

# 2021: A Surface Odyssey. Role of Oxygen Functional Groups on Activated Carbon-Based Electrodes in Vanadium Flow Batteries

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The market breakthrough of vanadium flow batteries is hampered by their low power density, which depends heavily on the catalytic activity of the graphite-based electrodes used. Researchers try to increase their performance by thermal, chemical, or electrochemical treatments but find no common activity descriptors. No consistent results exist for the so-called oxygen functional groups, which seem to catalyze mainly the  $V^{III}/V^{II}$  but rarely the  $V^{VO_2^+}/V^{VO^{2+}}$  redox reaction. Some studies suggest that the activity is related to graphitic lattice defects which often contain oxygen and are

therefore held responsible for inconsistent conclusions. Activation of electrodes does not change one property at a time, but rather surface chemistry and microstructure simultaneously, and the choice of starting material is crucial for subsequent observations. In this contribution, the literature on the catalytic and physicochemical properties of activated carbon-based electrodes is analyzed and evaluated. In addition, an outlook on possible future investigations is given to avoid the propagation of contradictions.

## 1. Introduction

Carbon-based materials are widely used as electrodes in vanadium flow batteries (VFBs). Especially graphite felt (GF) is applied on an industrial scale due to its porous structure, high surface area, and chemical stability in acidic media.<sup>[1]</sup> However, the properties that determine the electrochemical performance, *i.e.*, the ability to facilitate the negative ( $V^{III} + e^- \rightleftharpoons V^{II}$ ,  $E^0 = -0.26$  V vs. SHE) and positive ( $V^{VO_2^+} + 2H^+ + e^- \rightleftharpoons V^{VO^{2+}} + H_2O$ ,  $E^0 = 1.0$  V vs. SHE) vanadium half-cell redox reactions depend on several parameters such as the choice of precursor material, fiber preparation, carbonization temperature, and activation treatment. In Figure 1, the topmost surface layer of a graphite-based catalyst is divided into three different classes according to the preparation procedure and can either preserve a graphene, a graphene-oxide, or a reduced graphene oxide-like structure. The electrode shown in Figure 1a consists of an intact  $sp^2$  hybridized basal plane with a  $\pi$ -conjugated system and lacks contamination and functional groups. The structure of carbon-based materials is regularly studied by Raman spectroscopy, in which the intensity ratio of the defect-induced D and graphitic G band is used to quantify and qualify the degree of disorder.<sup>[2,3]</sup>

The catalytic activity of an electrode is studied in a three-electrode half-cell comprising the electrolyte with vanadium-containing species, *e.g.*,  $V^{VO^{2+}}$  for the positive or  $V^{III}$  for the negative half-cell. An electrode is considered active when reversible cyclic voltammetry (CV) curves close to the thermodynamic standard potential  $E^0$  can be obtained. For graphene, the overpotential is high since the basal plane is electrochemically inert for vanadium.<sup>[4,5]</sup> Many scientific and industrial activities focus on increasing the activity of an electrode by oxidative treatments such as thermal, chemical, or electrochemical activation to introduce so-called oxygen functional groups (OFGs) as surface moieties. The subsequently obtained graphene oxide-like material (Figure 1b) has a damaged surface, leading to a decreased  $sp^2$  content and the formation of OFGs. Their presence as hydroxyl, carbonyl, and carboxyl moieties is investigated by X-ray photoelectron (XPS) or IR spectroscopy. There exist contradictions in literature about the role of OFGs in the electrocatalysis of diluted vanadium ions. It was recently demonstrated that they are a poor activity descriptor because there was no correlation between half-cell activity and concentration of surface oxygen moieties before or after electrochemistry.<sup>[6]</sup> Oxidative activation creates pores and corrosion-like pits on the otherwise smooth pristine GF, as it is observed by scanning electron microscopy (SEM). If the damaging exceeds the mechanical tolerance of the material, its structural properties change and the long-range order is lost, resulting in an amorphous material with low electrical conductivity.<sup>[7]</sup> This material failure cannot be studied by surface sensitive methods, but requires bulk techniques such as X-ray diffraction (XRD).

By deoxygenating GF it was shown that the overall electrochemical performance was related to the presence and number of defects.<sup>[8]</sup> In contrast, OFGs, either present before or developing during electrochemistry, hindered the electron

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transfer. A deoxygenated electrode has a reduced graphene oxide structure with hydrogen-terminated edges (Figure 1c). The material surface is damaged by the ripping of carbon-oxygen moieties and reveals a more intense D to G ratio. In the displayed CV curves a higher catalytic activity can be observed by a  $V^{VO_2^+}/V^{VO^{2+}}$  redox peak which lies at lower potentials compared to graphene.

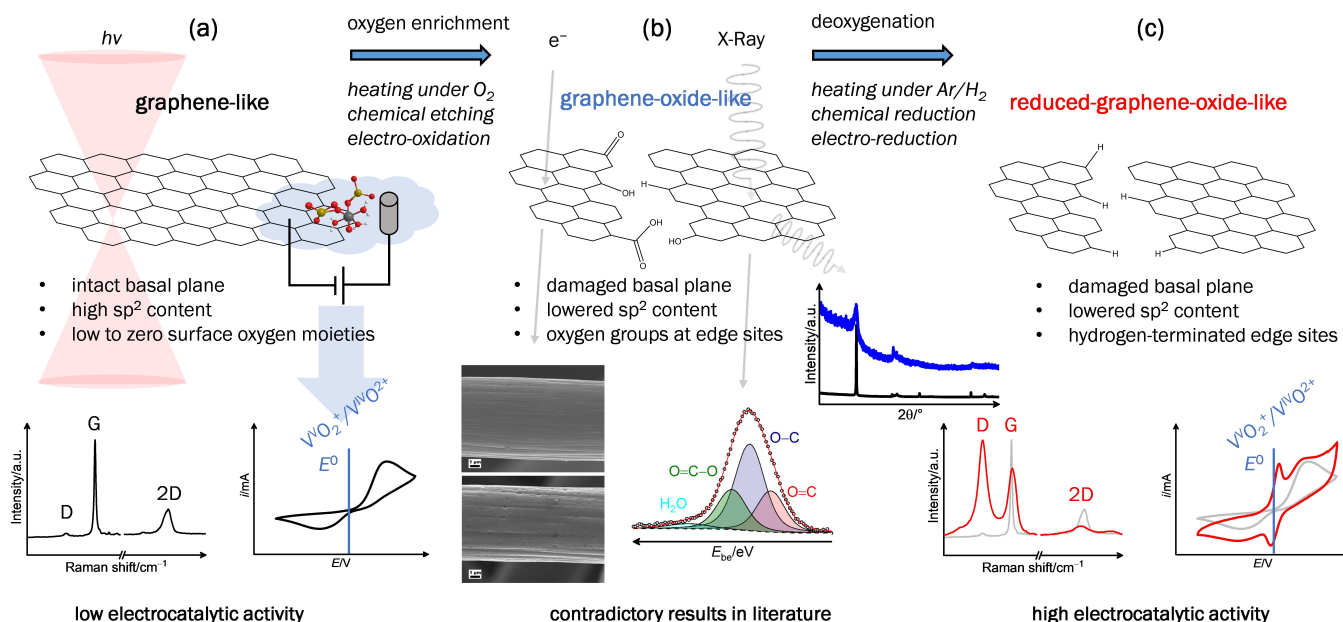
Herein, important previous research that specifically addressed the issue of OFGs and defects is summarized. Thereby the current state of knowledge is considered, and the previous conclusions are critically evaluated. The literature will be divided into segments based on the treatment, including thermal, (thermo-)chemical, electrochemical, and plasma/radiation activation. However, it is not the aim to review possible electrode treatments. Instead, particular attention is paid to the material used, its modified properties, and the associated interpretation of performance enhancement or degradation. The literature was selected by paying special attention to the interpretation of the physicochemical data and which material properties are made responsible for a change in activity. The findings and how they build on each other or contradict each other are outlined. In the end, a perspective on how to advance research on the fundamental catalysis of graphite electrodes while avoiding contradictions is given.

## 2. Review of Activation Treatments

### 2.1. Thermal Activation

Oxidation at elevated temperature in ambient is the most used method for the activation of GF. The herein discussed literature on thermal activation is summarized in Table 1. Other treatments must stand comparison with thermal activation for its simplicity and effectiveness. A major drawback, however, is the unreliability of the process, whose parameters not only depend on the material but can even change within two supply batches.<sup>[9]</sup> Thermal activation increases the electrical double layer capacitance (EDLC) and improves the wetting properties but these important parameters can diverge between two studied charges, which is related to their different surface chemistries.

To improve its electrochemical performance, Sun and Skyllas-Kazacos thermally treated GF, which improved the energy efficiency by 10% in a symmetrical full cell.<sup>[10]</sup> This increase was attributed to surface-active hydroxyl and carbonyl functional groups. A reaction sequence involving the formation of C–O–V intermediates facilitating electron and oxygen transfer was first proposed. However, the half-cell mechanism was based solely on full cell measurements. Therefore, Choi and co-workers aimed to separate the half-cells by investigating pristine and heat-treated carbon felt (CF) using impedance spectroscopy.<sup>[11]</sup> They found that the negative electrode was much more sensitive to heat treatment, and surprisingly the highest charge and discharge capacities were obtained by using activated CF as the negative and untreated CF as the positive electrode. They consequently suggested an inner-sphere mechanism for



**Figure 1.** Illustration of three fundamental graphitic surface structures commonly used to describe electrocatalysis in vanadium flow batteries, and typical characterization tools used for their analysis. (a) Graphene-like electrodes characterized by Raman spectroscopy and positive half-cell CV. (b) Graphene oxide-like electrodes imaged by SEM and investigated by XPS. (c) Reduced graphene oxide-like electrodes studied by XRD, Raman spectroscopy and positive half-cell CV.

**Table 1.** A chronologically ordered list of literature that dealt with thermal activation and claimed to as a result change the electrochemical performance of the investigated material.

Material	Environment	Investigated System	Improvement related to	Year	Ref.
GF	200–500 °C, 10–50 h, air	full cell	OFGs	1992	[10]
carbon-based <sup>[a]</sup>	400 °C, 20 h, air	V <sup>VO</sup> <sub>2</sub> <sup>+</sup> /V <sup>VO</sup> O <sup>2+</sup>	sp <sup>2</sup> content	2014	[7]
GF (PAN)	403–575 °C, n/a, air	EDLC	surface chemistry	2015	[9]
CP	400 °C, 15–35 h, 0–42% O <sub>2</sub>	single flow cell	surface area	2015	[16]
carbon-based <sup>[b]</sup>	400 °C, 30 h, air	V <sup>III</sup> /V <sup>II</sup> , V <sup>VO</sup> <sub>2</sub> <sup>+</sup> /V <sup>VO</sup> O <sup>2+</sup> , single flow cell	edge sites and OFGs	2015	[4]
GF (PAN) <sup>[c]</sup>	400–600 °C, n/a, air	V <sup>III</sup> /V <sup>II</sup>	OFGs, edge sites	2016	[18]
GF (PAN, Rayon)	400 °C, 1–20 h, <sup>[d]</sup> air	V <sup>III</sup> /V <sup>II</sup> , V <sup>VO</sup> <sub>2</sub> <sup>+</sup> /V <sup>VO</sup> O <sup>2+</sup>	OFGs, sp <sup>2</sup> content	2016	[14]
GF (PAN, Rayon) <sup>[e]</sup>	n/a, air	V <sup>III</sup> /V <sup>II</sup> , V <sup>VO</sup> <sub>2</sub> <sup>+</sup> /V <sup>VO</sup> O <sup>2+</sup> (single flow cell)	OFGs, none	2017	[17]
GF (Rayon)	400–600 °C, 9 h, air	V <sup>III</sup> /V <sup>II</sup> , V <sup>VO</sup> <sub>2</sub> <sup>+</sup> /V <sup>VO</sup> O <sup>2+</sup> , full cell	OFGs, none, OFGs	2018	[19]
CF	520 °C, 9 h, air	full cell (impedance)	OFGs <sup>[f]</sup>	2018	[11]
CF	400 °C, 30 h, air	V <sup>III</sup> /V <sup>II</sup> , V <sup>VO</sup> <sub>2</sub> <sup>+</sup> /V <sup>VO</sup> O <sup>2+</sup> , single cell	OFGs, none, OFGs	2019	[12]
GF	500–980 °C, Ar/H <sub>2</sub>	V <sup>III</sup> /V <sup>II</sup> , V <sup>VO</sup> <sub>2</sub> <sup>+</sup> /V <sup>VO</sup> O <sup>2+</sup>	edge sites, vacancies	2021	[8]

[a] Carbon black, graphite flakes, carbon fiber; [a] Graphite foil, highly oriented pyrolytic graphite, carbon felt; [c] Graphitized at 1500 and 2000 °C for 1 h; [d] PAN- and Rayon-based activated for 20 and 1 h, respectively; [e] Carbonized and graphitized; [f] Improvements are reported mainly for the negative electrode

the V<sup>III</sup>/V<sup>II</sup>, and an outer-sphere mechanism for the V<sup>VO</sup><sub>2</sub><sup>+</sup>/V<sup>VO</sup>O<sup>2+</sup> redox pair. This raises questions about whether there is a relationship between total oxygen content and activity or even specific OFGs necessary. Certain groups could complement the mechanism of the V<sup>III</sup>/V<sup>II</sup> reaction but not work accordingly for the V<sup>VO</sup><sub>2</sub><sup>+</sup>/V<sup>VO</sup>O<sup>2+</sup> reaction, which would explain previous results.

Different OFGs and their effects on CF were thus investigated, showing that thermal activation increased the hydroxyl, decreased the carbonyl, but did not affect the carboxylic group concentration.<sup>[12]</sup> In half-cell experiments with rotating disk electrodes, the V<sup>III</sup>/V<sup>II</sup> reaction rate constant and exchange current density were enhanced, but reduced for the V<sup>VO</sup><sub>2</sub><sup>+</sup>/V<sup>VO</sup>O<sup>2+</sup> reaction by heat treatment. In subsequent single-cell tests, the energy efficiency was increased by 15% after exchanging the negative electrode for a heat-treated sample. In contrast, by changing the positive electrode, the efficiency was decreased by 2%. The improvement of the negative electrode was attributed to the oxygen concentration supporting the inner-sphere electron transfer process of the V<sup>III</sup>/V<sup>II</sup> redox reaction, which was often discussed since electrodes without activation seemed to support the theory of an outer-sphere mechanism.<sup>[13]</sup> It was concluded that the efficiency of a full cell depends more on the negative than on the positive half-cell reaction. However, this was proven incorrect by Fink *et al.* and Friedl and Stimming, who investigated the rate constants of both vanadium redox reactions and proposed that they were of the same order of magnitude in both half-cells.<sup>[14,15]</sup> By studying different OFGs after thermal activation, they also concluded that all groups increase the wetted surface area and catalyze the V<sup>III</sup>/V<sup>II</sup> but hinder the V<sup>VO</sup><sub>2</sub><sup>+</sup>/V<sup>VO</sup>O<sup>2+</sup> kinetics. To investigate the limits of oxygenation, Pezeshki and co-workers doubled the atmospheric oxygen concentration during carbon paper (CP) heat treatment.<sup>[16]</sup> Since this resulted in an increased number of OFGs but lower cell performance, they concluded it is rather the increase in surface area responsible for the reduction of the activation overpotential.

It can be expected that the variety of materials studied is crucial, as different intrinsic and surface properties must be

considered. Even with the same graphitized felt material, the influence of thermal activation varies depending on the fiber precursor. This was shown by Schweiss and colleagues, who studied pristine and activated GF produced of polyacrylonitrile (PAN) and cellulose (Rayon) fibers.<sup>[17]</sup> The oxygenated felts had no or only slightly adverse effects on the cell resistances and polarization curves using the positive electrolyte, which was shown by double half-cell measurements. Because of the different results depending on the felt precursor, another influencing factor was highlighted: the degree of graphitization. This was further investigated by Langner *et al.* who graphitized and thermally activated felt electrodes at different temperatures.<sup>[18]</sup> The peak currents and peak potential separation in the negative half-cell were increased after thermal activation, regardless of the previous graphitization temperature. The treated samples exhibited an increased surface area, abundant OFGs, and a higher percentage of sp<sup>2</sup> hybridized carbon by the removal of amorphous carbon during the heat treatment. In addition, increased disorder was characterized by Raman spectroscopy. The specific influence of one factor was difficult to isolate, so no conclusive statement could be made whether it is OFGs, edge sites, or the sp<sup>2</sup> content that controls the V<sup>III</sup>/V<sup>II</sup> redox activity.

Model electrodes, such as highly oriented pyrolytic graphite (HOPG), are used to distinguish the electrocatalytic properties of the basal and edge plane, with the latter providing faster electron transfer for both vanadium redox pairs. Building on this knowledge, Pour *et al.* investigated defects on heat-treated CP and recognized higher peak currents and smaller peak separations for the negative half-cell, associating the enhanced activity with oxygen-containing defects.<sup>[4]</sup> The positive half-cell reaction could not be enhanced by heat-treatment for vanadium concentrations typically used in battery cells. Mazúr and colleagues specifically studied OFGs on GF and observed increased EDLC, disorder, and oxygen coverage, all of which subsided at higher temperatures because of destruction of the graphite structure.<sup>[19]</sup> They similarly observed a decrease in faradaic

resistances in the negative half-cell for functionalized electrodes. Whereas the oxygen-rich sample also had the best performance in the positive half-cell, in their full-cell impedance study using higher vanadium concentrations the oxygen-rich GF did not show decreased charge transfer resistances.

## 2.2. Chemical and Thermo-Chemical Activation

To conduct chemical or thermo-chemical activation, the sample is either treated in an aggressive environment or soaked in a solution and subsequently heated. Table 2 contains a summary of the chosen literature on this kind of treatment. Similar to their early study on thermal activation, Sun and Skyllas-Kazacos treated GF with hot sulfuric and nitric acid.<sup>[20]</sup> The full cell efficiencies were increased afterwards, and the activity of the best performing electrode attributed to the higher number of OFGs. Gao and co-workers used iron-containing H<sub>2</sub>O<sub>2</sub> solution to selectively hydroxylate GF.<sup>[21]</sup> They attributed the enhanced peak potential separation and cell efficiencies mainly to the increased number of surface oxygen, but found severely damaged electrodes using SEM. Jiang *et al.* made use of this damaging process and combined thermal activation with chemical etching to enable bi-porous GF.<sup>[22]</sup> The resulting electrode had more than twice the number of OFGs compared to thermally activated felt only, which was suspected to be the electrocatalytic motif in both half-cell reactions over the seven times larger surface area and changed morphology. However, their thermally activated sample for comparison had no defined redox peaks in the negative half-cell and was activated for a shorter period than the thermo-chemically treated felt.

Carbon cloth (CC) as possible electrode material was investigated by Zeng and colleagues using alkaline hydrothermal treatment.<sup>[23]</sup> In their SEM results, the surface was not affected by the activation but defects were observed by Raman spectroscopy. An increase in OFGs, mainly as hydroxyl and carbonyl groups, was revealed, and the active surface area, approximated by EDLC measurements, was nearly doubled for the treated material. In the positive half-cell, the treated and untreated sample were indistinguishable, which was explained by the lower number of OFGs compared to the literature. Activity enhancement in the negative half-cell reaction was fully

attributed to OFGs, although the activity had a local maximum and decreased again at higher oxidation.

Various research groups expressed doubts about the necessity of OFGs after chemical activation. Rümmler and colleagues studied graphitic carbon powders activated by oxygenating agents and found the activity of the electrode was not reflected by the respective oxygen concentration.<sup>[24]</sup> They concluded that the choice of material was more important than oxygenation, but activation was still necessary to create hydrophilic surfaces for improved diffusion and sorption kinetics. Friedl *et al.* investigated the electron transfer kinetics of the positive redox couple on multi-walled carbon nanotubes (MWCNTs).<sup>[25]</sup> While functionalization for the Fe<sup>III</sup>/Fe<sup>II</sup> system led to a tenfold increase in current density, the activity of the V<sup>VO</sup><sub>2</sub><sup>+</sup>/V<sup>VO</sup>O<sup>2+</sup> reaction was decreased by OFGs. They concluded that these groups played no role in the vanadium electrocatalysis, but slowed the mobility of vanadium ions. Zhang *et al.* modified GF with KOH and attributed increased wettability, lower peak potential separation and higher peak current ratios for both half-cells and higher efficiencies and capacities in the full cell to OFGs.<sup>[26]</sup> However, doubts were formulated by Radinger and co-workers for GF and MWCNTs etched with KOH.<sup>[6]</sup> The catalytic activity did not correspond to the surface composition before or after half-cell cycling. Rather, electrochemically stable edge sites correlated to the peak potential separation and reversibility.

## 2.3. Electrochemical Activation

Electrochemical activation is attractive for commercial applications, as it allows the input of pristine material followed by activation within the assembled cell. Many researchers perform potential-driven activation directly in the battery electrolyte. However, there are differences in terms of electrolyte concentration, electrochemical protocols, and the material studied, as illustrated in Table 3. The positive half-cell reaction kinetics were investigated by Wang *et al.* on oxidized graphite disks activated by anodic polarization.<sup>[27]</sup> The higher rate constant and activation energy was attributed to an increased number of OFGs, enhancing the wetting properties of the material and promoting charge transfer. The induced damage to the material increased with the applied potential and corresponded to the activity. Kabir and co-workers studied the negative half-cell using electrochemically oxidized HOPG.<sup>[28]</sup> Their sample exhib-

**Table 2.** A chronologically ordered list of literature that dealt with chemical or thermochemical activation and claimed to as a result change the electrochemical performance of the investigated material.

Material	Environment	Investigated System	Improvement related to	Year	Ref.
GF	H <sub>2</sub> SO <sub>4</sub> , HNO <sub>3</sub> , 3–15 h, inert gas	Full cell	OFGs	1992	[20]
GF (PAN)	Fenton's reagent	V <sup>VO</sup> <sub>2</sub> <sup>+</sup> /V <sup>VO</sup> O <sup>2+</sup> , full cell	OFGs	2013	[21]
MWCNTs	H <sub>2</sub> SO <sub>4</sub> , HNO <sub>3</sub> , 3–18 h, inert gas	V <sup>VO</sup> <sub>2</sub> <sup>+</sup> /V <sup>VO</sup> O <sup>2+</sup>	none	2013	[25]
GF (PAN)	KOH, 800 °C, 2 h, inert gas	V <sup>III</sup> /V <sup>II</sup> , V <sup>VO</sup> <sub>2</sub> <sup>+</sup> /V <sup>VO</sup> O <sup>2+</sup> , full cell	OFGs, edge sites	2016	[26]
CC	KOH, 6–12 M, 150 °C, autoclave	V <sup>III</sup> /V <sup>II</sup> , V <sup>VO</sup> <sub>2</sub> <sup>+</sup> /V <sup>VO</sup> O <sup>2+</sup> , full cell	OFGs	2017	[23]
GF (Rayon)	FeCl <sub>3</sub> , 0.5 M, 400 °C, 6 h, air	V <sup>III</sup> /V <sup>II</sup> , V <sup>VO</sup> <sub>2</sub> <sup>+</sup> /V <sup>VO</sup> O <sup>2+</sup> , full cell	OFGs, surface area	2017	[22]
graphitic carbon powder	H <sub>2</sub> SO <sub>4</sub> , HNO <sub>3</sub> , KMnO <sub>4</sub> , 100 °C, 1 h, inert gas	V <sup>VO</sup> <sub>2</sub> <sup>+</sup> /V <sup>VO</sup> O <sup>2+</sup>	choice of material	2018	[24]
GF (PAN) MWCNTs	KOH, 4–6 M, 600–1000 °C, inert gas	V <sup>III</sup> /V <sup>II</sup> , V <sup>VO</sup> <sub>2</sub> <sup>+</sup> /V <sup>VO</sup> O <sup>2+</sup>	edge sites	2020	[6]

**Table 3.** A chronologically ordered list of literature that dealt with electrochemical activation and claimed to as a result change the electrochemical performance of the investigated material.

Material	Environment	Investigated System	Improvement related to	Year	Ref.
GF (PAN)	1 M H <sub>2</sub> SO <sub>4</sub> , 5–15 V <sup>[a]</sup>	V <sup>VO</sup> <sub>2</sub> <sup>+</sup> /V <sup>VO</sup> O <sup>2+</sup> , full cell	OFGs (carboxylic) and surface area	2007	[29]
graphene oxide	PBS, <sup>[b]</sup> –0.8 to –1.6 V vs. SCE, 3 min	V <sup>III</sup> /V <sup>II</sup> , V <sup>VO</sup> <sub>2</sub> <sup>+</sup> /V <sup>VO</sup> O <sup>2+</sup> , full cell	OFGs (carbonyl)	2013	[30]
CF, GF	2 M vanadium, 4 M H <sub>2</sub> SO <sub>4</sub> , –2.0 to 1.5 V, 60 s	V <sup>III</sup> /V <sup>II</sup> , V <sup>VO</sup> <sub>2</sub> <sup>+</sup> /V <sup>VO</sup> O <sup>2+</sup> , full cell	OFGs	2016	[33]
carbon based <sup>[c]</sup>	1.5 M vanadium, 4.5 M H <sub>2</sub> SO <sub>4</sub> , –2.25 to 1.6 V vs. Hg/Hg <sub>2</sub> SO <sub>4</sub> , 60 s	V <sup>III</sup> /V <sup>II</sup> , V <sup>VO</sup> <sub>2</sub> <sup>+</sup> /V <sup>VO</sup> O <sup>2+</sup>	OFGs	2016	[32]
graphite disc	0.1 M V <sup>VO</sup> O <sup>2+</sup> + 3 M H <sub>2</sub> SO <sub>4</sub> , 1.5–1.9 V vs. SCE, 10 min	V <sup>VO</sup> <sub>2</sub> <sup>+</sup> /V <sup>VO</sup> O <sup>2+</sup>	OFGs	2016	[27]
HOPG	1.0 M H <sub>2</sub> SO <sub>4</sub> , 2.1 V vs. Ag/AgCl, 1 min	V <sup>III</sup> /V <sup>II</sup>	OFGs	2017	[28]
glassy carbon	2 M H <sub>2</sub> SO <sub>4</sub> , 0.5–2 V vs. Hg/Hg <sub>2</sub> SO <sub>4</sub> , 30 s	V <sup>III</sup> /V <sup>II</sup> , V <sup>VO</sup> <sub>2</sub> <sup>+</sup> /V <sup>VO</sup> O <sup>2+</sup>	OFGs (hydroxyl), OFGs (carboxylic)	2018	[31]
Graphite disc <sup>[d]</sup>	2 M H <sub>2</sub> SO <sub>4</sub> , 2.2 V vs. RHE, 5 min	V <sup>III</sup> /V <sup>II</sup>	OFGs and edge sites	2018	[5]

[a] A two-electrode setup was used (titanium as counter electrode); [b] PBS: phosphate buffer solution (KH<sub>2</sub>PO<sub>4</sub>/K<sub>2</sub>HPO<sub>4</sub>, pH 5.1–5.5); [c] Glassy carbon, carbon paper, carbon xerogel, carbon fibers. [d] Edge and basal plane exposed.

ited several oxygen-related functional groups after activation, which were held responsible for the enhanced electron transfer properties.

Many scientists who agree on the functionality of surface oxygen still discuss the differences in specific OFGs and believe that only one or two catalyze the vanadium redox reactions. Li *et al.* attributed an improvement of the positive half-cell reaction by oxidized GF to the increased number of carboxyl groups.<sup>[29]</sup> Other researchers reduced graphene oxide electrochemically and observed increased activity in both half-cells by implementing carbonyl groups.<sup>[30]</sup> Noack and co-workers studied polarized GF and found that the reaction rates increased.<sup>[31]</sup> However, the negative half-cell reaction was steadily improved with applied potential, while the positive half-cell reaction had a local kinetic minimum. A correlation was found between the activity of the V<sup>VO</sup><sub>2</sub><sup>+</sup>/V<sup>VO</sup>O<sup>2+</sup> redox couple and the number of hydroxyl groups. No such correlation was present for the negative half-cell, but due to the lack of links with roughness factors or surface area, the activity of carboxylic groups was discussed.

More detailed studies note the difference between the vanadium half-cells and investigate the influence of activation conditions. It was demonstrated by Bourke *et al.* for several carbon-based materials that the V<sup>III</sup>/V<sup>II</sup> reaction is enhanced by anodic, and the V<sup>VO</sup><sub>2</sub><sup>+</sup>/V<sup>VO</sup>O<sup>2+</sup> reaction by cathodic polarization.<sup>[32]</sup> In both cases, they suspected the influence of OFGs whose oxidized or reduced state would not correspond to the state in which the respective redox reaction occurs. In a later study, they reported that their results were not related to a change in surface area, but to a change in surface chemistry.<sup>[33]</sup> Anodic treatment, which inhibits the positive half-cell reaction,

leads to a highly oxidized surface. In contrast, cathodic treatment, which enhances the V<sup>VO</sup><sub>2</sub><sup>+</sup>/V<sup>VO</sup>O<sup>2+</sup> redox reaction, resulted in a composition similar to the untreated sample with rather low oxygen content.

The role of defective sites after electrochemical treatment is less prominently discussed, but Taylor and coworkers studied basal and edge exposed electrodes before and after electrochemical oxidation and stated that edges provided faster redox kinetics in the initial state.<sup>[5]</sup> After oxidation, the edge surfaces tended to catalyze the parasitic hydrogen evolution reaction and were subsequently less active for the V<sup>III</sup>/V<sup>II</sup> redox couple. For the oxidized basal surface, prolonged cycling resulted in a sharp drop in activity, which was attributed to instable OFGs.

#### 2.4. Plasma/Radiation Activation

To integrate abundant OFGs on the surface of GF, plasma or irradiation exposure, occasionally followed by a chemical treatment, has been considered (Table 4). Kim *et al.* investigated the influence of mild oxidation, plasma treatment and gamma-rays on the electrochemical performance of CF.<sup>[34]</sup> They concluded that the number and type of OFGs are crucial for the redox kinetics. In particular, the importance of hydroxyl groups is emphasized to enhance the efficiency of the V<sup>VO</sup><sub>2</sub><sup>+</sup>/V<sup>VO</sup>O<sup>2+</sup> reaction. In a later study, they enriched the surface of GF with OFGs by combining a plasma procedure to create dangling bonds with a subsequent H<sub>2</sub>O<sub>2</sub> treatment to saturate these bonds with oxygen.<sup>[35]</sup> According to their interpretation, the OFGs provided faster charge transfer and improved wettability.

**Table 4.** A chronologically ordered list of literature that dealt with plasma treatment or radiation and claimed to as a result change the electrochemical performance of the investigated material.

Material	Environment	Investigated System	Improvement related to	Year	Ref.
CF (PAN)	300–600 °C, 5 h, air; O <sub>2</sub> plasma, 1–10 min; gamma-ray, 50–200 kGy, RT, air	full cell	OFGs and surface area	2011	[34]
CF (PAN)	Corona discharge, 4 A, 15 s, air; H <sub>2</sub> O <sub>2</sub> (30%), 1 h	V <sup>III</sup> /V <sup>II</sup> , V <sup>VO</sup> <sub>2</sub> <sup>+</sup> /V <sup>VO</sup> O <sup>2+</sup> , full cell	OFGs	2014	[35]
GF (PAN)	O <sub>2</sub> plasma, 2–60 min; H <sub>2</sub> O <sub>2</sub> , 1 h	full cell	OFGs (carboxylic) <sup>[a]</sup>	2016	[36]
GF (PAN)	N <sub>2</sub> plasma, 40 min,	V <sup>III</sup> /V <sup>II</sup> , V <sup>VO</sup> <sub>2</sub> <sup>+</sup> /V <sup>VO</sup> O <sup>2+</sup> , full cell	defects	2019	[37]

[a] Negative effect for hydroxyl and carbonyl groups.

However, only an effect on the negative half-cell and almost no improvement of the peak current and potential separation in the positive half-cell is observed.

Estevez *et al.* combined oxygen plasma and chemical treatment and found that carboxylic groups improved the energy efficiency by about 8%, while hydroxyl and carbonyl groups had a negative impact.<sup>[36]</sup> No microstructural changes were observed on the electrodes by SEM after the procedure compared to the untreated felt. By switching from an oxygen to a nitrogen plasma treatment, Dixon and coworkers showed that the induction of structural defects can improve the half-cell redox kinetics, especially the  $V^{III}/V^{II}$  reaction.<sup>[37]</sup> Since the oxygen content on the surface remained unchanged, the increased charge and discharge capacities in a full cell were attributed to a higher degree of disorder.

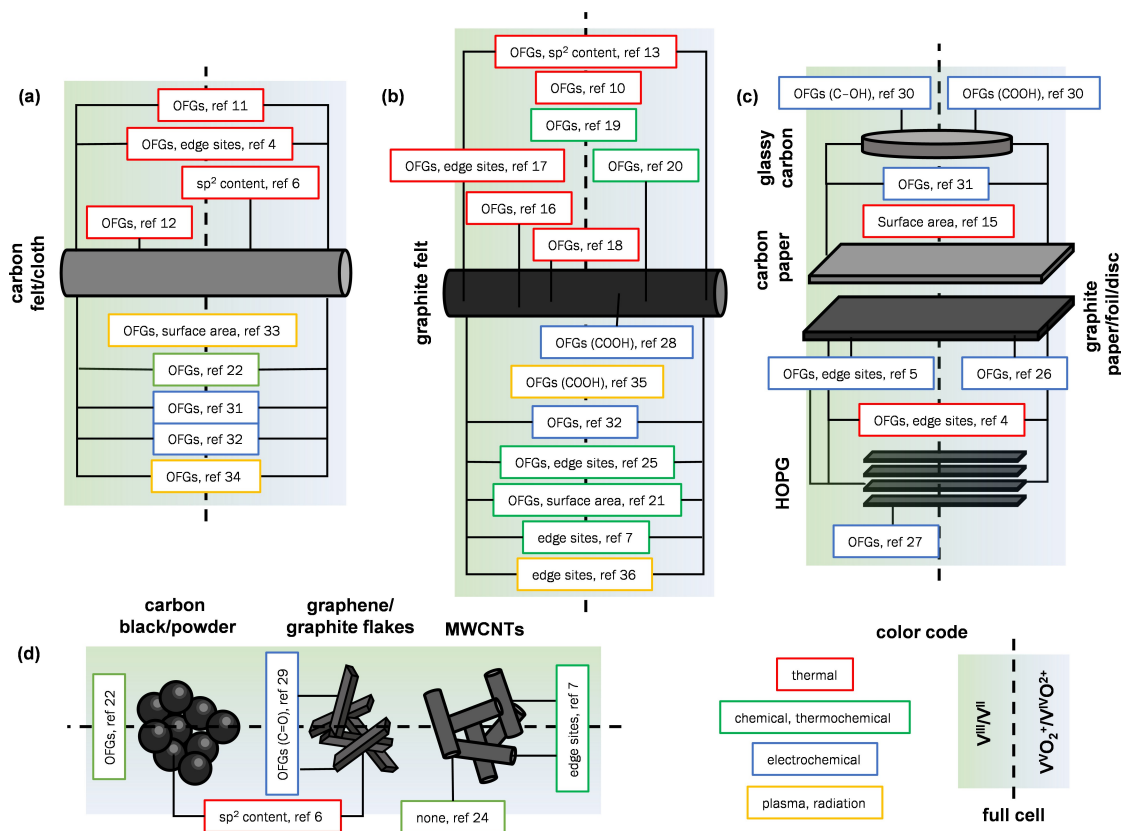
### 3. Perspective

The literature dealing with how the catalytic properties of carbon-based materials for vanadium redox reactions are affected by the integration of surface oxygen was summarized. The selected publications differed in their activation method, the material studied, the systems investigated, and the data

interpretation. A schematic overview is given in Figure 2, where the statements on the parameters are sorted according to the material. The conclusions drawn based on physicochemical characterization of the procedures are contradictory. OFGs are still held responsible for the demonstrated increased electrochemical performance, despite conclusive studies have shown the opposite, especially for the positive half-cell.

When discussing surface chemistry and associated changes after a treatment, it is important to note that such oxidized or reduced states are likely to be unstable over the potential ranges examined. This is evident from studies in which the surface chemistry was analyzed after electrochemical cycling.<sup>[6,38]</sup> When the oxygenated sample activated at positive potential is cycled in the negative half-cell, most of the previously introduced OFGs are expected to be removed, and the remaining bare edge sites take over the redox reactions, explaining the reduced concentration of surface oxygen after electrochemistry.<sup>[33]</sup> For prospective investigations, differential electrochemical mass spectrometry should be used as a technique to clarify the electrochemical stability of OFGs on graphite.

In contrast, OFGs are more persistent or are generated in the positive half-cell, thus hindering the positive half-cell reaction after anodic polarization. It was calculated that the



**Figure 2.** Scheme displaying the reason for enhanced electrochemical activity of different material as suggested by the literature. The position of the box indicates if the conclusion applies to the negative (green), positive (blue), both half-cells or the full cell, respectively (in between). The classification of the studies relates to the investigated material, *i. e.*, (a) carbon fiber and carbon cloth, (b) graphite felt, (c) model electrodes such as glassy carbon, carbon paper, graphite paper, graphite foil, HOPG, and (d) carbon-based nanomaterials such as carbon black, carbon and graphite powders or flakes, graphene (oxide), and MWCNTs. The publications are sorted according to their activation procedure by the given color code and the system they investigated.

$V^{V}O_2^{+}/V^{IV}O^{2+}$  redox reaction does not require the transfer of an oxygen atom, as several studies suggested.<sup>[39]</sup> Instead, proton exchange could occur *via* the oxygen atoms surrounding the vanadium ion or without the involvement of oxygen at all. A recent computational study suggests that  $sp^3$  groups at the surface are responsible for the acceleration of the positive half-cell redox reaction and oxygen groups can be considered a byproduct of this hybridization.<sup>[40]</sup> Instead, the authors suggest non-oxidative activations should be performed to maximize this effect. These procedures, such as polarization at negative potentials, create edges that can be considered active sites in both half-cell reactions.<sup>[8]</sup> The more resistant to oxidation, the higher and more durable the activity of the electrode consequently. Further computational studies should also consider the energy barriers for electron transfer at oxygen-free graphite defects.

Once a scientific theory is established in a community, it is difficult to seriously challenge it. Phenomenological observations by studying the physicochemical properties of catalysts are used to explain aspects of their activity. However, for complex systems such as graphite, not only one property should be held responsible since lots of changes can be monitored. Consequently, the established theory about the importance of OFGs for the catalysis of the vanadium redox couples might be reproduced while other properties are neglected. This may explain why several publications clearly demonstrate the enhanced activity of edge sites for the positive half-cell, but still attribute the performance to oxygen-containing defects. In our recent work, we demonstrated that hydrogen-containing edges better support vanadium redox reactions and OFGs in fact hinder charge transfer.<sup>[8]</sup> In catalysis research, it is common for mechanistic studies to examine the material postuse. However, this is rarely done within the VFB community, also due to the complexity of a heterogeneous graphite felt surface. But to develop reliable mechanisms, we need to paint a picture of the changing material properties during electrochemistry. We should thus use *operando* techniques to learn more about solid-liquid interactions and how molecules and atoms adsorb and migrate, how their coordination spheres develop, and how ions and charges are exchanged.

There are still open questions that need to be discussed, especially when it comes to graphitic defects. It is unclear how edge sites and vacancies behave differently in catalysis and how we can selectively introduce them into real electrodes. Armchair edges have different properties than zigzag edges, which affects their activity in other reactions such as oxygen evolution or reduction.<sup>[41,42]</sup> The effects on the vanadium redox reactions remain to be investigated. Furthermore, we did not accurately evaluate the contribution of the  $\pi$ -conjugated system. The correct balance between electrical conductivity and sufficient defect sites for electron transfer must be found. In addition, the interplay between microstructure and electronic structure needs to be understood. With an efficient activity descriptor from an electronic point of view that can be evaluated experimentally and theoretically, other parameters can be compared more easily.

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## Conflict of Interest

The authors declare no conflict of interest.

**Keywords:** electrocatalysis · electrode treatment · graphite felt · oxygen functional groups · vanadium flow batteries

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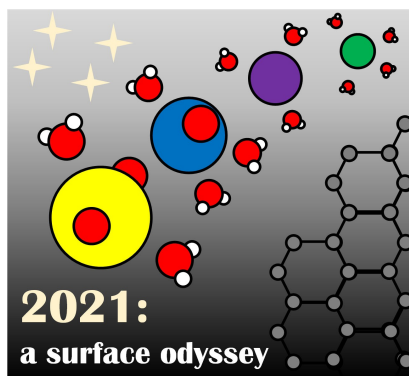
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## MINIREVIEWS

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There is a lack of common activity descriptors to understand the fundamental reaction processes occurring on carbon-based electrodes used in vanadium flow batteries. Most activation procedures do not change one property at a time but rather the surface chemistry and microstructure simultaneously. In this Minireview, selected literature on the electrochemical and physicochemical properties of treated electrodes is analyzed and an outlook on possible future investigations is provided.



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**2021: A Surface Odyssey. Role of Oxygen Functional Groups on Activated Carbon-Based Electrodes in Vanadium Flow Batteries**