

# Bubbles pinned on electrodes: friends or foes of aqueous electrochemistry?

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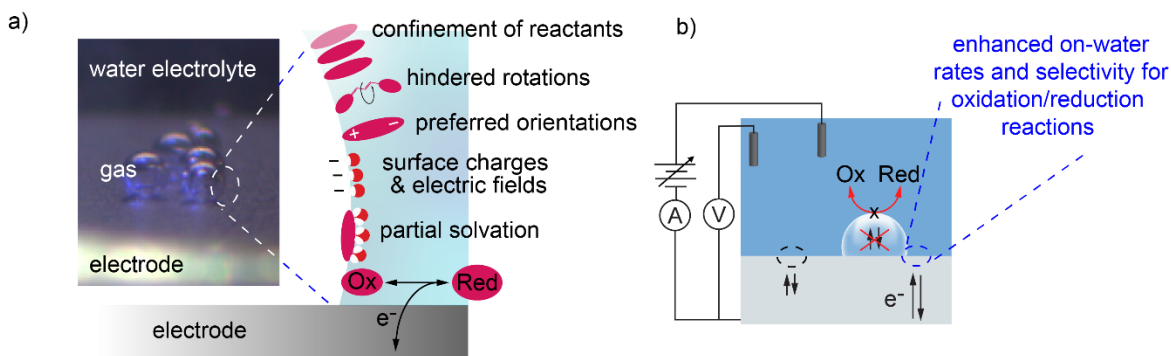
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**Abstract.** Electrochemists and engineers regard adherent gas bubbles as redox-inactive and therefore blocking entities. Adhesion of bubbles at electrodes generally carries an energy penalty. But this is not always the case: bubbles pinned on an electrode surface initiate the oxidation of water-soluble species under conditions where such reactions would normally be considered impossible. Here we critically review the recent literature that is beginning to unveil the novel concept of on-water electrochemistry. Harnessing electrochemical reactivity of the water–gas–electrode interface has the potential to become a game-changer in organic electrosynthesis, accelerating the transition toward a sustainable chemical industry by simplifying the direct integration of renewable electricity sources into the production of commodity chemicals.

## Introduction

The chemical industry is a major consumer of energy [1], and a transition toward more broadly adopted, renewables-driven chemical processes is urgently needed if we are to reach the goal of decarbonising the production of chemistry-based commercial products [2]. One obvious solution toward integrating renewable electricity into chemical manufacturing is to electrify industrial organic reactions – replacing conventional molecular reactants with electricity [3]. Low toxicity, scalability, and atom economy are additional advantages of organic electrochemical synthesis over purely chemical counterparts [4]. However, growth in the area

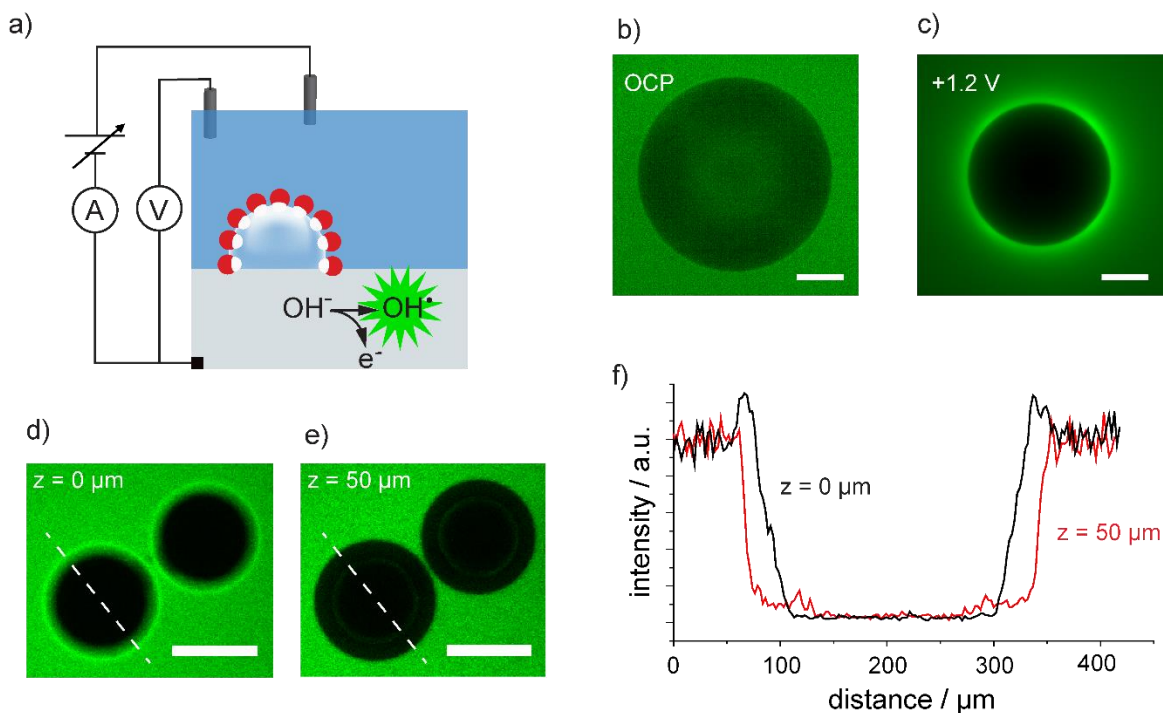


**Figure 1.** Static surface bubbles: detrimental electrode passivation or enabling a step change in electrosynthesis? (a) Schematic depiction of interfacial phenomena occurring on the aerial surface of water. At the three-phase boundary formed by electrode-adherent gas cavities few factors can contribute to enhance rates of redox (and non-redox) reactions. (b) For electrochemical reactions of both practical and conceptual value, current increase around non-conductive bubbles, enabling a new on-water path to mitigate constraints on the viability of electricity-driven organic reactions in aqueous electrolytes.

of organic electrosynthesis has never matched predictions. Of several hundreds of known organic electrosynthetic processes [4], only a handful have been implemented industrially [5,6]. The main cause of this limited industrial success is the difficulty of finding reactions that proceed with viable speed and selectivity in water – industry’s solvent of choice [7,8].

While limited viability in water is regarded as an insurmountable technical task, chemists are well aware of the dramatic acceleration reported for several reactions when they occur on the surface of water rather than in its bulk [9-11]. Over the past 15 years, “on-water” catalysis has become synonymous with enhanced reaction rates at the interface between water and hydrophobic materials such as gases and oils [9,12-16]. Important synthetic reactions, including condensation reactions [17], C–N and C–C bond-forming reactions [18], are accelerated several orders of magnitude at the water–air interface. Textbook chemical reactions such as Diels–Alder [19], Michael addition, Mannich condensation, and cross-linking of peptides [20] are faster on-water than in water. Biological relevant reactions that are unfavourable in bulk water, such as sugar phosphorylation and peptide bond formation, proceed spontaneously at the water–air interface of aqueous microdroplets [21,22]. Electrochemical reactions are no exception: Fenton reactions are accelerated by a factor of up to  $10^4$  at the water–air interface [23], hydrogen peroxide forms spontaneously in microdroplets of pure water [24], and also spontaneous is the reduction of biologically relevant metabolic intermediates in aqueous droplets [14]. Several other chemical reactions that proceed via charged intermediates are also accelerate near the aerial surface of water [11,25,26].

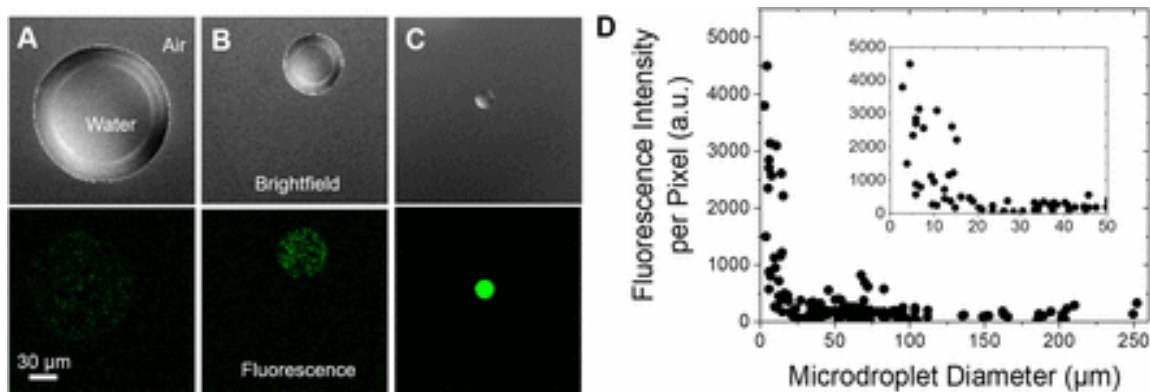
As schematically depicted in Figure 1a, driving the on-water acceleration is probably a combination of i) surface segregation [22,27]; ii) acid–base catalysis even in the absence of



**Figure 2.** The corona of a gas bubble promotes aqueous electro-oxidations. (a) Schematics of the electrochemical generation of hydroxyl radicals near an electrode-pinned bubble. (b–c) Epifluorescence microscopy images of an ITO electrode [(b), open-circuit potential; (c), electrode biased at +1.2 V vs SHE]. The electrolyte is aqueous sodium hydroxide (0.1 M) with an hydroxyl-sensitive fluorophore [3'-(p-hydroxyphenyl) fluorescein (10  $\mu$ M)]. Confocal microscopy images indicating that HO $\cdot$  formation is localized at point where water, gas and electrode meet (ITO biased at +1.2 V vs SHE) ITO slide. The confocal z-height, over the ITO surface, is indicated in figure. Scale bars in (b)–(e) are 200  $\mu$ m. (f) Fluorescence emission intensity profiles measured along the dashed lines marked in panels (d), (e), revealing a peak in fluorescence (hence larger OH $\cdot$  concentration) closer to the electrode. Adapted from Ref. [39], <https://doi.org/10.1038/s41467-019-12487-w>, under the terms of the CC BY 4.0 license, <http://creativecommons.org/licenses/by/4.0/>.

added acids and bases [10]; iii) inhibition of translational and intramolecular rotations [28]; iv) incomplete solvation and/or changes in hydration shells [23,29]; and v) large electric fields hypothesised to be present at the water's surface [30,31]. Regardless of a still poor fundamental understanding [10], on-water chemistry was promptly embraced by the synthetic community [9,32]. On the contrary, it remains almost entirely overlooked by electrochemists, despite the phenomena listed above being likely to impact heterogeneous electrochemical systems [33–36].

The reason for such overlook is simple: a catalytic and thermodynamic effect requiring an aqueous–gas interface appears irrelevant to the design of an electrode process. With the exception of electrochemical reactions with gaseous products [37], electrochemists unanimously regard bubbles adhering to an electrode as redox-inactive *blocking* entities [38]. A gas bubble will mask the portion of the electrode onto which it adheres, preventing any fresh

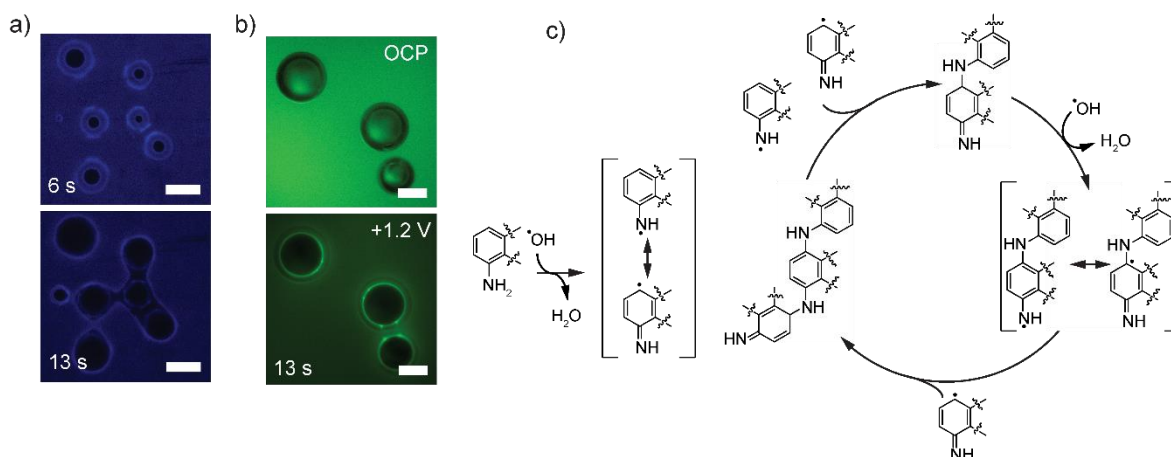


**Figure 3.** (a–c) Spontaneous formation of hydrogen peroxide inside in micro-scale water droplets, assessed as fluorescence intensity (PF-1 to fluorescein conversion) increasing as the droplet size decreases (d). The droplet diameter is 160  $\mu\text{m}$  in (a), 50  $\mu\text{m}$  in (b) and 16  $\mu\text{m}$  in (c). The plot in (d) depicts the relationship between fluorescence emission intensity and the diameter of the droplet. Reproduced from Ref. [24] with permission from The Authors, Copyright 2019.

reactant solution from reaching it (Figure 1b). The purpose of this article is to discuss recent research which is prompting a reassessment of the widespread view of bubbles being strictly blocking cavities [39].

### On-water augmented redox reactivity

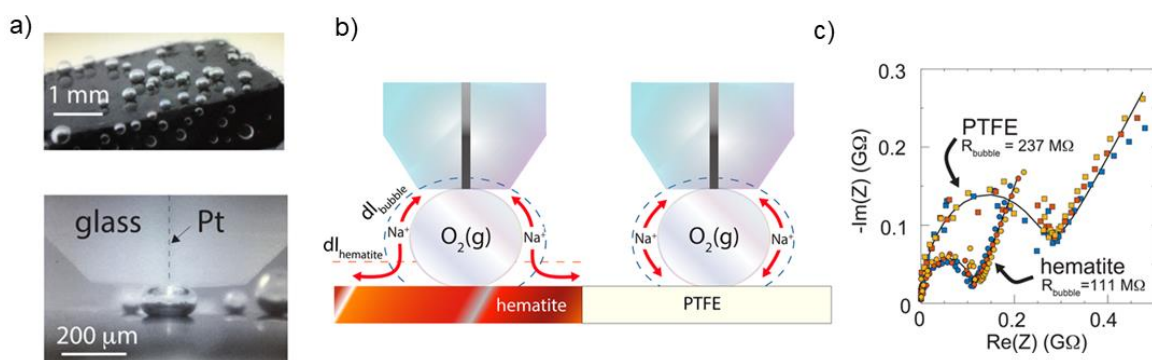
Surprising and counterintuitive, the electrode region surrounding a surface static bubble initiates oxidation of water-soluble species far more effectively than do electrode regions free of bubbles [39]. At the three-phase boundary – where electrode, gas, and an aqueous electrolyte meet – the oxidation of hydroxide anions to hydroxyl radicals occurs at potentials at least 0.7 V below those of tabulated redox values (Figure 2) [39]. This is likely due to electrostatic repulsions between neighbouring hydroxyl ions, which on the aerial water surface are unbalanced by cations [39]. The interface of water in contact with a hydrophobic substance, such as air but also oil, is negatively charged [40,41]. This charging does not require surfactants [40], and leads to an unbalanced ionic cloud extending away from the surface of water [42]. At the curved surface of a droplet the local concentration of unpaired ions can be large and even surpassing the Rayleigh limit. The “pull” by surface charges helps to balance the repulsion of the unpaired ions located inside the droplet. Chamberlayne and Zare have recently developed a computational model to analyze double layers (concentration gradients and electric fields) inside small water droplets, and shown that as their size decreases, the electric field penetrates surprisingly deeply into the droplet [43], and much farther than is predicted by one-dimensional models. This model explains for instance the spontaneous production of  $\text{H}_2\text{O}_2$  in droplets of



**Figure 4. Step polymerization initiated on-water.** (a) Time-stamped video frames capturing luminol chemiluminescence (emission at 440 nm) during the luminol polymerization reaction initiated at the electrode–gas–liquid interface of oxygen bubbles pinned on an ITO anode (+1.2 V vs SHE, potential step started at  $t = 0$  s). The polymer filaments, darker regions clearly visible after 13 s, grow anisotropically, linking adjacent bubbles following the gradient of reactive oxygen species. (b) Epifluorescence microscopy timeframes for the detection of reactive oxygen species around oxygen bubbles adhering on the ITO electrode (OCP and +1.2 V vs SHE). Scale bars in (a) and (b) are 200 μm. (c) The luminol polymerization begins on-water, prompted by the free oxygen radical attack to luminol. The film consist of 50% polyaminophthalate, and 50% of polyaminophthalazine and/or polyluminol (XPS data, not shown). Theoretical calculations suggest the polymerization mechanism is a stepwise radical process, in which a step is initiated via hydrogen transfer by the HO• radical from the aniline moiety in the monomer. Two of these radicals join to form an intermediate that undergoes a second H-transfer, followed by coupling with the radical of a further monomer unit to regenerate the active end group in its non-radical form. Adapted from Ref. [39], <https://doi.org/10.1038/s41467-019-12487-w>, under the terms of the CC BY 4.0 license, <http://creativecommons.org/licenses/by/4.0/>.

diameter smaller than 20 μm [24]. To unveil this spontaneous redox chemistry and the relationship to droplet size, Zare and co-workers used a hydrogen peroxide-sensitive fluorescent probe (peroxyfluor 1, PF-1, Figure 3) as well as the cleavage of 4-carboxyphenylboronic. This reaction happens in the absence of an external bias, and does not rely on the presence of dissolved or atmospheric oxygen. There are several possible sources of electrification leading to the formation of H<sub>2</sub>O<sub>2</sub>, the most obvious being triboelectric effects [44,45]. All of these factors were experimentally ruled out [14]. For example, if the electrification of water was due to simple streaming electrification [46], yields should be proportional to the capillary length and its material, which was not the case.

The recombination of hydroxyl radicals (OH•) is suggested as the most likely mechanism for the formation of H<sub>2</sub>O<sub>2</sub> in microdroplets, with OH• radicals likely to be generated by loss of an electron from OH<sup>-</sup>, which as mentioned above is favored on the surface of water [39], where large electric fields exist [30]. In the absence of an electrode acting as electron sink, the fate of the released electron is an open question, but noteworthy is a parallel with the atmospheric



**Figure 5. On-water gateway for ionic conduction.** (a) Direct measurement of the mobility of alkali metal ions on oxygen bubbles pressed between metal probes and semi-conducting (iron oxide) or gold surfaces. (b) This on-water ionic channel is lost on electrical insulators. (c) The gateway was identified by electrochemical impedance spectroscopy using an ultramicroelectrode in direct contact with bubbles pinned onto these solid surfaces. Adapted from Ref. [48], <https://doi.org/10.1038/s42004-021-00481-7>, under the terms of the CC BY 4.0 license, <http://creativecommons.org/licenses/by/4.0/>.

formation of  $\text{H}_2\text{O}_2$ , so crucial in maintaining the oxidative capacity of the atmosphere [47], but yet equally dense of open questions on the chemical identity of electron sinks and sources. There is then of course the captivating suggestion by Zare and co-workers whether microdroplets might have assisted prebiotic reduction reactions, before the evolution of biotic reducing systems.

Electrochemical reactions need intimate contact between liquid and electrified solid. This is certainly true, but what is becoming progressively clearer is that there is not a significant current (rate) penalty when bubbles pinned on an electrode interrupt such contact (Figure 1b). At the point where electrode, water, and gas meet, electrochemical currents counterintuitively do not diminish, but increase [39]. Beside introducing an energetic discount on the oxidation of hydroxide anions to hydroxyl radicals, there is also the recent proof of concept of the corona of a surface bubble catalysing the stepwise radical polymerisation of aniline analogues (Figure 4) [39], and of facilitated ionic conduction (compared to the water's bulk) on the surface of bubbles pinned on electrodes [48] (Figure 5). Noting that electrode kinetics is dominated by the efficiency of switching between ionic and electronic conduction [49], the discovery of an on-water gateway for ionic conduction adds another mechanism, beyond those listed in Figure 1a, to explain the unexpected on-water redox reactivity.

These recent experiments on electrochemistry around bubbles pinned on electrodes are overturning the long-held assumption that surface-adherent gas cavities are redox-inactive, but not recognising earlier this new form of multiphase electro-catalysis is unsurprising: the first

evidence of high currents around bubbles, and of large ionic motility on-water, have been obtained under conditions that are never deliberately targeted [39,48].

## Perspectives

Chemical reactivity triggered by the heat and pressure released as a bubble collapses fall within the field of sonochemistry [50,51]. In contrast, stationary air bubbles are generally perceived as inert entities. This is despite the established notion of the air–water interface carrying electric fields as high as  $0.01 \text{ V/\AA}$  [31]. The origin of this interfacial strong electric field is still debated [41]. Some authors argue it is associated with the accumulation of unbalanced hydroxide ions ( $\text{OH}^-$ ) at the interface between water and an hydrophobic media, such as air [41,52] or oil [40], while others believe is merely due to anionic impurities [53,54].

We believe that to capture this mechanism and harness the richness of on-water chemistry for electrosynthesis will require developing new methodologies to merge redox microscopy [55-57], fluorescence microscopy, and electrosynthesis [39]. What will also push further this exciting new branch of heterogeneous electrochemistry will be the development of methodologies to probe the interfacial electric field of the aqueous–hydrophobic interface. This is challenging as difficulties arise not only from instrumental limitations [58]. Voltage profiling is conceptually difficult for the reason that any voltage probe will carry its own excess of ions, and this ionic cloud will inevitably disturb the system under investigation. It is opinion of the authors that a way forward will be to explore the field-induced spectral tuning of some bioluminescent reactions [59], or shifts to the absorption spectra of vision pigments [60]. One can envision that the environment sensed by the excited state of a light-emitting molecule will affect the energy of its radiative decay and aided by computer modelling it will be possible to link spectral shifts to interfacial fields.

The aqueous–hydrophobic interface bears a net negative charge, as mentioned above of somewhat debated nature [41,61], but it is becoming increasingly clear that water-derived ions trapped at the water's surface, unlike Brønsted acids, lack local counterions, so will be significantly more reactive than contact ion pairs [11,39]. There is therefore the possibility of driving on-water electrochemical reactions which require a preceding acid–base step, without added acids or bases, or for instance develop methods to quantify surface charging by mapping [62], proton-coupled electron transfer reactions. One can also envision to rely on the water–air

interface to shift the equilibrium of the charged reactants towards their neutral form [27], perhaps using this to guide reaction selectivity [63].

Furthermore, the ubiquitous electrostatic imbalance at the gas–water interface could be of value to guide specific reactions by means of electrostatic destabilisation of reactants in crowded and charge-unbalanced environments. The role of electric fields in controlling chemical bonding and reactivity is rapidly entering mainstream chemical catalysis. While this form of catalysis has been demonstrated in specific environments – inside the active pocket of an enzyme [64], and in the electrified gap of a scanning tunnelling microscope (STM)[65,66] it is completely unexplored at aqueous–hydrophobic interfaces [30]. One of the open question is whether a field that can affect bond and bonding ( $> \text{MV/cm}$ ) [67] still exists close to the point of chemical electro-neutrality of the pinned bubbled, noting that the point of zero charge for surface water is met when the bulk is at  $\sim\text{pH } 3$ .

Lastly, water has a limited window of electrochemical stability, with significant energetic disadvantage. Rather than using additives to expand this voltage window, there is the possibility of lowering the energy requirement of the reaction of interest, so that it can occur on-water without additives. Non-aqueous alternatives, such as ionic liquids [68], suffer from large costs at scale. The recent discovery that reactions thermodynamically inaccessible in water become surprisingly feasible on-water – for example, the 0.7 V downward shift in the hydroxide oxidation potential in the corona of a surface bubble [39] – has started a paradigm-shift in the way water stability issues can be addressed.

## Conclusions

Electrochemists have built a wealth of knowledge on perfectly “wet” electrode–electrolyte junctions, and have developed a range of methods to manage the removal of bubbles from electrodes [69], but they have entirely overlooked the possibility of exploiting on-water catalytic effects [9].

By developing further our understanding of redox rates and equilibrium positions in electrode systems strategically balanced by the addition of surface bubbles, there exist an exciting opportunity to address the major shortcomings of purely “*in-water*” processes. To conclude with some specific examples, it is opinion of the authors that reactions of both conceptual and practical value, likely to perform well on-water, include for example the electrostatic catalysis cycloadditions between olefins and thionium species formed upon the oxidation of benzylic



dithioacetals, and the C–C biaryl coupling of phenols. The novel science of on-water electrochemistry [13,30,39,42,48,70,71] is one path, but we believe a very promising one, to address the major limitations of redox reactions in a water-based electrolytes: low rates, poor selectivity, and a limited electrochemical solvent window of stability.

### Conflict of interest statement

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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