supported by advanced surface-sensitive characterization techniques capable of unambiguous identification of individual oxygen species.

4.4 Chemical Derivatization of Oxygen Functional Groups on Hard Carbon

The previous chapter gave valuable insights on the functionalization of HC employing ozone. XPS analysis proved that ozone treatment introduces a high density of OFGs on the surface of HC. It offers a direct and quantitative access to the surface chemical composition, however a precise identification of individual OFG functionalities is limited by their spectral overlap.^[58] For example, the formal oxidation states of carbon in C=O and O–C–O groups are identical (+II), whereas their chemical reactivity can differ significantly. Similarly, carbon in O=C–O environments can occur in cyclic structures such as lactones or as free carboxyl functionalities that cannot be unambiguously resolved by XPS. To overcome these limitations, a chemical derivatization approach was employed to selectively label hydroxyl, carboxyl, and carbonyl functionalities with fluorinated marker molecules, which can be sensitively detected and quantified by XPS *via* the fluorine F 1s signal.^[66,162]

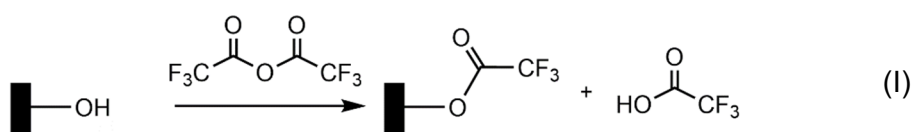
The chapter 4.4 is extracted from the manuscript in preparation entitled “Chemical Labeling of Oxygen Functional Groups Uncovers the Surface Chemistry of Hard Carbon and its Role in SEI Formation”.

4.4.1 Derivatization Protocol and Control Surfaces

Reliable interpretation of chemical derivatization requires that two conditions are met: First, the derivatization reagents must react selectively with their intended functional groups, meaning that, for example, hydroxyl groups must not undergo side reactions with a reagent designed for carboxyl groups. Second, the reactions must proceed quantitatively, ensuring that the amount of fluorine introduced during derivatization can be directly correlated with the concentration of the original surface functionalities. The following section therefore outlines the reaction mechanisms of the employed derivatization reagents and subsequently evaluates their selectivity and stoichiometric behavior using polymeric model substrates with well-defined OFGs.

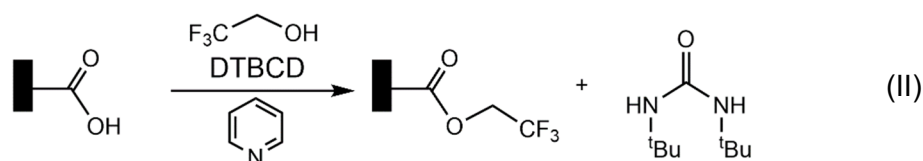
Hydroxyl Groups

Hydroxyl groups react with trifluoroacetic anhydride (TFAA) *via* direct esterification, forming trifluoroacetate esters and releasing trifluoroacetic acid as a byproduct (Reaction I).^[66] Due to their high volatility, excess anhydride and trifluoroacetic acid are removed during the vacuum drying step and are no longer present under the ultra-high vacuum conditions of the XPS measurement.



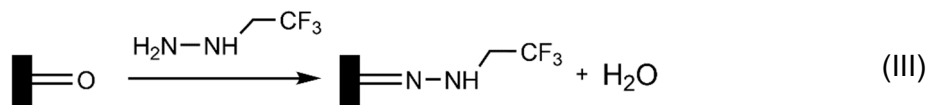
Carboxyl Groups

Carboxyl groups were derivatized using a mixture of trifluoroethanol (TFE), pyridine, and N,N'-di-tert-butylcarbodiimide (DTBCD) in a volumetric ratio of 100:45:36. The reaction proceeds *via* a carbodiimide-mediated esterification, forming trifluoroethyl esters and releasing N,N'-di-tert-butylurea as a byproduct (Reaction II).^[66] Pyridine acts in the reaction as a base to scavenge the proton released during ester formation and to suppress side reactions. Similar to the hydroxyl derivatization, excess reagents and volatile components, which are again removed during the vacuum drying step.



Carbonyl Groups

Carbonyl groups were derivatized using 70 % aqueous trifluoroethylhydrazine (TFEH) solution, forming hydrazone derivatives through nucleophilic addition of the hydrazine to the carbonyl carbon, followed by elimination of water (Reaction III).^[67]



To establish a reliable basis for the selective derivatization of surface OFGs on HC, selected polymer reference materials were tested. This validation step is essential to ensure that derivatization results obtained for HC can be interpreted in a meaningful manner. These polymers were chosen for their well-defined surface functional groups, enabling the assignment of characteristic XPS signals to hydroxyl, carboxyl, and carbonyl moieties.^[162] Each polymer exhibits a single type of OFG, serving as a model system for the derivatization strategy using fluorinated reagents. Specifically, poly(vinyl alcohol) (PVA) was used to represent hydroxyl groups, poly(acrylic acid) (PAA) for carboxylic acid groups, and poly(vinyl methyl ketone) (PVMK) for carbonyl functionalities in the form of ketones. In addition to these functionalized polymers, reference materials with OFGs expected to be unreactive toward the derivatization agents were tested. These negative controls serve to evaluate the selectivity of the derivatization approach and to identify potential non-specific interactions. Poly(ethylene glycol) (PEG), containing ether bonds, and poly(vinyl acetate) (PVAc), featuring ester functionalities, were selected for this purpose.

The chemical structures, abbreviations and C 1s peak assignments of all polymers used in this study are summarized in Figure 33a-e along with their C 1s detail spectra. All polymers exhibit the expected number of components and relative intensity ratios, consistent with their

respective chemical structures. The dominant peaks correspond well to the anticipated carbon environments, such as CC/CH, C–O, C=O, and O–C=O, depending on the polymer.^[163] Minor deviations from idealized structures were observed in the form of additional low-intensity peaks, which are attributed to unavoidable surface contamination like adventitious carbon (ad. C) or charging effects due to the non-conductivity of the polymer samples. These effects are however minor and do not interfere with the overall spectral interpretation. Most importantly, no fluorine-related signals were detected in the F 1s region for any of the samples, confirming the absence of unintentional derivatization or contamination prior to reagent exposure Figure 33f.

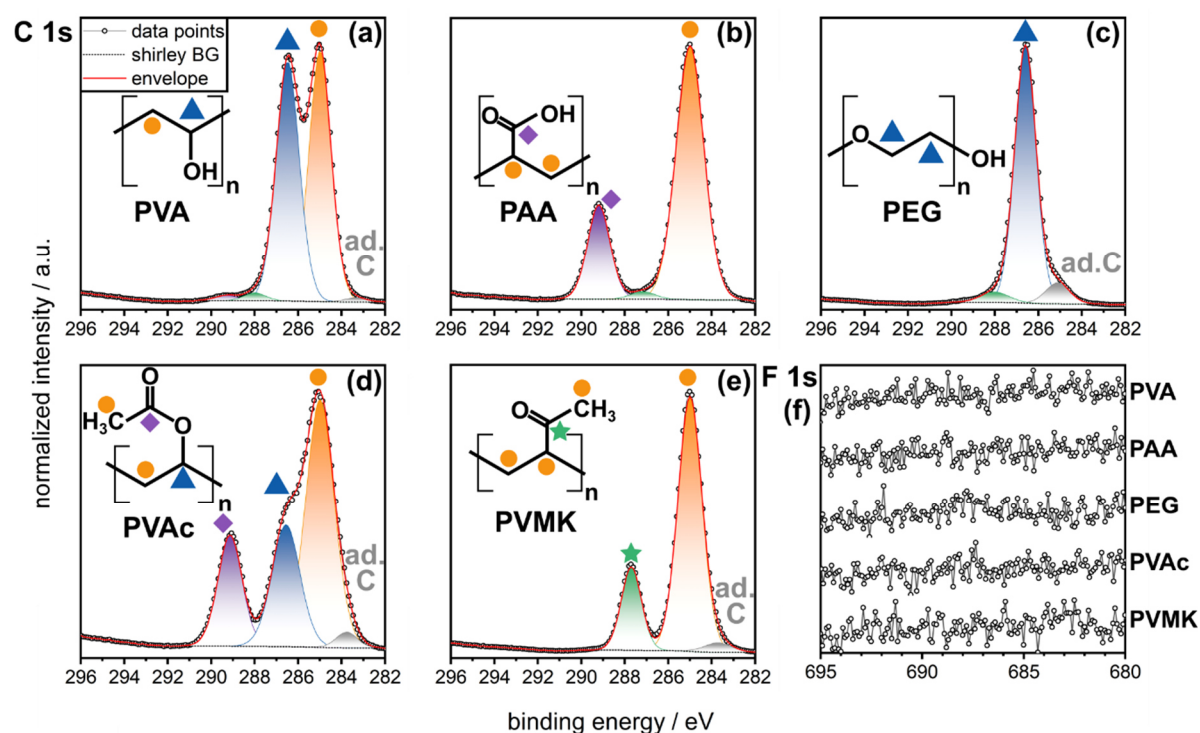


Figure 33. C 1s spectra of poly(vinyl alcohol) (PVA) (a), poly(acrylic acid) (PAA) (b), poly (ethylene glycole) (PEG) (c), poly (vinyl acetate) (PVAc) (d) and poly (vinyl methyl ketone) (PVMK) (e) with their corresponding molecular structures and peak assignments. Stacked F 1s spectra of the untreated polymers (f).

Polymer TFAA Derivatization

The reactivity of surface hydroxyl groups was probed *via* esterification with TFAA. Figure 34a illustrates the repeating unit of PVA before and after derivatization, in which the hydroxyl group is converted into a trifluoroacetate ester. The corresponding high-resolution C 1s spectra of pristine and TFAA-treated PVA (Figure 34b) confirm successful derivatization by the emergence of two new peaks at 289.5 eV (O=C–O) and 292.7 eV (CF₃) in a 1:1 ratio alongside to the peaks of pristine PVA. Comparison of F 1s spectra before and after TFAA treatment reveals a prominent, symmetric peak only after derivatization, further supporting the successful reaction (Figure 34c). Figure 34d compares the quantified fluorine content across the different polymer samples. PVA exhibits a fluorine content of 35 at.%, which is slightly higher than the theoretical value (33 at.%) expected for complete conversion. This deviation may be attributed

to residual TFAA or trifluoroacetic acid trapped within the polymer particles, or to non-specific interactions of the reagent with the PVA surface.^[162] Notably, other polymers also exhibit reactivity toward TFAA, consistent with literature reports of minor cross-reactivity with oxygen-containing polymers.^[162] Their reactivity can however be explained by the high electrophilicity of TFAA. PEG, for example, consists primarily of repeating C–O–C units, but terminal –OH groups can react with TFAA. The released trifluoroacetic acid may strongly polarize or even protonate bridging ether oxygens, rendering the C–O–C bond susceptible to a nucleophilic attack by the trifluoroacetate anion, potentially catalyzing ether bond cleavage. Figure S9a,b summarizes the proposed degradation mechanism and C 1s detail spectra of the TFAA treated PEG. However, in HC, ether-like linkages are more likely to be pyran-like and conjugated rather than sp³-hybridized, rendering such cleavage unlikely.^[59]

In the case of PAA, a cross-esterification reaction may occur, yielding trifluoroacetic acid and a mixture of trifluoroacetate and PAA-derived anhydride species. The high fluorine content observed in PVMK can be attributed to keto-enol tautomerism of the carbonyl group adjacent to the methyl substituent. While the tautomeric equilibrium is expected to lie strongly on the keto side under the given conditions, the enolic form may still be present in small amounts and react with TFAA to form a vinyl ester. Figure S10a shows the anticipated reaction mechanism and the corresponding C 1s detail spectra of TFAA treated PVMK (Figure S10b). Similar to PEG, the presence of enolizable carbonyl species on HC is considered unlikely due to the predominantly conjugated aromatic surface.

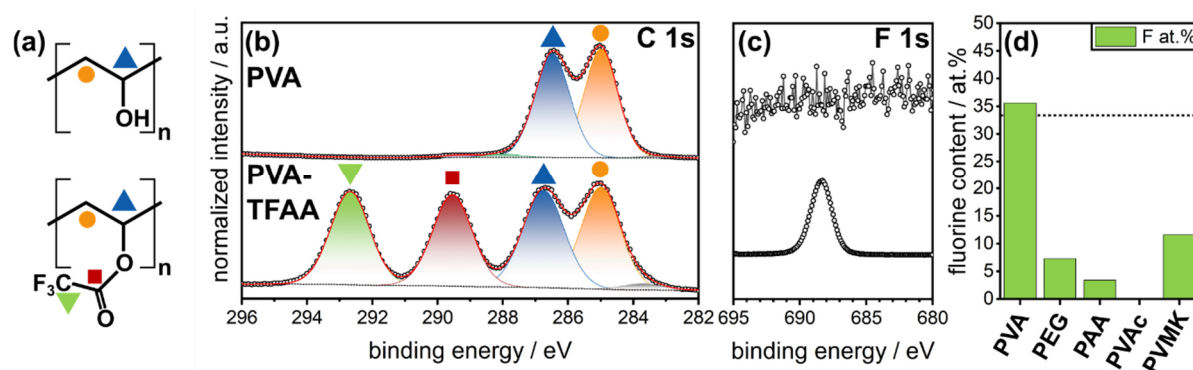


Figure 34. Molecular structure of PVA and its TFAA derivatized form (a). C 1s spectrum of PVA before and after the TFAA treatment (b) and corresponding F 1s spectra (c). Quantified fluorine content of polymers after TFAA treatment (d).

Table 10. Elemental quantification of PVA and PVA-TFAA with theoretical values for complete reaction in brackets.

	C / at. %	O / at. %	F / at. %
PVA	68.1 (66.7)	31.9 (33.3)	0 (0)
PVA-TFAA	43.7 (44.4)	19.9 (22.2)	35.8 (33.3)

Polymer TFE Derivatization

Carboxyl groups were targeted through derivatization using a mixture of TFE, pyridine and DTBCD. PAA served as the reference polymer and underwent esterification with TFE. The corresponding structures are shown in Figure 35a. Analogous to the derivatization of hydroxyl groups from PVA with TFAA, C 1s detail spectra in Figure 35b show the emergence of new peaks at 287 eV and 293 eV. The C–O peak at 287 eV appears at higher binding energies than typical C–O signals. This shift can be explained by the electron-withdrawing effect of the adjacent CF₃ group. The success of the derivatization is further confirmed by F 1s spectra shown in Figure 35c. The untreated sample shows no signal, while the derivatized sample exhibits a symmetric CF₃ peak at 688 eV. However, the expected ratio of 1:1:1:2 for CF₃, O=C–O, C–O and CC/CH components in the C 1s spectrum could not be observed, which means complete conversion of carboxyl groups was not achieved. Several factors may play into this incomplete conversion as the reaction mechanism is complex and involves multiple steps. It also requires stoichiometric amounts of the coupling agent DTBCD, which renders full conversion difficult.^[66] In addition, DTBCD is sterically hindered because of its spacious tert-butyl groups and carboxyl groups located beneath the polymer surface may not be accessible to the derivatization reagents. These inaccessible groups still contribute to the C 1s XPS signal, which can lead to an underestimation of the number of reactive carboxyl groups.

On the other hand, the complexity of the reaction makes it particularly selective toward carboxyl groups. This is evident in Figure 35d, where no fluorine signal is detected in F 1s spectra of PEG, PVAc and PVMK. Only traces are observed for PVA, as shown in Figure S12. In contrast, PAA exhibits a fluorine content of 23 at.%, which is approximately 10 at.% lower than the theoretical value of 33 at.%, which is expected for full conversion.

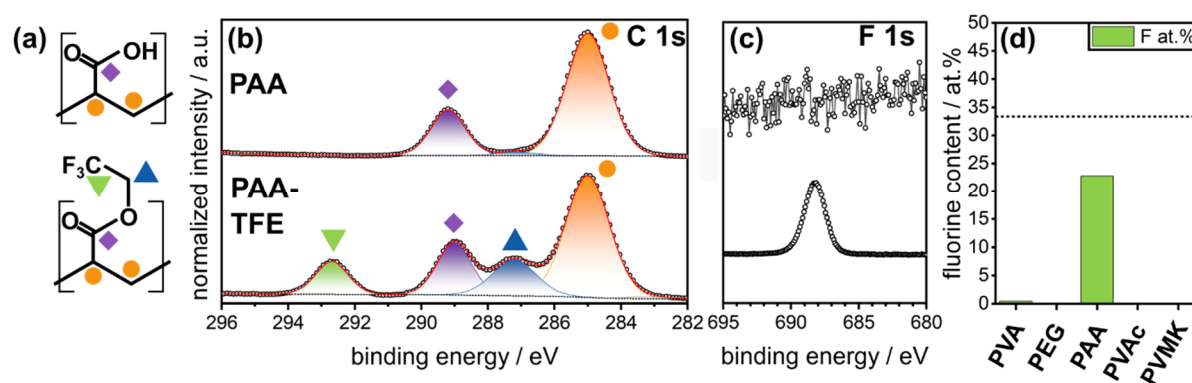


Figure 35. Molecular structure of PAA and its TFE derivatized form (a). C 1s spectrum of PAA before and after the TFE treatment (b) and corresponding F 1s spectra (c). Quantified fluorine content of polymers after TFE treatment (d).

Table 11. Elemental quantification of PAA and PAA-TFE with theoretical values for complete reaction in brackets.

	C / at.%	O / at.%	F / at.%
PAA	64.2 (60.0)	35.8 (40.0)	0 (0)
PAA-TFE	54.6 (50.0)	21.5 (20.0)	23.9 (30.0)

Polymer TFEH Derivatization

Carbonyl groups were derivatized using TFEH, which reacts with electrophilic carbonyl centers to form hydrazone derivatives. These functionalities are of particular relevance in sodium-ion batteries, as they may act as reversible redox-active sites and contribute to additional capacity during cycling.^[53,90,164] To validate the derivatization strategy, PVMK was selected as a model polymer. The structures of its native and derivatized forms are shown in Figure 36a. C 1s detail spectra Figure 36b reveal the anticipated disappearance of the original C=O peak at approximately 288 eV, accompanied by the emergence of new signals at 286.1 eV (C=N), 287.1 eV (CF₃-C*-NH), and 293 eV (CF₃), characteristic for hydrazone functionalities.^[163] Complete conversion would yield a peak ratio of 1:1:1:3 for the CF₃, CF₃-C*-N, C=N, and CC/CH components, which is not observed experimentally. One possible explanation is the use of TFEH as a 70% aqueous solution, where water, also formed as a reaction byproduct, may shift the equilibrium to the educts. However, this does not account for the complete disappearance of the C=O signal, suggesting the involvement of side reactions. Crosslinking between the hydrazone and a second carbonyl group may occur, as illustrated in Figure S14a. This reaction explains the near-complete loss of oxygen (1.4 at.%), the elevated nitrogen and reduced fluorine content (Figure S14c). Additional side-product formation is observed as a shoulder in the F 1s spectrum, possibly arising from alternative fluorine species such as F-N bonds (Figure 36b). The reaction shows limited selectivity, as fluorine is detected in all polymers, indicating that TFEH may react with functionalities other than carbonyls (Figure 36d). Although PVMK yields the highest fluorine content, the presence of fluorine in the other polymers confirms that the reaction is not exclusively specific to carbonyl groups. Consequently, quantification of carbonyl groups on HC surfaces based on fluorine content should be interpreted with caution, as reactivity from other OFGs cannot be excluded.

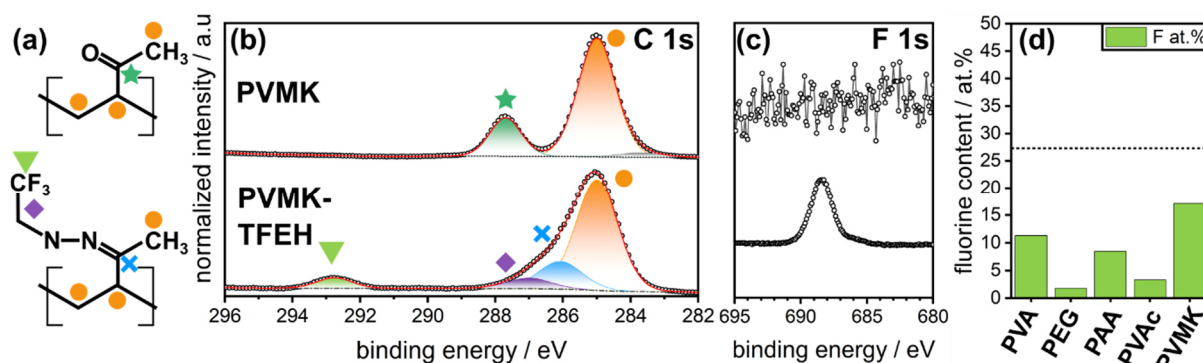


Figure 36. Molecular structure of PVMK and its TFEH derivatized form (a). C 1s of PVMK before and after the TFEH treatment (b) and corresponding F 1s spectra (c). Quantified fluorine content of all polymers after TFEH treatment (d).

Table 12. Elemental quantification of PAA and PAA-TFE with theoretical values for complete reaction in brackets.

	C / at.%	O / at.%	F / at.%	N / at.%
PVMK	79.4 (80.0)	20.6 (20.0)	0 (0)	0 (0)
PVMK-TFEH	60.0 (54.5)	1.4 (0)	24.6 (27.3)	14.0 (18.2)

4.4.2 Surface Composition of Hard Carbon

Building on the insights gained from polymer systems, this section focuses on the derivatization of pristine and ozone treated HC powders.

Hard Carbon TFAA Derivatization

In C 1s high-resolution spectra of TFAA treated HC powders, shown in Figure 37a, no distinctive peaks at ~ 293 eV indicative of CF_3 groups can be seen for all samples. This suggests a very low concentration of free hydroxyl groups across the HC powders. This observation is noteworthy, as ozone-assisted oxidation of the HC surface can plausibly generate hydroxyl groups *via* ozonolysis of $\text{C}=\text{C}$ double bonds. Figure 37b,c compare F 1s spectra of the untreated samples and those subjected to TFAA treatment. While no fluorine signal is observed for the untreated samples, a small but distinct peak appears at ~ 689 eV after derivatization, corresponding to the CF_3 moiety introduced by TFAA, which confirms the presence of a small number of reactive hydroxyl groups on the HC surface.

Figure 37d shows that the fluorine content remains low across all samples after derivatization: Pristine HC contains ~ 1.7 at.% F, which increases to 3.4 at.% for ozone treatment at 25°C and to 2.5 at.% for treatment at 100°C . Because esterification with TFAA proceeds in a 1:1 stoichiometry and introduces three fluorine atoms per hydroxyl group, the corresponding C–OH content can be estimated as one-third of the fluorine concentration. This translates to $\sim 0.6\%$ for the pristine HC, $\sim 1.1\%$ for the 25°C sample, and $\sim 0.83\%$ for the 100°C sample. These values indicate that ozone treatment at 25°C generates the highest amount of free hydroxyl groups, whereas elevated temperatures likely drive further oxidation toward O–C–O, C=O, or O=C–O species. Therefore, the C–O signal in C 1s spectra may also arise from cyclic oxygen functionalities such as pyran rings, which do not react with TFAA. While ozone can oxidize both surface and subsurface regions, TFAA derivatization targets only hydroxyl groups, which are accessible through wetting. This difference likely explains why the C–O intensity in C 1s spectra exceeds the comparatively weak fluorine signal in F 1s spectra.

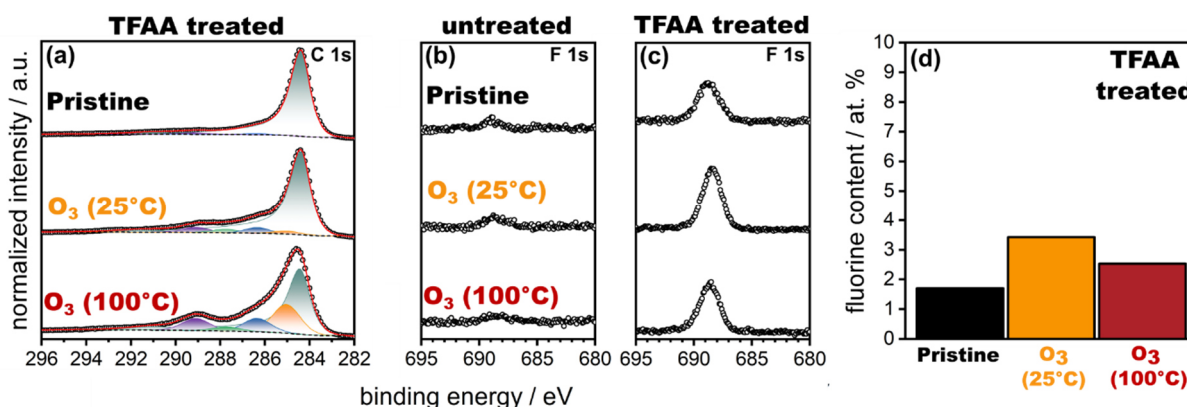


Figure 37. C 1s spectra of pristine and ozone functionalized HC samples subjected to TFAA treatment (a). F 1s spectra of untreated (b) and TFAA treated (c) HC powders. Quantified fluorine content of the TFAA treated HC powders (d).

Hard Carbon TFE Derivatization

TFE derivatization reveals a strong, temperature-dependent formation of surface carboxyl groups upon ozone treatment: The C 1s spectra of the TFE-treated pristine HC show no signal attributable to CF_3 groups, indicating that the untreated material contains negligible amounts of accessible carboxyl functionalities (Figure 38a). In contrast, a small peak at 293 eV appears after ozone treatment at 25 °C, and a pronounced peak attributed to CF_3 is observed following treatment at 100 °C, confirming the reaction of TFE with accessible carboxyl groups. A second peak emerges at 289.6 eV in the ozone-treated samples, corresponding to esterified carboxyl groups whose binding energy is shifted due to the derivatization reaction. This interpretation is supported by F 1s spectra, which display a peak at ~689 eV assigned to the introduced CF_3 moiety (Figure 38b). The intensity of this signal increases with ozone treatment and reflects the formation of free surface carboxyl groups. As the derivatization of PAA does not proceed to full conversion for the aforementioned reasons, the actual concentration of carboxyl groups on HC is likely underestimated by the fluorine signal.

Figure 38c summarizes the quantified fluorine contents of pristine and ozone-treated HC powders after derivatization with TFE. Evident from the F 1s spectra, the fluorine level in the pristine HC is low (~0.7 at.%), translating to a carboxyl concentration of 0.23 at.%. Ozone treatment at 25 °C increases the fluorine content to 2.8 at.%, which corresponds to 0.93 at.% of carboxyl functionalities. The highest value of 14.0 at.% is measured after ozone exposure at 100 °C, which equivalent to a carboxyl concentration of 4.67 at.%. Although the derivatization reaction may not proceed stoichiometrically, the measured fluorine content provides a semi-quantitative estimate and a lower-limit of the electrolyte accessible carboxyl group concentration. These results clearly show that ozone treatment introduces accessible carboxyl functionalities on the HC surface dependent on the treatment temperature. This agrees very well with the observations from Chapter 4.3 and the postulated Criegee-like functionalization mechanism.

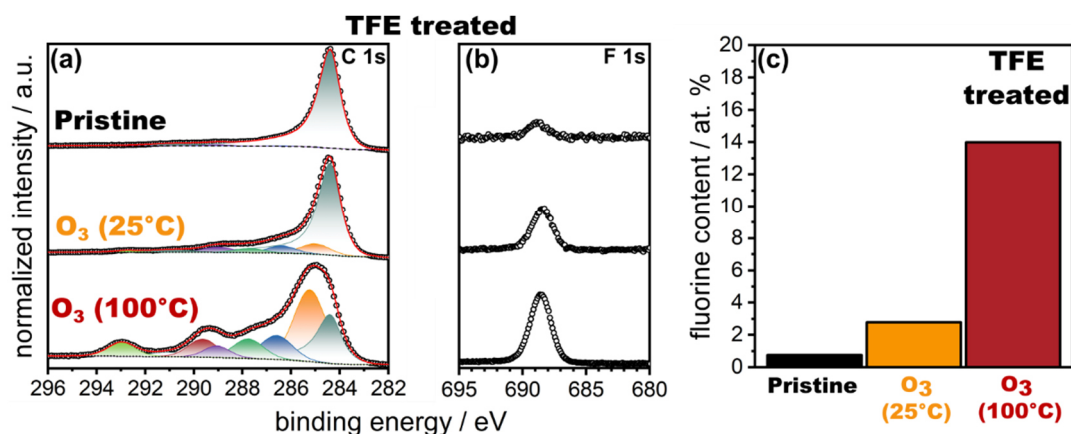


Figure 38. C 1s (a) and F 1s spectra (b) of TFE treated HC samples and quantified fluorine content (c).

Hard Carbon TFEH Derivatization

Although TFEH was intended to selectively derivatize carbonyl groups, C 1s spectra of the TFEH-treated pristine HC indicate that additional surface sites participate in the reaction or that non-specific interactions occur between TFEH and the HC surface. Besides the expected CF_3 feature, two prominent signals appear at 285.7 eV and 286.9 eV, which can be assigned to C–N and to C=N, N–C–N, or N–C*– CF_3 environments.^[163] Since the pristine HC C 1s spectrum does not exhibit spectral evidence of carbonyl groups, these findings suggest that TFEH reacts with other surface OFGs as predicted by the polymer reference samples. Additionally, reaction with defects can occur, which are not explicitly considered here.

The 25 °C ozone-treated HC exhibits similar spectral features but with higher intensities, consistent with the notion that mild oxidation conditions generate carbonyl groups that subsequently react with TFEH (Figure 39a). This observation aligns with the previously proposed ozone-functionalization mechanism. In contrast, the sample treated at 100 °C shows a broad C 1s signal in the CC/CH region, which may arise from LOCs formed during ozone exposure and their subsequent reaction with ambient moisture. F 1s spectra contain two distinct signals: a main peak at 688.5 eV and a secondary peak at 686 eV with lower intensity (Figure 39b). The latter increases for the 25 °C ozone-treated sample and may indicate the formation of alternative fluorine-containing species such as F–N bonds from surface-bound fluorinated nitrogen fragments, complicating interpretation of the derivatization results.

Fluorine quantification yields 15.7 at.% for pristine HC, 27.1 at.% for the 25 °C ozone-treated sample, and 11.6 at.% for the 100 °C sample (Figure 39c). The highest fluorine content observed for the 25 °C ozone treated sample supports the hypothesis that mild oxidation preferentially forms carbonyl groups, whereas higher temperatures promote the formation of carboxyl functionalities, consistent with results from TFE derivatization. However, given the observed reactivity of TFEH across multiple reference polymers and the presence of fluorine in all HC samples, these results must be interpreted with caution.

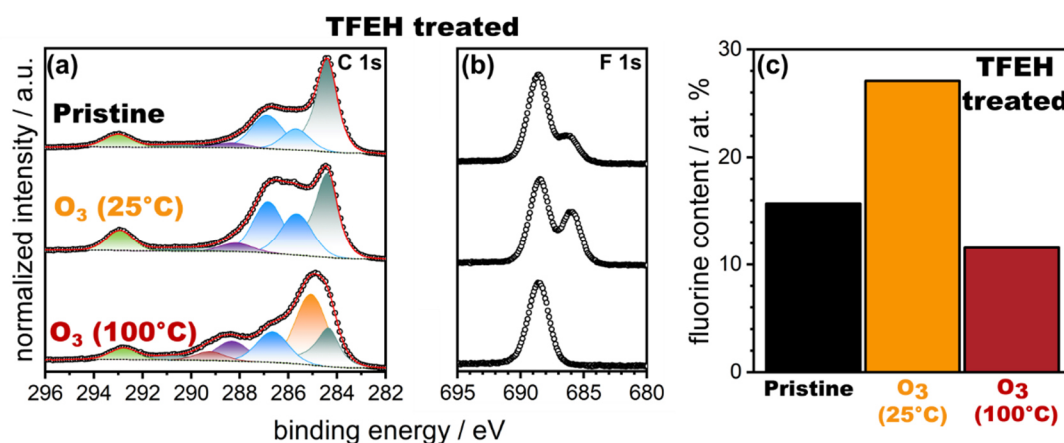


Figure 39. C 1s (a) and F 1s spectra (b) of TFEH treated HC samples and quantified fluorine content (c).

The combined derivatization experiments on polymer reference materials and HC samples allow a comprehensive assessment of the surface chemistry of pristine and ozone-treated HCs. Figure 40 summarizes the total oxygen contents of the HC samples as determined by XPS together with the distribution of individual oxygen-containing functional groups obtained from derivatization.

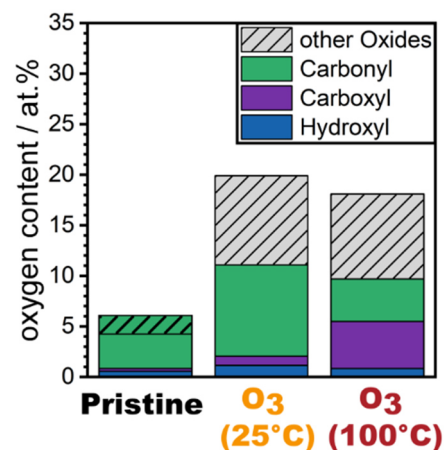


Figure 40. Calculated content of oxygen functional groups on pristine and ozone treated HC powders. The green-shaded region marks the portion attributed to an overestimation of carbonyl groups in the pristine HC.

The pristine HC contains 4 at.% oxygen, which is exceeded by the sum of quantified derivatized functionalities. Although derivatization is designed to provide quantitative information, the results likely overestimate carbonyl groups due to limited selectivity and possible side reactions. In contrast, the quantified concentrations of carboxyl and hydroxyl groups appear more reliable. This is consistent with the different probing depths of the methods: XPS detects both surface- and subsurface oxygen species several nanometers into the carbon matrix, whereas derivatization is confined to the wetted and chemically accessible surface. Since this interfacial region is most relevant for electrochemical processes, derivatization provides relevant informations for battery applications. For the ozone-treated samples, the sum of derivatized oxygen functionalities does not match the total oxygen detected by XPS. This discrepancy likely arises from surface OFGs that do not react with the derivatization reagents, as well as from subsurface oxygen. These oxygen species are detectable by XPS but inaccessible to derivatization and cannot be quantified.^[67]

Overall, the derivatization strategy developed in this work enables the selective identification and relative quantification of hydroxyl and carboxyl groups on HC surfaces, whereas carbonyl functionalities could not be reliably analyzed. Validation with polymer reference materials and application to pristine and ozone-treated HC demonstrate the utility of the approach; however, the results should be interpreted in a semi-quantitative manner. Incomplete conversion during derivatization reactions, such as carbodiimide-activated esterification with TFE and reduced selectivity of TFEH due to side reactions with other nucleophilic sites still impose inherent limitations. Additionally, morphological and microstructural characteristics of HC can influence the comparison between XPS and derivatization, since XPS may probe regions which are not accessible to liquid-phase reagents. Despite these constraints, the method provides valuable insight into the surface chemistry of HC and its modification through oxidative treatments, particularly in the context of SEI formation and sodium storage behavior.

4.4.3 Electrochemical Characterization

As outlined in Chapter 4.3, surface OFGs of ozone functionalized HCs exhibit differences SEI formation, reversible capacity and ICE of SIBs depending on the temperature of the treatment. Therefore, electrodes of pristine and ozone functionalized samples were subjected to an identical derivatization treatment to decouple the contributions of individual OFGs and evaluate their electrochemical activity. Covalent modification of hydroxyl, carboxyl, and carbonyl functionalities *via* derivatization is expected to reduce their participation in SEI formation, as the reactive sites are chemically saturated through covalent attachment of the derivatization reagent, thereby lowering their reactivity.

However, electrodes contain among the active material also components, which are needed for structural integrity like binders or additives for conductivity (e.g. conductive carbon). In this study, carboxymethyl cellulose (CMC) and styrene–butadiene rubber (SBR) were employed as binder components. Due to the presence of intrinsic hydroxyl and carboxyl functionalities, CMC is also susceptible to reactions with the derivatization reagents. However, since the resulting ester bonds from derivatized HC powders are prone to hydrolysis upon contact with water, this represents the most practical approach under the constraints of aqueous processing prior to electrode coating. To ensure direct comparability with previous investigated samples, the overall electrode composition was kept unchanged.

SEM analysis of electrodes before and after TFAA treatment reveals no observable morphological changes (Figure 41a). C 1s spectra of the pristine electrode show apart from the dominant HC sp^2 peak features, which are attributable to the binder components. Upon treatment in TFAA, peaks corresponding to trifluoroacetate esters are observable, which confirms the reactivity of CMC with the derivatization reagents (Figure 41b). CMC exhibits free hydroxyl and carboxyl functionalities, which can react with the derivatization reagents (Figure 41c). Therefore, derivatization of electrodes will cover the contributions from binder and active material induced interactions of OFGs during SEI formation.

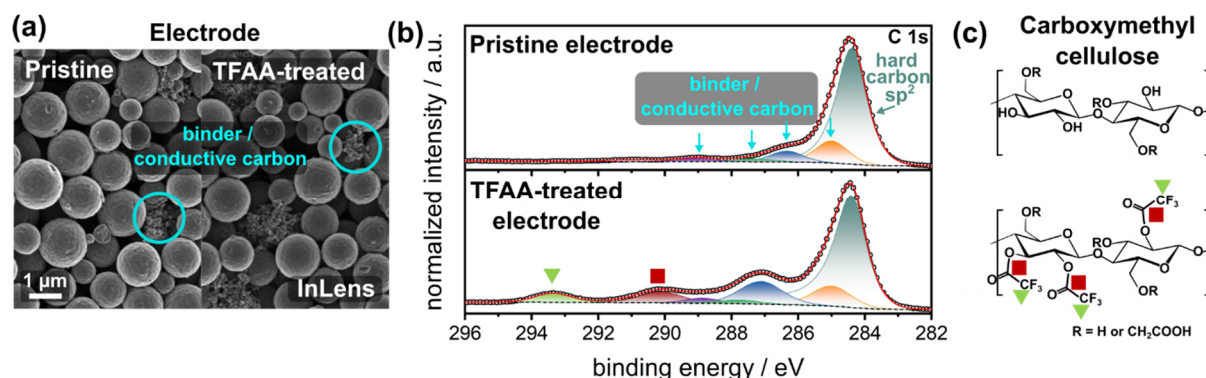


Figure 41. SEM InLens images (a) and C 1s spectra (b) of a pristine and a TFAA treated electrodes. Molecular structure of CMC binder before and after TFAA treatment.

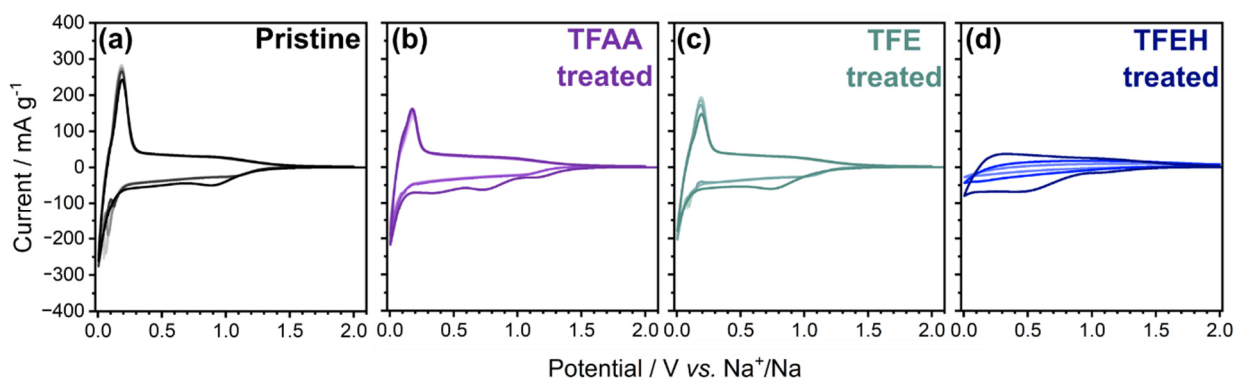


Figure 42. First five CV scans at 0.1 mV s^{-1} of pristine (a), TFAA (b), TFE (c) and TFEH (d) derivatized electrodes

CV measurements were conducted to investigate the interfacial processes of pristine and derivatized HC electrodes with a focus on the influence of OFGs on SEI development during the initial cycles (Figure 42a-d). In the first cathodic scan for the pristine HC electrode, a distinct reduction peak emerges at $\sim 0.9 \text{ V vs. Na}^+/\text{Na}$, which disappears in subsequent cycles and can therefore be attributed to initial SEI film formation.^[95,103] In agreement with previous measurements, the highest current densities are observed below 0.1 V , corresponding to reversible sodium storage *via* insertion in pseudo-graphitic domains and pore filling.^[99] TFAA treated electrodes exhibit an earlier current onset and a high-potential SEI formation peak at $\sim 1.2 \text{ V}$. Additional reactions associated with SEI formation occur at ~ 0.7 and $\sim 0.4 \text{ V}$ indicating that SEI formation proceeds sequentially. It should be noted however that these features may not solely originate from SEI formation, but can also include contributions from the electrochemical reduction of the derivatization species.

TFE treated electrodes lack these features, implying they are specific for TFAA treated electrodes. A possible explanation is that a small number of reactive sites governs SEI formation and their derivatization by TFAA induces a redistribution of reaction pathways toward less efficient sites. This would also explain the multi-step SEI formation process and the concomitant decrease in (de-)insertion currents at low potentials. The difference could also be to the varying selectivity of the derivatization reactions. As demonstrated in the preliminary model polymer studies, TFE has high selectivity and reacts exclusively with carboxyl groups, which are present only in low surface concentrations on pristine HC. Consequently, TFE treatment induces only minor changes in surface chemistry and the resulting electrochemical behavior. In contrast, TFAA and TFEH exhibit lower selectivity and modify a broader range of surface functionalities, leading to more pronounced changes in the CV response.

Derivatization with TFE does not significantly alter the CV response of pristine HC. This suggests that carboxyl functionalities do not represent the key reactive sites for SEI initiation, which is instead governed by other surface functionalities or defect-related structures. TFEH treated electrodes exhibit a nearly complete loss of electrochemical activity, with no distinct SEI related features and no evidence of sodium insertion at low potentials. This behavior can

be attributed to the low selectivity of the derivatization reaction combined with the steric impact of the bulky derivatization agent, which likely results in extensive surface passivation. As a consequence, electrochemically active sites are blocked and ion transport across the interface is hindered, leading to suppressed charge-transfer processes.

Figure 43a compares the first galvanostatic charge–discharge cycles of pristine HC electrodes with those subjected to different derivatization treatments. Pristine, TFAA-, and TFE-treated electrodes all exhibit first-cycle discharge capacities of $\sim 300 \text{ mAh g}^{-1}$. However, their potential profiles differ noticeably. These differences directly reflect differences in SEI formation pathways induced by selective modification of surface sites. The distinctions become more evident in the corresponding differential capacity plots shown in Figure 43b and its inset. The pristine and TFE treated electrode both share a single SEI related peak during the first cycle, however the position shifts from 0.9 to 0.7 V, indicating again that carboxyl functionalities do not represent the dominant reactive sites governing SEI formation. The TFAA-treated sample exhibits three distinct peaks, which are in good agreement with the positions of SEI related peaks observed in the CV measurements and corroborate the sequential SEI development. The TFEH treated electrode exhibits no plateau capacity and demonstrates a negligible desodiation capacity during discharge. In addition to that, no signs of sodium insertion at low potentials can be observed for TFEH treated electrodes in differential capacity plots.

Rate tests further corroborate these findings: TFE derivatization preserves the capacity retention and ICE relative to pristine HC (Table 13), whereas derivatization of hydroxyl groups by TFAA leads to a reduced reversible capacity and an impeded ICE. This behavior is attributed to the formation of a less ion-conductive SEI, which introduces additional interfacial resistance and increases electrode polarization, thereby lowering the apparent reversible capacity, which is reflected by a decrease in both the slope and plateau capacity in addition to lower capacities at increasing current loads. In contrast, derivatization with TFEH results in severe capacity decay over the first five cycles, an ICE as low as 46.6% and a complete loss of electrochemical activity after cycle five. It should be noted that the surface concentration of carboxyl and hydroxyl functionalities are marginal, as identified by the derivatization of the pristine HC powder ($<1 \text{ at.}\%$) and TFEH treatment certainly overestimated contributions from carbonyl functionalities. Taking this into account, it is plausible that binder components may also contribute to the observed interfacial behavior and should be considered when interpreting the results.

Overall, the electrochemical response of derivatized HC electrodes reflects not only changes in intrinsic surface reactivity, but also contributions from the chemical nature, selectivity, and possible electrochemical instability of the derivatization species themselves.

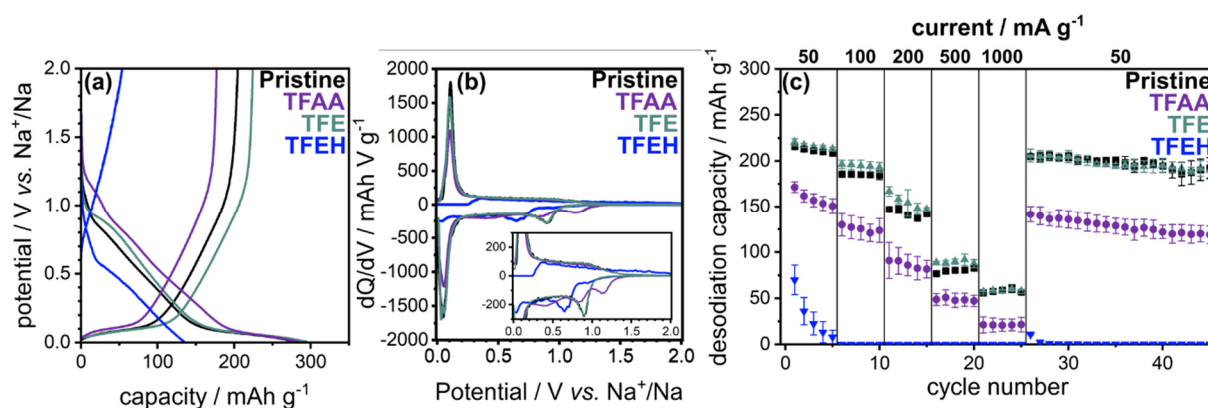


Figure 43. First-cycle charge-discharge profile of pristine HC and its derivatized electrodes at 50 mA g⁻¹ (a) with corresponding differential capacity plot (b) and rate test of the electrodes (c).

Table 13. Overview of HC and derivatized electrodes with their specific capacities, slope- and plateau capacities, and initial coulomb efficiencies (mean $\pm$ standard deviation).

	reversible capacity at 50 mA g ⁻¹	slope capacity	plateau capacity	slope / plateau ratio	ICE
	/ mAh g ⁻¹	/ mAh g ⁻¹	/ mAh g ⁻¹		/ %
HC	221 $\pm$ 4	111 $\pm$ 2	110 $\pm$ 2	1.01	77.0 $\pm$ 1.2
+TFAA	161 $\pm$ 9	89 $\pm$ 4	72 $\pm$ 5	1.23	61.8 $\pm$ 0.7
+TFE	220 $\pm$ 4	109 $\pm$ 2	111 $\pm$ 3	0.98	76.3 $\pm$ 0.3
+TFEH	-	-	-	-	46.6 $\pm$ 6.6

In agreement with prior observations, ozone functionalization at 25 °C results in enhanced sodium insertion currents at low potentials and induces a shift of SEI formation to higher potentials, which can be seen in CV measurements (Figure 44a-c). These effects are attributed to a modified (pore) surface chemistry due to the presence of OFGs, which can improve interfacial properties and facilitate ion transport as discussed in Chapter 4.3.

Despite the fact that the concentration in quantified hydroxyl and carboxyl functionalities is nearly doubled, no significant differences are observed between the untreated and TFAA derivatized electrodes in the overall CV profile. This is somewhat unexpected and suggests that the impact of derivatization on electrochemically relevant surface sites is limited.

One possible explanation is that derivatization primarily occurs at the outer particle surface, which is probed by XPS, while the internal pore network, which governs sodium storage and transport, remains largely unaffected. This may be further corroborated by changes in surface polarity induced by ozone treatment, which could hinder the penetration of derivatization reagents and solvents into the internal structure of the HC particles. OFGs may also be generated by ozone treatment in regions, which are not accessible to the derivatization reagents, but contribute electrochemically to SEI formation. The kinetic diameter of the ozone molecule is approximately ~0.33-0.36 nm based on values of O₂ and SO₂, which would be small enough to access also ultramicropores (<1 nm).^[35,157] In contrast, molecules employed in the derivatization procedures (TFAA, TFE, DTBCD, *etc.*) are all much more spacious and

can therefore not enter the pores, which have been functionalized by ozone, further supporting the hypothesis that electrochemically active sites may reside in regions inaccessible to derivatization. Na^+ ions on the other hand with a diameter of ~ 0.25 nm are very well known to access these pores.^[157,165]

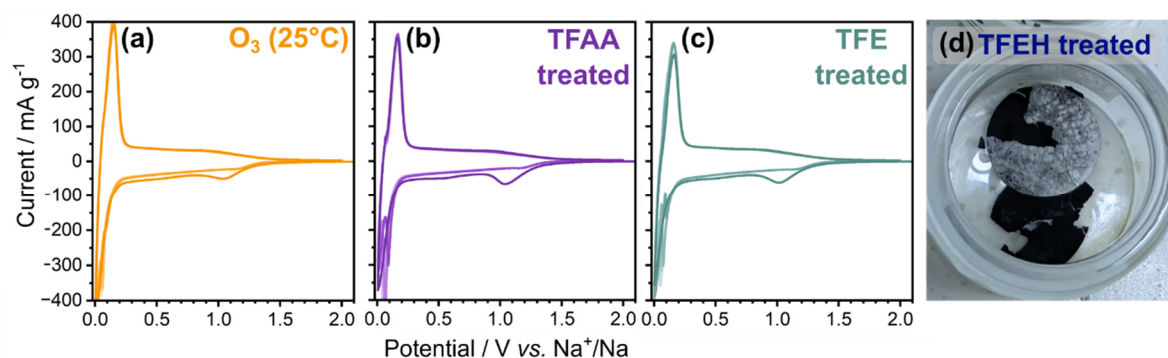


Figure 44. First five CV scans of a 25°C O₃ treated sample (a) as well as TFAA (b) and TFE (c) derivatized electrodes at 0.1 mV s⁻¹. Photograph of delaminated electrode after immersion in TFEH.

Contrary to expectations, derivatization with TFAA and TFE does not affect the position of the SEI formation peak in the first cycle, and de-insertion currents closely resemble those of the unmodified ozone functionalized electrode. This observation contrasts with the behavior of the pristine HC and suggests that a highly functionalized surface is less sensitive to chemical modification in terms of its electrochemical response. It would be expected that TFAA and TFE electrodes exhibit multiple pronounced features associated with SEI formation in CV measurements, similar to the pristine HC treated with TFAA. However, CV measurements cannot distinguish between individual irreversible reactions, if the reactions proceed at the same potential, which may obscure subtle changes induced by derivatization.

The contrasting impact of TFAA derivatization on pristine and ozone-treated HC indicates that SEI formation in pristine HC is governed by a limited number of highly reactive surface sites. Derivatization of these sites disrupts the dominant reaction pathways, resulting in multiple competing SEI processes and reduced reversible capacity due to inferior SEI development. In contrast, ozone treatment generates a higher density of surface distributed OFGs, leading to a transition from site-controlled to OFG ensemble-controlled SEI formation. In such a system, the contribution of individual surface sites becomes less critical, rendering the system largely insensitive to selective chemical modification by derivatization.

Electrodes treated with TFEH could not be analyzed due to detachment of the coating from the current collector during immersion (Figure 44d). The observed delamination of TFEH-treated electrodes suggests an additional contribution from structural or binder-related effects, potentially linked to interactions between derivatization products and ozone treatment-derived LOCs. These effects may further complicate the interpretation of electrochemical data and

highlight the sensitivity of the system toward chemical modification. Therefore, derivatization utilizing TFEH was excluded from further investigation.

Galvanostatic cycling of the mild ozone-functionalized electrode and derivatized samples provides additional insight into the role of OFGs in the early cycles of HC. As determined by XPS, the oxygen content is almost five times higher, the ICE remains unchanged, which corroborates the hypothesis that OFGs primarily influence the onset of SEI formation without significantly increasing irreversible sodium consumption (Table 14). Both TFAA- and TFE-derivatized electrodes display almost identical reversible capacities in the first cycle compared to the untreated ozone-functionalized reference (Figure 45a). Selective masking of oxygen functionalities is expected to mitigate irreversible capacity losses during initial cycling without detrimentally affecting reversible sodium storage, however no significant changes can be observed for the 25°C treated ozone sample and its derivatized electrodes.

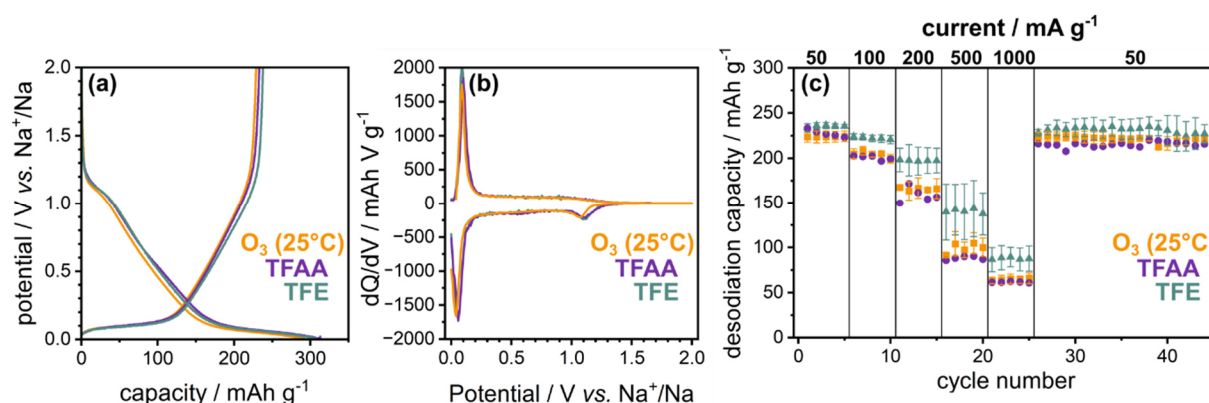


Figure 45. First-cycle charge-discharge profile of 25°C ozone treated HC and its TFAA/TFE derivatized electrodes at 50 mA g⁻¹ (a) with corresponding differential capacity plot (b) and rate test of the electrodes (c).

Table 14. Overview of HC-O3-25 and derivatized electrodes with their specific capacities, slope- and plateau capacities, and initial coulomb efficiencies (mean ± standard deviation, only a single measurement was available for TFAA).

	reversible capacity at 50 mA g ⁻¹	slope capacity	plateau capacity	slope / plateau ratio	ICE
	/ mAh g ⁻¹	/ mAh g ⁻¹	/ mAh g ⁻¹		/ %
HC-O3-25	228 ± 6	119 ± 3	109 ± 3	1.10	77.2 ± 1.3
+TFAA	231	120	111	1.07	74.5
+TFE	241 ± 2	129 ± 4	112 ± 2	1.16	76.4 ± 0.6

To further probe the limits of the derivatization approach and extend the mechanistic framework, electrodes based on HC treated with ozone at 100 °C were investigated. CV measurements of the ozone treated HC and its derivatized counterparts show similar profiles, with only a slightly broader and more pronounced SEI formation feature for the TFAA-treated electrode, indicating more extensive and less controlled electrolyte decomposition (Figure 46).^[90] Instabilities are observed for the TFE treated electrode, especially in the lower potential regime in the first cycle. Because of the high degree of oxygen functionalization

demonstrated by XPS and abundance of non-quantifiable oxides, it is very likely that LOCs govern the SEI formation process, which are either not accessible or not reactive towards the derivatization reagents, which explains the similarity of CV profiles.

In contrast to the behavior observed for pristine HC, the electrochemical response of the 100°C treated HC appears insensitive to selective chemical modification. This indicates that SEI formation is no longer governed by a limited number of reactive surface sites, but rather by a highly oxidized and structurally disordered surface. Under these conditions, derivatization of individual functionalities does not significantly alter the overall interfacial behavior.

Galvanostatic measurements further support this interpretation. The first-cycle voltage profiles reveal pronounced irreversible losses and a strong dominance of sloping capacity, as reflected by slope-to-plateau capacity ratios exceeding 2 (Table 15). This indicates that sodium storage in the samples is predominantly surface-controlled, while the contribution from insertion sites like pores is significantly reduced. The corresponding low ICE values summarized in Table 15 confirm extensive irreversible reactions.

These observations underline the findings from Chapter 4.3 that ozone treatment at elevated temperature induces not only a high density of OFGs but also significant structural degradation of the carbon framework. The resulting loss of pore-attributed sodium storage domains and increase in disordered surface regions fundamentally changes the electrochemical behavior: The system transitions from a balanced slope and plateau controlled (pristine HC) to ensemble-controlled (mildly oxidized HC) and finally to structurally degraded behavior, in which neither individual functional groups nor their selective modification dominate the electrochemical response.

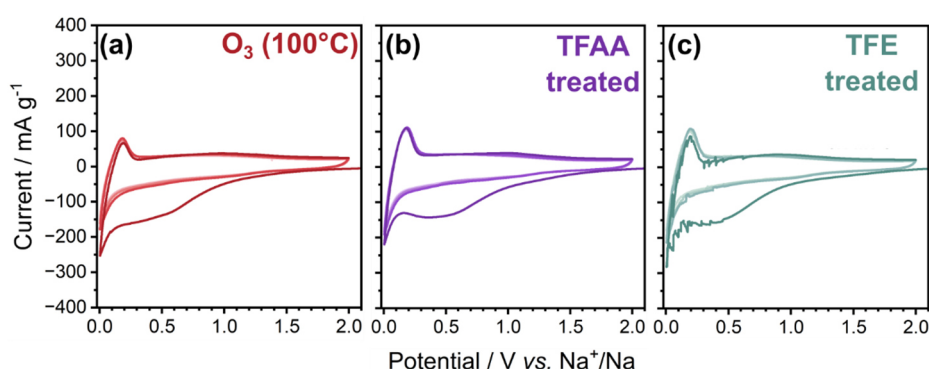


Figure 46. First five CV scans of a 100°C O₃ treated sample (a) as well as TFAA (b) and TFE (c) derivatized electrodes at 0.1 mV s⁻¹.

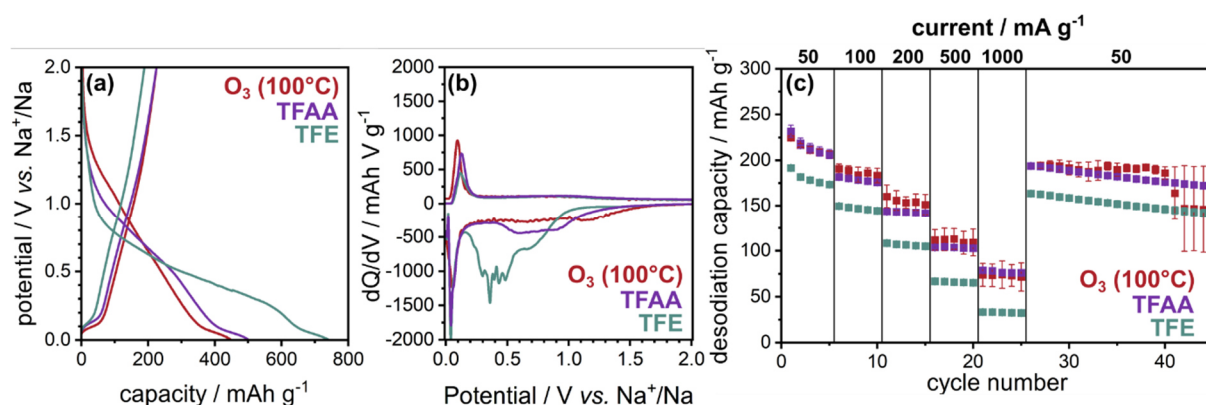


Figure 47. First-cycle charge-discharge profile of 100°C ozone treated HC and its TFAA/TFE derivatized electrodes at 50 mA g⁻¹ (a) with corresponding differential capacity plot (b) and rate test of the electrodes (c).

Table 15. Overview of HC-O3-100 and derivatized electrodes with their specific capacities, slope- and plateau capacities, and initial coulomb efficiencies (mean $\pm$ standard deviation).

	reversible capacity at 50 mA g ⁻¹	slope capacity	plateau capacity	slope / plateau ratio	ICE
	/ mAh g ⁻¹	/ mAh g ⁻¹	/ mAh g ⁻¹		/ %
HC-O3-100	219 $\pm$ 8	150 $\pm$ 8	69 $\pm$ 1	2.21	50.4 $\pm$ 0.1
+TFAA	242 $\pm$ 15	163 $\pm$ 10	79 $\pm$ 4	2.06	44.0 $\pm$ 1.1
+TFE	209 $\pm$ 12	137 $\pm$ 8	72 $\pm$ 4	1.91	25.9 $\pm$ 0.4

4.4.4 Conclusion

The derivatization approach developed in this work demonstrates that selective chemical labeling enables the identification of individual OFGs on HC surfaces with high specificity for hydroxy and carboxy functions. As a complementary technique to conventional surface analysis methods, derivatization provides direct insights into chemical environment and distribution of electrochemically relevant surface functionalities. A key advantage lies in its operational simplicity and the ability to selectively label only those OFGs that are accessible to the electrolyte, thereby directly linking surface chemistry to electrochemical behavior. Future studies on HC materials focusing on surface functionalization should therefore expand their analysis repertoire by this facile method. While this approach shows good selectivity for hydroxyl and carboxyl groups, the derivatization of carbonyl functionalities with TFEH remains less specific. Finding of an alternative carbonyl derivatization reagent (e.g. pentafluorophenylhydrazine) or transition to gas-phase derivatization procedures could overcome the drawbacks observed for derivatization with TFEH.

It could be demonstrated that pristine HC with ~4 at.% oxygen content has a low amount of chemically accessible surface OFGs in the form of hydroxy and carboxyl functionalities (<1 at.%). Ozone treatment at 25°C raises the total oxygen functionalization to 20 at.% and increases concentrations of hydroxyl and carboxyl functionalities, whereas treatment at 100°C significantly increases the carboxyl share to 4.7 at.%.

Beyond its analytical capabilities, this study deepens more fundamental insights into the role of OFGs in sodium-ion batteries. Results from electrodes subjected to derivatization reactions demonstrate that OFGs do not primarily determine the total extent of SEI formation, but rather govern its onset and reaction pathways. In pristine HC, SEI formation is controlled by a limited number of reactive surface sites, rendering the system highly sensitive to selective chemical modification. Upon mild ozone treatment (25 °C), this behavior shifts toward an ensemble-controlled regime, where a higher density of distributed OFGs leads to a more uniform SEI formation, because of a redundant surface functionalization. At more aggressive oxidation conditions (100 °C), structural degradation of the carbon matrix dominates, resulting in a disordered system with reduced insertion capacity and extensive irreversible reactions.

These findings highlight that the electrochemical relevance of OFGs is not solely determined by their concentration, but by their accessibility, chemical environment, and structural context. Consequently, derivatization selectively probes only a subset of electrochemically relevant functionalities, which must be considered when interpreting results. Future work should extend this methodology to well-defined model electrodes like HOPG and glassy carbon electrodes or to HC materials with systematically varied structural and chemical properties.

Imaging techniques could be developed to complement the chemically selective derivatization approach. While chemical labeling allows for the identification of accessible OFGs, it does not provide direct information on their spatial distribution across the carbon surface. One promising strategy could involve organosilane-based functionalization, enabling the introduction of heavier elements onto specific OFGs. Such labeling could subsequently be visualized using electron microscopy techniques, for example *via* energy-selective backscattered (ESB) detectors, providing contrast based on atomic number differences. This approach may allow direct visualization of the spatial distribution and clustering of surface functionalities, thereby offering deeper insight into the relationship between surface heterogeneity and SEI formation. However, this method will likely face similar challenges related to chemical selectivity and sterical accessibility as well as spatial resolution of the ESB detector.

Overall, this work establishes chemical derivatization as a powerful diagnostic tool for probing surface chemistry in carbon-based battery materials and provides a unified mechanistic framework linking OFGs, structural evolution, and electrochemical performance in hard carbon anodes.

5 Summary

The surface properties of hard carbon materials are becoming an increasingly important research topic in the sodium-ion battery research community. A comprehensive understanding of the relationship between surface chemistry and electrochemical performance requires the separation of surface-related effects from morphological contributions, which is often not sufficiently addressed in the literature. The targeted modification of oxygen functional groups on the surface has been identified as a promising approach to improve the electrochemical properties of hard carbon with regard on initial capacity losses from solid electrolyte interphase formation.

In this work, the surface chemistry of hard carbon is systematically tailored using both non-covalent functionalization *via* pyrene-based molecules and covalent modification through ozone treatment, while avoiding significant changes to the particle morphology. By correlating detailed surface characterization with electrochemical performance, this thesis provides fundamental insights into the role of oxygen surface functionalization in hard carbon and its impact on SEI formation in SIBs.

Pyrenes bearing different oxygen functional groups were adsorbed on the surface of hard carbon as model compounds to introduce well-defined surface functionalities. Using complementary characterization techniques such as UV–Vis spectrophotometry, XPS, and electrochemical measurements, the presence and redox activity of the pyrene species on the hard carbon surface were clearly confirmed. Despite this controlled modification, no direct correlation between surface oxygen functionalization and the ICE could be established. These results demonstrate that the electrochemical impact of oxygen functional groups is not intrinsic to their chemical identity, but governed by the interfacial environment created by their spatial distribution, surface coverage, and electronic properties. While pyrene-derived functionalities significantly influence SEI formation and interfacial transport, their effect on reversible capacity is indirect and mediated through the interphase. Accordingly, differences in pore-attributed capacity arise from variations in interfacial accessibility rather than changes in intrinsic sodium storage.

Ozone treatment of hard carbon was investigated as a facile surface functionalization method to introduce a variety of oxygen functional groups. Surface functionalization is effectively achieved by ozone already at room temperature, leading to an increase in oxygen content by ~15 at.% as quantified by XPS. Additionally, it was found that the treatment temperature governs the degree of functionalization and structural degradation, as for high temperature treatments a decrease in particle size and formation of highly oxidized carbon fragments could be observed. A Criegee-type ozonolysis inspired reaction mechanism was proposed, which coherently describes the formation of functional groups identified by XPS.

Most importantly, the results refute the common assumption that a high surface oxygen content inherently leads to a poor initial coulombic efficiency. Instead, the results highlight that both initial coulombic efficiency and reversible capacity are governed primarily by the accessibility of the internal porosity. While ozone functionalization at 25 °C enhances ion-transport kinetics, as evidenced by reduced charge-transfer resistance, high-temperature ozone treatment promotes structural degradation and the formation of carbon fragments that obstruct the internal pore networks, thereby lowering the reversible capacity of HC.

Finally, a chemical derivatization approach was pursued to identify individual oxygen functional groups on the surface of hard carbon, which would otherwise remain impossible to determine due to the spectral overlap of XPS signals. This derivatization approach enables reliable insights into the nature and distribution of electrochemically relevant surface groups including hydroxyl, carboxyl and carbonyl functionalities by selective reactions with fluorinated marker molecules. While derivatization reactions provided robust evidence for hydroxyl and carboxyl groups, the analysis of carbonyl groups remained inconclusive. Quantification of the fluorine content following derivatization enabled the estimation of the respective oxygen functional group levels. It was further demonstrated that pristine hard carbon features low amounts of accessible surface hydroxyl and carboxyl functionalities, which can be significantly increased by ozone treatment.

In summary, this work thoroughly investigated the surface properties of hard carbon and linked the electrochemical performance in electrochemical cells with surface functionalization by oxygen groups. The results evidence that a high degree of surface oxygen functionalization does not correlate with a low initial coulombic efficiency and impeded reversible capacity. In contrast, it was found that a surface oxygen content as high as 20 at.% can decrease interfacial resistances and facilitate charge-transfer kinetics, while maintaining a high reversible capacity and initial coulombic efficiency. It was further found that the accessibility of pores is critical for a high reversible capacity, as the low-potential plateau capacity is reduced for samples with blocked internal porosity as observed for pyrene functionalized samples and hard carbon subjected to ozone treatment at elevated temperatures.

6 Outlook on Future Research Possibilities

This work focused on developing a profound understanding of hard carbon surface properties and on how oxygen functional groups influence the electrochemical structure-property relationships in sodium-ion batteries. Within the current research landscape, there is a lack of fundamental studies investigating the interplay between oxygen functional groups and electrochemical activity. Existing literature often fails to decouple effects of surface functionalization and concomitant structural disintegration of the carbon framework.

Future studies can build on the facile functionalization framework of hard carbon with ozone. However, the reaction mechanism of ozone with hard carbon surfaces still needs a deeper mechanistic investigation to enable a targeted introduction of surface functionalities. Here, theoretical studies (*e.g.* DFT simulations) could elucidate the molecular interaction of graphene sheets or defects with ozone molecules to further corroborate experimental findings.

In analogy to established methods in organic chemistry, controlled ozonolysis could achieve precise surface tuning and thus aid rational SEI development. Oxygen functionalized surfaces could further serve as a gateway for subsequent reactions, *i.e.* introduction of other heteroatoms to the hard carbon surface. Similar to the derivatization of electrodes described in Chapter 4.4.3, nitrogen groups may be introduced. Possibly, the treatment of ozone-functionalized hard carbons with ammonia at elevated temperatures could be used to investigate the impact of surface nitrogen doping. Particular emphasis should be placed on developing new methods that allow functionalization without inducing structural change to the surface, like ozone treatment at elevated temperatures.

In addition to surface functionalization efforts, the concurrent implementation of surface-sensitive analytical methods is essential. In this context, derivatization reactions using fluorinated marker molecules followed by XPS quantification were shown to provide a solid foundation for the complementary detection and quantification of oxygen functional groups and should become a standard diagnostical tool. However, beyond the described derivatization approaches for quantification, it is of great interest to explore the potential of imaging techniques regarding oxygen functional groups. For instance, the use of organosilanes could enable spatially resolved mapping of oxygen functionalization, utilizing the energy selective backscattered electron detector in a scanning electron microscope to visualize chemical contrasts.

7 References

- [1] C.-X. Zu, H. Li, “Thermodynamic analysis on energy densities of batteries” *Energy Environ. Sci.* **2011**, 4, 2614–2624.
- [2] U. S. G. Survey, *Mineral commodity summaries 2020*, U.S. Geological Survey, **2020**.
- [3] U. S. G. Survey, *Mineral commodity summaries 2025*, U.S. Geological Survey, **2025**.
- [4] O. Velázquez-Martínez, J. Valio, A. Santasalo-Aarnio, M. Reuter, R. Serna-Guerrero, “A Critical Review of Lithium-Ion Battery Recycling Processes from a Circular Economy Perspective” *Batteries* **2019**, 5, 68.
- [5] G. D. J. Harper, E. Kendrick, P. A. Anderson, W. Mrozik, P. Christensen, et. al., “Roadmap for a sustainable circular economy in lithium-ion and future battery technologies” *J. Phys. Energy* **2023**, 5, 021501.
- [6] H. S. Hirsh, Y. Li, D. H. S. Tan, M. Zhang, E. Zhao, Y. S. Meng, “Sodium-Ion Batteries Paving the Way for Grid Energy Storage” *Adv. Energy Mater.* **2020**, 10, 2001274.
- [7] K. Hans Wedepohl, “The composition of the continental crust” *Geochim. Cosmochim. Acta* **1995**, 59, 1217–1232.
- [8] C. Vaalma, D. Buchholz, M. Weil, S. Passerini, “A cost and resource analysis of sodium-ion batteries” *Nat Rev Mater* **2018**, 3, 1–11.
- [9] S. Roberts, E. Kendrick, “The re-emergence of sodium ion batteries: testing, processing, and manufacturability” *NSA* **2018**, Volume 11, 23–33.
- [10] P. Voß, B. Gruber, M. Mitterfellner, J.-D. Plöpst, F. Degen, R. Schmuck, S. Lux, “Benchmarking state-of-the-art sodium-ion battery cells – modeling energy density and carbon footprint at the gigafactory-scale” *Energy Environ. Sci.* **2025**, 18, 8104–8129.
- [11] A. Ponrouch, E. Marchante, M. Courty, J.-M. Tarascon, M. R. Palacín, “In search of an optimized electrolyte for Na-ion batteries” *Energy Environ. Sci.* **2012**, 5, 8572.
- [12] A. Ponrouch, D. Monti, A. Boschini, B. Steen, P. Johansson, M. R. Palacín, “Non-aqueous electrolytes for sodium-ion batteries” *J. Mater. Chem. A* **2015**, 3, 22–42.
- [13] S. J. An, J. Li, C. Daniel, D. Mohanty, S. Nagpure, D. L. Wood, “The state of understanding of the lithium-ion-battery graphite solid electrolyte interphase (SEI) and its relationship to formation cycling” *Carbon* **2016**, 105, 52–76.
- [14] Z. Xue, D. Zhu, M. Shan, H. Wang, J. Zhang, G. Cui, Z. Hu, K. C. Gordon, G. Xu, M. Zhu, “Functional separator materials of sodium-ion batteries: Grand challenges and industry perspectives” *Nano Today* **2024**, 55, 102175.
- [15] K. Kubota, S. Komaba, “Review—Practical Issues and Future Perspective for Na-Ion Batteries” *J. Electrochem. Soc.* **2015**, 162, 2538–2550.
- [16] H. He, D. Sun, Y. Tang, H. Wang, M. Shao, “Understanding and improving the initial Coulombic efficiency of high-capacity anode materials for practical sodium ion batteries” *Energy Storage Materials* **2019**, 23, 233–251.
- [17] X. Huang, Z. Wang, “Precursor-Dependent Initial Coulombic Efficiency of Hard Carbon Anodes for Sodium-Ion Batteries: A Comparative Review” *Materials* **2026**, 19, 2132.

- [18] M. Hosseinzadegan, F. Bauer, L. Nyholm, G. Hernández, D. R. Maibach, "Separating Nucleation and Growth: High-Overpotential Pretreatment Pulses for Sodium-Metal Electrodes" *Advanced Energy Materials* **2025**, *15*, e03627.
- [19] B. Qin, A. Schiele, Z. Jusys, A. Mariani, T. Diemant, X. Liu, T. Brezesinski, R. J. Behm, A. Varzi, S. Passerini, "Highly Reversible Sodiation of Tin in Glyme Electrolytes: The Critical Role of the Solid Electrolyte Interphase and Its Formation Mechanism" *ACS Appl. Mater. Interfaces* **2020**, *12*, 3697–3708.
- [20] D. A. Stevens, J. R. Dahn, "The Mechanisms of Lithium and Sodium Insertion in Carbon Materials" *J. Electrochem. Soc.* **2001**, *148*, 803.
- [21] Y. Nishi, "Lithium ion secondary batteries; past 10 years and the future" *Journal of Power Sources* **2001**, *100*, 101–106.
- [22] S. Aronson, F. J. Salzano, D. Bellafiore, "Thermodynamic Properties of the Potassium–Graphite Lamellar Compounds from Solid-State emf Measurements" *J. Chem. Phys.* **1968**, *49*, 434–439.
- [23] Y. Li, Y. Lu, P. Adelhelm, M.-M. Titirici, Y.-S. Hu, "Intercalation chemistry of graphite: alkali metal ions and beyond" *Chem. Soc. Rev.* **2019**, *48*, 4655–4687.
- [24] Z. Wang, S. M. Selbach, T. Grande, "Van der Waals density functional study of the energetics of alkali metal intercalation in graphite" *RSC Adv.* **2013**, *4*, 4069–4079.
- [25] H. Moriwake, A. Kuwabara, C. A. J. Fisher, Y. Ikuhara, "Why is sodium-intercalated graphite unstable?" *RSC Adv.* **2017**, *7*, 36550–36554.
- [26] Y. Liu, B. V. Merinov, W. A. Goddard, "Origin of low sodium capacity in graphite and generally weak substrate binding of Na and Mg among alkali and alkaline earth metals" *Proceedings of the National Academy of Sciences* **2016**, *113*, 3735–3739.
- [27] K. Nobuhara, H. Nakayama, M. Nose, S. Nakanishi, H. Iba, "First-principles study of alkali metal-graphite intercalation compounds" *J. Power Sources* **2013**, *243*, 585–587.
- [28] Y. Cao, L. Xiao, M. L. Sushko, W. Wang, B. Schwenzer, J. Xiao, Z. Nie, L. V. Saraf, Z. Yang, J. Liu, "Sodium ion insertion in hollow carbon nanowires for battery applications" *Nano Lett.* **2012**, *12*, 3783–3787.
- [29] Z.-L. Xu, J. Park, G. Yoon, H. Kim, K. Kang, "Graphitic Carbon Materials for Advanced Sodium-Ion Batteries" *Small Methods* **2019**, *3*, 1800227.
- [30] X. Dou, I. Hasa, D. Saurel, C. Vaalma, L. Wu, D. Buchholz, D. Bresser, S. Komaba, S. Passerini, "Hard carbons for sodium-ion batteries: Structure, analysis, sustainability, and electrochemistry" *Mater. Today* **2019**, *23*, 87–104.
- [31] J. Li, T. Li, C. Peng, J. Li, H. Zhang, "Molecular Structure Evaluation and Image-Guided Atomistic Representation of Hard Carbon Electrodes" *J. Electrochem. Soc.* **2022**, *169*, 070517.
- [32] J. S. McDonald-Wharry, M. Manley-Harris, K. L. Pickering, "Reviewing, Combining, and Updating the Models for the Nanostructure of Non-Graphitizing Carbons Produced from Oxygen-Containing Precursors" *Energy Fuels* **2016**, *30*, 7811–7826.
- [33] T. W. Surta, E. Koh, Z. Li, D. B. Fast, X. Ji, P. A. Greaney, M. R. Dolgos, "Combining Experimental and Theoretical Techniques to Gain an Atomic Level Understanding of

- the Defect Binding Mechanism in Hard Carbon Anodes for Sodium Ion Batteries” *Advanced Energy Materials* **2022**, *12*, 2200647.
- [34] K. Kubota, S. Shimadzu, N. Yabuuchi, S. Tominaka, S. Shiraishi, M. Abreu-Sepulveda, A. Manivannan, K. Gotoh, M. Fukunishi, M. Dahbi, S. Komaba, “Structural Analysis of Sucrose-Derived Hard Carbon and Correlation with the Electrochemical Properties for Lithium, Sodium, and Potassium Insertion” *Chem. Mater.* **2020**, *32*, 2961–2977.
- [35] A. Beda, F. Rabuel, M. Morcrette, S. Knopf, P.-L. Taberna, P. Simon, C. Matei Ghimbeu, “Hard carbon key properties allow for the achievement of high Coulombic efficiency and high volumetric capacity in Na-ion batteries” *J. Mater. Chem. A* **2021**, *9*, 1743–1758.
- [36] J. R. Dahn, W. Xing, Y. Gao, “The ‘falling cards model’ for the structure of microporous carbons” *Carbon* **1997**, *35*, 825–830.
- [37] D. A. Stevens, J. R. Dahn, “High Capacity Anode Materials for Rechargeable Sodium-Ion Batteries” *J. Electrochem. Soc.* **2000**, *147*, 1271.
- [38] X. Chen, C. Liu, Y. Fang, X. Ai, F. Zhong, H. Yang, Y. Cao, “Understanding of the sodium storage mechanism in hard carbon anodes” *Carbon Energy* **2022**, *4*, 1133–1150.
- [39] J. M. Stratford, A. K. Kleppe, D. S. Keeble, P. A. Chater, S. S. Meysami, C. J. Wright, J. Barker, M.-M. Titirici, P. K. Allan, C. P. Grey, “Correlating Local Structure and Sodium Storage in Hard Carbon Anodes: Insights from Pair Distribution Function Analysis and Solid-State NMR” *J. Am. Chem. Soc.* **2021**, *143*, 14274–14286.
- [40] E. Olsson, J. Cottom, Q. Cai, “Defects in Hard Carbon: Where Are They Located and How Does the Location Affect Alkaline Metal Storage?” *Small* **2021**, *17*, 2007652.
- [41] Z. Li, C. Bommier, Z. S. Chong, Z. Jian, T. W. Surta, X. Wang, Z. Xing, J. C. Neufeind, W. F. Stickle, M. Dolgos, P. A. Greaney, X. Ji, “Mechanism of Na-Ion Storage in Hard Carbon Anodes Revealed by Heteroatom Doping” *Adv. Energy Mater.* **2017**, *7*, 1602894.
- [42] A. Agrawal, S. Janakiraman, K. Biswas, A. Venimadhav, S. K. Srivastava, S. Ghosh, “Understanding the improved electrochemical performance of nitrogen-doped hard carbons as an anode for sodium ion battery” *Electrochim. Acta* **2019**, *317*, 164–172.
- [43] X. Yin, Y. Zhao, X. Wang, X. Feng, Z. Lu, Y. Li, H. Long, J. Wang, J. Ning, J. Zhang, “Modulating the Graphitic Domains of Hard Carbons Derived from Mixed Pitch and Resin to Achieve High Rate and Stable Sodium Storage” *Small* **2022**, *18*, 2105568.
- [44] H. Au, H. Alptekin, A. C. S. Jensen, E. Olsson, C. A. O’Keefe, T. Smith, M. Crespo-Ribadeneyra, T. F. Headen, C. P. Grey, Q. Cai, A. J. Drew, M.-M. Titirici, “A revised mechanistic model for sodium insertion in hard carbons” *Energy Environ. Sci.* **2020**, *13*, 3469–3479.
- [45] M. Gabrijelčič, B. Tratnik, G. Kapun, E. Tchernychova, N. Z. Logar, A. Krajnc, R. Dominko, A. Vizintin, “Probing sodium structures and dynamics in hard carbon for Na-ion batteries using ^{23}Na operando solid-state NMR spectroscopy” *Journal of Materials Chemistry A* **2025**, *13*, 1042–1056.
- [46] M. P. Mercer, S. Affleck, E. M. Gavilán-Arriazu, A. A. Zülke, P. A. Maughan, S. Trivedi, M. Fichtner, A. Reddy Munnangi, E. P. M. Leiva, H. E. Hoster, “Sodiation Of Hard

- Carbon: How Separating Enthalpy And Entropy Contributions Can Find Transitions Hidden In The Voltage Profile" *ChemPhysChem* **2022**, *23*, e202100748.
- [47] M. P. Mercer, M. Nagarathinam, E. M. Gavilán-Arriazu, A. Binjrajka, S. Panda, H. Au, M. Crespo-Ribadeneyra, M.-M. Titirici, E. P. M. Leiva, H. E. Hoster, "Sodiation energetics in pore size controlled hard carbons determined via entropy profiling" *J. Mater. Chem. A* **2023**, *11*, 6543–6555.
- [48] C. Bommier, T. W. Surta, M. Dolgos, X. Ji, "New Mechanistic Insights on Na-Ion Storage in Nongraphitizable Carbon" *Nano Lett.* **2015**, *15*, 5888–5892.
- [49] E. Olsson, G. Chai, M. Dove, Q. Cai, "Adsorption and migration of alkali metals (Li, Na, and K) on pristine and defective graphene surfaces" *Nanoscale* **2019**, *11*, 5274–5284.
- [50] F. Sun, H. Wang, Z. Qu, K. Wang, L. Wang, J. Gao, J. Gao, S. Liu, Y. Lu, "Carboxyl-Dominant Oxygen Rich Carbon for Improved Sodium Ion Storage: Synergistic Enhancement of Adsorption and Intercalation Mechanisms" *Advanced Energy Materials* **2021**, *11*, 2002981.
- [51] J. Bourke, M. Manley-Harris, C. Fushimi, K. Dowaki, T. Nunoura, M. J. Antal, "Do All Carbonized Charcoals Have the Same Chemical Structure? 2. A Model of the Chemical Structure of Carbonized Charcoal" *Ind. Eng. Chem. Res.* **2007**, *46*, 5954–5967.
- [52] C. Qiu, L. Jiang, Y. Gao, L. Sheng, "Effects of oxygen-containing functional groups on carbon materials in supercapacitors: A review" *Materials & Design* **2023**, *230*, 111952.
- [53] Y. He, D. Liu, Q. Li, Z. Zhu, R. Wu, "Advances in oxygen-containing functional groups-modified hard carbon anodes for sodium-ion batteries" *Materials Science and Engineering: R: Reports* **2026**, *168*, 101143.
- [54] M. Jerigová, M. Odziomek, N. López-Salas, "'We Are Here!' Oxygen Functional Groups in Carbons for Electrochemical Applications" *ACS Omega* **2022**, *7*, 11544–11554.
- [55] H. Zhao, J. Ye, W. Song, D. Zhao, M. Kang, H. Shen, Z. Li, "Insights into the Surface Oxygen Functional Group-Driven Fast and Stable Sodium Adsorption on Carbon" *ACS Appl. Mater. Interfaces* **2020**, *12*, 6991–7000.
- [56] C. Matei Ghimbeu, J. Górka, V. Simone, L. Simonin, S. Martinet, C. Vix-Guterl, "Insights on the Na⁺ ion storage mechanism in hard carbon: Discrimination between the porosity, surface functional groups and defects" *Nano Energy* **2018**, *44*, 327–335.
- [57] J. Zhou, P. Yang, P. A. Kots, M. Cohen, Y. Chen, C. M. Quinn, M. D. de Mello, J. Anibal Boscoboinik, W. J. Shaw, S. Caratzoulas, W. Zheng, D. G. Vlachos, "Tuning the reactivity of carbon surfaces with oxygen-containing functional groups" *Nat Commun* **2023**, *14*, 2293.
- [58] J. Zhou, P. Yang, P. A. Kots, M. Cohen, Y. Chen, C. M. Quinn, M. D. de Mello, J. Anibal Boscoboinik, W. J. Shaw, S. Caratzoulas, W. Zheng, D. G. Vlachos, "Tuning the reactivity of carbon surfaces with oxygen-containing functional groups" *Nat Commun* **2023**, *14*, 2293.
- [59] C. Hofer, V. Skákalová, T. Görlich, M. Tripathi, A. Mittelberger, C. Mangler, M. R. A. Monazam, T. Susi, J. Kotakoski, J. C. Meyer, "Direct imaging of light-element impurities in graphene reveals triple-coordinated oxygen" *Nat Commun* **2019**, *10*, 4570.

- [60] E. Olsson, J. Cottom, H. Au, M.-M. Titirici, Q. Cai, "Investigating the effect of edge and basal plane surface functionalisation of carbonaceous anodes for alkali metal (Li/Na/K) ion batteries" *Carbon* **2021**, 177, 226–243.
- [61] H. Zhao, D. Zhao, J. Ye, P. Wang, M. Chai, Z. Li, "Directional Oxygen Functionalization by Defect in Different Metamorphic-Grade Coal-Derived Carbon Materials for Sodium Storage" *ENERGY & ENVIRONMENTAL MATERIALS* **2022**, 5, 313–320.
- [62] J. Zheng, C. Guan, H. Li, D. Wang, Y. Lai, S. Li, J. Li, Z. Zhang, "Unveiling the Microscopic Origin of Irreversible Capacity Loss of Hard Carbon for Sodium-Ion Batteries" *Advanced Energy Materials* **2024**, 14, 2303584.
- [63] P. Zhang, J. Fan, Y. Wang, Y. Dang, S. Heumann, Y. Ding, "Insights into the role of defects on the Raman spectroscopy of carbon nanotube and biomass-derived carbon" *Carbon* **2024**, 222, 118998.
- [64] D. J. Morgan, "Comments on the XPS Analysis of Carbon Materials" *C* **2021**, 7, 51.
- [65] G. H. Major, T. G. Avval, B. Moeini, G. Pinto, D. Shah, V. Jain, V. Carver, W. Skinner, T. R. Gengenbach, C. D. Easton, A. Herrera-Gomez, T. S. Nunney, D. R. Baer, M. R. Linford, "Assessment of the frequency and nature of erroneous x-ray photoelectron spectroscopy analyses in the scientific literature" *J. Vac. Sci. Technol. A* **2020**, 38, 061204.
- [66] M. Bauer, S. Beratz, K. Ruhland, S. Horn, J. Moosburger-Will, "Anodic oxidation of carbon fibers in alkaline and acidic electrolyte: Quantification of surface functional groups by gas-phase derivatization" *Applied Surface Science* **2020**, 506, 144947.
- [67] L. A. Langley, D. H. Fairbrother, "Effect of wet chemical treatments on the distribution of surface oxides on carbonaceous materials" *Carbon* **2007**, 45, 47–54.
- [68] C. Buono, P. R. Davies, R. J. Davies, T. Jones, J. Kulhavý, R. Lewis, D. J. Morgan, N. Robinson, D. J. Willock, "Spectroscopic and atomic force studies of the functionalisation of carbon surfaces: new insights into the role of the surface topography and specific chemical states" *Faraday Discuss.* **2014**, 173, 257–272.
- [69] G. Hotová, V. Slovák, O. S. G. P. Soares, J. L. Figueiredo, M. F. R. Pereira, "Oxygen surface groups analysis of carbonaceous samples pyrolysed at low temperature" *Carbon* **2018**, 134, 255–263.
- [70] J. L. Figueiredo, M. F. R. Pereira, M. M. A. Freitas, J. J. M. Órfão, "Modification of the surface chemistry of activated carbons" *Carbon* **1999**, 37, 1379–1389.
- [71] A. Beda, C. Vaultot, F. Rabuel, M. Morcrette, C. Matei Ghimbeu, "The role of specific and active surface areas in optimizing hard carbon irreversible capacity loss in sodium ion batteries" *Energy Adv.* **2022**, 1, 185–190.
- [72] C. Nita, B. Zhang, J. Dentzer, C. Matei Ghimbeu, "Hard carbon derived from coconut shells, walnut shells, and corn silk biomass waste exhibiting high capacity for Na-ion batteries" *J. Energy Chem.* **2021**, 58, 207–218.
- [73] Z. Zhang, D. W. Flaherty, "Modified potentiometric titration method to distinguish and quantify oxygenated functional groups on carbon materials by pKa and chemical reactivity" *Carbon* **2020**, 166, 436–445.
- [74] S. Komaba, W. Murata, T. Ishikawa, N. Yabuuchi, T. Ozeki, T. Nakayama, A. Ogata, K. Gotoh, K. Fujiwara, "Electrochemical Na Insertion and Solid Electrolyte Interphase for

- Hard-Carbon Electrodes and Application to Na-Ion Batteries” *Advanced Functional Materials* **2011**, *21*, 3859–3867.
- [75] J. B. Goodenough, Y. Kim, “Challenges for Rechargeable Li Batteries” *Chem. Mater.* **2010**, *22*, 587–603.
- [76] P. Peljo, H. H. Girault, “Electrochemical potential window of battery electrolytes: the HOMO–LUMO misconception” *Energy Environ. Sci.* **2018**, *11*, 2306–2309.
- [77] M. Carboni, J. Manzi, A. R. Armstrong, J. Billaud, S. Brutti, R. Younesi, “Analysis of the Solid Electrolyte Interphase on Hard Carbon Electrodes in Sodium-Ion Batteries” *ChemElectroChem* **2019**, *6*, 1745–1753.
- [78] Y. Rangom, R. R. Gaddam, T. T. Duignan, X. S. Zhao, “Improvement of Hard Carbon Electrode Performance by Manipulating SEI Formation at High Charging Rates” *ACS Appl. Mater. Interfaces* **2019**, *11*, 34796–34804.
- [79] J. Meng, G. Jia, H. Yang, M. Wang, “Recent advances for SEI of hard carbon anode in sodium-ion batteries: A mini review” *Front. Chem.* **2022**, *10*.
- [80] C. Bommier, D. Leonard, Z. Jian, W. F. Stickle, P. A. Greaney, X. Ji, “New Paradigms on the Nature of Solid Electrolyte Interphase Formation and Capacity Fading of Hard Carbon Anodes in Na-Ion Batteries” *Advanced Materials Interfaces* **2016**, *3*, 1600449.
- [81] K. Hankins, M. H. Putra, J. Wagner-Henke, A. Groß, U. Krewer, “Insights on SEI Growth and Properties in Na-Ion Batteries via Physically Driven Kinetic Monte Carlo Model” *Advanced Energy Materials* **2024**, 2401153.
- [82] F. A. Soto, P. Yan, M. H. Engelhard, A. Marzouk, C. Wang, G. Xu, Z. Chen, K. Amine, J. Liu, V. L. Sprenkle, F. El-Mellouhi, P. B. Balbuena, X. Li, “Tuning the Solid Electrolyte Interphase for Selective Li- and Na-Ion Storage in Hard Carbon” *Advanced Materials* **2017**, *29*, 1606860.
- [83] G. G. Eshetu, T. Diemant, M. Hekmatfar, S. Grugeon, R. J. Behm, S. Laruelle, M. Armand, S. Passerini, “Impact of the electrolyte salt anion on the solid electrolyte interphase formation in sodium ion batteries” *Nano Energy* **2019**, *55*, 327–340.
- [84] A. Bouibes, N. Takenaka, K. Kubota, S. Komaba, M. Nagaoka, “Development of advanced electrolytes in Na-ion batteries: application of the Red Moon method for molecular structure design of the SEI layer” *RSC Advances* **2022**, *12*, 971–984.
- [85] E. Olsson, J. Cottom, H. Alptekin, H. Au, M. Crespo-Ribadeneyra, M.-M. Titirici, Q. Cai, “Investigating the Role of Surface Roughness and Defects on EC Breakdown, as a Precursor to SEI Formation in Hard Carbon Sodium-Ion Battery Anodes” *Small* **2022**, *18*, 2200177.
- [86] P. Watthaisong, S. Suthirakun, P. Hirunsit, “Mechanistic Study of the Effect of Epoxy Groups on Ethylene Carbonate Decomposition Reaction on Carbon Anodes of Sodium-Ion Batteries” *J. Phys. Chem. C* **2021**, *125*, 8031–8044.
- [87] H. Kumar, E. Detsi, D. P. Abraham, V. B. Shenoy, “Fundamental Mechanisms of Solvent Decomposition Involved in Solid-Electrolyte Interphase Formation in Sodium Ion Batteries” *Chem. Mater.* **2016**, *28*, 8930–8941.
- [88] E. Peled, D. Golodnitsky, G. Ardel, “Advanced Model for Solid Electrolyte Interphase Electrodes in Liquid and Polymer Electrolytes” *J. Electrochem. Soc.* **1997**, *144*, L208.

- [89] H. Alptekin, H. Au, E. Olsson, J. Cottom, A. C. S. Jensen, T. F. Headen, Q. Cai, A. J. Drew, M. Crespo Ribadeneyra, M. Titirici, "Elucidation of the Solid Electrolyte Interphase Formation Mechanism in Micro-Mesoporous Hard-Carbon Anodes" *Advanced Materials Interfaces* **2022**, 9, 2101267.
- [90] M. Liu, F. Wu, Y. Gong, Y. Li, Y. Li, X. Feng, Q. Li, C. Wu, Y. Bai, "Interfacial-Catalysis-Enabled Layered and Inorganic-Rich SEI on Hard Carbon Anodes in Ester Electrolytes for Sodium-Ion Batteries" *Advanced Materials* **2023**, 35, 2300002.
- [91] M. Ma, H. Cai, C. Xu, R. Huang, S. Wang, H. Pan, Y.-S. Hu, "Engineering Solid Electrolyte Interface at Nano-Scale for High-Performance Hard Carbon in Sodium-Ion Batteries" *Advanced Functional Materials* **2021**, 31, 2100278.
- [92] Y. Pan, Y. Zhang, B. S. Parimalam, C. C. Nguyen, G. Wang, B. L. Lucht, "Investigation of the solid electrolyte interphase on hard carbon electrode for sodium ion batteries" *Journal of Electroanalytical Chemistry* **2017**, 799, 181–186.
- [93] U. Purushotham, N. Takenaka, M. Nagaoka, "Additive effect of fluoroethylene and difluoroethylene carbonates for the solid electrolyte interphase film formation in sodium-ion batteries: a quantum chemical study" *RSC Advances* **2016**, 6, 65232–65242.
- [94] W. Chen, C. Chen, X. Xiong, P. Hu, Z. Hao, Y. Huang, "Coordination of Surface-Induced Reaction and Intercalation: Toward a High-Performance Carbon Anode for Sodium-Ion Batteries" *Advanced Science* **2017**, 4, 1600500.
- [95] Y. Zhao, J. Ye, P. Zhang, Z. Li, H. Zhao, "Abnormal preferential oxygen functionalization on the surface of soft/hard carbon for sodium storage" *Applied Surface Science* **2022**, 602, 154336.
- [96] H. Wang, F. Sun, Z. Qu, K. Wang, L. Wang, X. Pi, J. Gao, G. Zhao, "Oxygen Functional Group Modification of Cellulose-Derived Hard Carbon for Enhanced Sodium Ion Storage" *ACS Sustainable Chem. Eng.* **2019**, 7, 18554–18565.
- [97] C. Shen, C. Wang, T. Jin, X. Zhang, L. Jiao, K. Xie, "Tailoring the surface chemistry of hard carbon towards high-efficiency sodium ion storage" *Nanoscale* **2022**, 14, 8959–8966.
- [98] H. Xie, Z. Wu, Z. Wang, N. Qin, Y. Li, Y. Cao, Z. Lu, "Solid electrolyte interface stabilization via surface oxygen species functionalization in hard carbon for superior performance sodium-ion batteries" *J. Mater. Chem. A* **2020**, 8, 3606–3612.
- [99] G. Zhao, X. Deng, Z. Wang, X. Wang, "Boosting sodium storage performance of hard carbons by regulating surface oxygen functionalities" *Materials Letters* **2025**, 396, 138783.
- [100] W. Shao, F. Hu, T. Zhang, S. Liu, C. Song, N. Li, Z. Weng, J. Wang, X. Jian, "Engineering Ultramicroporous Carbon with Abundant C=O as Extended 'Slope-Dominated' Sodium Ion Battery Anodes" *ACS Sustainable Chem. Eng.* **2021**, 9, 9727–9739.
- [101] D. Sun, B. Luo, H. Wang, Y. Tang, X. Ji, L. Wang, "Engineering the trap effect of residual oxygen atoms and defects in hard carbon anode towards high initial Coulombic efficiency" *Nano Energy* **2019**, 64, 103937.
- [102] X. Li, G. Liu, B. Liu, P. Sun, Z. Wang, C. Wang, Z. Wang, F. Wu, H. Wang, Y. Cao, F. Zhang, Z. Mo, H. Cheng, D. Luo, G. Liu, Z. Lu, "Oxygen Plasma-Treated Hard Carbon

- for High-Rate and Durable Sodium-Ion Storage” *ACS Appl. Mater. Interfaces* **2025**, *17*, 46989–46997.
- [103] Y. Zhu, M. Chen, Q. Li, C. Yuan, C. Wang, “A porous biomass-derived anode for high-performance sodium-ion batteries” *Carbon* **2018**, *129*, 695–701.
- [104] A. Ponrouch, M. R. Palacín, “On the high and low temperature performances of Na-ion battery materials: Hard carbon as a case study” *Electrochemistry Communications* **2015**, *54*, 51–54.
- [105] Y. Li, S. Xu, X. Wu, J. Yu, Y. Wang, Y.-S. Hu, H. Li, L. Chen, X. Huang, “Amorphous monodispersed hard carbon micro-spherules derived from biomass as a high performance negative electrode material for sodium-ion batteries” *J. Mater. Chem. A* **2014**, *3*, 71–77.
- [106] L. A. Romero-Cano, H. García-Rosero, F. Carrasco-Marín, A. F. Pérez-Cadenas, L. V. González-Gutiérrez, A. I. Zárate-Guzmán, G. Ramos-Sánchez, “Surface functionalization to abate the irreversible capacity of hard carbons derived from grapefruit peels for sodium-ion batteries” *Electrochimica Acta* **2019**, *326*, 134973.
- [107] C.-X. Yu, Y. Li, Z.-H. Wang, X.-R. Wang, Y. Bai, C. Wu, “Surface engineering based on in situ electro-polymerization to boost the initial Coulombic efficiency of hard carbon anode for sodium-ion battery” *Rare Met.* **2022**, *41*, 1616–1625.
- [108] B. He, L. Feng, G. Hong, L. Yang, Q. Zhao, X. Yang, S. Yin, Y. Meng, D. Xiao, Y. Wang, J. Ai, “A generic F-doped strategy for biomass hard carbon to achieve fast and stable kinetics in sodium/potassium-ion batteries” *Chemical Engineering Journal* **2024**, *490*, 151636.
- [109] Y. Sun, D. Zuo, C. Xu, B. Peng, J.-C. Li, J. Yang, S. Xu, X. Sun, H. Zhou, S. Guo, “A ‘grafting technique’ to tailor the interfacial behavior of hard carbon anodes for stable sodium-ion batteries” *Energy Environ. Sci.* **2025**, *18*, 1911–1919.
- [110] C. Müller, Z. Wang, A. Hofmann, P. Stueble, X. Liu-Théato, J. Klemens, A. Smith, “Influences on Reliable Capacity Measurements of Hard Carbon in Highly Loaded Electrodes” *Batteries & Supercaps* **2023**.
- [111] W. Weppner, R. A. Huggins, “Determination of the Kinetic Parameters of Mixed-Conducting Electrodes and Application to the System Li₃Sb” *J. Electrochem. Soc.* **1977**, *124*, 1569.
- [112] M. Cao, A. Fu, Z. Wang, J. Liu, N. Kong, X. Zong, H. Liu, J. J. Gooding, “Electrochemical and Theoretical Study of π – π Stacking Interactions between Graphitic Surfaces and Pyrene Derivatives” *J. Phys. Chem. C* **2014**, *118*, 2650–2659.
- [113] H. Radinger, V. Trouillet, F. Bauer, F. Scheiba, “Work Function Describes the Electrocatalytic Activity of Graphite for Vanadium Oxidation” *ACS Catal.* **2022**, *12*, 6007–6015.
- [114] H. Radinger, F. Bauer, F. Scheiba, “Edge Site Catalyzed Vanadyl Oxidation Elucidated by Operando Raman Spectroscopy” *Batteries & Supercaps* **2023**, *6*, e202200440.
- [115] B. Anothumakkool, P.-L. Taberna, B. Daffos, P. Simon, Y. Sayed-Ahmad-Baraza, C. Ewels, T. Brousse, J. Gaubicher, “Improved electro-grafting of nitropyrene onto onion-like carbon via in situ electrochemical reduction and polymerization: tailoring redox energy density of the supercapacitor positive electrode” *J. Mater. Chem. A* **2017**, *5*, 1488–1494.

- [116] M. Bauer, P. Konnerth, H. Radinger, K. Pfeifer, Y. Joshi, F. Bauer, H. Ehrenberg, F. Scheiba, "Crucial interactions of functional pyrenes with graphite in electrodes for lithium-ion batteries" *Nano Select* **2023**.
- [117] R. Criegee, "Mechanism of Ozonolysis" *Angewandte Chemie International Edition in English* **1975**, *14*, 745–752.
- [118] Y. Mulyana, M. Uenuma, Y. Ishikawa, Y. Uraoka, "Reversible Oxidation of Graphene Through Ultraviolet/Ozone Treatment and Its Nonthermal Reduction through Ultraviolet Irradiation" *J. Phys. Chem. C* **2014**, *118*, 27372–27381.
- [119] P. Magne, N. Dupont-Pavlovsky, "Graphite-ozone surface complexes" *Carbon* **1988**, *26*, 249–255.
- [120] K. Peng, L.-Q. Liu, H. Li, H. Meyer, Z. Zhang, "Room temperature functionalization of carbon nanotubes using an ozone/water vapor mixture" *Carbon* **2011**, *49*, 70–76.
- [121] J. Yao, H. Wang, J. Liu, K.-Y. Chan, L. Zhang, N. Xu, "Preparation of colloidal microporous carbon spheres from furfuryl alcohol" *Carbon* **2005**, *43*, 1709–1715.
- [122] J. Klemens, L. Schneider, D. Burger, N. Zimmerer, M. Müller, W. Bauer, H. Ehrenberg, P. Scharfer, W. Schabel, "Process and Drying Behavior Toward Higher Drying Rates of Hard Carbon Anodes for Sodium-Ion Batteries with Different Particle Sizes: An Experimental Study in Comparison to Graphite for Lithium-Ion-Batteries" *Energy Technology* **2023**, *11*, 2300338.
- [123] D. Weingarth, M. Zeiger, N. Jäckel, M. Aslan, G. Feng, V. Presser, "Graphitization as a Universal Tool to Tailor the Potential-Dependent Capacitance of Carbon Supercapacitors" *Advanced Energy Materials* **2014**, *4*, 1400316.
- [124] J. H. Scofield, "Hartree-Slater subshell photoionization cross-sections at 1254 and 1487 eV" *J. Electron. Spectrosc. Relat. Phenom.* **1976**, *8*, 129–137.
- [125] M. Thompson, Q. Xia, Z. Hu, X. S. Zhao, "A review on biomass-derived hard carbon materials for sodium-ion batteries" *Mater. Adv.* **2021**, *2*, 5881–5905.
- [126] S. Xiao, Y.-J. Guo, H.-X. Chen, H. Liu, Z.-Q. Lei, L.-B. Huang, R.-X. Jin, X.-C. Su, Q. Zhang, Y.-G. Guo, "Insight into the Role of Closed-Pore Size on Rate Capability of Hard Carbon for Fast-Charging Sodium-Ion Batteries" *Advanced Materials* **2025**, *37*, 2501434.
- [127] Q. Li, X. Liu, Y. Tao, J. Huang, J. Zhang, C. Yang, Y. Zhang, S. Zhang, Y. Jia, Q. Lin, Y. Xiang, J. Cheng, W. Lv, F. Kang, Y. Yang, Q.-H. Yang, "Sieving carbons promise practical anodes with extensible low-potential plateaus for sodium batteries" *Natl Sci Rev* **2022**, *9*, nwac084.
- [128] Q. Meng, Y. Lu, F. Ding, Q. Zhang, L. Chen, Y.-S. Hu, "Tuning the Closed Pore Structure of Hard Carbons with the Highest Na Storage Capacity" *ACS Energy Lett.* **2019**, *4*, 2608–2612.
- [129] A. O. C. Iroegbu, S. S. Ray, "On the chemistry of furfuryl alcohol polymerization: A review" *Journal of Polymer Science* **2024**, *62*, 1044–1060.
- [130] M. Choura, N. M. Belgacem, A. Gandini, "Acid-Catalyzed Polycondensation of Furfuryl Alcohol: Mechanisms of Chromophore Formation and Cross-Linking" *Macromolecules* **1996**, *29*, 3839–3850.

- [131] Z. Ding, V. Trouillet, S. Dsoke, "Are Functional Groups Beneficial or Harmful on the Electrochemical Performance of Activated Carbon Electrodes?" *J. Electrochem. Soc.* **2019**, *166*, A1004.
- [132] R. Blume, D. Rosenthal, J.-P. Tessonier, H. Li, A. Knop-Gericke, R. Schlögl, "Characterizing Graphitic Carbon with X-ray Photoelectron Spectroscopy: A Step-by-Step Approach" *ChemCatChem* **2015**, *7*, 2871–2881.
- [133] P. Stüble, C. Müller, J. Klemens, P. Scharfer, W. Schabel, M. Häring, J. R. Binder, A. Hofmann, A. Smith, "Enabling Long-term Cycling Stability of Na₃V₂(PO₄)₃/C vs. Hard Carbon Full-cells" *Batteries & Supercaps* **2024**, *7*, e202300375.
- [134] K. Pfeifer, S. Arnold, J. Becherer, C. Das, J. Maibach, H. Ehrenberg, S. Dsoke, "Can Metallic Sodium Electrodes Affect the Electrochemistry of Sodium-Ion Batteries? Reactivity Issues and Perspectives" *ChemSusChem* **2019**, *12*, 3312–3319.
- [135] A. Hofmann, Z. Wang, S. P. Bautista, M. Weil, F. Müller, R. Löwe, L. Schneider, I. U. Mohsin, T. Hanemann, "Comprehensive characterization of propylene carbonate based liquid electrolyte mixtures for sodium-ion cells" *Electrochimica Acta* **2022**, *403*, 139670.
- [136] R. Mogensen, D. Brandell, R. Younesi, "Solubility of the Solid Electrolyte Interphase (SEI) in Sodium Ion Batteries" *ACS Energy Lett.* **2016**, *1*, 1173–1178.
- [137] P. Stüble, C. Müller, N. Bohn, M. Müller, A. Hofmann, T. Akçay, J. Klemens, A. Koeppel, S. Kolli, D. Rajagopal, H. Geßwein, W. Schabel, P. Scharfer, M. Selzer, J. R. Binder, A. Smith, "From Powder to Pouch Cell: Setting up a Sodium-Ion Battery Reference System Based on Na₃V₂(PO₄)₃/C and Hard Carbon" *Batteries & Supercaps* **2024**, *7*, e202400406.
- [138] A. Smith, P. Stüble, L. Leuthner, A. Hofmann, F. Jeschull, L. Mereacre, "Potential and Limitations of Research Battery Cell Types for Electrochemical Data Acquisition" *Batteries & Supercaps* **2023**, *6*, e202300080.
- [139] T. Waldmann, A. Innocenti, V. Scheck, K. Bischof, R. V. Feser, P. Moosmann, M. Kasper, M. Marinaro, A. Hoffmann, M. Wohlfahrt-Mehrens, R.-G. Scurtu, I. Jipa, P. Axmann, M. Hölzle, "From Laboratory to Application – Differences between Small and Large Battery Cells" *J. Electrochem. Soc.* **2026**, *173*, 050501.
- [140] S. Ghosh, X. An, R. Shah, D. Rawat, B. Dave, S. Kar, S. Talapatra, "Effect of 1- Pyrene Carboxylic-Acid Functionalization of Graphene on Its Capacitive Energy Storage" *J. Phys. Chem. C* **2012**, *116*, 20688–20693.
- [141] H. Itoi, K. Takagi, H. Ohmi, T. Usami, Y. Nagai, C. Matsuoka, R. Suzuki, S. Kugimiya, H. Iwata, Y. Ohzawa, "Metal-Free Homocoupling of Pyrene inside the Pores of Mesoporous Carbons via Electrochemical Oxidation: Application for Electrochemical Capacitors" *ACS Omega* **2022**, *7*, 35245–35255.
- [142] L. Maddii Fabiani, T. Reiker, H. Zacharias, "Vuv/vis absorption spectroscopy of different PAHs" *Appl. Phys. A* **2024**, *130*, 815.
- [143] S. E. Wheeler, J. W. G. Bloom, "Toward a More Complete Understanding of Noncovalent Interactions Involving Aromatic Rings" *J. Phys. Chem. A* **2014**, *118*, 6133–6147.
- [144] R. P. Matthews, T. Welton, P. A. Hunt, "Competitive pi interactions and hydrogen bonding within imidazolium ionic liquids" *Phys. Chem. Chem. Phys.* **2014**, *16*, 3238–3253.

- [145] A. D. Delman, B. B. Simms, A. E. Ruff, "On the mechanism of ozone degradation of SBR" *Journal of Polymer Science* **1960**, *45*, 415–434.
- [146] J. Hoigné, H. Bader, "The role of hydroxyl radical reactions in ozonation processes in aqueous solutions" *Water Research* **1976**, *10*, 377–386.
- [147] L. Li, X. Yao, H. Li, Z. Liu, W. Ma, X. Liang, "Thermal Stability of Oxygen-Containing Functional Groups on Activated Carbon Surfaces in a Thermal Oxidative Environment" *Journal of Chemical Engineering of Japan* **2014**, *47*, 21–27.
- [148] S. Kundu, Y. Wang, W. Xia, M. Muhler, "Thermal Stability and Reducibility of Oxygen-Containing Functional Groups on Multiwalled Carbon Nanotube Surfaces: A Quantitative High-Resolution XPS and TPD/TPR Study" *J. Phys. Chem. C* **2008**, *112*, 16869–16878.
- [149] T. Du, A. S. Adeleye, T. Zhang, N. Yang, R. Hao, Y. Li, W. Song, W. Chen, "Effects of ozone and produced hydroxyl radicals on the transformation of graphene oxide in aqueous media" *Environ. Sci.: Nano* **2019**, *6*, 2484–2494.
- [150] S. D. Razumovskii, V. N. Gorshenev, A. L. Kovarskii, A. M. Kuznetsov, A. N. Shchegolikhin, "Carbon Nanostructure Reactivity: Reactions of Graphite Powders with Ozone" *Fullerenes, Nanotubes and Carbon Nanostructures* **2007**, *15*, 53–63.
- [151] M. J. Webb, P. Palmgren, P. Pal, O. Karis, H. Grennberg, "A simple method to produce almost perfect graphene on highly oriented pyrolytic graphite" *Carbon* **2011**, *49*, 3242–3249.
- [152] V. Meunier, A. G. Souza Filho, E. B. Barros, M. S. Dresselhaus, "Physical properties of low-dimensional sp²-based carbon nanostructures" *Rev. Mod. Phys.* **2016**, *88*, 025005.
- [153] D. B. Schuepfer, F. Badaczewski, J. M. Guerra-Castro, D. M. Hofmann, C. Heiliger, B. Smarsly, P. J. Klar, "Assessing the structural properties of graphitic and non-graphitic carbons by Raman spectroscopy" *Carbon* **2020**, *161*, 359–372.
- [154] F. Tuinstra, J. L. Koenig, "Raman Spectrum of Graphite" *The Journal of Chemical Physics* **1970**, *53*, 1126–1130.
- [155] A. Eckmann, A. Felten, A. Mishchenko, L. Britnell, R. Krupke, K. S. Novoselov, C. Casiraghi, "Probing the Nature of Defects in Graphene by Raman Spectroscopy" *Nano Lett.* **2012**, *12*, 3925–3930.
- [156] J.-M. Atebamba, J. Moskon, S. Pejovnik, M. Gaberscek, "On the Interpretation of Measured Impedance Spectra of Insertion Cathodes for Lithium-Ion Batteries" *J. Electrochem. Soc.* **2010**, *157*, A1218.
- [157] K. Wang, Y. Xu, Y. Li, V. Dravid, J. Wu, Y. Huang, "Sodium storage in hard carbon with curved graphene platelets as the basic structural units" *J. Mater. Chem. A* **2019**, *7*, 3327–3335.
- [158] Y. Yamada, Y. Iriyama, T. Abe, Z. Ogumi, "Kinetics of Lithium Ion Transfer at the Interface between Graphite and Liquid Electrolytes: Effects of Solvent and Surface Film" *Langmuir* **2009**, *25*, 12766–12770.
- [159] Y. Youn, B. Gao, A. Kamiyama, K. Kubota, S. Komaba, Y. Tateyama, "Nanometer-size Na cluster formation in micropore of hard carbon as origin of higher-capacity Na-ion battery" *npj Comput Mater* **2021**, *7*, 48.

- [160] M. Anji Reddy, M. Helen, A. Groß, M. Fichtner, H. Euchner, "Insight into Sodium Insertion and the Storage Mechanism in Hard Carbon" *ACS Energy Lett.* **2018**, 3, 2851–2857.
- [161] H. Radinger, A. Ghamlouche, H. Ehrenberg, F. Scheiba, "Origin of the catalytic activity at graphite electrodes in vanadium flow batteries" *J. Mater. Chem. A* **2021**, 9, 18280–18293.
- [162] L. A. Langley, D. E. Villanueva, D. H. Fairbrother, "Quantification of Surface Oxides on Carbonaceous Materials" *Chem. Mater.* **2006**, 18, 169–178.
- [163] G. Beamson, D. Briggs, *High resolution XPS of organic polymers: The Scienta ESCA300 database*, Chichester, **1992**.
- [164] J.-L. Xia, D. Yan, L.-P. Guo, X.-L. Dong, W.-C. Li, A.-H. Lu, "Hard Carbon Nanosheets with Uniform Ultramicropores and Accessible Functional Groups Showing High Realistic Capacity and Superior Rate Performance for Sodium-Ion Storage" *Advanced Materials* **2020**, 32, 2000447.
- [165] A. Karatrantos, S. Khan, T. Ohba, Q. Cai, "The effect of different organic solvents on sodium ion storage in carbon nanopores" *Phys. Chem. Chem. Phys.* **2018**, 20, 6307–6315.

8 Appendix

Supplementary Figures

8.1 Experimental Methods

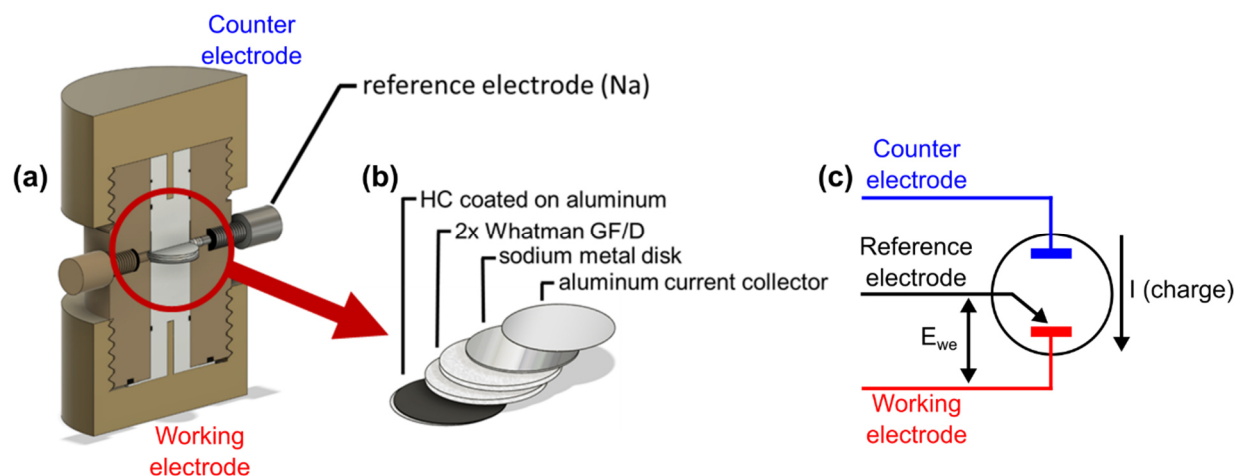


Figure S1. Sectional view of the PEEK cell body used in this work (a), electrode arrangement inside the cell (b) and electrode connections showing the current flow and potential measurement between the electrodes (c).

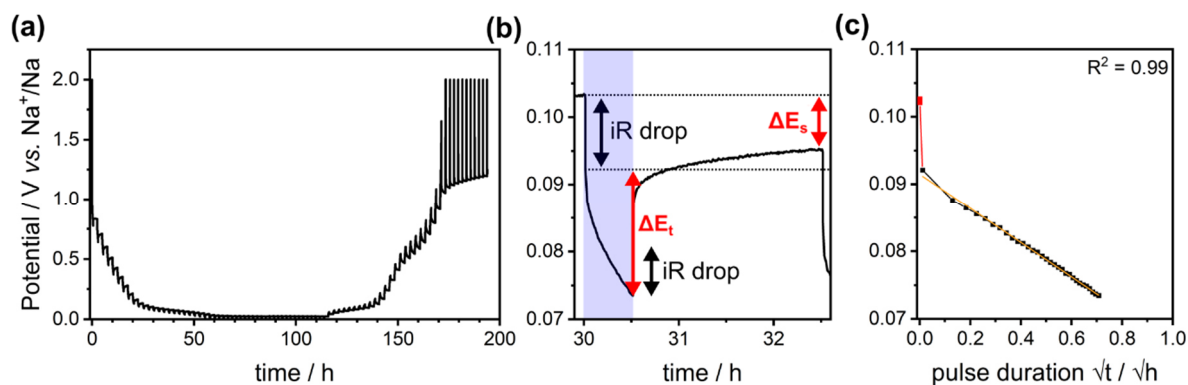


Figure S2. GITT curve of the pristine hard carbon (a). GITT step illustrating the galvanostatic pulse and the following relaxation interval (b). Potential response of the HC electrode during a GITT current pulse plotted against the square root of time (c). After correction for the initial iR drop, a linear regression (orange line) was fitted to the data, confirming the $\sqrt{t}$ dependence expected for semi-infinite diffusion and validating the applicability of the GITT diffusion model.

8.2 Ozone treatment as a covalent Functionalization Method

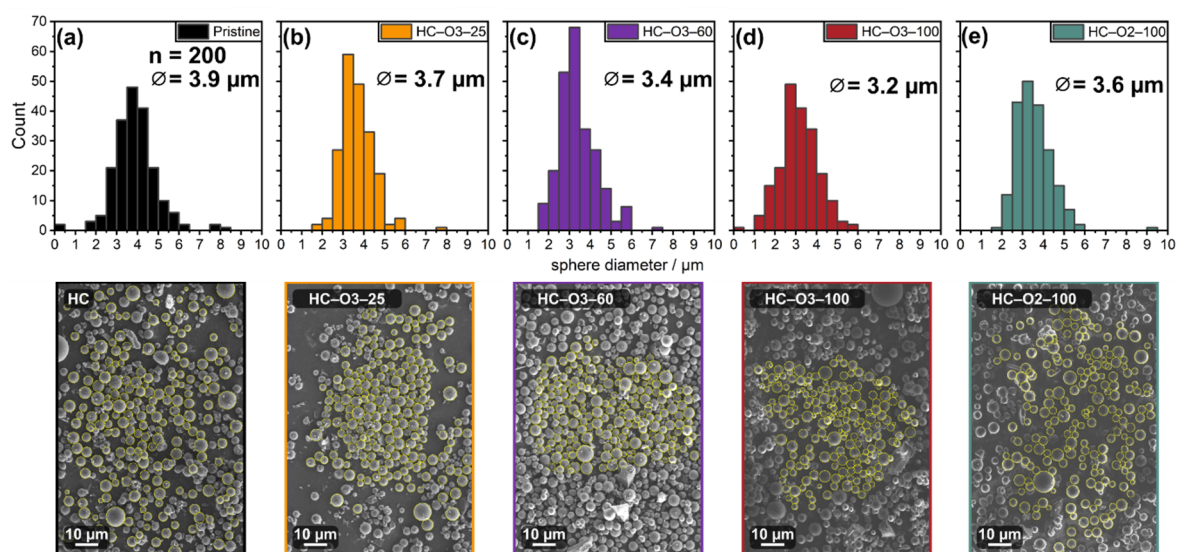


Figure S3. Histograms of measured sphere diameters and annotated SEM images (a-d).

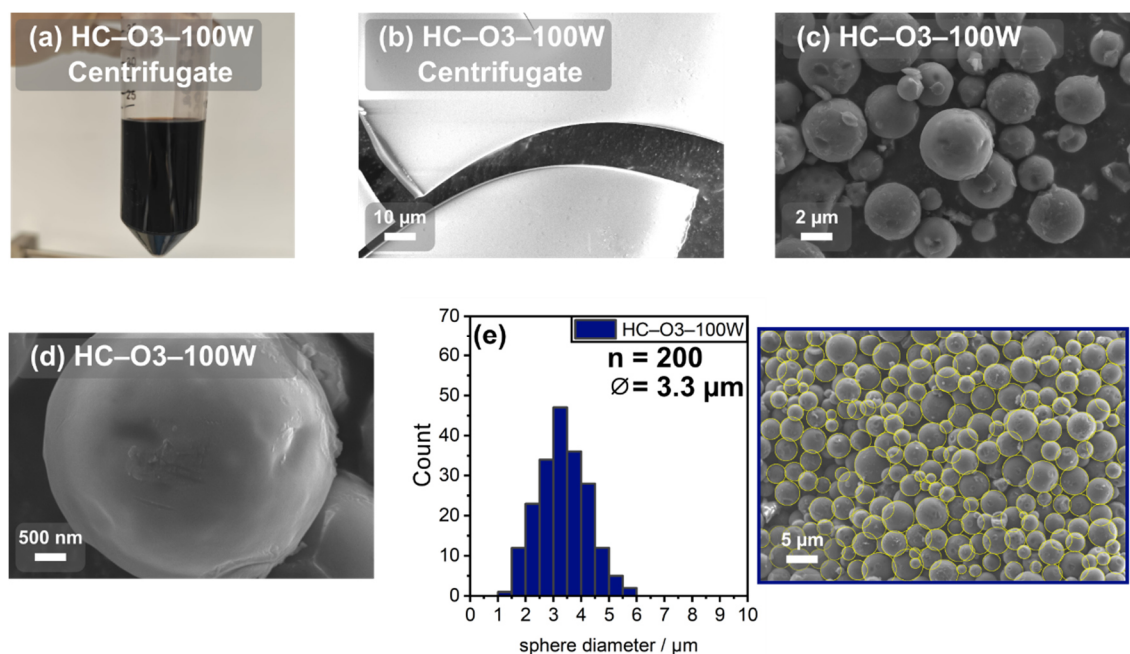


Figure S4. Image centrifugate of HC-O3-100W in water (a) and SEM image of the centrifugate (b). SEM images of HC-O3-100W (c,d) and histogram of sphere diameter distribution with annotated SEM image (e).

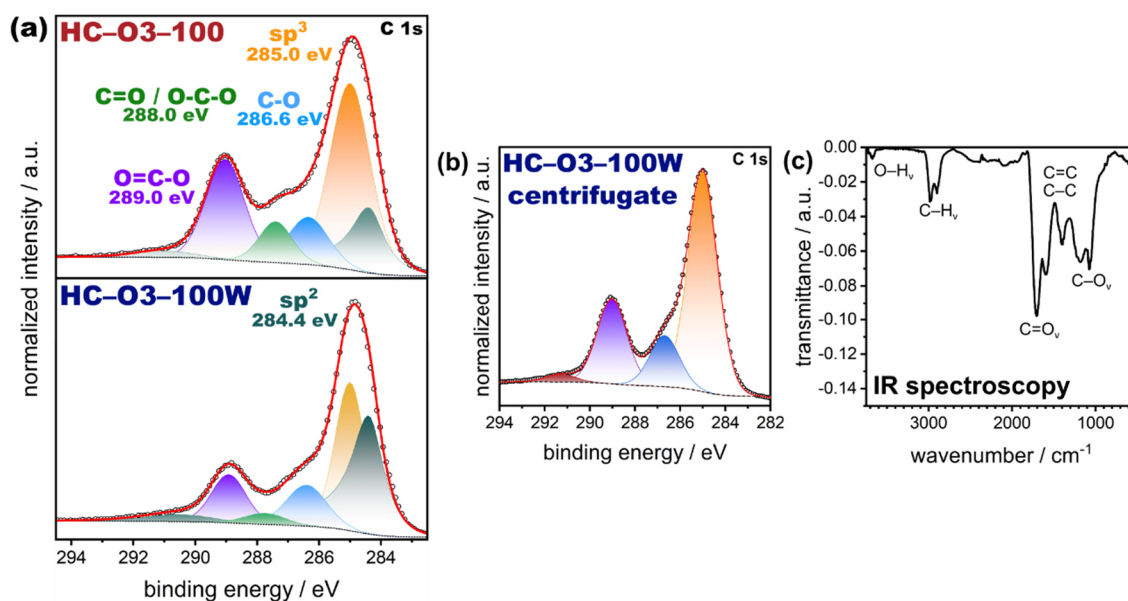


Figure S5. Comparison of HC-O3-100 and HC-O3-100W C 1s spectra (a) and the centrifugate recovered after washing of HC-O3-100 (b) as well as IR spectra of the centrifugate (c).

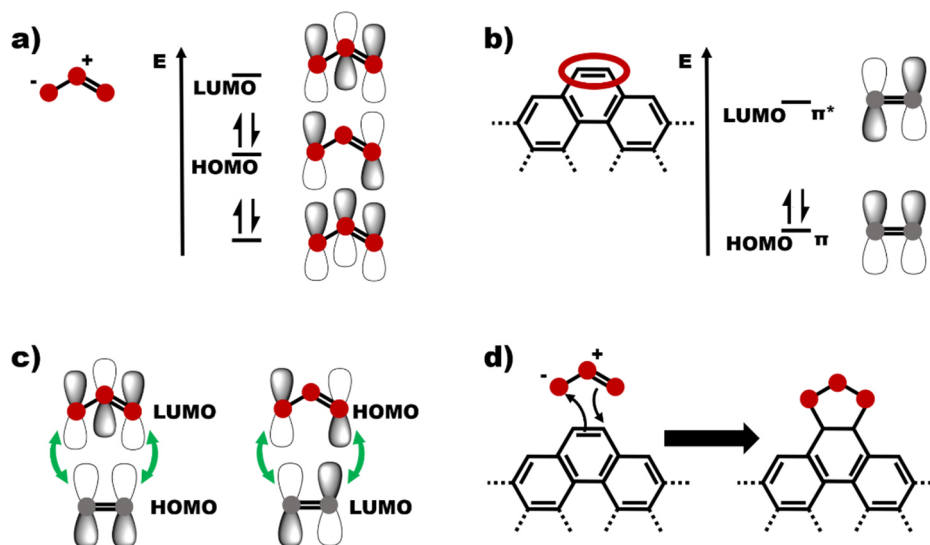


Figure S6. Molecular orbital diagrams of ozone (a) and a sp^2 hybridized carbon-carbon double bond (b). HOMO-LUMO interactions between ozone and the sp^2 bond during the 1,3-dipolar cycloaddition (c) and first reaction step of the concerted reaction of molozonide formation (d).

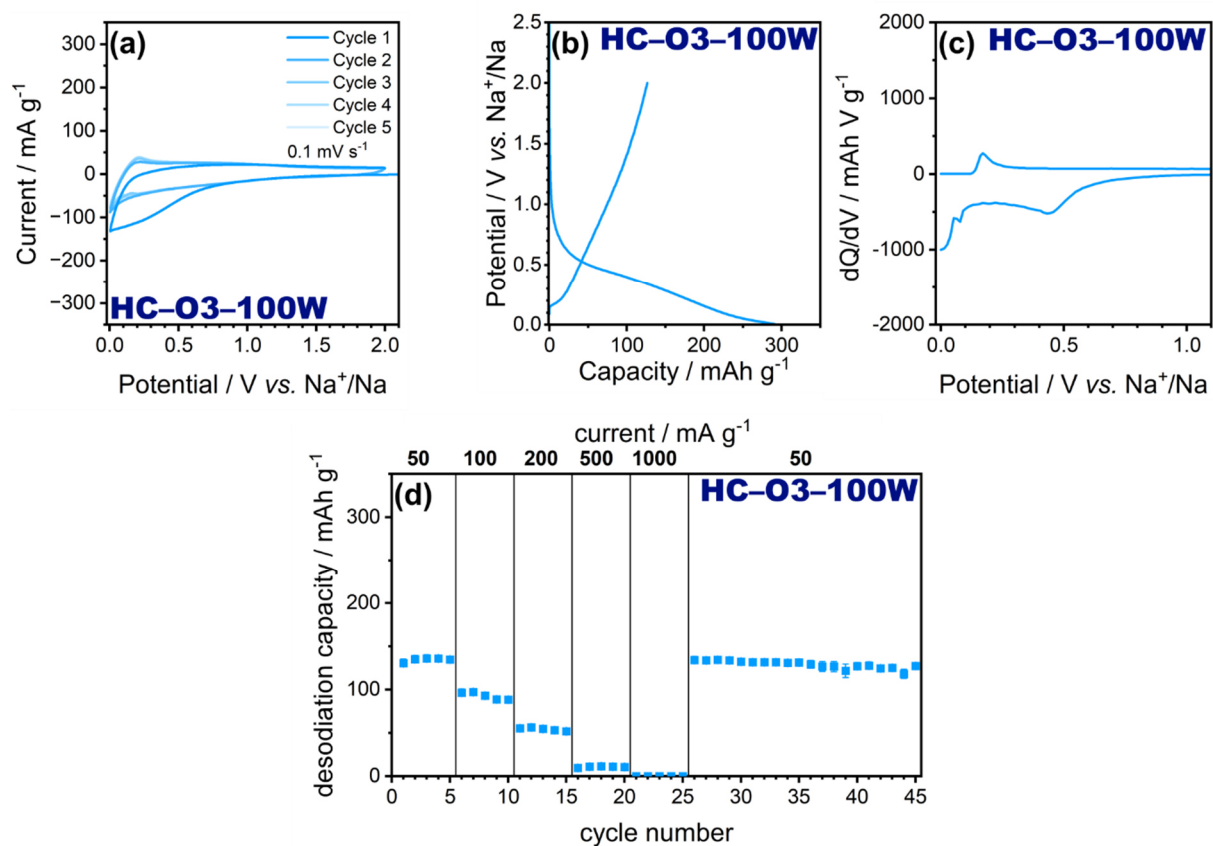


Figure S7. First five CV scans at 0.1 mVs⁻¹ (a), first-cycle galvanostatic cycling (b) and corresponding dQ/dV profile (c) and rate test of HC-O3-100W.

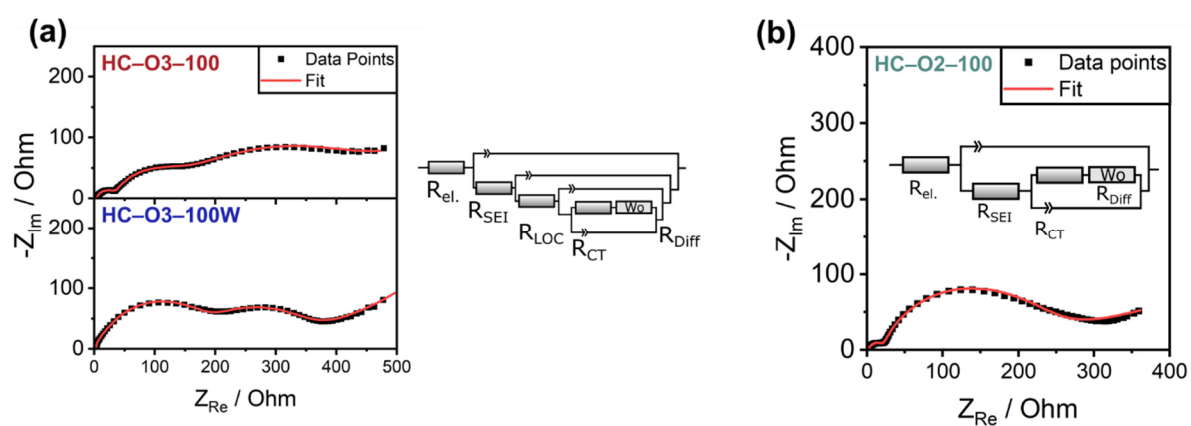


Figure S8. Nyquist plot comparison of HC-O3-100 and HC-O3-100W (a) and HC-O2-100 (b).

8.3 Chemical Derivatization of Oxygen Functional Groups on Hard Carbon

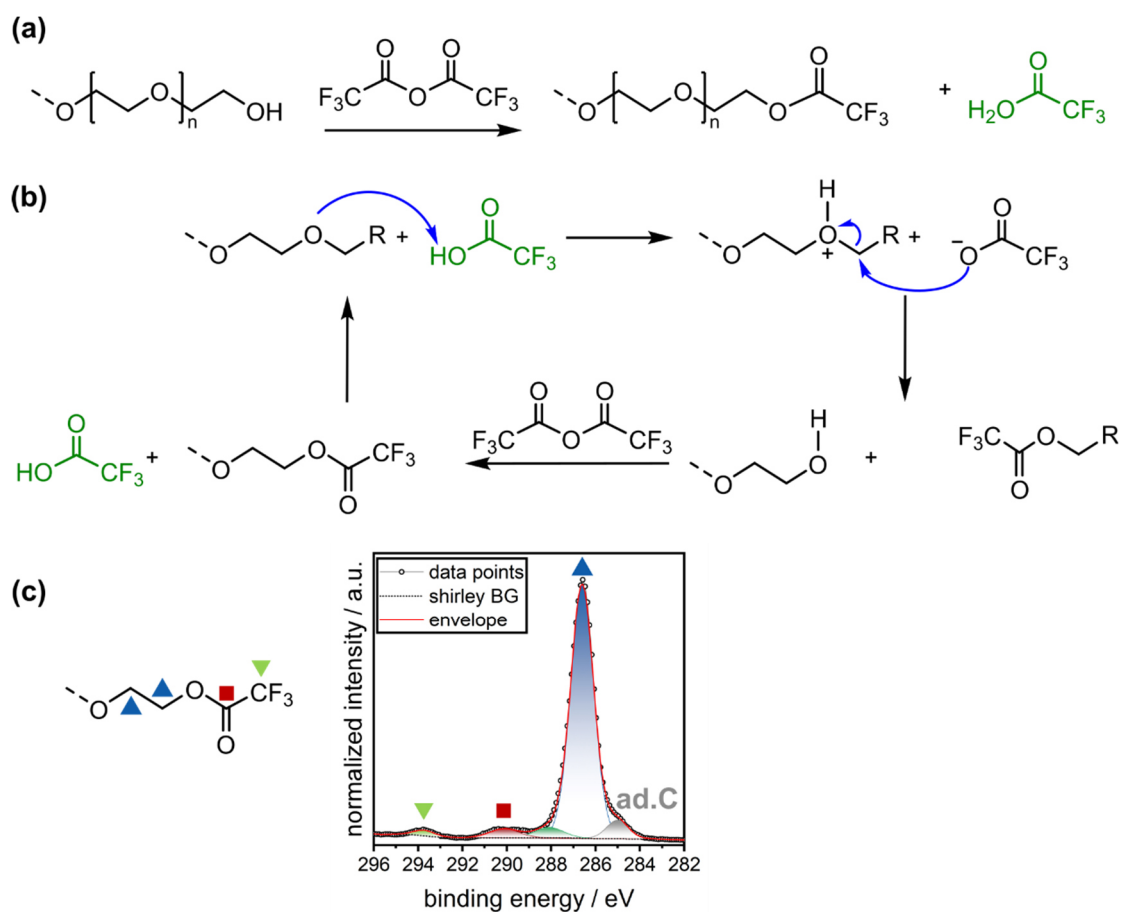


Figure S9. Reaction of TFAA with PEG (a) and proposed mechanism of TFAA mediated degradation of the PEG chains (b). Panel (c) shows the corresponding C 1s spectrum of the TFAA-treated polymer.

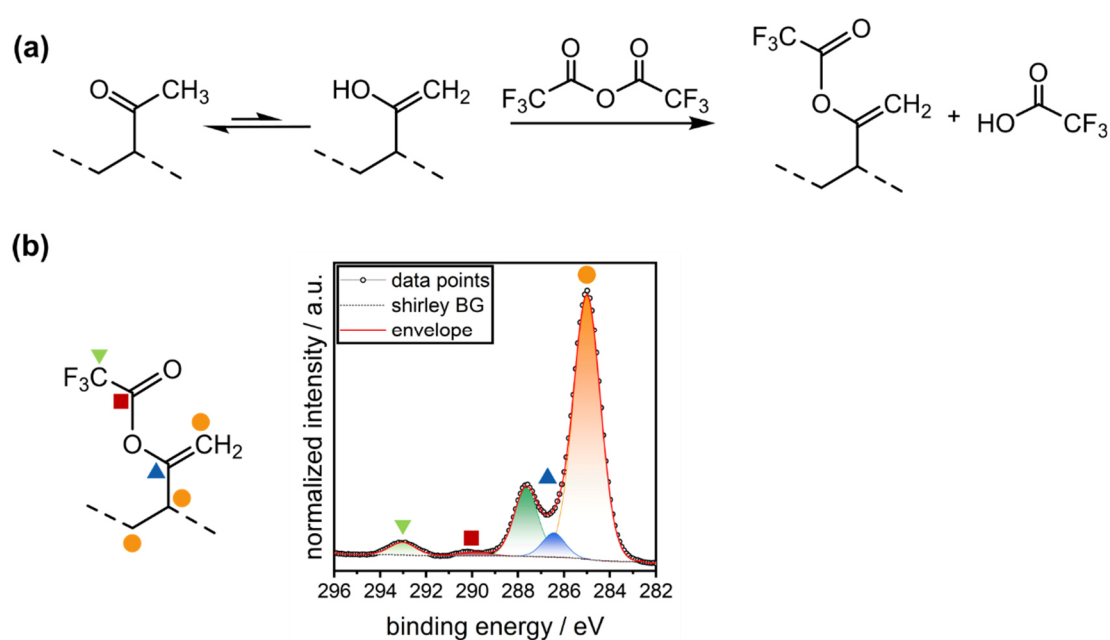


Figure S10. Keto-enol tautomerism of PVMK and reaction with TFAA (a) and corresponding C 1s spectrum of the TFAA-treated polymer (b)

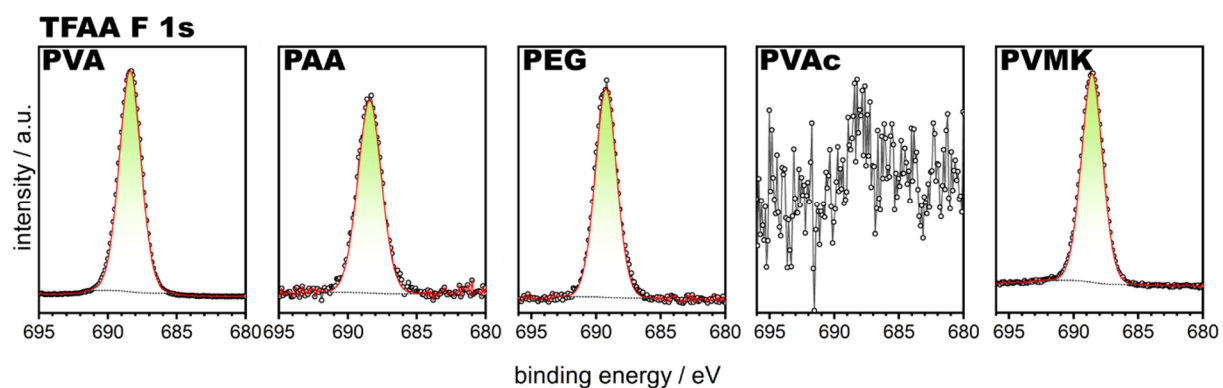


Figure S11. F 1s spectra of polymers after immersion in TFAA.

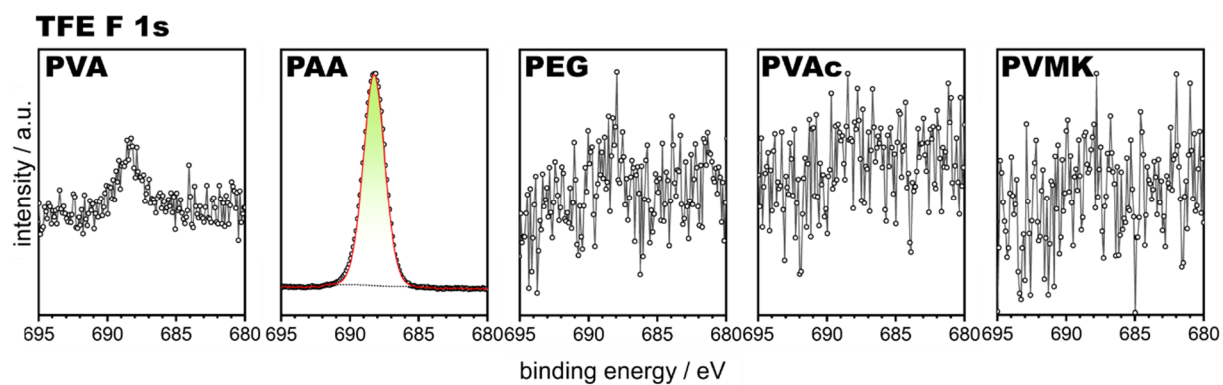


Figure S12. F 1s spectra of polymers after immersion in TFE.

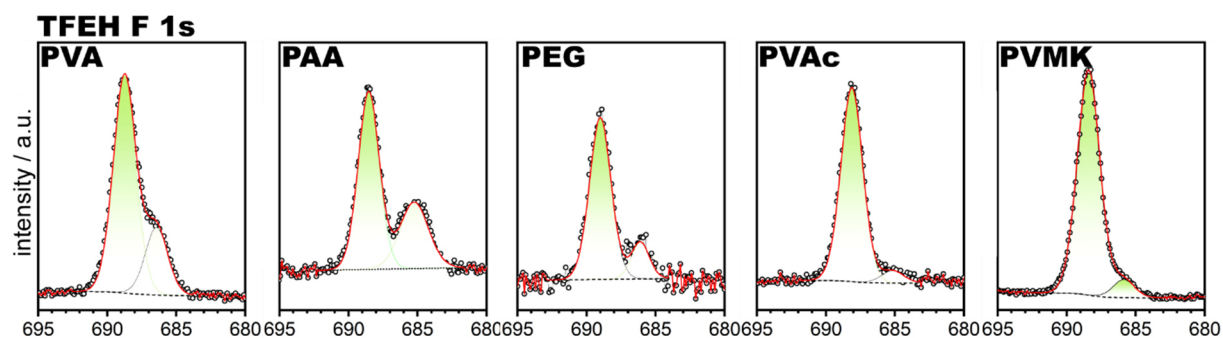


Figure S13. F 1s spectra of polymers after immersion in TFEH.

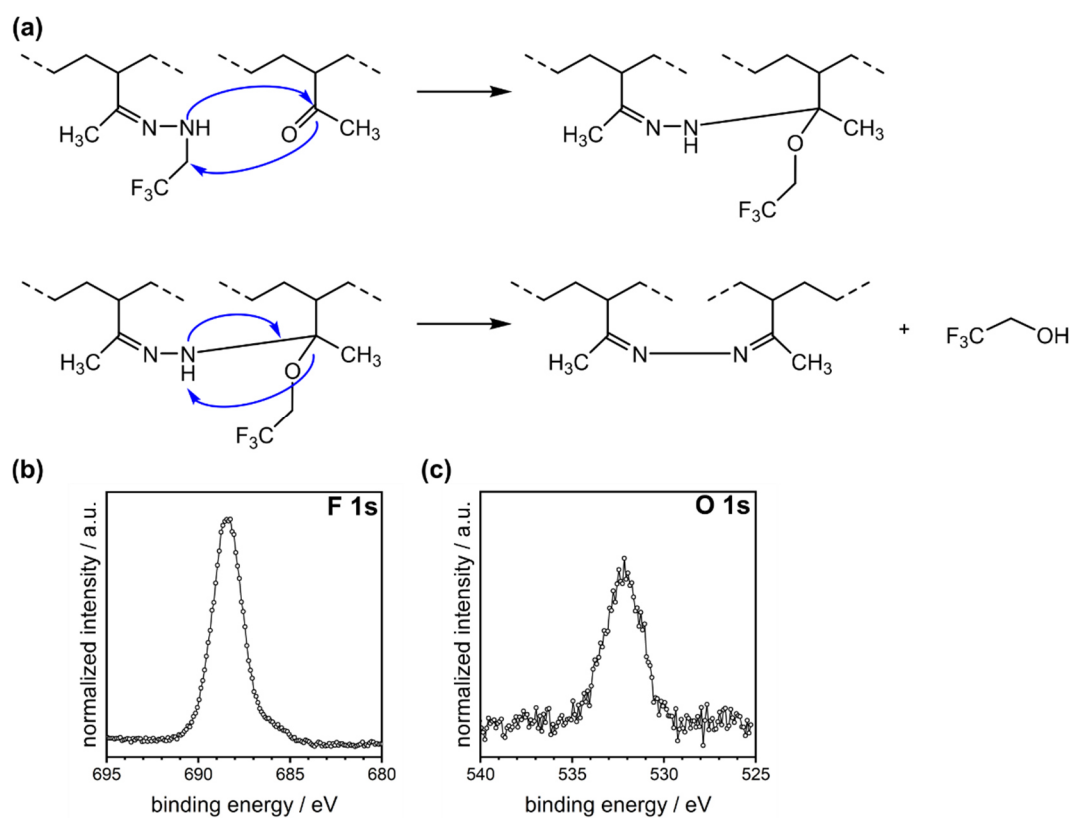


Figure S14. Proposed condensation mechanism of PVMK with TFEH (a), C 1s and O 1s spectra of the TFEH treated polymer (b,c).

9 Authorship

The following persons contributed to this thesis with the respective contributions outlined below:

Felix Bauer:	Lead author, performed all electrochemical experiments and data analysis. Authored the manuscripts with supervision and guidance from Frieder Scheiba.
Frieder Scheiba:	Supervision.
Marius Ast:	Performed SEM image acquisition.
Bijian Deng:	Performed SEM image acquisition.
Mattes Renner	Review and Feedback
Vanessa Trouillet:	Guidance on XPS experiments and data analysis.
Dominik-Marcel Schwarz:	Bachelor Thesis, conducted experiments in chapter 4.2.
Tabea Sostmann:	Performed XRD data acquisition.
Alperen Kahraman:	Student research assistant, support in the laboratory.
Ebru Halim:	Student research assistant, support in the laboratory.
Clemens Seifert:	Student research assistant, support in the laboratory.

Chapter 4.2 is based on the results of the Bachelor's thesis by Dominik-Marcel Schwarz entitled "Surface Modification of Hard Carbon with Pyrene for Sodium-Ion Batteries". The original idea for this work was conceived by Frieder Scheiba. The experimental concept, methodology and data analysis was done by Felix Bauer, and all experimental work was carried out by Dominik-Marcel Schwarz.

Chapters 4.3 and 4.4 are based on ideas developed and conceptualized by Felix Bauer and form part of the manuscript in submission entitled "Ozone-Induced Surface Functionalization of Hard Carbon for Sodium-Ion Batteries: Mechanism, Composition, and Electrochemical Impact" and the manuscript in preparation entitled "Chemical Labeling of Oxygen Functional Groups Unveils the Surface Chemistry of Hard Carbon and its Role in SEI Formation". Felix Bauer conducted all experimental work with support from the aforementioned student research assistants. SEM measurements were carried out by Marius Ast and Bijian Deng. Vanessa Trouillet assisted with the design of the XPS experiments and supervised data analysis. Frieder Scheiba contributed to data interpretation and the writing process.

During the preparation of this work, the author used the AI assistant Microsoft Copilot to aid in the linguistic refinement and writing process. The author explicitly states that no data analysis, interpretation of results, or drawing of conclusions were performed by AI. After using this tool, the author thoroughly reviewed and edited the content as needed and takes full responsibility for the integrity and accuracy of the entire work.

10 Scientific Contributions

Peer-reviewed Articles:

- [1] H. Radinger, V. Trouillet, F. Bauer, F. Scheiba, ACS Catalysis, **2022**, 12, (10), 6007-6015.
- [2] H. Radinger, F. Bauer, F. Scheiba, Batteries & Supercaps **2023**, 6, e202200440.
- [3] M. Bauer, P. Konnerth, H. Radinger, K. Pfeifer, Y. Joshi, F. Bauer, H. Ehrenberg, F. Scheiba, Nano Select., **2023**, 4, 278.
- [4] S. McArdle, F. Bauer, S.F. Granieri, M. Ast, F. Di Fonzo, A.T. Marshall, H. Radinger, ChemElectroChem, **2024**, 11, e202300512.
- [5] M. Hosseinzadegan, F. Bauer, L. Nyholm, G. Hernández, D. R. Maibach, Adv. Energy Mater., **2025**, 15, 44, e03627.
- [6] F. Bauer, M. Ast, A. Kahraman, F. Scheiba, *manuscript in submission*.
- [7] F. Bauer, M. Ast, A. Kahraman, F. Scheiba, *manuscript in preparation*.

Oral Presentations:

- [1] 245th Meeting of the Electrochemical Society, ECS Meeting, “Systematic Investigations of Surface Oxygen Functional Groups on Spherical Hard Carbon for Sodium-Ion Batteries”, **2024**, San Francisco, USA.
- [2] POLiS Conclave, “Deciphering the Effect of Surface Oxygen Functionalities on Hard Carbon”, **2025**, Karlsruhe, Germany.
- [3] Deakin University International Energy Symposium, “Deciphering the Effect of Surface Oxygen Functionalities on Hard Carbon”, **2025**, Melbourne, Australia.

Poster Presentations:

- [1] 5th International Sodium Battery Symposium, SBS-5, “Exploring Hard Carbon Surface Functionalization with Ozone”, **2024**, Berlin, Germany.
- [2] 10th International Conference on Sodium Batteries, ICNaB, “Deciphering the Effect of Surface Oxygen Functionalities on Hard Carbon”, **2025**, Sydney, Australia. (Poster-Award)