

Membraneless Energy Conversion and Storage using Immiscible Electrolyte Solutions

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Abstract

Breakthrough alternative technologies are urgently required to alleviate the critical need to decarbonise our energy supply. We showcase non-conventional approaches to battery and solar energy conversion and storage (ECS) system design that harness key attributes of immiscible electrolyte solutions, especially the membraneless separation of redox active species and ability to electrify certain liquid-liquid interfaces. We critically evaluate the recent development of membraneless redox flow batteries based on biphasic systems, where one redox couple is confined to an immiscible ionic liquid or organic solvent phase, and the other couple to an aqueous phase. Common to all solar ECS devices are the abilities to harvest light, leading to photo-induced charge carrier separation, and separate the products of the photo-reaction, minimising recombination. We summarise recent progress towards achieving this accepted solar ECS design using immiscible electrolyte solutions in photo-ionic cells, to generate redox fuels, and biphasic “batch” water splitting, to generate solar fuels.

Keywords

Membraneless redox flow battery; energy storage; solar energy conversion; liquid-liquid interfaces; immiscible electrolyte solutions; redox fuel; solar fuel

Introduction

The enormous scale and complexity of storing energy generated renewably means that one certain type of battery (*e.g.*, Li-ion or redox flow) or approach (*e.g.*, solar fuel generation or pumped-hydro) will never be able to fulfil the need due to element scarcity, scale-up and economic issues, safety concerns, *etc.*. The storage of energy will only be satisfied by a multitude of simultaneous approaches all serving different niches (*e.g.*, mobile *versus* large scale storage). Thus, despite its high-risk nature, the sustained exploration of approaches to battery and solar energy conversion and storage (ECS) technology beyond the conventional remains a grand scientific challenge [1–3].

A critical issue that affects the performance of redox flow batteries (RFBs) is cross-over of redox active materials and solvents. Transfer of redox species through the membrane will result in decreased capacity and self-discharge. Typical RFBs use ion exchange membranes, like Nafion. However, these membranes were usually designed for other applications with different functional requirements and, as a consequence, in RFBs lead to performance shortcomings [4]. For example, Donnan failure in highly concentrated salt solutions decreases the selectivity of the membrane [5]. The cross-over rate can be decreased by increasing the membrane thickness, but this leads to increased cell resistance [6]. Also, membranes have a significant economic cost, of up to 40 % of the stack costs [7,8]. In this review, we discuss recent progress towards the development of membraneless RFBs using immiscible electrolyte solutions [9].

We outline recent progress towards achieving solar ECS using immiscible electrolyte solutions. For example, photo-ionic cells [10] apply the theory and methodologies developed to study electrochemistry at the *interface* between *two immiscible electrolyte solutions* (ITIES) [11,12] to convert and store solar energy as redox fuels. The latter are oxidised and reduced photo-products spatially separated by an immiscible liquid-liquid interface. These redox fuels can be either discharged immediately, to generate electricity, or temporarily stored until required in a similar fashion to traditional RFBs. Another concept, known as biphasic “batch” water splitting [13], involves the design and coupling of two photo-driven half-reactions, the biphasic hydrogen evolution reaction (HER) and biphasic water oxidation reaction (WOR), to generate molecular hydrogen (H₂) as a solar fuel.

Scale-up of all the technologies discussed is feasible, not requiring complicated manufacturing processes or expensive solid-state architectures and materials, *i.e.*, separation membranes.

Furthermore, the development of enabling tools for liquid-liquid reactions is likely to increase due to the growing field of flow chemistry [13].

Membraneless batteries with immiscible electrolyte solutions

A variety of membraneless RBFs based on biphasic systems, where one redox couple is confined to an immiscible ionic liquid or organic solvent phase, and the other couple is confined to an aqueous phase have recently been proposed. The first such system was realised by Gong *et al.* in 2016 [14], employing a Zn^{2+}/Zn redox couple in the aqueous phase and the ferrocenium/ferrocene (Fc^+/Fc) redox couple in an immiscible organic phase composed of butyl acetate and “Aliquat 336” (an ionic liquid composed of a mixture of tricaprylmethylammonium chloride and trioctylmethylammonium chloride). However, this system suffered from poor Coulombic efficiency due to the partition of Fc^+ to the aqueous phase [15], and the rather high resistance of the organic phase. Since then, Navalpotro *et al.* demonstrated a biphasic system with parabenzoquinone (pBQ) in a hydrophobic ionic liquid for the negative side and the hydroquinone (H_2Q) redox couple in an aqueous HCl solution for the positive side [9], see Figure 1. A similar approach was proposed by Bamgbopa *et al.* [16], who used an iron acetylacetonate complex in a hydrophobic ionic liquid phase as the negative electrolyte and iron sulfate in aqueous K_2SO_4 solution as the positive electrolyte. Various solvents such as butanone and propylene carbonate, and different redox couples (anthraquinone derivatives for the negative side and 4-hydroxyl-TEMPO for the positive side) have also been tested [17].

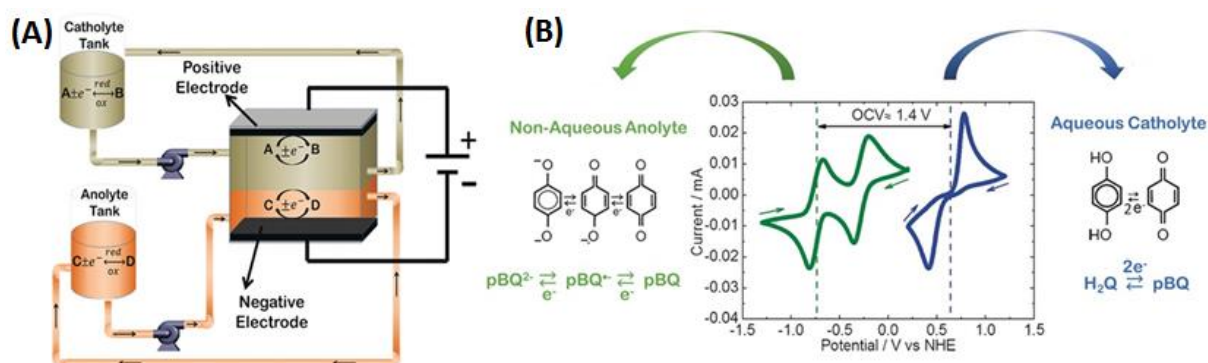


Figure 1. (A) Schematic of a membraneless redox flow battery (RFB) using immiscible electrolyte solutions. The upper aqueous electrolyte is the catholyte and the lower ionic liquid electrolyte (1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide; $PYR_{14}TFSI$) is the anolyte. (B) Cyclic voltammograms (CVs) of parabenzoquinone (pBQ) dissolved in $PYR_{14}TFSI$ (green CV) and hydroquinone (H_2Q) in 0.1 M HCl (blue CV). CVs were performed

in 3-electrode electrochemical cells at a scan rate of $10 \text{ mV} \cdot \text{s}^{-1}$, and 20 mM of the redox-active species present. This figure is reproduced with modifications from ref. [9].

Alternative approaches based on “all-aqueous” biphasic systems were proposed for biphasic energy storage. In these cases, the biphasic systems were formed from a ternary mixture of water and two phase-forming components above certain concentrations, in which the two phases were water rich. Phase forming components such as different ionic liquids/ Na_2SO_4 [18] and poly(ethylene glycol)/ Na_2SO_4 [19] have been investigated for biphasic batteries, with methyl viologen as the negative electrolyte partitioning into the Na_2SO_4 rich phase and 2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (TEMPO) as the positive electrolyte partitioning into the ionic liquid or and poly(ethylene glycol) rich phase.

The membraneless RBF systems discussed *vide supra* share some similarities with bromine flow batteries, where bromine complexing agents (typically quaternary ammonium salts) are utilised to form bromine rich fused phases containing polybromides [20]. This property can also be used to realise biphasic membraneless bromide batteries, either by utilising organic solvents [21] (as described in Figure 2A) or nitrogen doped graphite felt [22] to retain the polybromide species.

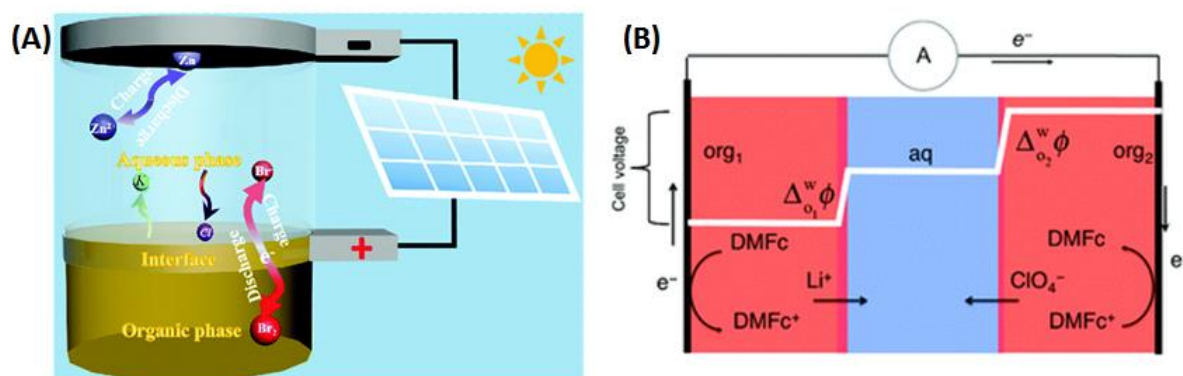


Figure 2. (A) Schematic of a biphasic battery using zinc/bromine as the redox couples. The ZnBr_2 aqueous solution serves as the negative electrolyte, while the positive electrolyte is Br^-/Br_2 in the organic phase. Reproduced from Ref. [21] with permission from The Royal Society of Chemistry. (B) Schematic of an ion transfer battery, illustrating the Galvani potential profile in the cell and the battery reactions upon discharge. DMFc refers to decamethylferrocene. The charge is stored by transferring a salt (LiClO_4) from the aqueous phase into the organic phases in ion transfer coupled electron transfer reactions. Reproduced from Ref. [23] with permission from The Royal Society of Chemistry.

Peljo *et al.* designed a battery based on ion transfer between immiscible electrolytes to store charge [23]. The system consisted of two liquid-liquid interfaces formed using two organic

electrolytes separated by an aqueous electrolyte. The aqueous electrolyte simply contained a salt (lithium perchlorate, LiClO_4), whereas both organic phases contained a lipophilic redox couple, decamethylferrocenium/decamethylferrocene ($\text{DMFc}^+/\text{DMFc}$) with very limited solubility in the aqueous phase. During charging/discharging of the ion transfer battery, oxidation and reduction of the $\text{DMFc}^+/\text{DMFc}$ redox couple was linked with an ion transfer reaction to maintain electroneutrality in each organic phase, see Figure 2B outlining the operating principle. The interfacial Galvani potential difference ($\Delta_0^W \phi$) across one interface was controlled by the partition of Li^+ , at ca. 0.55 V, while the other interface was polarised by ClO_4^- at ca. -0.2 V, resulting in a cell voltage of ca. 0.8 V [23]. Both the redox reactions of the $\text{DMFc}^+/\text{DMFc}$ couple and the ion transfer reactions are facile and reversible, requiring low overpotential. Furthermore, the cycling of the battery was achieved with a Coulombic efficiency of ca. 100% and energy efficiencies up to 80%. However, the cycling stability was limited by evaporation of the organic solvents [23].

Solar energy conversion and storage with immiscible electrolyte solutions

(i) Photo-ionic cells

Photo-ionic cells were inspired by photogalvanic cells in a biphasic configuration [24–27]. A photoreaction between photo-excited dye (D) and quencher (Q) redox couples takes place in one bulk electrolyte solution. The hydrophobicity gradient at the ITIES enhances charge separation and minimises recombination by spatially separating the resulting photoproducts, with one photoproduct transferring to the adjacent electrolyte. To date, studies have focussed on homogeneous aqueous reductive quenching followed by extraction of a neutral dye to an immiscible organic electrolyte solution, either 1,2-dichloroethane (DCE) or propylene carbonate (PC), see Case (i) in Figure 3A [10,28,29]. However, several other system configurations for photo-ionic cells are possible and yet to be exploited (Figure 3A). After separation of the phases, the redox fuels, e.g., Q^{2+} and D for Case (i), can be stored and then converted to electricity on demand by electrochemical discharge in a biphasic fuel cell (Figure 3B).

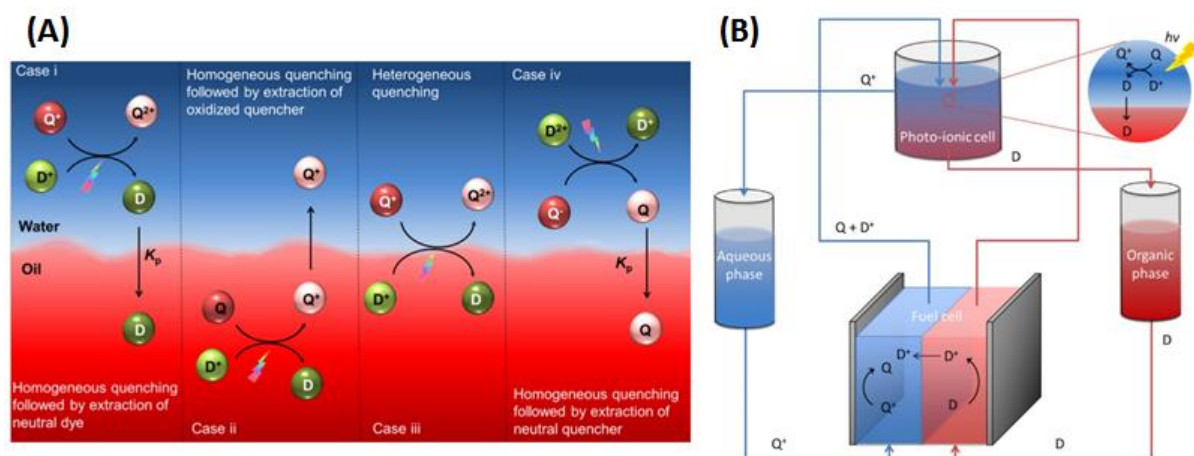


Figure 3. Solar energy conversion and storage with a photo-ionic cell. **(A)** Possible system configurations for a photo-ionic cell. D refers to dye and Q refers to quencher. **(B)** Photo-charging the redox electrolytes and a fuel cell recovering the energy as electricity. Reprinted from ref. [29] with permission from Elsevier.

The $[\text{Co}^{\text{III}}\text{EDTA}]^-/[\text{Co}^{\text{II}}\text{EDTA}]^{2-}$ redox couple, originally proposed for photogalvanic cell studies [24], has also been used as the quencher in recent photo-ionic cell experiments. This is primarily due to its stability at neutral to mildly basic pH conditions ($\text{pH} < 9$), optimal pH conditions to neutralise dyes belonging to the phenothiazine family, such as thionine (Th) and Azure B. These dyes exhibit characteristics representative of an ideal chromophore to achieve maximum quantum yields in a photo-ionic cell [10,28,29]. Both Th and Azure B have a high molar absorptivity and long triplet excited state lifetime (tens of microseconds). The latter depends on the solution pH and significantly reduces upon dye aggregation [28]. Practical energy storage densities require the dye concentration to be maximised while preventing dye aggregation. For a system based on reductive quenching of Azure B by $[\text{Co}^{\text{II}}\text{EDTA}]^{2-}$, Bourdon *et al.* demonstrated that the presence of chaotropic agents that break the structure of water, such as urea, minimised the extent of dye aggregation leading to an order of magnitude increase in the quantum yield [28]. In a separate study employing ITIES methodologies and molecular modelling, Peljo *et al.* highlighted that the presence of chaotropic agents was found to enhance the solvation of a series of phenothiazine dyes in the aqueous phase [30]. An additional $2 - 3 \text{ kJ} \cdot \text{mol}^{-1}$ was required to transfer the ionic form of the dyes (D^+) to the organic phase [30], impacting the design of the photo-ionic cells. Furthermore, recently a flow battery utilizing a 1.5 M solution of phenothiazine dye has been demonstrated, indicating that practical dye concentrations could indeed be achievable [31].

Finite element simulations of the efficiency of the photo-ionic cell and photo-reduced dye extraction by Méndez *et al.* revealed that the neutral dye's partition coefficient should optimally be >100 [10]. Unfortunately, the partition coefficients of neutral leucothionine and leuco-Azure B to DCE or PC solvents are ca. 15 [10] and <10 [29], respectively. Simulations also indicated that efficient photoconversion requires the photoreaction to preferably take place very close to the liquid–liquid interface. Experimentally this necessitates the interfacial surface area to be maximised, for example by dispersion of organic phase into small droplets [28,32] or creating micro-emulsions [33,34].

The partition of ionic species across the liquid-liquid interface can be suppressed or enhanced electrochemically [11,12]. Thus, photo-ionic cells should be designed to take advantage of polarising the ITIES by varying $\Delta_o^w \phi$. The latter has a dual-role to (i) control the partition of ions during the photoreaction and (ii) boost the biphasic fuel cell voltage. $\Delta_o^w \phi$ may be varied by distribution of a common ion (*i*) between both electrolyte solutions. For instance, with a common cation C^+ in both the aqueous (w) and organic (o) phases [11]:

$$\Delta_o^w \phi = \Delta_o^w \phi_{C^+}^{\ominus'} + \frac{RT}{z_i F} \ln \left(\frac{c_{C^+}^o}{c_{C^+}^w} \right) \quad (1)$$

Assuming C^+ is equally distributed between both phases ($c_{C^+}^o = c_{C^+}^w$), then $\Delta_o^w \phi$ is equivalent to the formal ion transfer potential of C^+ , $\Delta_o^w \phi_{C^+}^{\ominus'}$. To comprehensively determine $\Delta_o^w \phi$, the equilibrium interfacial concentrations of all species present in the biphasic system, and their dynamic variation with time, should be considered [35]. However, the simple use of Equation (1) is accurate once the common ion is in excess over other species.

Ideally, to maximise photoproduct separation efficiency, Q^+ , Q^{2+} and D^+ in Case (i) should all remain in the aqueous phase. In this regard, polarisation of the ITIES negatively, through distribution of a common ion with a negative standard ion transfer potential ($\Delta_o^w \phi_i^{\ominus}$), such as tetrabutylammonium (TBA^+ , $\Delta_{DCE}^w \phi_{TBA^+}^{\ominus} = -0.280$ V) or tetrahexylammonium ($THxA^+$, $\Delta_{DCE}^w \phi_{THxA^+}^{\ominus} = -0.470$ V) cations [36], has been demonstrated to be highly effective [10,28,29]. The biphasic fuel cell voltage for Case (i) is defined as [29]:

$$E = \left(\left[E_{Q^{2+}/Q^+}^{\ominus'} \right]_{SHE}^w + \frac{RT}{nF} \ln \left(\frac{c_{Q^{2+}}^w}{c_{Q^+}^w} \right) \right) - \left(\left[E_{D^+/D}^{\ominus'} \right]_{SHE}^o + \frac{RT}{nF} \ln \left(\frac{c_{D^+}^o}{c_D^o} \right) \right) + \left(\Delta_o^w \phi_i^{\ominus'} + \frac{RT}{z_i F} \ln \left(\frac{c_i^o}{c_i^w} \right) \right) \quad (2)$$

where $\left[E_{Q^{2+}/Q^+}^{\ominus'} \right]_{SHE}^w$ and $\left[E_{D^+/D}^{\ominus'} \right]_{SHE}^o$ are the formal redox potentials of the quencher (Q^{2+}/Q^+) and dye (D^+/D) redox couples in the aqueous and organic phases, respectively, on the standard hydrogen electrode (SHE) scale, and i is the common ion. This expression can be simplified to:

$$E = E_w - E_o + \Delta_o^w \phi = \Delta E_{w-o} + \Delta_o^w \phi \quad (3)$$

where E_w and E_o are the Nernst potentials of the aqueous (Q^{2+}/Q^+) and organic (D^+/D) redox couples, respectively.

Ideally, to maximise the biphasic fuel cell voltage, ΔE_{w-o} should be as large as possible and the ITIES should be polarised positively. However, a compromise is required since increasing ΔE_{w-o} also increases the driving force for recombination. Furthermore, for Case (i), another compromise exists between maximising photoproduct separation efficiency (favoured by negative polarisation) or the biphasic fuel cell voltage (favoured by positive polarisation). A study by Vladimirova *et al.* of the influence of the applied $\Delta_o^w \phi$, compared the performance of photo-ionic cells prepared with different organic solvents, DCE and PC [29]. The water-DCE interface is polarisable and thus a negative $\Delta_o^w \phi$ can be applied. Conversely, the water-PC interface is non-polarisable and $\Delta_o^w \phi \approx 0$ V since mutually saturated water and PC solvate ions very similarly. Under otherwise identical experimental conditions, the maximum biphasic cell voltage and kinetics of the photoreaction improved with the non-polarisable water-PC system. The rapid separation of the two phases after emulsion formation, by stopping the vigorous stirring of the biphasic system, is another critical step to minimise photoproduct recombination. However, the latter was much slower for the water-PC system [29]. Further investigations are required to find alternative solvents that exhibit a $\Delta_o^w \phi$ approaching 0 V, yet facilitate rapid separation after the photoreaction. The latter may be achieved by the presence of additives in the aqueous or organic phase. As an example, the addition of excess electrolyte salt to an aqueous phase results in normally miscible biphasic systems, such as water and acetonitrile,

becoming immiscible [37,38]. Indeed, Marken and co-workers [37] demonstrated that ultrasonic agitation can be employed to produce unstable acetonitrile | aqueous 2 M NaCl emulsions which rapidly separate upon cessation of agitation.

(ii) Biphasic “batch” water splitting

Illustrated in Figure 4A is a conceptual membraneless biphasic approach to photo-driven water splitting. This approach overcomes problems encountered at solid electrode/liquid interfaces, such as corrosion [39,40]. Two separate biphasic compartments are designed, one carrying out the photo-driven WOR in the presence of a recyclable electron acceptor “A” in the organic phase and the other carrying out the photo-driven HER with a reversible electron donor (D) in the organic phase. The reversible redox natures of “A” and “D” are the key as, in theory, both photosystems will be “reset” by mixing the oil phases after photo-irradiation (*i.e.*, $D^+ + A^- \rightarrow D + A$) [39,40]. To date, the chemistry underpinning each biphasic compartment has been studied separately.

In a series of articles, Rastgar *et al.* [41–43] achieved the biphasic photo-driven WOR by assembling hyperbranched bismuth vanadate (BiVO₄) semiconductor nanostructures at a water-butyrone nitrile interface. As per the scheme in Figure 4B, oxidative quenching was achieved by an oil-soluble Co^(III) complex, [Co(bpy)₃](PF₆)₃, *via* interfacial photo-induced electron transfer (ET) from the conduction band of BiVO₄. The latter was simultaneously coupled with hole-transfer from the valence band of BiVO₄ to the water molecules, liberating molecular oxygen. The kinetics of interfacial photo-induced ET were probed by recycling the electrochemically reversible Co^(III)/Co^(II) species at the tip of a microelectrode immersed in the organic phase using an *in situ* scanning electrochemical microscopy (SECM) configuration. Previously, Li *et al.* [44] demonstrated that SECM represents a significant step forward in overcoming the resistive, capacitive and sluggish mass transport issues that limit the kinetic resolution of interfacial photo-induced ET studies at macro-sized (>millimetre) liquid-liquid interfaces in a 4-electrode configuration. Recent progress in the area of local studies of photoelectrochemical reactions using a variety of scanning probe setups has been reviewed by Wittsock *et al.* [45]. Rastgar *et al.* [42] clearly demonstrated that the kinetics of interfacial photo-induced electron transfer can be tuned, in accordance with Equation (1), by varying $\Delta_o^W \phi$ through adjustment of the concentration ratio of the common ion (ClO₄⁻ in their case).

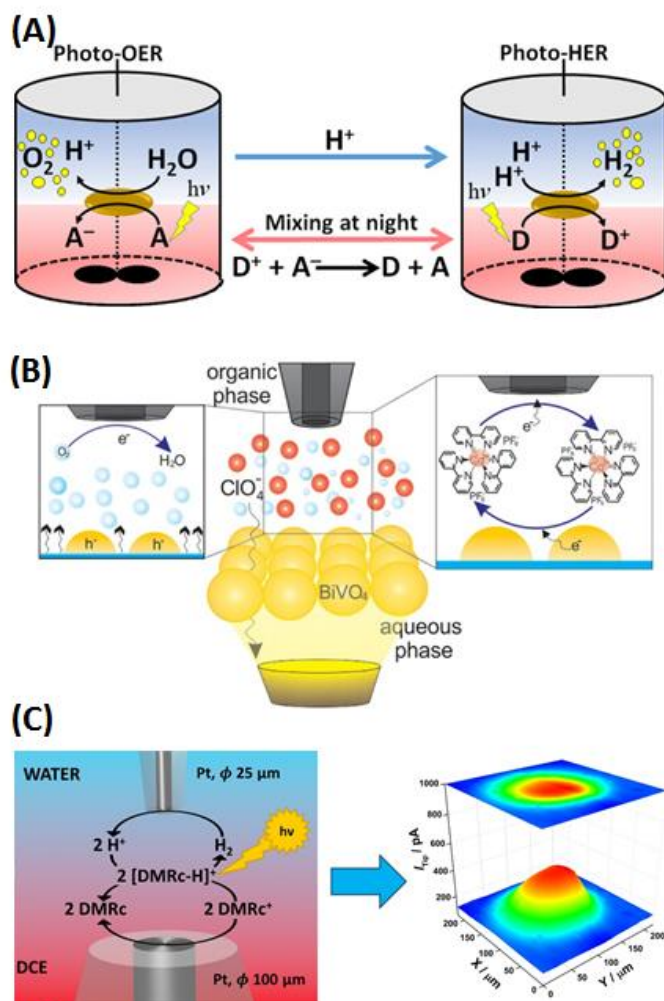


Figure 4. (A) Schematic of biphasic “batch” water splitting. A is a recyclable electron acceptor that is photo-reduced to oxidise water in the anodic compartment, and D is a recyclable electron donor photo-oxidised to reduce protons in the cathodic compartment. This figure has been reproduced with permission from ref. [39]. (B) Schematic of the photo-driven biphasic water oxidation reaction (WOR) at BiVO_4 nanoparticles assembled at a polarised liquid–liquid interface. The kinetics of the photocatalytic reaction (recycling of the $[\text{Co}(\text{bpy})_3]^{3+/2+}$ redox couple on the BiVO_4 nanoparticle surface) were probed by scanning electrochemical microscopy (SECM). Reproduced with permission from ref. [42] Copyright 2017 American Chemical Society. (C) Schematic of the photo-driven biphasic hydrogen evolution reaction (HER) at a polarised liquid-liquid interface using photo-excited decamethylruthenocene (DMRc) as the electron donor. SECM demonstrated that DMRc regeneration, by electro-reduction of DMRc^+ at the microelectrode in the organic phase, resulted in an increase in hydrogen photogeneration, determined by electro-oxidation of hydrogen at the microelectrode in the aqueous phase. Reprinted from ref. [46] with permission from Elsevier.

Girault and co-workers identified the decamethylruthenocenium/decamethylruthenocene ($\text{DMRc}^+/\text{DMRc}$) redox couple as a suitable candidate to act as D^+/D in a biphasic photo-driven HER system [39,47,48]. DMRc is capable of reducing organic protons through a photoactive hydride intermediate ($[\text{DMRc-H}]^+$). Importantly, due to the photoactivation of the hydride

intermediate, DMRC evolves hydrogen at an appreciable rate despite being a weak reductant; $\left[E_{\text{DMRC}^+/\text{DMRC}}^{\ominus'}\right]_{\text{SHE}}^{\text{DCE}} = 0.750 \text{ V}$. The relatively positive reduction potential of DMRC is key to ensure A^- can successfully regenerate D^+ upon mixing of the organic phases. Indeed, based on their formal reduction potentials, DMRC^+ will be reduced by $[\text{Co}(\text{bpy})_3]^{2+}$, $\left[E_{[\text{Co}(\text{III})(\text{bpy})]^{3+}/[\text{Co}(\text{II})(\text{bpy})]^{2+}}^{\ominus'}\right]_{\text{SHE}}^{\text{DCE}} = 0.594 \text{ V}$ [49]. A crucial finding by Rivier *et al.* was a set of experimental conditions to stabilise DMRC^+ on a time-scale sufficient to permit its electrochemical regeneration [48]. Furthermore, Jedraszko *et al.* illustrated the suitability of DMRC towards continuous biphasic photo-driven hydrogen production by positioning a water-DCE interface between two platinum microelectrodes, one in each phase and both in close proximity to the ITIES [46], see Figure 4C. Using a bi-potentiostatic SECM configuration, DMRC was constantly regenerated by reduction of DMRC^+ at the tip of the oil-based microelectrode and photo-evolved hydrogen was detected by its oxidation at the tip of the water-based microelectrode. Other metallocenes were identified that photo-evolve hydrogen through a photoactive hydride intermediates, such as osmocene (Oc) [50] and decamethylsmocene (DMOc) [51], but ultimately deemed unsuitable for biphasic “batch” water splitting. Osmocene is a weak reductant $\left[E_{\text{Oc}^+/\text{Oc}}^{\ominus'}\right]_{\text{SHE}}^{\text{DCE}} = 1.03 \text{ V}$ [50], capable of being regenerated by A^- . However, the quantities of hydrogen evolved with Oc were very low. Meanwhile, substantial quantities of hydrogen were evolved with DMOc upon photo-activation. However, DMOc is a stronger reductant, $\left[E_{\text{DMOc}^+/\text{DMOc}}^{\ominus'}\right]_{\text{SHE}}^{\text{DCE}} = 0.480 \text{ V}$ [51], and incapable of being regenerated by A^- .

Conclusions and future directions

Some of the membraneless RBF systems discussed in this review show reasonable or even excellent cell voltages of $> 2 \text{ V}$, and reasonable solubility's of redox species of $> 0.1 \text{ M}$ can be obtained. However, all of these systems share similar problems currently limiting their widespread adoption. Current and power densities are almost one order of magnitude lower than obtained from state-of-the-art RBFs, mostly due to the high resistance of the system. The latter is due to the poor ionic conductivity of the non-aqueous phase or the ionic liquid/polymer rich phase in the case of aqueous biphasic systems, leading to high Ohmic losses. Also, partitioning of ions and interfacial electron transfer between the aqueous and organic redox

pairs leads to self-discharge and lower Coulombic efficiencies. Currently, no information is available regarding the partition of the redox species in their charged states. This needs to be determined and optimised to reduce the rate of self-discharge, for example by employing polarisable liquid-liquid interfaces and establishing a distribution potential with a common ion. Solubility studies are yet to be performed in detail. Such studies are crucial since the energy storage density will depend on the solubility's of the redox compounds. Investigations of the effect of additives such as hydrophobic salts may improve the systems conductivity, but may affect the phase composition and will increase the cost. Aqueous biphasic systems are one interesting research direction, if they can be prepared from inexpensive components. Still, both power and energy storage densities need to be significantly improved to reach reasonable performance. The cost issues and practical aspects require careful evaluation to see whether further development of the biphasic flow batteries can offer practical solutions for energy storage.

Future work is required to design photo-ionic cells incorporating multiple dyes, each absorbing a different portion of the electromagnetic spectrum, are required. Furthermore, for practical energy storage and power densities, synthetic dyes with 2 – 3 orders of magnitude higher solubility compared with phenothiazine dyes are required. Another issue is the need to replace the current volatile, and even toxic (*e.g.*, DCE), organic phase with alternatives. Finally, research into the biphasic “batch” water splitting concept has now reached a threshold where the optimised chemistries for both photo-driven biphasic half-reactions, the WOR and HER, respectively, need to be incorporated into a single prototype system for rigorous testing as a viable approach to solar fuel generation.

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