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Electrochemically Generated Platform Oxidizers: An Enabler for the Hydrogen Economy

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CONSPECTUS: A highly attractive alternative anode reaction for electrochemical hydrogen production is the formation of platform oxidizers instead of molecular oxygen. These platform oxidants are high-value products and can therefore help cofinance hydrogen production. For most electro-organic reactions, the electrochemical conditions for hydrogen production would be incompatible, due to the high current density required, whereas the anodic production of platform oxidizers demonstrates technical complementarity. The broad range of applications for such platform oxidants and versatility allow for broad applications and large-scale use, including the synthesis of complex, high-value target products. For platform oxidizing agents that utilize elements that are in limited supply or pose environmental concerns, a closed-loop system must be established between their production and recycling. The recovery and regeneration of reaction waste into platform oxidizing agents must ensure that no cross-contamination occurs during the production of the target products and that these platform oxidizing agents can be transported and stored safely. Among many other platform oxidants, periodates and peroxodicarbonates are the most promising. This is because either a wide range of applications is already known, or the resulting byproducts serve as critical reactants for processes involving biogenic feedstock. Periodates have also been demonstrated to work in a closed-loop system: if these platform oxidants are used on-site, much simpler and easier-to-store starting compounds can be used, which then yield harmless coproducts that do not need to be recovered, e.g., alkali carbonates. In most cases, these platform oxidizers can be produced in an undivided electrolytic cell. This improves the energetics of the electrolytic reaction. The anodic reaction typically occurs at electrodes with a high overpotential for the oxygen-evolution reaction. Due to the temporary storage of the platform oxidants, this approach can contribute efficiently to the transformation of the chemical industry, as it allows safe hydrogen generation on demand and is tailored to the electricity supply.



KEY REFERENCES

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- Seitz, A. K.; Kohlpaintner, P. J.; van Lingen, T.; Dyga, M.; Sprang, F.; Zirbes, M.; Waldvogel, S. R.; Goossen, L. J. Concentrated Aqueous Peroxodicarbonate: Efficient Electrosynthesis and Use as Oxidizer in Epoxidations, *S*-, and *N*-Oxidations. *Angew. Chem., Int. Ed.* **2022**, *61* (25), e202117563, 10.1002/anie.202117563.[2] This publication describes the design of a flow electrolyzer that allows for the preparation of aqueous peroxodicarbonate solutions in unprecedented concentrations of up to 1 M. Peroxodicarbonate generation is established as a viable counterreaction to electrochemical hydrogen generation.
- Schupp, N.; Rücker, T.; Glockner, E.; Wittgens, B.; Waldvogel, S. R. Highly Concentrated Peroxodicarbonate for Efficient Oxidative Degradation of Kraft Lignin. *ChemSusChem* **2025**, *18* (14), e202500741, 10.1002/cssc.202500741.[3] In this publication, peroxodicarbonate is shown to be an effective reagent for the degradation of

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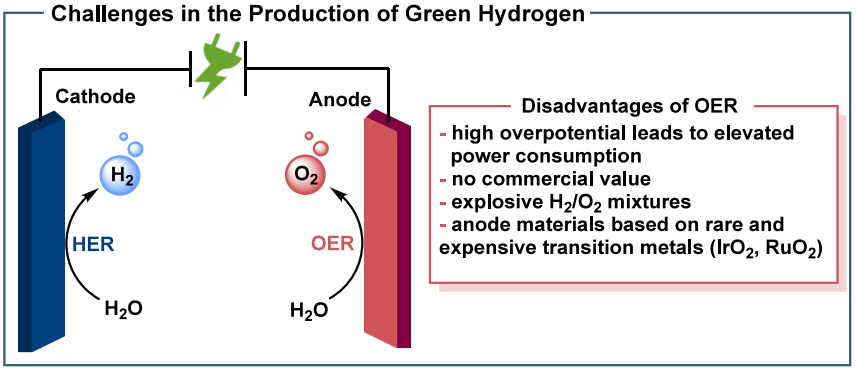


Figure 1. Challenges associated with the oxygen evolution reaction (OER) as a counter reaction to the hydrogen evolution reaction (HER).

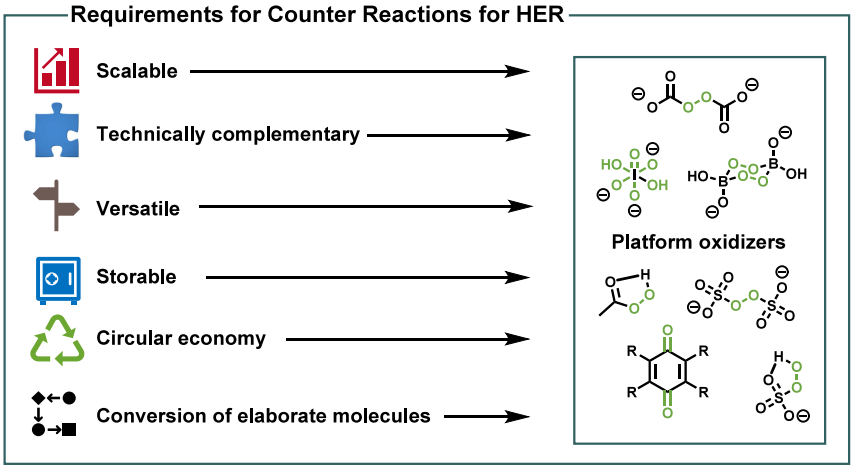


Figure 2. Technical constrains for platform oxidizers in order to be compatible with HER.

biomass, illustrating it to be a highly attractive reagent with versatile applications. Highlighting its potential as a coproduct of hydrogen electrolysis.

- Kisukuri, C. M.; Bednarz, R. J.; Kampf, C.; Arndt, S.; Waldvogel, S. R. Robust and Self-Cleaning Electrochemical Production of Periodate. *ChemSusChem* **2022**, *15* (16), e202200874, 10.1002/cssc.202200874.[4] In this publication, the production of periodate is feasible from a variety of starting materials and in the presence of impurities. This illustrates the reusability of platform oxidizers, which would reduce the amount of waste generated from the oxidation reactions.

INTRODUCTION

The current climate crisis has led to rising sea levels, increases in global temperature, and an increase in extreme weather phenomena.[5,6] This alarming change is caused by the large-scale emission of CO_2 from the combustion of fossil fuels. In order to combat this development, a variety of solutions have been proposed, with a hydrogen economy being one of the most feasible to implement.[7,8] However, in order for a hydrogen-based economy to be truly sustainable, it needs to be produced in a green way and, most importantly, be able to compete economically with fossil fuels to make its use attractive.[9] This could be achieved by electrochemical water splitting instead of the currently dominant steam methane reforming and coal gasification, which are associated with high CO_2 emissions.[10]

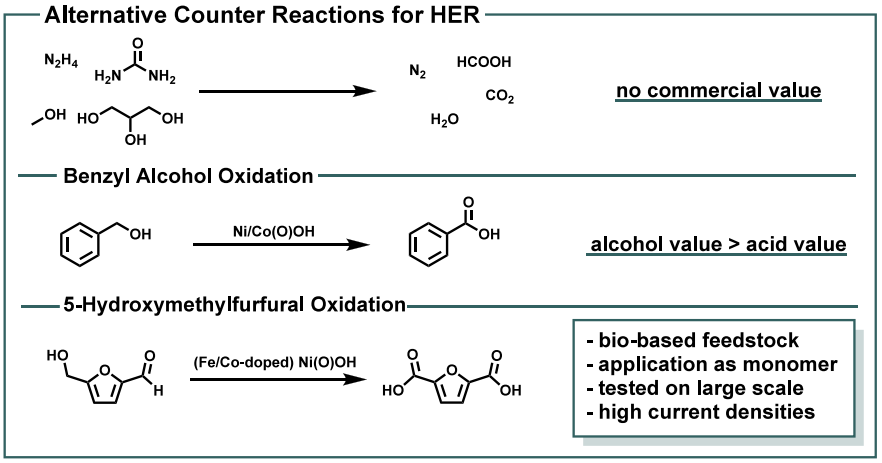
However, the cathodic hydrogen evolution reaction (HER) is accompanied by a corresponding counterreaction,[11] which is the oxygen evolution reaction (OER) in the case of water splitting. This anodic reaction has major drawbacks that limit the broad industrial implementation of electrolytic hydrogen production (Figure 1): First, most electrode materials show a high overpotential for the OER, leading to an elevated power consumption and heat formation.[12] Second, while there is an established market and future demand for hydrogen, the market for oxygen is narrow, e.g., medicinal oxygen.[13] As such, the cost of producing hydrogen like this would have to be entirely offset by the hydrogen itself, so the incentive is high, to develop processes with a more valuable counter reaction to make the production of green hydrogen compatible with conventional processes. Additionally, a simultaneous generation of O_2 and H_2 necessitates a strict separation of both electrolytic compartments due to the hazardous nature of O_2/H_2 mixtures. When anodically generating a nonvolatile oxidizer, undivided cells can be operated with lower terminal voltages and at increased energy efficiency.

Alternative anodic reactions seem to be a choice but have some requirements for a successful combination and implementation (Figure 2): these restrictions apply to a single anodic process or making a platform oxidizer that can be made on scale by a broad employment in following up processes. First and foremost, scalability and an overall large scale have to be achieved, otherwise, it cannot contribute significantly to the hydrogen economy. It also needs to exhibit technical complementarity with the hydrogen evolution process. In

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Scheme 1. Different State-of-the-Art Alternative Anodic Reactions for the Green Production of Hydrogen



other words, it has to operate at high current density up to 300−3000 mA/cm^2. By engineering a maximum of 2 orders of magnitude of current density can be adjusted. Thus, it is a viable option to anodically generate oxidizers, which should be usable as platform reagents with a high versatility in subsequent uses. Corresponding to the demand and applications of these platform oxidizers, they should be safely storable, so they can be used at different production sites and value chains. This will be particularly interesting for when generating a high-performance oxidizer that can be used in the chemical synthesis of highly value-added compounds, where reliable business cases are given. Regarding the bigger picture of the process, it should be able to be implemented in a circular economy or use abundant starting materials that are of no environmental concern. Thus, the anodically generated platform oxidizer will be the value creator of the electrolysis, enabling low-cost hydrogen by cofinancing the electrolysis process.

Several efforts have already been made to develop processes that address these challenges (Scheme 1). One possibility is the use of additives in the electrolyte, which get oxidized at lower potentials than water improving the efficiency of the process. For this, the oxidation of various small inorganic and organic molecules has been studied: hydrazine,[14−16] methanol,[17,18] urea,[19−21] and glycerol.[22−24] Nevertheless, the downside of these strategies is that the oxidation products are of low value and commercial interest. Another approach is the oxidation of more elaborate organic molecules for the synthesis of commodity or fine chemicals. The oxidation of alcohols presents one of the most studied examples, demonstrated on benzyl alcohol which was oxidized to benzoic acid, but industrial application is not feasible since the starting material is of higher value than the product.[25−27] An outstanding exception is the oxidation of renewable 5-hydroxymethylfurfural, yielding 2,5-furandicarboxylic acid, a monomer for biobased polyesters.[28−30] Schüth et al. were able to develop a novel type of electrode, by depositing Fe/Co(O)OH on nickel foam, which showed high activity for the conversion of 5-hydroxymethylfurfural, and allowed the use of industrial current densities up to 1000 mA/cm^2 without significant OER.[31,32] A similar process was used for a pilot-scale production of 2,5-furandicarboxylic acid with a productivity of 33 kg/d, underlining the scalability of the method.[33]

All of the aforementioned oxidation processes, with the exception being the oxidation of 5-hydroxymethylfurfural, suffer from significant drawbacks, associated either with low value or demand of the generated products, elaborate catalyst systems requiring laborious synthesis, and rare metals, or are only investigated on laboratory scale with limitations in their scalability. This hinders an implementation of the process on an industrial scale, which is critical to enable the production of green hydrogen. Among the many possibilities for alternative anodic reactions, the generation of platform oxidizers fulfills all of these requirements and could serve as a key enabler for a sustainable and green hydrogen economy.

THE CONCEPT OF PLATFORM OXIDIZERS

With platform oxidizers, oxidative power is stored in chemical bonds. These reagents could be produced at scale[1] and allow for facile downstream processing of the hydrogen, as it is often the only gaseous product, allowing the use of simple, undivided cells. Additionally, the electrogeneration of these species takes place at high current density,[3] making them technically compatible with the hydrogen evolution reaction.

The anodic production of oxidizing reagents has further advantages due to their versatility (Figure 3): Oxidizers can subsequently be used for the destruction of pollutants in water,[34−36] but more importantly, they find application in the synthesis of elaborate molecules,[37,38] including active pharmaceutical ingredients, agrochemicals, fragrances, and synthetic intermediates. Particularly, for the modification of such complex molecules, the use of a chemical oxidant has the advantage that these often sensitive species are not exposed to the high-energy environment inside an electrochemical cell, which gives rise to selective conversion of the organic substrate.

Furthermore, electrochemical platform oxidizers require only simple setups for their generation,[39,40] such as simple electrolyzers and aqueous electrolytes, enabling their production both on-site and on-demand. Finally, electrogenerated platform oxidizers can often be used in a circular fashion: after their anodic generation, they can be used in a variety of reactions, in the course of which these oxidizers get reduced. These reduced species can subsequently be used as substrates for the regeneration of new oxidizers by electrolysis (Figure 3).

These species have been of major interest to the Waldvogel lab, with multiple species being investigated to serve as

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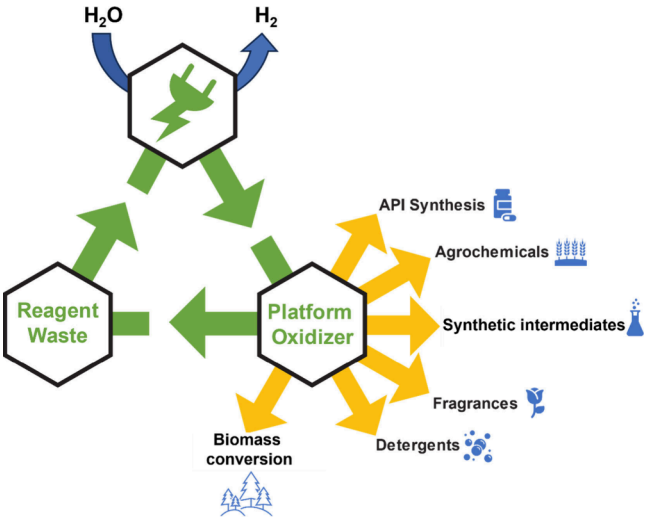


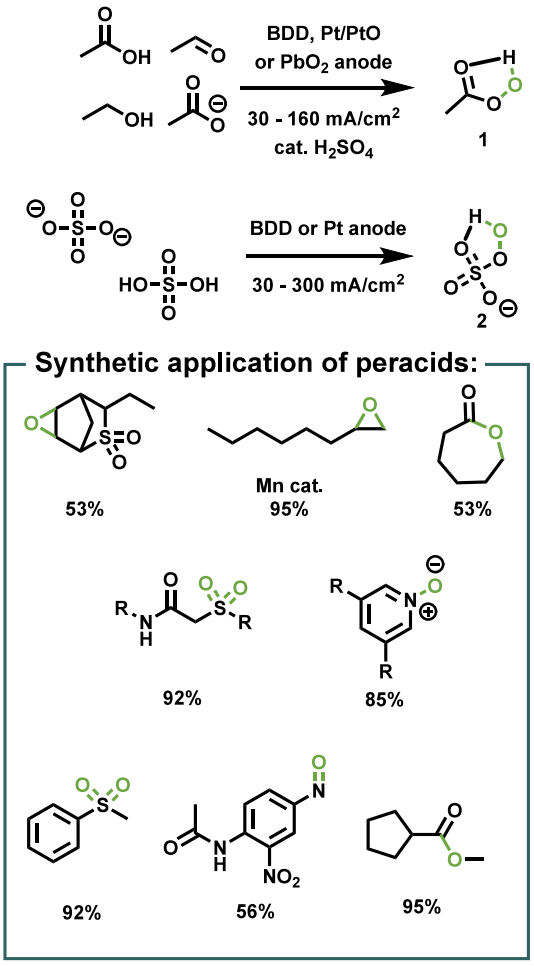
Figure 3. Schematic representation of the circular use of platform oxidizers and their versatility.

platform oxidizers. The compounds of interest include peroxyacids, particularly peracetic acid and Caro's acid, as well as peroxo-salts, such as peroxodisulfate, perborate, and peroxodicarbonate. Furthermore, hypervalent halo compounds, such as trichlorides and periodate are also of interest alongside quinones. Both the electrogeneration and application of these species will be further illuminated in the following:

Peracids or peroxyacids are a class of peroxides that represent strong oxidants[41,42] that derive their stability from intermolecular hydrogen bonding. Both organic and inorganic peracids exist. In the context of this Review, the focus will be on peracetic acid (CH_3CO_3H) and peroxymonosulfuric acid (H_2SO_5). Traditionally, these compounds can be generated through the addition of hydrogen peroxide to the parent acid, alongside an acid catalyst.[43] However, this reaction is exothermic and highly hazardous, which makes it challenging to scale.

Alternatively, peracids can be generated through the electrosynthesis of reactive oxygen moieties in the presence of acids or similar building blocks in solution (Scheme 2). For peracetic acid, this can be achieved from multiple starting materials and using different anode materials: The Bairachnyi group investigated the oxidation of acetic acid using Pt/PtO and PbO_2 anodes[44] using a current density of up to 160 mA/cm^2, with platinum-based electrodes showing significantly higher current efficiencies than their lead counterparts. Alternatively, other starting materials, such as ethanol, acetaldehyde, or sodium acetate, can be used, as illustrated by Rodrigo and co-workers.[45] They compared the generation of peracetic acid from these feedstocks using a boron-doped diamond (BDD) anode and found sodium acetate to be the most promising starting material. However, using this approach, the concentration of the peracid would barely reach 1 mM, because of the equilibrium between the peracid and hydrogen peroxide. In order to reach higher concentrations, Saha and co-workers used both the cathode and anode in the generation of the peracid:[46] Parallel to generation of peracid at the anode, they used a gas-diffusion electrode to reduce oxygen to hydrogen peroxide, thus shifting the equilibrium to the peracid and reaching concentrations of 6.4 mM. Using this approach, peracetic acid can also be generated in parallel to another oxidant.[47] Canizares and co-workers

Scheme 2. Electrogeneration and Synthetic Applications of Peracetic Acid 1 and Caro's Acid 2[a]



[a]Oxygen atoms that are electrochemically installed and then transferred onto organic substrates are indicated in green.

investigated the influence of the reactor geometry for the electrogeneration of peracetic acid,[40] reporting that a high anode surface-to-volume ratio was beneficial.

Peroxymonosulfuric acid, also known as Caro's acid, can also be generated electrochemically, by oxidation of aqueous sulfuric acid (Scheme 2). Particularly high efficiency is observed when diamond anodes are used,[48] while other anode materials with high overpotentials for the oxygen evolution reaction, such as platinum, were also successful.[49] The electrode influence was further elaborated on by the group of Rodrigo, who showed that BDD on a Nb support is even more effective than diamond electrodes prepared using other support materials.[50] Using these electrodes, in a bespoke, 3D-printed reactor allowed them to achieve peroxymonosulfuric acid concentrations of up to 200 mM at a current density of up to 300 mA/cm^2. Both of these peracids are stored as stock solutions.

In biomass conversion, peracetic acid is an effective bleaching agent for lignin.[51] In synthesis, both peracetic acid **1** and Caro's acid **2** can be used for traditional peracid chemistry[52] resulting in good to excellent yields. These oxidants have been shown to be effective in epoxidations,[53,54] which can be made more rapid and selective using transition-metal catalysts,[55] as well as Baeyer–Villiger oxidations,[56,57] and

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oxidations of sulfides,[58,59] and pyridines[60,61] (Scheme 2). Additionally, Caro's acid is also used in the selective oxidation of amines[62] and the generation of ketones.[63] However, due to their thermal instability, an integrated system for the peracid production and use is advantageous. This was realized in a flow system by the Kappe group in order to affect a direct oxidative esterification of aldehydes with alcohols.[64]

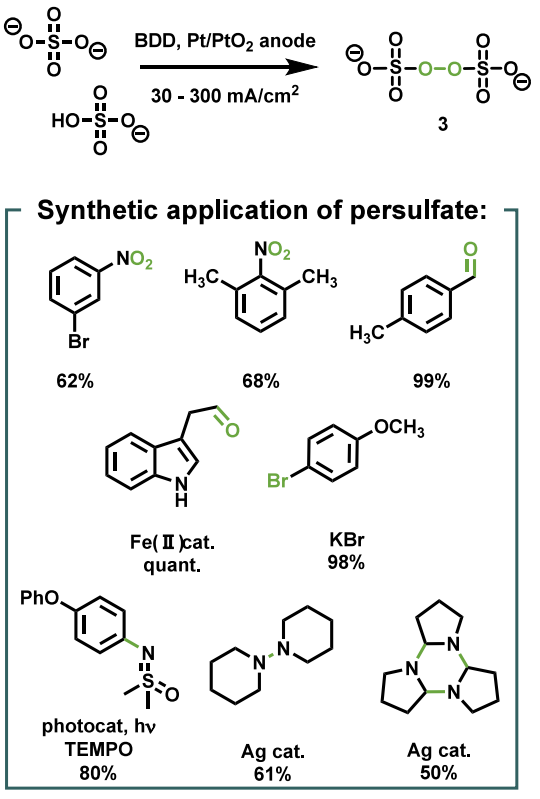
PEROXO SALTS

Peroxodisulfate ($S_2O_8^{2-}$) is a strong and relatively stable oxidizing agent that can serve as a source of strongly oxidizing sulfate radicals ($SO_4^{\bullet -}$). Persulfate salts, with sodium, potassium, or ammonium cations, are predominantly generated via the electrochemical oxidation of sulfate ions in sulfuric acid or sulfate solutions under high anodic potentials and a current density of 30−300 mA/cm^2. This process has been proposed to take place via either direct oxidation of the sulfate species[65−68] or through intermittently formed hydroxyl radicals.[69−72] Electrode materials with high overpotentials for OER, such as platinum-group metals, their mixed metal oxides, as well as oxides of lead, tin, and tungsten have been used.[69,70,73] Among these materials, Pt remains the benchmark anode due to its high OER overpotential and excellent physicochemical stability.[74] More recently, carbon electrodes have also found application, with BDD in particular being promising.[75,76] Peroxodisulfate is stored as a solid, often in the form of sodium or potassium salts.

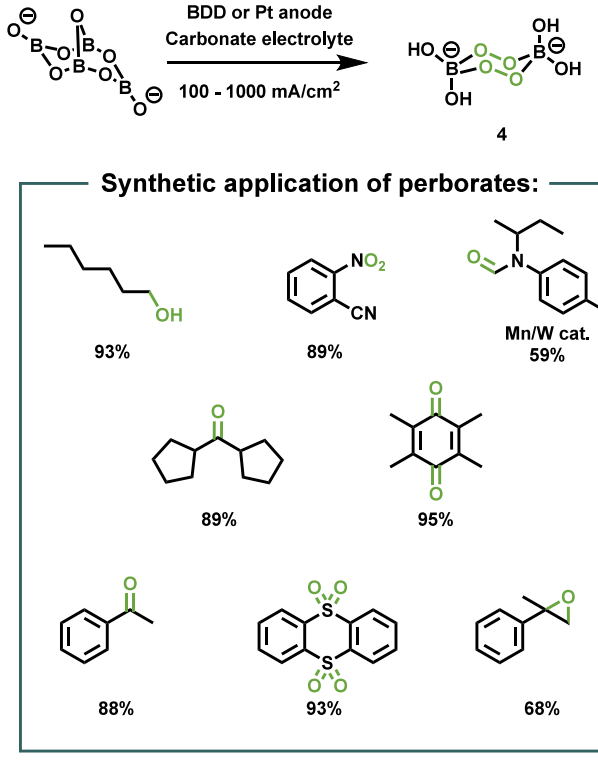
Persulfate has been investigated for the degradation of pollutants in aqueous media. While initial studies in this direction have been promising,[77−81] significant questions remain concerning the environmental risks associated with excessive persulfate dosage and sulfate residues.[78,79] Simultaneously, persulfate has found application in synthesis (Scheme 3), including as a source of sulfate radicals: As an exceptionally strong oxidant, persulfate is used in the oxidative formation of nitro groups.[82] Additionally, persulfate allows for the simultaneous deprotection and oxidation of alcohols bearing a TMS or THP protecting group, as well as the cleavage of C═N bonds, forming aldehydes and ketones in both cases in excellent yields.[83] Such oxidative processes could be significantly accelerated using transition-metal species, such as a Fe(II) catalyst in the oxidation of tryptophan.[84] Furthermore, persulfate was shown to allow for the bromination in *para* of aromatic substrates using bromide salts as a halogen source.[85] Persulfate has also been used in late-stage modification, such as the photocatalytic sulfoximidation of arenes,[86] and the dimerization and trimerization of cyclic secondary amines.[87] Lastly, persulfate can serve as a radical initiator for the polymerization of styrene.[77]

Perborates derive their oxidative activity from a tetrahedral borate framework incorporating a stabilized peroxy moiety (Scheme 4).[88] As alkali-metal salts, particularly as sodium perborate (**4**, $NaBO_3{\cdot}xH_2O$; x = 1, 3, or 4), they offer enhanced storage stability, facile handling, low cost, and moderate oxidative strength suitable for the use as a detergent, bleaching agent and selective chemical oxidant.[88−91] Industrial production of sodium perborate is well-established. In the conventional route, borax ($Na_2B_4O_7{\cdot}10H_2O$) is converted to soluble metaborate species under strongly alkaline conditions, followed by reaction with hydrogen peroxide or sodium peroxide to form sodium perborate, which is typically isolated as the tetrahydrate and subsequently dried to obtain the monohydrate.[92−95] Product isolation involves precipitation, filtration, and conditioning to obtain a stable powder. While robust and industrially mature, this process is energy-intensive, because it depends on external alkaline and oxidation reagents.

Scheme 3. Electrogeneration and Synthetic Applications of Peroxodisulfate 3



Scheme 4. Electrogeneration and Synthetic Applications of Perborate 4



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The necessary hydrogen peroxide itself is produced via the anthraquinone process.[96] Moreover, the process is highly exothermic and requires strict temperature control—often below 20 °C and in some cases near 2 °C—to prevent decomposition and maintain product quality.[92,93,95] The handling of concentrated oxidizers, wastewater treatment, and stabilizer usage further increase safety, environmental, and economic burdens.

Electrochemical synthesis represents an alternative approach that has been explored for more than a century. Early studies demonstrated that perborate can be generated electrochemically from borax in carbonate-containing alkaline electrolytes, with bicarbonate often identified as an accelerating component.[90,92,97−101] Most reports indicate that very high carbonate concentrations (typically 120−150 g L^{-1} Na_2CO_3) are required, and perborate yield generally increases with carbonate concentration.[92,102] Consequently, the process has traditionally been rationalized by formation of a peroxodicarbonate intermediate generated from carbonate oxidation.[92,100−102]

While the electrosynthesis of perborate has significant advantages over traditional synthesis pathways, such as the elimination of terminal oxidizers, it still faces significant challenges: Due to the high current density (100−1000 mA/cm^2) that is employed, the parasitic OER needs to be mitigated to prevent a loss of current.[90,92,97−102] Historically, platinum anodes have been used for this process, but their high cost and limited availability make them unsuitable for large-scale processes.[103−109]

More recently, Waldvogel and co-workers[110] reported an improved electrochemical strategy employing BDD anodes, which enhances selectivity toward the formation of peroxo species and enables direct precipitation of solid **4** with yields approaching 80%. This oxidizer is stored as a solid, usually as the sodium salt.

Perborates have found various applications, particularly due to their high active oxygen content of up to 16 wt% (in sodium perborate monohydrate), which is an order of magnitude higher than that of commonly used, labile 3 wt% aqueous hydrogen peroxide.[102] This, alongside its mild oxidation properties, has established sodium perborate as a versatile reagent in both industrial and academic contexts, with an annual production of approximately 750 000 tons.[88] In sustainable oxidation chemistry,[111,112] perborate has been used in the oxidation of organoboranes,[89] carboxylic acids,[112] sulfides,[113] oximes to carbonyl compounds,[114] and N-hydroxylation of azoles (Scheme 4).[115] However, it has also found uses beyond synthesis as it is used in detergents, textiles, paper processing, cosmetics, disinfection, hydraulic fracturing, and aquaculture.[116−118]

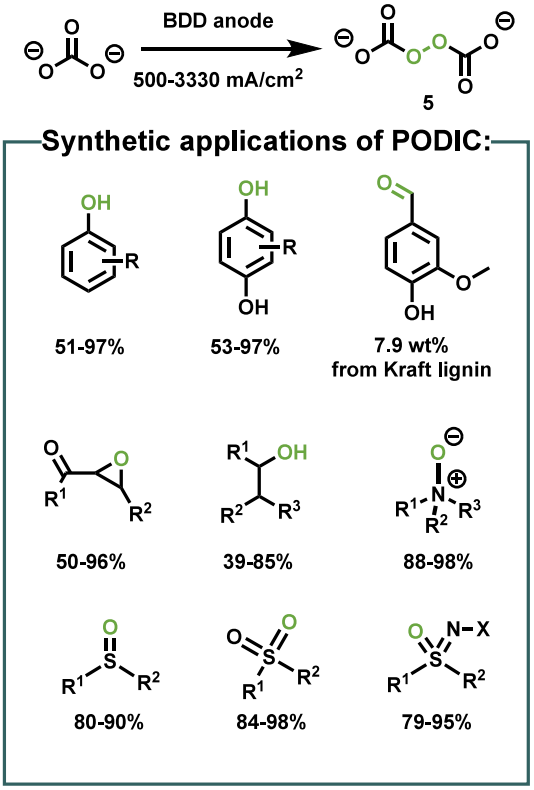
Peroxodicarbonate (PODIC) is a dianion formally constituted of two carbonate moieties, which are linked by a peroxide bond.[119] This compound can only be obtained through electrolysis of concentrated carbonate solutions, whereas the addition of hydrogen peroxide to a carbonate solution results in the formation of percarbonate (e.g., $Na_2CO_3 \cdot 1.5\ H_2O_2$), an adduct with different chemical properties.[120]

Peroxodicarbonate was first reported in 1896 upon electrolysis of saturated K_2CO_3 solutions in a divided cell setup with platinum electrodes at a current density ranging from 1 to 3000 mA/cm^2. It was isolated as a light blue salt, with highly concentrated carbonate solutions and low temperatures being crucial to obtain good yields and prevent thermal decomposition.[121] This method was improved by switching to an undivided cell equipped with a BDD anode,[122] which led to an improvement of the current efficiency from 16% (Pt anode) to 49% (BDD anode) at 500 mA/cm^2, resulting in peroxodicarbonate solutions of up to 0.045 M.[123] Further studies from Zhang, Meas, Rodrigo, and Ruiz−Ruiz focused on reaction optimization,[124−126] kinetic studies,[127] additives for enhanced thermal stability,[124,125] and improved Faradaic efficiency.[127] However, the total concentration of the synthesized oxidant remained below 0.1 M. In 2017, Chardon et al. implemented an undivided flow setup.[128] Electrolysis of a 1.5 M Na_2CO_3 solution at 720 mA/cm^2 below room temperature (<18 °C) and at high flow rates (170 cm/s) showed oxidant concentrations of up to 0.28 M with current efficiencies up to 76%.[128] Maintaining 76% Faradaic efficiency, Ziogas et al. were able to increase the concentration of oxidants up to 0.38 M, using an actively cooled sandwich flow cell.[129] By designing a cell with improved heat transfer equipped with a BDD anode and stainless-steel cathode, Waldvogel and Gooßen improved the process further: Using a 2.25 M triple salt mixture (Na_2CO_3, K_2CO_3, $KHCO_3$) solution and high current density (3330 mA/cm^2) they could generate 0.919 M solutions at 0 °C and even 1 M solutions, using D_2O as a solvent.[2]

Peroxodicarbonate can be stored as a stock solution at low temperature.

These highly concentrated PODIC solutions enabled various synthetic applications, which can be categorized into oxygenations of carbon moieties, oxygenations of heteroatoms and processing of biomaterials (Scheme 5): Waldvogel and

Scheme 5. Electrogeneration and Synthetic Applications of Peroxodicarbonate 5



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Gooßen reported a catalyst-free Weitz-Scheffer-type epoxidation of unsaturated α,β-enones, which tolerates sensitive quinones as well as sterically demanding cyclic ketones.[2] In 2023, Waldvogel introduced hydroxylation protocols: Phenols were obtained by the treatment of aromatic boronic acids with PODIC in high yields.[130] The methodology was demonstrated on multigram scale with high functional group tolerance. Furthermore, alkenes like norbornene can be used as substrates in a one-pot hydroboration-oxygenation sequence. In a second hydroxylation approach, hydroquinones and catechols were obtained from hydroxybenzaldehydes in a Dakin-type reaction sequence, with peroxodicarbonate acting as both oxidizer and base.[131]

Peroxodicarbonate also enables the oxidation of heteroatoms. Highly concentrated oxidizer solutions enabled the synthesis of N-oxides in excellent yields and without additives.[2] Using ethanol as a cosolvent and phenyloxy succinimide as activator, this method could be extended to water-insoluble amines.[132] PODIC can also be used for the selective pH-dependent oxidation of sulfur moieties to sulfoxides and sulfones,[2] which was also extended to the oxidation of sulfilimines to sulfoximines.[133] Additionally, peroxodicarbonate is an ideal makeup chemical for pulping factories allowing for the generation of vanillin and other monoaromatics[134−136] from lignin in up to 15.6 wt%.[3] A different example is the replacement of harmful chlorine bleaching of shellac, a natural resin used, e.g., in food coatings, wood varnish, and pharmaceutical coatings.[132]

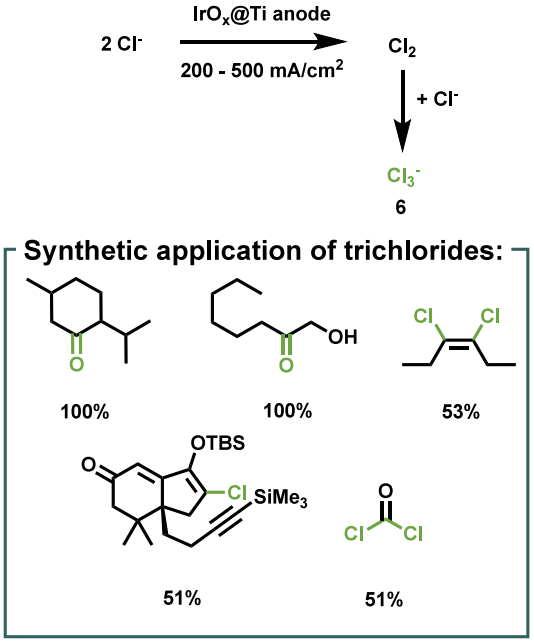
HYPERVALENT HALO COMPOUNDS

Polychlorides (Cl_n^-, n = 3, 5, 7, 11, 13) are anions that are formed from the reaction of one or more molecules of chlorine with chloride, albeit under ambient conditions, the trichloride is the most stable polychloride.[137,138] These compounds will release chlorine upon heating or under low pressure but can also directly serve as a reagent as well as a safe option for the storage and transport of chlorine.[139] The electrochemical generation of chlorine is a mature process,[140] which is performed in membrane electrolyzers, allowing for the simultaneous production of chlorine and sodium hydroxide at high purity.[141] These devices traditionally employ cation exchange membranes, allowing for the selective migration of Na ions, and anodes made from IrO_2-coated Ti. Industrially, this process is operated at high current densities of 200−500 mA/cm^2. Novel processes toward the electrochemical formation of chlorine from different substrates, such as PVC,[142] are also under investigation but are performed at significantly lower current density.

Riedel and co-workers have shown that chlorine can be simply and easily transformed into trichlorides, particularly if the resulting salt is an ionic liquid, such as triethylmethylammonium trichloride.[143] In this easy-to-handle form, trichlorides can be used in the oxidation of alcohols to form both aldehydes and ketones (Scheme 6). Particularly, they allow for the selective oxidation of secondary alcohols in the presence of primary alcohols.[144] Additionally, they can also serve as chlorinating agents to achieve dichlorination of both alkenes and alkynes, C−H chlorination, electrophilic aromatic substitutions,[144,145] and even the generation of phosgene from CO.[146]

Periodates are highly oxidized iodide species with particularly sodium para-periodate ($Na_3H_2IO_6$, **7**) finding abundant use as a platform oxidizer. Commonly, periodate is

Scheme 6. Electrogeneration of Chlorine, Subsequent Formation of Trichloride 6, and Its Synthetic Applications



prepared via the oxidation of iodine, iodide, or iodate, using a variety of strong oxidizing agents or harsh conditions. These methods suffer from limitations related to safety, waste generation, and high energy consumption.[38]

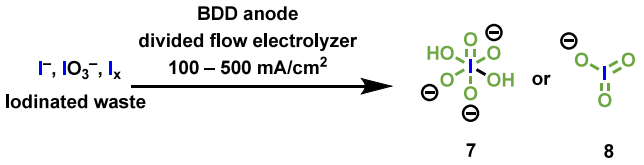
While other approaches to synthesize periodate are also being investigated,[147] the electrochemical generation of periodate offers several advantages, since the method is both facile and scalable and the iodine species involved can directly be recycled. The electrosynthesis of periodates uses a broad spectrum of iodate sources (e.g., $NaIO_3$, HIO_3, and $LiIO_3$) as substrates and oxidizes them at either lead dioxide (PbO_2) or boron-doped diamond (BDD) anodes (Scheme 7),[4,38] with the latter having the advantage that they avoid heavy-metal contamination.[148−151] Waldvogel and co-workers reported the development of an electrochemical continuous-flow process for the synthesis of *para*-periodate from iodide at BDD anodes, using a divided flow cell.[1] The process produced periodate with yields of up to 94% and a purity of >97%, respectively. The scalability of this approach was also established, with production of sodium *para*-periodate at hecto-gram scale resulting in 86% yield with a current efficiency of 69%. Due to the low solubility of the *para*-periodate, the system was further improved by combining a steady-state CSTR (continuous stirred-tank reactor) design with flow electrolysis,[39] in which the product would settle in the reservoir, allowing for a continuous process through the simulation of late-stage electrolysis conditions. This setup enabled the electrolysis of (oxo)iodo species (NaI, $NaIO_3$, and I_2), covering oxidation states from −I to +V without changes to the protocol or parameters, and permitted the direct recycling of the electrolytes. The electrochemically produced *para*-periodate was obtained in yields of up to 98% and 99% purity. Using a high current density and flow rate, **7** was produced in 94% yield and a current efficiency of 57%.

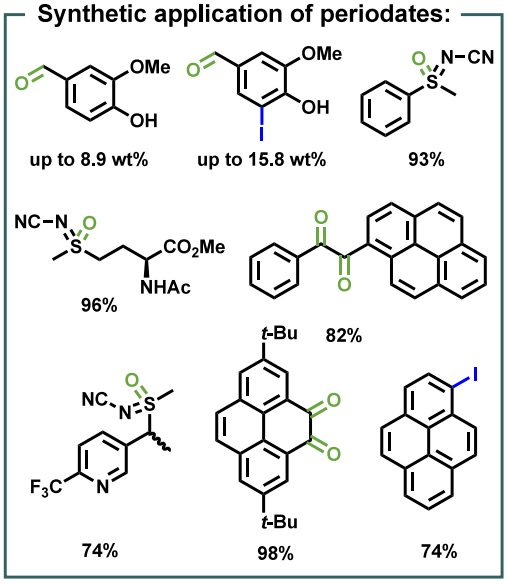
This electrochemical approach was also employed for the reoxidation of iodate generated during the ruthenium-catalyzed synthesis of levetiracetam, a compound used for the treatment

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Scheme 7. Electrogeneration and Synthetic Applications of Periodate 7 or Iodate 8





of epilepsy.[37] Periodate, initially used as the terminal oxidant in the synthesis of levetiracetam, was quantitatively recovered as iodate by crystallization with methanol or isopropanol and could subsequently be reused as a starting material for the generation of 7. Such recovery approaches are often limited by organic impurities in recovered iodine species. The electrochemical generation of para-periodate does not suffer from this drawback, as organic impurities could directly be mineralized to CO_2 and H_2O in a hydroxyl-radical-mediated environment, while iodine functionalities are directly converted into the desired platform oxidizer.[4]

The applications of periodate are numerous (Scheme 7) and have been extensively summarized,[152−154] illustrating the broad synthetic utility of periodate in both well-established reactions, such as the Malaprade reaction, and more novel approaches, such as the oxidation of sulfides, phenols, or nitrogen-containing heterocycles.

The selective oxidation of sulfur species has been showcased in the work of Waldvogel, for example, sulfilimines, which were generated electrochemically, were selectively oxidized with periodate to result in sulfoximines in up to 96% yield.[155] This method allowed for the synthesis of the commercial herbicide sulfoxaflor in 74% yield. Furthermore, periodate can be employed as an oxidizer to transform renewable feedstocks, such as lignin-based materials, into value-added products. Waldvogel and co-workers produced either vanillin or 5-iodovanillin from side-stream lignin types (lignosulfonate, Kraft, and organosolv) using electrochemically generated *para*-periodate.[156] Reactions were conducted at 160 °C in 2 M NaOH for 24 h, and product selectivity was controlled by simple pH adjustment, which allowed access to each compound in yields of up to 15.8wt %.

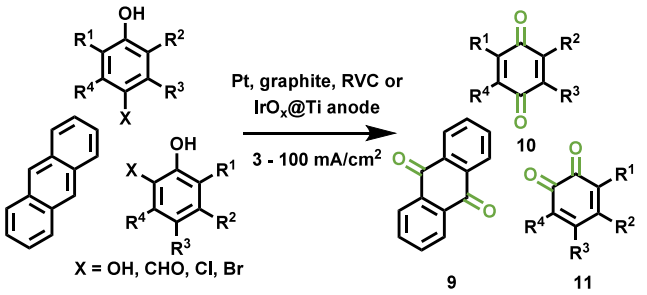
Reactions in a H_2O/MTBE mixture at 45 °C furnished quinolones and a pyrrolo[3,2-*b*]quinolone in up to 87% yield.[157] Periodate was recovered by simple filtration, likely as the disodium salt ($Na_2H_3IO_6$),[158] and reused in place of fresh 7 by adding the required equivalents of NaOH, with no loss in yield. A 40-fold scale-up was also achieved, demonstrating the feasibility of this one-pot/one-step protocol.

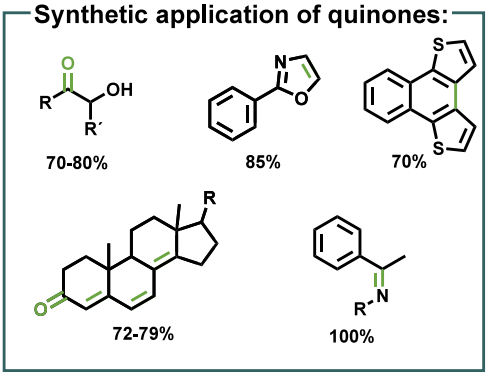
Periodate only has a limited solubility, making it an interesting reagent for solvent-free approaches like mechanochemistry. Using mechanochemistry, oxidations leading to ketones[159] and diones could be achieved with excellent yields, whereas solution-phase approaches led to different results.[160]

■ QUINONES

The oxidative power of quinones highly depends on the concentration of Brønsted or Lewis acids in the reaction mixture. Due to the reversible oxidation to quinones and their reduction to hydroquinones, the electrochemical synthesis must be conducted in divided cells.[161] They can be made electrochemically from phenols, 4-halophenols,[162] 4-hydroxybenzaldehydes,[163] or even from naphthalene (Scheme 8).[164]

Scheme 8. Electrogeneration of Quinone Species 9−11 and Examples of Their Synthetic Applications





The resulting platform oxidizers can be isolated as either solids or liquids, depending on the starting material. Corresponding to these diverse starting materials, many anode materials are used as well, with both noble metal (Pt, IrOx@Ti) and carbon materials (graphite, RVC) finding uses. The employed current density ranges from 2 mA/cm^2 to 100 mA/cm^2.[165] Quinones, due to their tunable oxidation potentials, are of particular interest for the synthesis of active pharmaceutical ingredients.[166] They are capable of transforming alcohols into ketones, which may even be applied to the modification of steroids.[167] Additionally, since the reduction of quinones involves protons as well, they are versatile dehydrogenation reagents, which has been leveraged in the formation of large π-systems. Due to their high redox reversibility,[168] quinone-

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based oxidizers are prime candidates to be recycled; however, the purity of these species due to cross contamination may be a hindrance in this case. However, for the production of the same target compound, regeneration still seems to be a viable option.

CONCLUSION AND PERSPECTIVE

The use of platform oxidizers will not only enable by the coproduct hydrogen a cost-efficient access but also allows the valorization of electricity when hydrogen is needed or intermittent electricity is available.[169] This kind of flexible operation will open up new business models that have been previously less attractive. Most likely, periodates and quinones as high-performance oxidizers might be exploited as oxidation equivalents that can be used in catalysis and traded in a leasing model. The chlorine production was, for a long time, not that value-creating. Since chlorine is needed in a vast amount, the polychlorides offer new options with the ionic liquids which allow transport under ambient conditions. The future of fine chemical production will be electric, and the platform oxidizers will represent an indispensable tool for it.[170,171] Which one will be employed will strongly depend on the follow-up reactions.[11,172]

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Author Contributions

D.F.N. and S.R.W. conceptualized the manuscript. D.F.N., F.M., A.A.B., F.M.F., and Z.T. conducted the literature search and drafted the initial manuscript. S.R.W. and D.F.N. edited the manuscript. S.R.W. supervised the project and acquired the funding. All authors have given approval to the final version of the manuscript.

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Notes

The authors declare no competing financial interest.

Biographies

Dr. Darryl F. Nater studied chemistry at ETH Zurich, where he obtained his Ph.D. under the supervision of Prof. Dr. Christophe Copéret in 2022. Afterward, he joined the group of Prof. Siegfried Waldvogel as a Postdoc with a postdoc.mobility fellowship of the Swiss National Science Foundation. Afterward, he continued as a Group Leader in the Department of Electrosynthesis, where the focus of his research is on the development of (halo-mediated) electrosynthetic reactions, advanced screening tools for reaction optimization and the scale-up of electro-organic transformations.

Finn Moeller studied chemistry at the university of Mainz, where he subsequently started his doctoral studies in the group of Prof. Siegfried Waldvogel. He accompanied the group when it moved to the Max-Planck Institute for Chemical Energy Conversion. Now part of the Department of Electrosynthesis, his research interests include synthetic organic electrochemistry, biomass valorization, and sustainable chemical processes.

Dr. Aloisio de Andrade Bartolomeu received a B.Sc. degree in Chemistry and an M.Sc. degree in Materials Science and Technology from São Paulo State University (UNESP). He completed his Ph.D. in Science (Organic Chemistry) at the Federal University of São Carlos (UFSCar), during which he conducted part of his doctoral research in the Noël Group at Eindhoven University of Technology (TU/e). He then joined the Obesity and Comorbidities Research Center (OCRC) at the State University of Campinas (UNICAMP) as a postdoctoral fellow under the supervision of Prof. Ronaldo A. Pilli. During this period, he carried out part of his postdoctoral research as a guest researcher in the Waldvogel Group at Johannes Gutenberg University Mainz (JGU). He is currently a postdoctoral fellow at the Max Planck Institute for Chemical Energy Conversion (MPI CEC) under the supervision of Prof. Siegfried R. Waldvogel, with research focused on the electrochemical synthesis of periodate and its application in organic transformations.

Felix M. Fuchs received his degrees in chemistry, B.Sc. at Universty of Bonn and M.Sc. at University of Göttingen. Subsequently, he joined the Department of Electrosynthesis at the Max-Planck Institute for Chemical Energy Conversion as a Ph.D. student, under the supervision of Prof. Dr. Siegfried Waldvogel. His research interests include the generation and stability of electrogenerated oxidizers.

Ziqi Teng received her B.Sc. degree in Chemistry from Nanjing Tech University, China, and her M.Sc. degree in Chemistry from Ruhr University Bochum, Germany. After completing her Master's research at the Max-Planck Institute for Chemical Energy Conversion, she continued there as a doctoral researcher under the supervision of Prof. Dr. Siegfried R. Waldvogel. Her research interests focus on synthetic organic electrochemistry, electrosynthesis of inorganic oxidants, boron chemistry, and the scaleup of sustainable electrochemical processes.

Prof. Dr. Siegfried R. Waldvogel studied chemistry in Konstanz, and in 1996, he received his Ph.D. from the Ruhr University Bochum/

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Max Planck Institut für Kohlenforschung. After postdoctoral research in La Jolla, CA, he started his own research at the University of Münster, the University of Bonn, and the University of Mainz. In 2023, he became director at the Max-Planck Institute for Chemical Energy Conversion. His research focuses on electro-organic transformations on different scales, including biobased feedstocks. He initiated and coordinated large research projects such as the BMBFTR future cluster Electrifying Technical Organic Syntheses (ETOS). In 2018, he cofounded ESy-Labs GmbH, which provides custom electrosynthesis and contract R&D.

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■ ABBREVIATIONS

BDD, boron-doped diamond; HER, hydrogen evolution reaction; MTBE, *tert*-butyl methyl ether; OER, oxygen evolution reaction; PODIC, peroxodicarbonate; PVC, poly(vinyl chloride); RVC, reticulated vitreous carbon; TMS, trimethylsilyl; THP, tetrahydropyradyl

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