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Review Article

Electrocatalysis at the polarised interface between two immiscible electrolyte solutions

Alonso Gamero-Quijano¹, Grégoire Herzog², Pekka Peljo³ and Micheál D. Scanlon⁴**Abstract**

Electrocatalysis at the interface between two immiscible electrolyte solutions (ITIES) is an emerging field of research, which allows the separation of reactants according to their lipophilicity. Electrocatalysts of various natures (noble metals, carbon-based and inorganic nanomaterials, enzymes, and supramolecular ensembles) are assembled at the ITIES, either spontaneously or following the application of an interfacial Galvani potential difference. While primarily used for the electrocatalysis of the oxygen reduction reaction (ORR) and hydrogen evolution reaction (HER), recent work has focused on the electrocatalysis of the oxygen evolution reaction (OER) and the electrocatalytic oxidation of elemental sulfur (S_8) and an organosulfur compound. Protocols to compare electrocatalytic performances at the ITIES call for careful data analysis and a detailed knowledge of the catalyst's morphological parameters (e.g., active surface area and catalyst loading). However, standardisation of such protocols at the ITIES has yet to be implemented and is required to allow better comparison of the results from individual biphasic systems.

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Keywords

Electrocatalysis, Polarised liquid|liquid interfaces, Interface between two immiscible electrolyte solutions, Hydrogen evolution reaction, Oxygen reduction reaction, Oxygen evolution reaction.

Introduction

Biphasic systems allow the electrocatalysis of reactants which are separated according to their lipophilicity [1]. Catalytic nanomaterials and supramolecular films can be assembled at the polarised interface between Two Immiscible Electrolyte Solutions (ITIES) spontaneously, or by the application of an external driving force, e.g., in the form of an interfacial Galvani potential difference ($\Delta_0^w \phi$) [2–7]. Furthermore, electrochemistry at the ITIES allows direct probing of the electrocatalytic activity of the nanomaterials or films free from the influence of an underlying support [8].

The two main electrocatalytic processes investigated at the ITIES to date, using metallic or inorganic nanomaterials, are of the energy-related oxygen reduction reaction (ORR) [9–15] and hydrogen evolution reaction (HER) [16–34]. The electrocatalytic oxidation of elemental sulfur (S_8) and the organosulfur compound 2,5-dimercapto-1,3,4-thiadiazole (DMcT) by gold nanoparticles (AuNPs) [35,36], photoelectrocatalysis of the oxygen evolution reaction (OER) [37–43], HER [44–49], and ORR [50–57] by a series of diverse strategies, and bioelectrocatalysis of the ORR using the redox-active protein cytochrome *c* (Cyt *c*) [58,59] at the ITIES have also been reported. In this review, recent progress for each of these biphasic electrocatalytic processes is overviewed. An in-depth discussion is also provided on the need for stricter standard protocols for electrocatalysis at the ITIES, to allow better comparison of the results from individual biphasic systems. Electrocatalysis of the ORR at the ITIES using molecular catalysts, such as cobalt or iron porphyrins and phthalocyanines dissolved in the aqueous phase, is not discussed in detail herein, as a detailed description of this research is provided in a recent review by Opallo et al. [60].

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Electrocatalysis at the ITIES by metallic, carbon-based, or inorganic nanomaterials

In the liquid|liquid interface configuration, both the ORR and HER require: (i) a lipophilic electron donor dissolved in the organic phase, which is typically a ferrocene derivative (ferrocene Fc, dimethylferrocene DiMFc, or decamethylferrocene DcMFc) or tetrathiafulvalene; and (ii) protons available from the aqueous phase and oxygen dissolved in either phase to diffuse freely towards the 2D or 3D assemblies of catalysts. Although the interfacial electron transfer (IET) reaction is thermodynamically possible between the oxidising species dissolved in the aqueous phase (H^+ or O_2) and the electron donor present in the organic phase, the reaction kinetics are greatly improved by the presence of nanocatalysts in the ITIES. Thanks to Fermi level equilibration, conducting nanoparticles (NPs) adsorbed at the ITIES allow direct electron transfer by acting as bipolar electrodes and facilitating catalytic reactions [12,61]. Catalytically improved electron transfer through an AuNP film was demonstrated through the investigation of electron transfer between lipophilic ferrocenium cation/ferrocene and hydrophilic ferri-ferrocyanide redox couples (Figure 1a(i)) [62]. The peak-to-peak separation was greater than 90 mV in the absence of a catalyst (Figure 1a(ii)) but decreased down to 70 mV when the AuNP film was present at the ITIES (Figure 1a(iii)).

Catalysts made of noble metals (*e.g.*, Au [10,12], Pt [14], and Pd [10]) or purely carbon-based (*in situ* generated reduced graphene oxide [11], graphene [13] and even lithium-ion battery waste [15]) were mainly used for the ORR, whereas a larger selection of inorganic materials were tested for the HER: MoS_2 [16,17,27,28,31,32] Mo_2C [18,19], Cu [21,25,34], Cu_2CoSnS_4 [22], Cu_2WS_4 [23], CoS [24], black phosphorus [33], NiS [26], W_2S [20] and W-based ternary metal sulfides [29]. These catalysts were adsorbed as such at the ITIES or were supported onto carbon-based materials, *e.g.*, carbon nanotubes [17,19,24–26] and reduced graphene oxide [27,34]. Carbon-based nanomaterials, on which the catalysts were immobilised, helped to efficiently transfer electrons between the lipophilic electron donor and the hybrid materials (and not exclusively from the catalytically active site) leading to an increased HER rate (Figure 1b).

Over the past decade, the study of single NPs by their collision with microelectrodes has been exploited to size NPs, determine their shape, and provide insights into NP agglomeration or aggregation phenomena [63,64]. Such single-entity electrochemical measurements at a micron-sized ITIES were demonstrated by Stockmann *et al.* [14] by recording current spikes, that were rationalised by a COMSOL 2D simulation, and attributed to the electrocatalytic ORR upon impact of Pt NPs

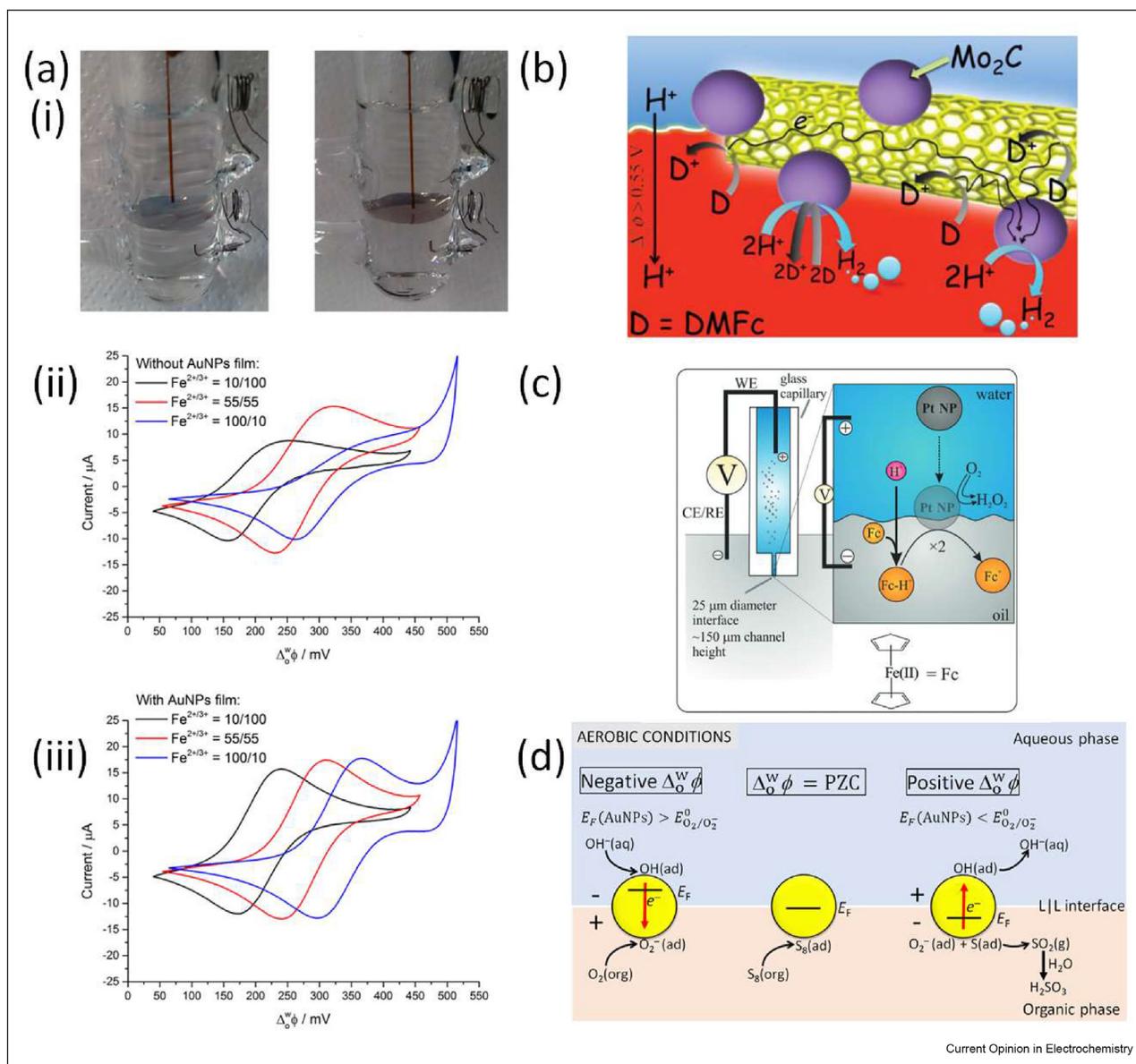
at the ITIES with ferrocene acting as the electron donor (Figure 1c). A major advantage of this approach to single-entity electrochemistry is the more facile and reproducible preparation of microITIES, supported at the tip of a micropipette filled with either the aqueous or organic phase, *versus* microelectrodes [14,65]. Nevertheless, single-entity electrochemistry remains underexplored at microITIES *versus* microelectrodes due to the relatively small community of researchers actively working on this topic presently.

Suárez-Herrera *et al.* used a film of AuNPs at the ITIES to act as a catalytic surface onto which O_2 and elemental sulfur (S_8) can adsorb [35]. Electrocatalytic oxidation of S_8 by O_2 was then achieved by providing an electrochemical driving force through polarisation of the ITIES and tuning the Fermi level of the interfacial AuNPs by the adsorption of aqueous anions (Figure 1d). This system mimics biochemical sulfur oxidation under ambient conditions with the ITIES being the ideal environment to oxidise S_8 , overcoming the incompatible solubilities of the hydrophobic reactants (O_2 and S_8) and hydrophilic products (H^+ , SO_3^{2-} , SO_4^{2-} , *etc.*). In a separate study, Suárez-Herrera *et al.* also used a film of AuNPs at the ITIES to electrocatalyse the oxidation of the organic soluble organosulfur molecule 2,5-dimercapto-1,3,4-thiadiazole (DMcT) by O_2 , yielding a floating interfacial AuNP/poly(DMcT) film by oxidative electrosynthesis [36]. Raman spectroscopy strongly suggested the AuNP/poly(DMcT) film is surface-enhanced Raman spectroscopy (SERS)-active and a coordination polymer of poly(DMcT) with AuNPs.

Photoelectrocatalysis at the ITIES

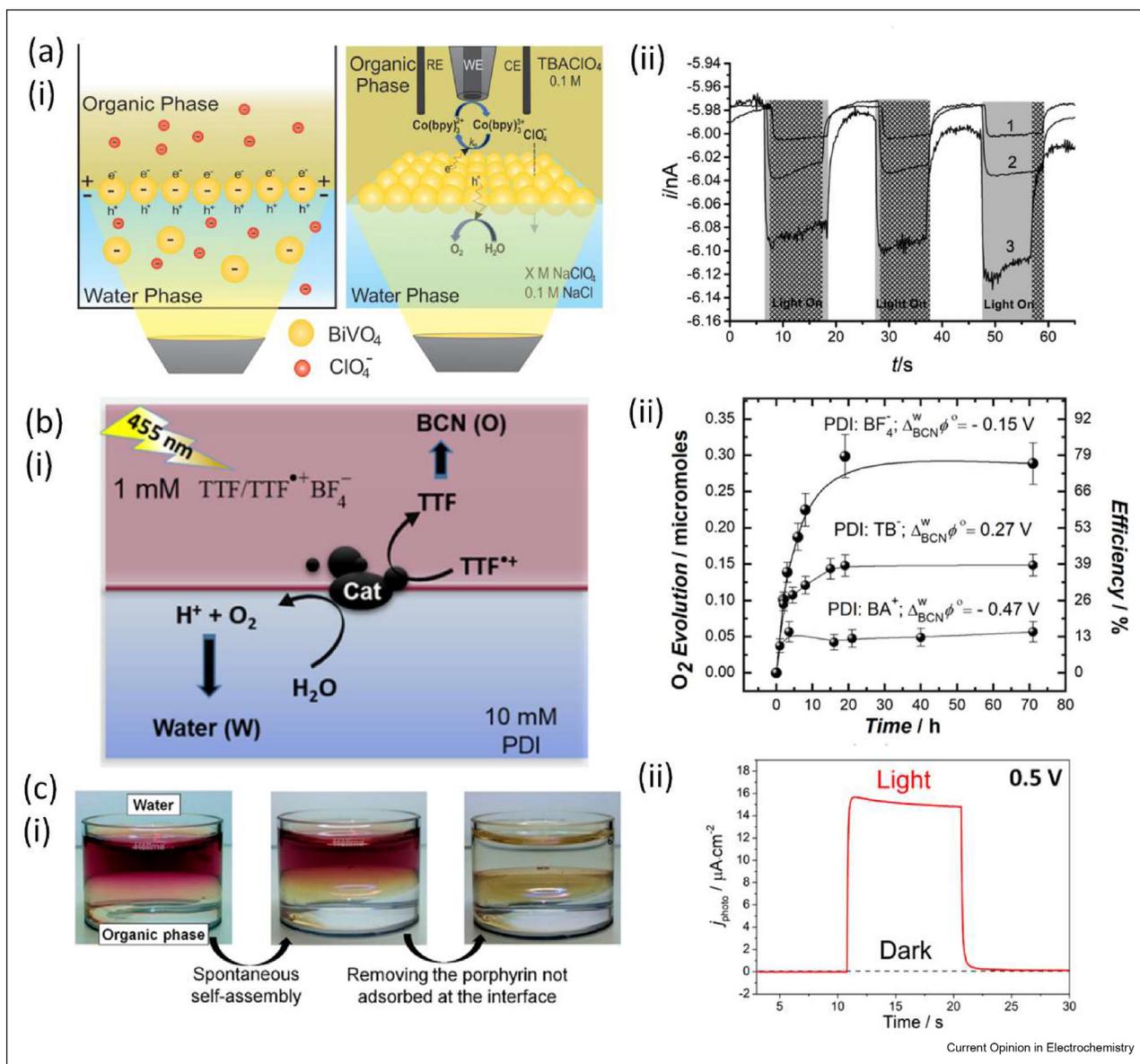
To date, all photoelectrocatalytic OER experiments at the ITIES have been performed with butyronitrile as the organic solvent due to its stability under strongly oxidising conditions [37–43]. Using a film of $BiVO_4$ photocatalyst with a specific hyperbranched structure at the ITIES, Rastgar *et al.* added $[Co(bpy)_3](PF_6)_3$ to the organic phase with the dual role of acting as the redox-active oxidant, scavenging conduction band electrons from $BiVO_4$ upon illumination and thereby enhancing the separation efficiency of photogenerated charge carriers, and as a scanning electrochemical microscopy (SECM) redox probe [37,38]. The latter permits the kinetics of the photoinduced interfacial electron transfer (IET) reaction to be probed by recording SECM feedback approach curves using a microelectrode that approaches the ITIES from the organic side and re-oxidises the photo-generated $[Co(bpy)_3]^{2+}$ (Figure 2a(i)). Additional SECM feedback approach curves directly detected the O_2 evolved upon oxidation of water by the valence band holes of $BiVO_4$ during illumination [38]. By tuning the applied $\Delta\phi^w$ by varying the concentration ratio of the potential determining perchlorate anion (ClO_4^-) in each phase, increased rates of $[Co(bpy)_3]^{2+}$

Figure 1



Electrocatalysis at the ITIES by metallic, carbon-based, or inorganic nanomaterials at the ITIES. (a) (i) Images of AuNP films prepared at a polarisable water| α,α,α -trifluorotoluene (TFT) interface in a four-electrode electrochemical cell using AuNPs with mean diameters of 12 nm (left panel) and 38 nm (right panel). (ii), (iii) Cyclic voltammograms of interfacial electron transfer between organic soluble ferrocenium cation/ferrocene and aqueous soluble ferri-ferrocyanide redox couples, with various ratios between Fe^{2+} and Fe^{3+} investigated, both (ii) in the absence and (iii) in the presence of an interfacial AuNP nanofilm. The scan rate used was 10 mV s^{-1} . (b) Schematic of the biphasic HER in the presence of a CNT/ Mo_2C nanocomposite adsorbed at a polarisable liquid|liquid interface. The electron donor, decamethylferrocene (DcMFC), may inject electrons anywhere on the carbon support and not necessarily directly at the Mo_2C active site. (c) Schematic of a Pt NP impact leading to a measurable current spike at a micron-sized ITIES due to the electrocatalysis of the biphasic ORR using ferrocene as the electron donor. (d) An overview of the electrochemically driven biphasic sulfur oxidation reaction under aerobic conditions when the interfacial Galvani potential difference ($\Delta\phi^W$) is polarised negatively, positively, or equal to the potential of zero charge (PZC). (a) is reproduced with permission from ref. [62]. Copyright 2015 American Chemical Society. (b) is reproduced from ref. [19] with permission from the Royal Society of Chemistry. Copyright 2013. (c) is reproduced with permission from ref. [14]. Copyright 2017 Wiley-VCH. (d) is reproduced from ref. [35] with permission from Elsevier. Copyright 2022.

Figure 2



Photoelectrocatalysis at the ITIES. **(a) (i)** Schematic of scanning electrochemical microscopy (SECM) approach curves for the photoelectrocatalytic O_2 evolution reaction (OER) using a film of $BiVO_4$ photocatalyst at the ITIES and organic soluble $[Co(bpy)_3]^{2+}$ as both a sacrificial oxidant and SECM redox probe. **(ii)** Photocurrent transients of increased magnitude upon reduction of O_2 at a microelectrode positioned in the organic phase at a fixed distance away from the ITIES as the applied $\Delta\phi^w$ was tuned to less positive potentials using perchlorate anions (ClO_4^-) as the potential determining ion (PDI); the $[ClO_4^-]_{aq}/[ClO_4^-]_{org}$ ratios are 1:1, 1:2 and 1:10 for the transients labelled 1, 2 and 3, respectively. **(b) (i)** Composition of a biphasic cell used to evaluate the effect of polarisation of an aqueous/butyronitrile (BCN) interface on the photoelectrocatalytic OER by tetrathiafulvalene (TTF), TTF^{2+} and tetrafluoroborate anions (BF_4^-) molecular assemblies adsorbed on the surface of Pt microparticles. **(ii)** O_2 produced in the biphasic cells described in (b) (i) with BF_4^- , tetrakis(pentafluorophenyl)borate anions (TB^-) or bis(triphenylphosphoranylidene)ammonium cations (BA^+) as the PDI. The O_2 evolved was quantified by sampling the headspace of septum-sealed glass vials using a lock-in syringe with a push-pull valve and injecting the sample on to a gas chromatography-mass spectroscopy (GC-MS) instrument. **(c) (i)** Optical images of the formation of a film of ZnTPPc interfacial nanostructures at an aqueous/ α, α, α -trifluorotoluene (TFT) interface with the pH of the aqueous phase precisely matching the pK_a of the carboxyphenyl-substituents (pH 5.8). **(ii)** Comparison of photocurrent transients due to the photoelectrocatalytic O_2 reduction reaction (ORR) measured in the presence of a film of ZnTPPc interfacial nanostructures with and without LED illumination, at an applied $\Delta\phi^w$ of 0.5 V with decamethylferrocene as the organic electron donor. The supporting organic electrolyte was bis(triphenylphosphoranylidene)ammonium tetrakis(pentafluorophenyl)borate (BATB). **(a)** is reproduced with permission from ref. [38]. Copyright 2017 American Chemical Society. **(b)** is reproduced from ref. [42] with permission from Elsevier. Copyright 2022. **(c)** is reproduced with permission from ref. [57]. Copyright 2020 American Chemical Society.

oxidation and O₂ reduction were recorded as the applied $\Delta_0^w\phi$ shifted to less positive potentials. These observations may be due to an increased thermodynamic driving force for the photoelectrocatalytic OER (*i.e.*, following Butler-Volmer theory), more efficient electron-hole separation, or an increased surface coverage of BiVO₄. The photoelectrocatalytic effect of the BiVO₄ nanoparticles was further demonstrated by obtaining photocurrent transients upon reduction of O₂ at a microelectrode positioned in the organic phase at a fixed distance away from the ITIES (Figure 2a(ii)) [38]. Additionally, the formation and decay of the OH[•] intermediates during the OER at the surface of the BiVO₄ nanoparticles was quantified *in situ* by a surface interrogation mode of SECM involving the approach of a microelectrode to a micropore orifice that supported the BiVO₄ modified ITIES [39].

Girault and co-workers employed *in situ* self-assembled *p*-type semiconductors, consisting of tetrathiafulvalene (TTF), TTF^{•+} and BF₄⁻ or PF₆⁻ molecular assemblies adsorbed on the surface of Co₃O₄ or Pt nanoparticles, as an electron acceptor/photosensitiser redox OER photoelectrocatalyst at the ITIES (Figure 2b(i)) [40–42]. Initial studies in a non-polarisable fully miscible water/ acetonitrile system were hampered by protonation of the molecular assemblies, triggering competing reactions such as the HER and ORR, and preventing electrochemical recycling of TTF^{•+} [40]. However, polarisation of an ITIES formed between water and butyronitrile using the potential determining BF₄⁻ anion increased the efficiency of the photoelectrocatalytic OER by enhancing the separation of the photoproducts (protons and TTF) by pumping protons to the aqueous phase [42]. Polarisation at the negative extreme, using the bis(triphenylphosphoranylidine)ammonium cation (BA⁺), or positive extreme, using the tetrakis(pentafluorophenylborate) anion (TB⁻), of the potential window yielded sub-optimal efficiency (Figure 2b(ii)). With BA⁺, the TTF^{•+} was extracted to the aqueous phase and the resultant TTF/TTF^{•+}Cl⁻ assemblies formed were less photocatalytic, while with TB⁻ a stable “ionosome” emulsion [66] formed that scattered the light. Deposition of the TTF/TTF^{•+}BF₄⁻ molecular assembly on a carbon electrode in the anodic compartment of a water-splitting H-cell permitted the electrochemical recycling of the electron acceptor TTF^{•+} in a water|butyronitrile emulsion [41]. Girault and co-workers also reported OER at the ITIES simply using photo-excitabile fluorinated 7,7,8,8-tetracyanoquinodimethane (F₄TCNQ) aggregates as an electron acceptor [43]. In the proposed mechanism, four photo-excited TCNQF₄^{•+} radical cations stacked in an aggregate oxidise water to release O₂ and four protons, with the latter neutralising the TCNQF₄²⁻ dianions to form H₂TCNQF₄ [43].

Photoelectrocatalysis of the HER at the ITIES has been achieved using organic soluble osmocene [44],

decamethylsmocene [45] and decamethylruthenocene [46–49]. Based on their standard redox potentials, none of these metallocenes reduce protons pumped across a positively polarised ITIES spontaneously. However, all act as photo-redox catalysts and evolve H₂ to varying degrees *via* the corresponding hydride species when illuminated. The ability to generate H₂ with weak reductants makes these molecules highly suited for integration into the cathodic compartment of a biphasic H-cell as the oxidised form can be reduced at very positive redox potentials, thereby requiring less electrochemical driving force [67].

Photoelectrocatalysis of the ORR at the ITIES has been achieved by introducing photoactive porphyrin molecules to the aqueous phase [50,51,54] and by assembling either porphyrin-based supramolecular nanostructures [57] or bare [52,55,56] and dye-sensitised [53] colloidal TiO₂ semiconductor NPs at the ITIES. Aqueous soluble porphyrins, for example zinc(II) meso-tetrakis(4-carboxyphenyl)porphyrins (ZnTPPc), act as a photo-redox catalyst at the ITIES. Upon illumination, the excited state is reductively quenched by IET from an organic soluble ferrocene-derivative. The ground state of the porphyrin is then regenerated by binding O₂ and reducing it. Only porphyrins present at the ITIES are photoelectrocatalytically active and therefore the efficiency of the photoelectrocatalytic ORR, as monitored by the magnitude of photocurrent transients recorded at the ITIES, is limited by the interfacial surface coverage of the porphyrin molecules. By optimally tuning the pH of the aqueous phase to match the pK_a of the carboxyphenyl-substituents on ZnTPPc, Scanlon and co-workers have self-assembled ZnTPPc into films of highly ordered supramolecular nanostructures at a polarisable aqueous|TFT interface (Figure 2c(i)) [57,68–70]. Due to the huge increase in interfacial porphyrin surface coverage, the multilayers of interfacial nanostructures are more efficient light harvesters, with the photocurrent due to the photoelectrocatalytic ORR increasing an order of magnitude compared to studies with ZnTPPc simply dissolved in the bulk aqueous phase (Figure 2c(ii)) [57].

Colloidal TiO₂ semiconductor NPs can be electrostatically assembled at ITIES by tuning the aqueous pH and applied $\Delta_0^w\phi$ [52,55]. Upon illumination, O₂ is photoelectrocatalytically reduced by the conduction band electrons of TiO₂, while a ferrocene-derivative is oxidised by interfacial hole-transfer across the ITIES mediated by surface OH[•] radicals. Plana *et al.* developed a methodology involving sonication and the use of relatively high aqueous electrolyte concentrations to prepare thick interfacial films of coalesced TiO₂ NPs at the ITIES [56]. Despite the mesoporous nature of the interfacial TiO₂ film, cyclic voltammograms indicated that the ITIES retained a characteristic molecular sharpness. Using this setup, incident photon-to-current

efficiencies (IPCE) of 75% were reported [56], far beyond the ca. 1% achieved for ITIES modified with sub-monolayer coverages of photoactive porphyrin molecules or TiO₂ NPs. In an early contribution to this field, Fermín et al. demonstrated that photocurrent responses originating from the photoelectrocatalytic OER and associated oxidation of a ferrocene-derivative can be extended into the visible region by dye sensitisation of TiO₂ NPs assembled at the ITIES [53].

Bioelectrocatalysis at the ITIES

Polarised liquid|liquid interfaces provide the required fluidic, amphipathic environment for redox protein adsorption, and can replicate the electrostatic and/or hydrophobic interactions required to mimic the biological membrane [71]. Furthermore, the electric fields of up to 10⁹ V·m⁻¹ experienced by peripheral membrane proteins are replicated at the ITIES without the need to introduce any solid electrode architectures [72]. In this context, the electrocatalytic activity of the model protein cytochrome *c* (Cyt *c*) towards the ORR has recently been demonstrated at the ITIES [58,59]. Cyclic voltammograms with Cyt *c* in an aqueous phosphate buffer solution and the reductant DcMFC in an organic electrolyte solution show two voltammetric signals, one reversible and the other irreversible (Figure 3a). The irreversible signal at positive potentials is attributed to the electrocatalytic ORR, while the reversible peak at negative potentials is attributed to the ion transfer of DcMFC⁺ cations produced during O₂ reduction [58]. This bioelectrocatalytic IET reaction was facilitated at positive potentials due to electrostatic and hydrophobic interactions between Cyt *c* and tetrakis(pentafluorophenyl)borate (TB⁻) organic electrolyte anions in the mixed solvent region. UV/vis spectroscopy in total internal reflection (TIR-UV/vis) configuration demonstrated that Cyt *c* adsorbs and is partially denatured at a positive applied $\Delta_0^w\phi$ (ca. 0.5 V). In contrast, no adsorbed Cyt *c* species were detected at negative applied $\Delta_0^w\phi$ [58]. These findings were supported by Molecular dynamic (MD) computational modelling, where positive potentials promoted interactions between cationic lysine residues that surround the active site of Cyt *c* and TB⁻ (Figure 3b). The consequences of these interactions are two-fold: (i) causing a conformational change of the adsorbed Cyt *c* from its native state that exposes the redox-active heme to O₂ and (ii) ensuring the partially exposed heme-pocket is orientated perpendicular to the liquid|liquid interface to favour interfacial electron transfer with DcMFC. The intensity of the irreversible ORR signal decreases with each cycle (Figure 3a) as Cyt *c* becomes progressively more denatured and redox inactive due to its continued interactions with the organic solvent and TB⁻. The electrochemical behaviour of Cyt *c* at a positively polarised ITIES mimics Cyt *c*'s *in vivo* peroxidase activity in the inner mitochondrial membrane at the onset

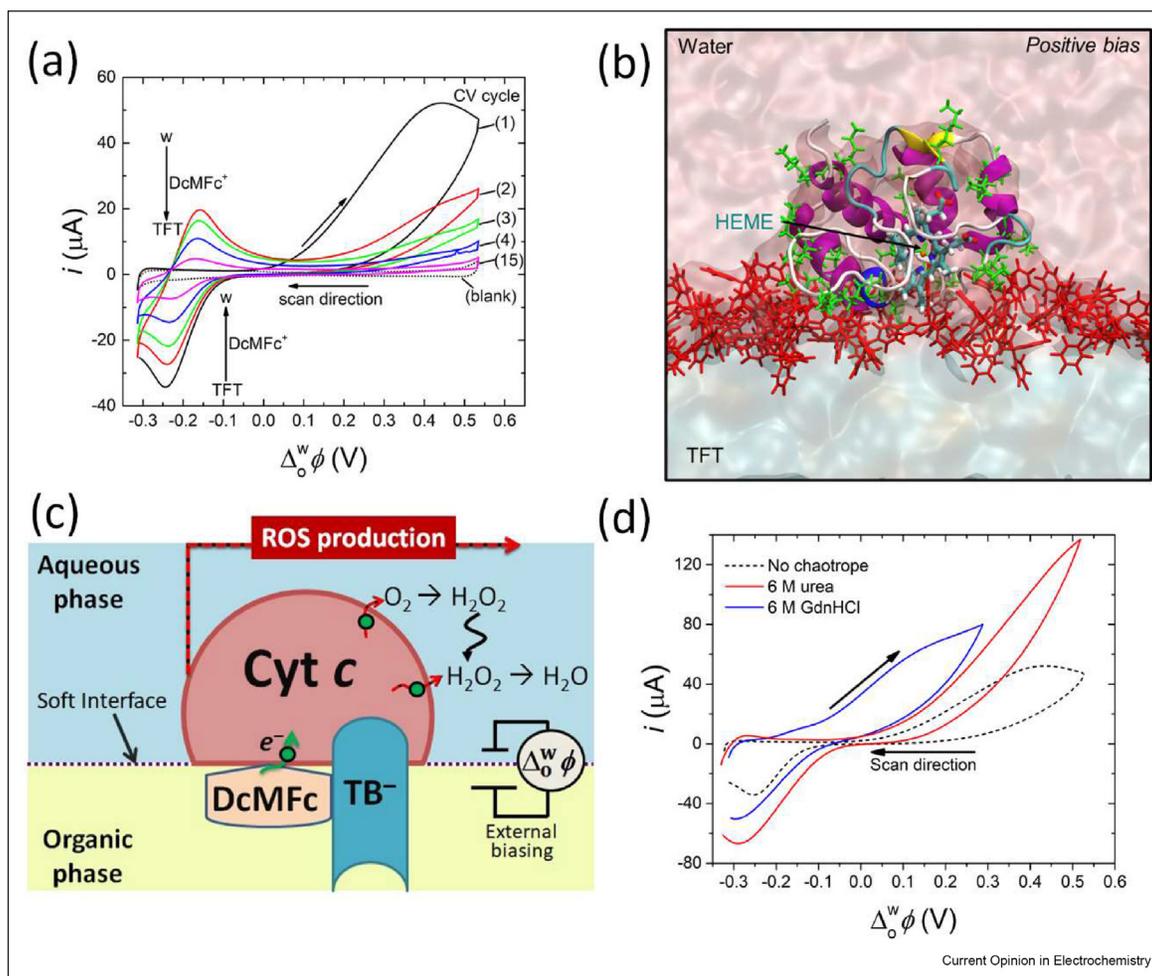
of apoptosis in which reactive O₂ species (ROS; such as H₂O₂) are reduced at the heme [58]. Specifically, the dual biological roles of the anionic phospholipid cardiolipin in this process, as a disrupter of the tertiary structure of Cyt *c* and sacrificial oxidant, are played by TB⁻ and DcMFC, respectively (Figure 3c).

Cyt *c*'s electrocatalytic activity towards the ORR at the ITIES is enhanced in the presence of denaturing agents such as guanidinium chloride (GdmCl) and urea (Figure 3d) [59]. The magnitude of this enhancement is correlated with physicochemical changes to the liquid|liquid interface and, most importantly, conformational changes to the adsorbed Cyt *c* specific to each chaotrope. MD modelling revealed that the distinct Cyt *c* unfolding mechanism with GdmCl leads to a more open heme pocket structure than when urea is added, and thus GdmCl shows a greater enhancement in electrocatalytic activity towards the ORR [59]. Additionally, Gdm⁺ cations penetrate the interface, creating a more hydrophobic environment that increases the interfacial concentration of DcMFC in the mixed solvent region and thereby enhances IET. Conversely, urea partially impedes access of the organic solvent to the water phase and hinders IET.

Normalising electrocatalytic performance at the ITIES

As outlined in the previous sections, over the years, many different catalyst materials have been investigated for the HER and ORR at polarised liquid|liquid interfaces. Unfortunately, there has been very little discussion in the field on how to normalise and compare the electrocatalytic performance of different materials at the ITIES. Experiments have been performed in vastly different experimental conditions, with very different catalyst amounts. Also, catalysts may be added as a powder (*e.g.*, [16,27]) or formed *in situ* by reduction from the precursors (*e.g.*, [9,21]). Therefore, to allow better comparison of the results, we believe that stricter standards are required and recently suggested best practises for reporting electrocatalytic performance of nanomaterials should also be applied for electrocatalytic work at the ITIES [73]. One of the recommendations was to report the turnover frequency, but this is challenging to estimate as typically the number of active sites per area is not known. Unlike for catalysts attached on an electrode surface, even estimation of the electrochemically active surface area of catalyst dispersed in solution or attached at the ITIES remains a challenge. As a compromise, we suggest at least normalising the reaction rates by the mass or the molar amount of the catalyst. As an example, we have analysed the data on the biphasic HER presented in the literature in so-called “shake-flask experiments” (Figure 4). The latter involved DcMFC dissolved in a 1,2-dichloroethane phase reacting under stirring with protons transferred to the

Figure 3



Bioelectrocatalysis at the ITIES. (a) Cyclic voltammetry with 10 μM Cyt *c* in a phosphate buffer solution (60 mM Na_2HPO_4 and 20 mM KH_2PO_4 at pH 7) and 500 μM DcMfc in a solution of 5 mM bis(triphenylphosphoranylidene)ammonium tetrakis(pentafluorophenyl)borate (BATB) organic electrolyte in TFT under aerobic conditions. The scan rate used was 20 mV s^{-1} . (b) Representative molecular dynamics snapshots showing the orientation of the Cyt *c* heme active site at a positively polarised liquid|liquid interface. The Lys residues on the surface of Cyt *c* are shown as green ball and sticks, while the BA^+ and TB^- ions from the electrolyte in the TFT organic phase are shown as blue and red ball and sticks, respectively. (c) Schematic of the biomimetic electrified aqueous|organic interface at which DcMfc and TB^- anions activate Cyt *c* for reduction of reactive O_2 species. The electrons are represented by green circles. (d) Cyclic voltammetry of 10 μM Cyt *c* and 1 mM DcMfc under aerobic conditions, as described in part (a), with and without 6 M urea or GdmCl. The scan rate was 20 mV s^{-1} . (a), (b) and (c) are reproduced with permission from ref. [58]. Copyright 2021 American Association for the Advancement of Science (AAAS). (d) is reproduced from ref. [59] with permission from the Royal Society of Chemistry. Copyright 2022. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

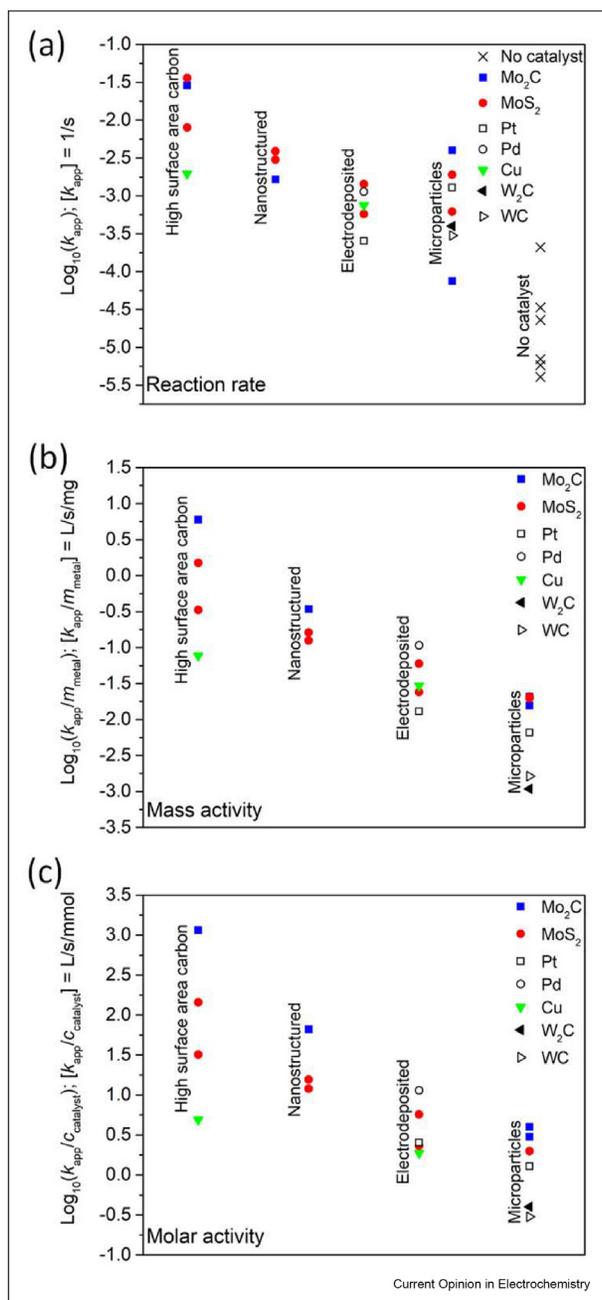
aqueous phase after positive polarisation of the liquid|liquid interface by distribution of lithium tetrakis(pentafluorophenyl)borate (LiTB ; initially dissolved in the organic phase) between the phases.

For analysis of the data extracted from the literature [9,16–19,21,31,32,34], we have assumed that first-order kinetics with respect to the DcMfc concentration is followed initially, and the catalyst affects the rate constant of the reaction. This assumption is not strictly true, as some of the catalysts have shown different kinetics [18], but it serves as a first approximation.

Apparent first-order reaction rate constants (unit of 1/s) have been extracted for all the catalysts and in the absence of a catalyst (Figure 4a), and the rate constants have been normalised by the mass of the metal (mg/L; Figure 4b), or the concentration of the catalyst (mmol/L; Figure 4c) and divided into catalysts deposited on high-surface-area carbon, as nanomaterials, as catalysts formed by electrodeposition and as microparticles.

The reaction rates depend on the number of active sites, so nanostructuring of the catalysts leads to enhanced normalised reaction rates. Additionally, deposition of the

Figure 4



Normalising electrocatalytic performance at the ITIES. (a) Apparent first-order reaction rate constants (k_{app} with a unit of 1/s) extracted in the absence and presence of the catalysts Mo₂C, MoS₂, metallic (Pt, Pd and Cu) nanoparticles, W₂C and WC, either deposited on high-surface-area carbon, as nanomaterials, as catalysts formed by electrodeposition, or as microparticles. The rate constants were normalised (b) by the mass (mg/L) of the metal ($k_{\text{app}}/m_{\text{metal}}$ with a unit of L/s/mg) and (c) the concentration (mmol/L) of the active catalyst ($k_{\text{app}}/c_{\text{catalyst}}$ with a unit of L/s/mmol). The data was extracted from references [9,16–19,21,31,32,34] and is available on Zenodo (<https://doi.org/10.5281/zenodo.7400926>) to download.

catalyst on a high-surface-area carbon leads to the highest normalised rates. This is because both hydrogen evolution and DcMfc oxidation need to take place at the

redox electrocatalyst at the same rate. The overpotential for each reaction depends on the area available for the reactions, as explained in a recent review [8]. For supported catalysts, the area available for DcMfc oxidation taking place at the support is much higher than for the HER taking place mostly at the catalyst. For unsupported particles, the areas available for both reactions can be considered similar. Therefore, the driving force will be higher on the supported catalysts, leading to higher rates.

Analysis of only the reaction rates can lead to misinterpretation of the activities. For example, Mo₂C microparticles show very different reaction rates because the catalyst concentration varied between 25 μM and 1 mM, but this difference disappears when the activities are normalised either by catalyst mass or concentration. Concentration normalised data shows slightly higher activity for Mo₂C than for MoS₂ while the difference is smaller for metal mass normalised data, as the carbide contains twice the mass of the metal.

The data also shows high variability in the reaction rates measured in the absence of catalyst. This might indicate that some chemicals, flasks or even stir bars [74] may very easily cause contamination. Therefore, the practise to compare acceleration to the uncatalysed reaction can lead to inaccurate conclusions. We highlight that carefully cleaned glassware and stir bars should be used for these experiments.

Conclusions and outlook

The diversity of reactions electrocatalysed at the ITIES remains low, with the overwhelming majority of studies pertaining to the HER and ORR, followed by more challenging OER studies [60]. Scope clearly exists to electrocatalyse other reactions that may benefit from a biphasic environment, as shown by the electrocatalytic oxidation of S₈ [35], or lead to the direct electrocatalytic oxidation of DMcT by AuNPs [36]. A particularly important reaction that is conspicuous by its absence in the literature is the carbon dioxide reduction reaction (CO₂RR) at the ITIES. A key challenge limiting the efficiency of the (photo)electrochemical CO₂RR is the low solubility of CO₂ in water at standard conditions (~ 35 mM). However, organic solvents permit higher CO₂ solubility and enable different reaction products, including value-added C₂+ hydrocarbons like oxalate [75]. Furthermore, aprotic organic solvents eliminate the competing HER, an arduous task in aqueous electrolytes [76]. Thus, biphasic systems may simultaneously harness desirable attributes of both the aqueous phase (proton source) and organic phase (inhibit H₂ evolution, increase access to C₂+ hydrocarbons, reservoir of CO₂) towards the CO₂RR. To date,

biphasic CO₂RR systems have been studied using water-miscible organic solvents, *e.g.*, acetonitrile [75,77], immiscible aqueous|organic emulsions [78] and supercritical CO₂|ionic liquid biphasic systems [79–81]. However, the benefits of polarisation of an ITIES to drive the biphasic (photo)electrochemical CO₂RR towards selective C₂+ hydrocarbon production have never been explored. Additionally, nitrogen reduction reactions should also be explored [82].

SECM is a powerful methodology to probe the redox kinetics of any (photo)electrocatalyst as a function of the applied $\Delta\phi^w$, as clearly demonstrated by the series of articles by Rastgar *et al.* to photoelectrocatalyse the OER by an interfacial film of BiVO₄ [37–39]. Thus, the further development of SECM as a key methodology to combine with (photo)electrocatalysis at the ITIES will allow the measurement of the “true” (photo)electrocatalytic activity of specific materials without interfering effects arising from interactions of the (photo)electrocatalyst with an underlying solid electrode surface, *e.g.*, contact resistance [8].

The field of bioelectrocatalysis at the ITIES is still in its infancy. Thus, studies with proteins beyond the model Cyt *c* system, such as oxidases [83] and dehydrogenases [84], are required to clarify the limitations and advantages of this new research topic. Furthermore, major scope exists to modify the liquid|liquid interface with phospholipid monolayers to enhance the biocompatibility of the ITIES and optimise IET with proteins. Electrochemical activation of a proteins’ enzymatic activities at the ITIES will open exciting new avenues to realise biofuel cell and artificial photosynthesis-based energy conversion and storage, drug screening for medical applications, and (bio)sensing.

Two-phase shake flask methods offer a quick and simple method to test the activity of powdered catalysts for different reactions. For a more careful comparison of the catalysts, the active surface area should be known. For supported catalysts, the loading of the catalyst will also have a significant effect on the measured rates. Additionally, methods to evaluate the stability of the catalysts should be developed, for example, based on electrochemical setups [67].

Declaration of competing interest

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.

Data availability

The data extracted from references [9,16–19,21,31,32,34] to prepare Figure 4 is available on Zenodo (<https://doi.org/10.5281/zenodo.7400926>) to download.

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