



Solvent effect in photo-ionic cells

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ABSTRACT

Photo-ionic cells convert solar energy into redox fuels. Unlike in photovoltaic devices where the photo-induced charge transfer reactions occur at an electrode, the photoreaction takes place in one bulk solution of a biphasic liquid-liquid system, and the charge separation is realised by the transfer of one of the photoproducts into the adjacent phase to avoid recombination. After separation of the two phases, the redox fuels can be stored and then converted to electricity on demand with a biphasic fuel cell. Here, we compared the effect of the two organic solvents, 1,2-dichloroethane and propylene carbonate, on the performance of the photo-ionic cell. By replacing 1,2-dichloroethane, the maximum cell voltage was increased to 0.6 V. Additionally, propylene carbonate helps to reduce aggregation of dyes and it shows faster kinetics for the photoreaction.

1. Introduction

Solar energy conversion is one of the global challenges for a sustainable economy. At present, two major routes are being followed: photovoltaic (PV) systems to generate electricity [1] and solar thermal collectors to generate heat [2]. State-of-the-art semiconductor based PV cells can reach conversion efficiencies of 20 to even 30% [1], and dye-sensitized solar cells can reach conversion efficiencies of 11 up to 14% [3–5] at the laboratory scale. However, all PV technologies must immediately distribute the produced electricity either to a storage system or to the electrical grid, irrespective of demand. A common electricity storage in mountain regions like Switzerland is pumped-hydro, where excess electricity is used to pump water to reservoirs located in high areas [6]. The electricity is then regained as hydropower with a turn-around yield of about 80%. This, however, is unpractical in many parts of the world. An upcoming strategy is based on the use of Megawatt batteries, either solid state like Li-Ion [6] or redox flow such as the all Vanadium redox flow battery [7–10].

Another strategy is to directly produce solar fuels. Various concepts have been proposed, like photo-biological solar fuel production with different micro-organisms [11], artificial photosynthesis in molecular systems [12–14] and solar fuel production in nanostructured and semiconductor based systems [12,15–17], as well as solar energy harvesting utilizing PV cells coupled with electrolysis [18]. The energy harvesting from biomass suffers from losses in the cellular metabolism, and transforming the produced biomass into energy is far from simple. Alternative approaches have been proposed to utilize different micro-organisms to generate hydrogen or carbon sources directly from solar

energy, but these methods are not yet commercially viable [11]. Artificial photosynthesis and solar fuel production by nanostructured and semiconductor based systems are both rather difficult and requires highly demanding procedures for synthesis of catalysts or for preparation of nanostructured platforms [12,15–17], so scale-up of these systems is even more challenging and the impact of photocatalytic systems has been limited [19]. This clearly demonstrates that alternatives are needed.

Alternative routes for electrochemical solar energy harvesting have been proposed. Chief among these is the photogalvanic approach, where a photoinduced electron transfer reaction occurs in the bulk of an electrolyte solution sandwiched between two electrodes [20,21]. This approach was pioneered by Rabinowitch et al. [22–25] and Albery et al. [20,26–28]. Photogalvanic cells have been recently reviewed by Halls et al. [29]. Briefly, a photoinduced electron transfer reaction occurs not at an electrode but in the bulk of an electrolyte solution between two electrodes to collect the current from the photoproducts. It represents an alternative strategy to photovoltaic cells based on photoelectrochemistry, as in a photogalvanic cell the photochemical reaction is coupled to two classical dark electrochemical reactions. In the case of a reductive quenching, the reduced sensitizer and the oxidized quencher diffuse to the electrodes to be oxidized and reduced, respectively. Here, the recombination is avoided mainly by kinetic factors, setting up concentration gradients. Albery et al. have shown that an optimum efficiency of 18% is theoretically possible [27], albeit never experimentally achieved with most reported systems operating at an efficiency below 1% [20,21]. Photosystems comprising an aqueous dye, such as thionine (Th^+), and an aqueous redox quencher, such as Fe(II)

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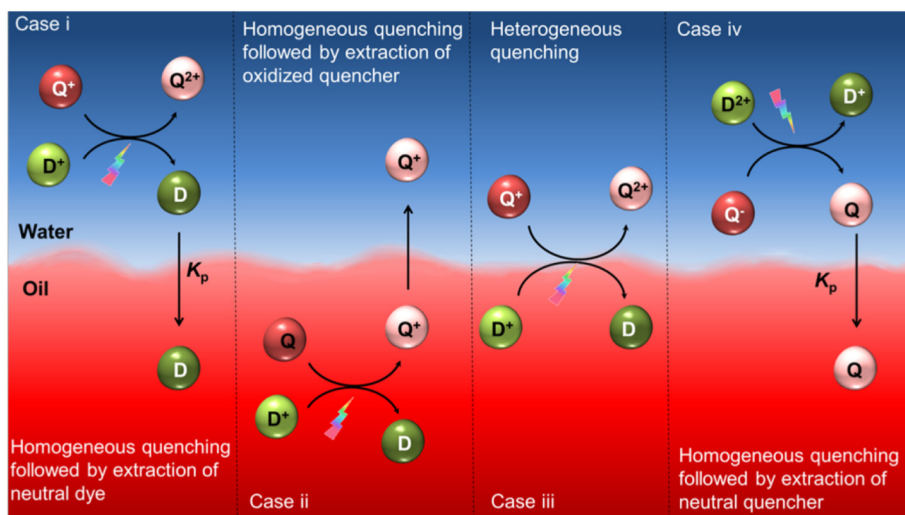


Fig. 1. Possible system configurations for photo-ionic cell. D refers to dye and Q refers to quencher.

have been investigated as early as 1940 as a photogalvanic cell [22,23]. Charge storage has been achieved by precipitation of Fe(III) produced in the photoreaction, or by charge separation at the interface between two immiscible electrolyte solutions. In 1962, Rabinowitch et al. showed that if the photoreaction is carried out in a biphasic water–ether emulsion, the reduced dye is extracted to the organic phase, while the oxidized quencher remains in the aqueous phase [24]. In 1970, the same authors showed that if the aqueous redox quencher is [Co(II)EDTA]²⁻, then a 54% separation of the photoproducts is possible when working at pH 7.2 [25]. Much of the later work has been focused on using irreversible quenchers, i.e. performing photo-assisted combustion of organic molecules [21,29]. However, this approach is not sustainable, as the system cannot be cycled.

Surfactants can be used to improve the separation of the photoproducts, as shown for example by Grätzel [30,31]. In general, photogalvanic systems containing a surfactant produced higher relative values for photocurrent, photopotential, and conversion efficiency than systems without surfactants. Fendler et al. [32] and Atwood et al. [33] have attributed this to the ability of a surfactant to solubilize certain molecules (i.e. the photosensitizing dye) and the catalytic effect that carefully chosen surfactants induce on particular chemical reactions. Furthermore, Rohatgi-Mukherjee et al. theorized that addition of a surfactant into a photogalvanic system increases conversion efficiency via facilitating the separation of photogenerated products by hydrophobic-hydrophilic interaction of the products with the surfactant interface [34]. More recently, Halls et al. have presented a photogalvanic cell based on lyotropic liquid crystal layers entrapping a sensitizer. In this lamellar biphasic approach, a 2% efficiency was demonstrated [35].

We have recently revisited this concept for solar energy storage, photogalvanic cells, using methodologies developed to study electrochemistry at Interfaces between Two Immiscible Electrolyte Solutions (ITIES) [36,37]. Instead of homogeneous solutions or surfactants, we proposed charge separation by transfer of the photoproducts into adjacent phases, and we have named these systems photo-ionic cells [38,39]. Here, the partition of ionic species across the liquid-liquid interface can be controlled electrochemically. The operating principle is that solar energy is converted to redox fuels that are separated into different phases to prevent recombination. The redox fuels can then be converted to electricity when needed, and the process is also producing heat. As the technology does not require complicated manufacturing processes or expensive materials, it could be easy to scale up. We have demonstrated the relevance of polarised ITIES for the charge separation processes for the Th⁺-[Co(II)EDTA]²⁻ system. Thanks to the long

triplet excited state lifetime of thionine (ca. 20 μs) and an appreciable partition coefficient of neutral HTh between water and DCE (ca. 15), 86% of the reduced dye could be extracted in a biphasic system under vigorous stirring [38]. Also, we have optimized the system by exploring other dyes of the phenothiazines family and have reached a quantum yield of 13.8% (moles of reduced dye produced/moles of photons absorbed) with Azure B as chromophore when utilizing urea as a chaotrope to reduce aggregation of the dyes [39]. We have identified, experimentally and theoretically, the photophysical properties of the chromophores (i.e. molar absorptivity, excited triplet state lifetime, aggregates formation, etc.), the hydrophobicity of the photoproducts, the solubility of the light absorber in the aqueous phase and the potential difference across the interface as the main factors affecting the efficiency of the charge separation [38–40]. To maximize the interfacial surface area available for the transfer of photo-products, dispersion of organic phase into small droplets [39,40] or micro-emulsions has been proposed [41,42]. Recently, amphiphilic mesoporous grapheme was proposed as an efficient material to immobilize dye molecules for photoredox reactions [43]. This approach allows replacement of the organic solvent with a solid material in a system where cationic Azure B dye is trapped by the negatively charged amphiphilic mesoporous grapheme by electrostatic interactions [43]. Dye modified mesoporous grapheme was shown to photoreact with Co(II)EDTA, allowing approximately 100% separation of the reduced dye [43].

Currently, photo-ionic cells with extraction of the neutral dye have been investigated, but other configurations are possible as shown in Fig. 1. In all the cases presented, the Galvani potential difference can be used both to control the partition of ions and to boost the cell voltage, and this has to be taken into account when designing a photo-ionic system.

For conversion of the produced redox fuels into electricity, we have recently proposed a new concept for charge storage in liquid batteries, where the charge is stored as the energy required to transfer a salt (e.g. LiClO₄) from an aqueous phase into organic phases [44]. The system consists of two organic phases separated by an aqueous electrolyte. Both organic phases contain a redox couple that is almost insoluble in the aqueous phase. Oxidation and reduction of this redox couple is coupled with an ion transfer reaction to maintain the electroneutrality of the phases. The Galvani potential across one interface is controlled by the partition of Li⁺, at ca. 0.55 V while the other interface is polarised by ClO₄⁻ at ca. -0.2 V, resulting in secondary battery with a cell voltage of ca. 0.8 V [44]. The combination of the photo-ionic cell with a fuel cell is shown schematically in Fig. 2.

Photo-ionic systems have nevertheless some serious drawbacks, like

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