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A Bio-Inspired, Small Molecule Electron-Coupled-Proton Buffer for Decoupling the Half-Reactions of Electrolytic Water Splitting

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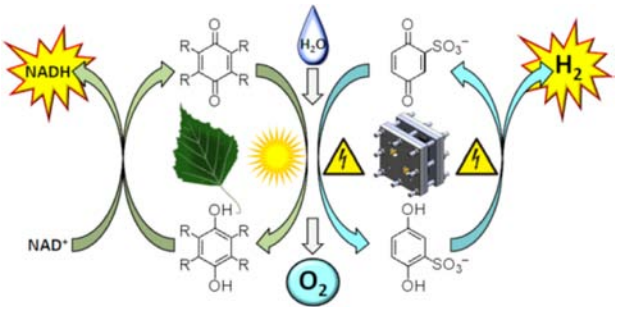
Supporting Information

ABSTRACT: Electron-coupled-proton buffers (ECPBs) allow H_2 and O_2 evolution to be separated from each other in time during the electrolysis of water. Natural photosynthetic systems achieve an analogous feat during water splitting and employ a range of intermediate redox mediators such as quinone derivatives to aid this process. Drawing on this natural example, we show that a low molecular weight quinone derivative is capable of decoupling H_2 evolution from O_2 evolution at scale during electrochemical water splitting. This work could significantly lower the cost of ECPBs, paving the way for their more widespread adoption in water splitting.

Hydrogen has great potential as a clean fuel and energy storage medium in the putative "hydrogen economy".[1] Currently, however, the majority of the world's H_2 is produced by the reformation of fossil fuels, which is neither sustainable nor environmentally friendly.[2] An alternative and sustainable source of H_2 is water, via electrolysis driven by renewable power inputs such as wind and solar.[3] If this approach is to become more widespread, it must be made more economical, and hence there is an imperative to investigate new paradigms in electrolytic H_2O splitting and electrolyzer design.[4]

Recently, we introduced the concept of the electron-coupled-proton buffer (ECPB), which allows H_2 and O_2 to be produced at separate times during electrolytic water splitting.[5] By decoupling the oxygen-evolving reaction (OER) from the hydrogen-evolving reaction (HER) in this way, it may prove possible to replace (or significantly improve the lifespan of) Nafion in proton electrolyte membrane electrolyzers, with implications for the durability and price of such devices.[6] Likewise, decoupling the OER and HER gives greater flexibility over when, and how fast, the products of water splitting are made. In an ECPB electrolysis cell, water is oxidized at the anode to give O_2, protons, and electrons. At the cathode, these protons and electrons are used to reversibly reduce and protonate the ECPB (instead of making H_2 directly), meaning that no H_2 is produced during the water oxidation phase. Subsequently, the reduced and protonated ECPB (hereafter termed ECPB*) is reoxidized, regenerating oxidized ECPB and releasing protons and electrons which combine at the cathode to give H_2 that is completely free of O_2. This train of events is summarized in Scheme 1 and Figure 1. In our initial study,[5] we used the all-inorganic polyoxometalate phosphomolybdic acid ($H_3Mo_{12}PO_{40}$, MW > 1800 g mol^{-1}) as an ECPB but noted that ECPBs with lower molecular weights and based on more abundant elements would be beneficial. However, given the demands required of an effective ECPB (an appropriately positioned reversible redox wave, high solubility in water, stability in both oxidized and reduced forms, ability to buffer the pH during water splitting, and low cost of the components), it was far from obvious that the concept could be extended beyond the polyoxometalates. Herein, we show that quinones can be used as ECPBs, combining the requisites listed above with low molecular weight (MW), abundance of the components, and production on an industrial scale, features which are essential if the promise of ECPB-mediated water splitting is to be realized.

Scheme 1. Analogies between Natural Water Splitting during Photosynthesis (Green Cycle) and an Artificial ECPB-Mediated Water Splitting Cycle (Blue Arrows)



Quinone derivatives, such as plastoquinone and coenzyme Q10, are known to act as mitochondrial redox carriers in the photosynthetic electron transport chain in bacteria and green plants.[7] They,[8] and other biomimetic redox mediators,[9] have also recently been used as redox-active components in the electrolyte of dye-sensitized solar cells. Plastoquinone accepts electrons from Photosystem II during water oxidation and protons from the chloroplast stromal matrix, such that an initially oxidized benzoquinone derivative undergoes a reversible two-electron, two-proton-transfer process to form a reduced hydroquinone. These electrons and protons stored on the hydroquinone are then ultimately used to generate H_2 equivalents in the form of NADH (Scheme 1).[10−12] Inspired by these natural examples, we hypothesized that water-soluble quinone derivatives could function as low MW, organic ECPBs in electrolytic cells, allowing effective decoupling of the OER from the HER.

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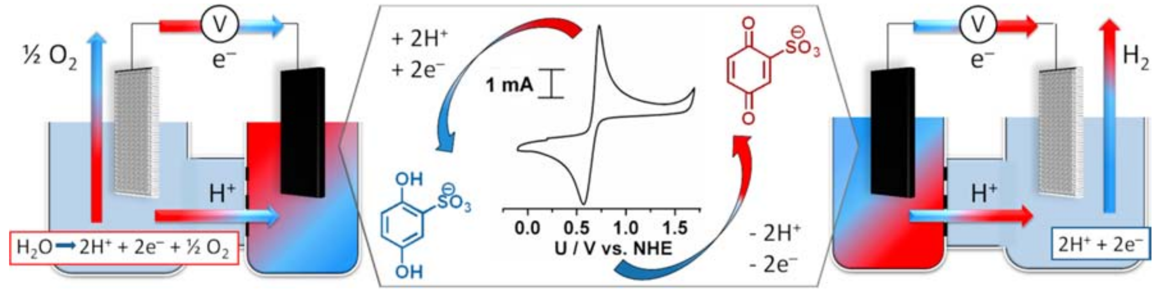

Figure 1. ECPB-mediated H_2O splitting with decoupled OER and HER. The colorless hydroquinone (shown in blue) is oxidized at a carbon electrode (black rectangle) to form the red benzoquinone. During this process, two protons and two electrons are released per hydroquinone molecule (right). The protons migrate across the membrane, while the electrons pass through the external circuit. The protons and electrons recombine on the Pt electrode (gray rectangle) to form H_2. When the process is reversed, H_2O is oxidized to give O_2, protons, and electrons on the Pt electrode. The H^+ and electrons are used to reduce and protonate the benzoquinone, re-forming the hydroquinone. Cyclic voltammetry (center) shows a 10 mM solution of the hydroquinone sulfonate in 1.8 M H_3PO_4 (pH 0.7), at a modified glassy carbon working electrode (area 0.071 cm^2), using Pt counter and Ag/AgCl reference electrodes at a scan rate of 0.1 V s^{-1}.

Herein we show that the commercially available 1,4-hydroquinone derivative potassium hydroquinone sulfonate is suitable as an ECPB. The 1,4-hydroquinone precursor is manufactured by oxidative cleavage of diisopropylbenzene, oxidation of aniline, or hydroxylation of phenol on a scale of 40 000−50 000 tons annually.[13] By aromatic sulfonation, a sulfonic group can be added to the aromatic ring system such that both the reduced hydroquinone sulfonate and the oxidized benzoquinone sulfonate are very water-soluble. This allows access to suitably high concentrations of the ECPB in aqueous solutions (0.5 M).

An effective ECPB should have a reversible redox wave between the OER and HER onsets and should attenuate the large fluctuations in pH which would otherwise arise as a result of water oxidation and proton reduction being decoupled from one another.[5] The parent 1,4-hydroquinone/*p*-benzoquinone redox couple lies at around +0.7 V (vs NHE) under standard conditions,[14] and cyclic voltammetry (see the center of Figure 1) shows that the redox couple of the sulfonate derivative used in this work is at +0.65 V (all three-electrode potentials vs NHE) in 1.8 M H_3PO_4 at pH 0.7 on a modified glassy carbon electrode.[15] The peak current for this wave increases linearly with the square root of the scan rate (see Supporting Information, Figure S1), indicating a solution-phase process that is limited by diffusion effects.

The efficacy of hydroquinone sulfonate as an ECPB was then probed by examining the voltages required to produce a given current density in the ECPB electrolysis cell. To be able to study both oxidations and reductions of the ECPB under conditions where both forms were present at high concentrations, a 0.5 M solution of hydroquinone sulfonate in 1.8 M H_3PO_4 (pH 0.7) was oxidized until a statistical 50:50 mix of the oxidized and two-electron-reduced states (hereafter termed ECPB/ECPB*) had been produced.[16] The low pH was found necessary in order to ensure adequate reversibility in the redox wave (Figures S2−S10). Figure 2 shows how the current densities obtained in a three-electrode configuration at a Pt working electrode in 1.8 M H_3PO_4 compare with the current densities that can be achieved at a glassy carbon electrode in an ECPB/ECPB* solution (see Supporting Information for details). At a benchmark current density of 50 mA cm^{-2}, Figure 2a shows that reduction of ECPB to ECPB* on glassy carbon will proceed at 50 mA cm^{-2} when a bias of +0.23 V is applied, while −0.39 V is required to reduce protons to H_2 on Pt at this current density. Conversely, Figure 2b shows that the oxidation of the ECPB* on a glassy carbon proceeds at +0.90 V, whereas the oxidation of water on a Pt electrode at 50 mA cm^{-2} requires +2.23 V.

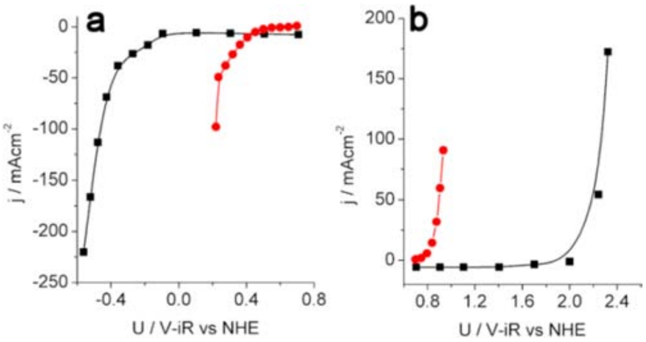

Figure 2. Three-electrode *i*−*V* curves with an Ag/AgCl reference electrode and a large-area Pt mesh counter electrode: (a) reduction of ECPB or protons; (b) oxidation of ECPB* or water. Black line and squares: 1.8 M H_3PO_4 (pH 0.7) and a Pt disc working electrode (area = 0.0314 cm^2). Red line and circles: 0.5 M ECPB/ECPB* in 1.8 M H_3PO_4 (pH 0.7) and a glassy carbon working electrode (area = 0.071 cm^2).

Given that the use of a three-electrode configuration minimizes the effects of resistance,[17] it is possible to compare the expected energetics of a two-step ECPB system (where a glassy carbon electrode oxidizes and reduces the ECPB and a Pt electrode alternately oxidizes water and reduces protons) with a single-step system that uses two Pt electrodes to produce O_2 and H_2 simultaneously, by simply summing the voltages required to produce a given current density. Hence, to oxidize water and reduce the ECPB at 50 mA cm^{-2} requires 2.23 − 0.23 = 2.00 V, with the reverse step (reoxidation of ECPB* and simultaneous proton reduction to H_2) needing +0.9 − (−0.39) = 1.29 V. This gives an overall voltage requirement of 3.29 V for the two-step process, compared to 2.62 V (+2.23 − (−0.39)) for the single-step reaction.

This gives an expected efficiency of 80% for the two-step process relative to the single-step process in the absence of resistive factors, although we note that the single-step reaction requires two precious metal electrodes, compared to just one precious metal electrode when an ECPB is used. Similarly, Figure S11 shows that to reduce protons at 50 mA cm^{-2} on a glassy carbon electrode requires a potential of −0.77 V, which means that a single-step process for generating H_2 on a carbon cathode and O_2 on a Pt anode requires a total voltage of 3.0 V to run at 50 mA cm^{-2} (giving the ECPB-mediated process 91% efficiency relative to a one-step process that uses a single Pt electrode). Moreover, as the two-step ECPB process uses two smaller power inputs to split water (compared to a single larger power input in a non-ECPB cell), using an ECPB reduces the instantaneous power required to do a productive step in the water-splitting reaction, potentially allowing lower power and more diffuse energy inputs to be used to generate hydrogen from water.

Next, we moved from the ideal situation found with three-electrode configurations to a two-electrode configuration such as that shown in Figure 1. Hence, a 0.5 M solution of ECPB/ECPB* (in 1.8 M H_3PO_4) was placed into one compartment of a two-compartment H-cell, and the second compartment was filled with pure 1.8 M H_3PO_4 (pH 0.7). The two compartments were separated by a Nafion 118 membrane. A Pt "working" electrode (area = 0.031 cm^2) was placed into the chamber filled with pure 1.8 M H_3PO_4, while a large area carbon felt was used for reduction/oxidation of the ECPB. Various potentials were then applied across this cell, and the current densities (normalized to the area of the Pt electrode performing the gas evolution reactions) were recorded as shown in Figures 3a and 4a.

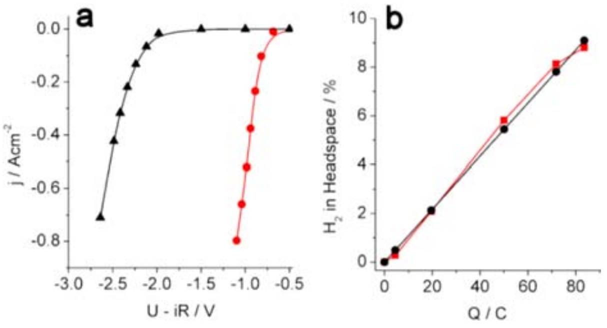

Figure 3. (a) Two-electrode *i*−*V* curves for a two-compartment cell containing a 0.5 M solution of ECPB/ECPB* in H_3PO_4 (1.8 M, pH 0.7) in one compartment and 1.8 M H_3PO_4 in the other (red line and circles), or 1.8 M H_3PO_4 in both sides (black line and triangles). In each case the gas-evolving electrode was a Pt-disc working electrode (area = 0.0314 cm^2) in 1.8 M H_3PO_4. Using the ECPB, the other electrode was a large-area carbon felt in the ECPB/ECPB* solution, while a large-area Pt-mesh was used in the cell containing 1.8 M H_3PO_4 in both sides to avoid oxidative degradation of the anode. (b) A representative trace showing %H_2 expected in the cell headspace (calculated on the basis of the amount of charge passed, black line and circles) compared to the %H_2 in the headspace measured by GCHA (red line and squares).

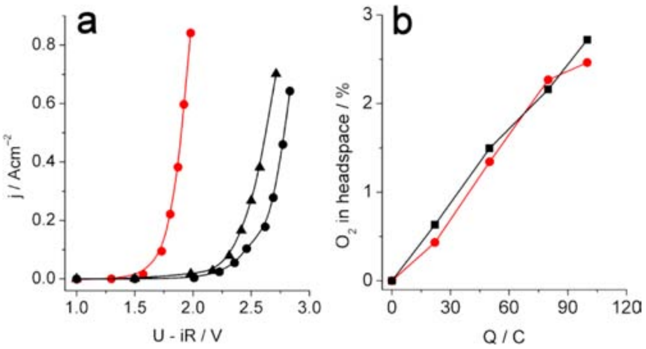

Figure 4. (a) Two-electrode *i*−*V* curves for a two-compartment cell containing a 0.5 M solution of ECPB/ECPB* in H_3PO_4 (1.8 M, pH 0.7) in the counter electrode compartment and 1.8 M H_3PO_4 in the working electrode compartment (red line and circles), or 1.8 M H_3PO_4 in both sides (black lines). In each case the gas-evolving electrode was a Pt-disc working electrode (area = 0.0314 cm^2) in 1.8 M H_3PO_4. Using the ECPB, the counter electrode was a large-surface carbon felt in the ECPB/ECPB* solution. When 1.8 M H_3PO_4 was used in both compartments, data were collected using both a large-area Pt mesh (black line and triangles) and a large-area carbon cloth (black line and circles) in the counter electrode compartment. (b) A representative trace showing %O_2 expected in the cell headspace (calculated on the basis of the amount of charge passed, black line and squares) compared to the %O_2 in the headspace measured by GCHA (red line and circles).

As shown in Figure 3a, current densities of 0.5 A cm^{-2} could be achieved when an *iR*-corrected voltage of 0.98 V was applied across the ECPB cell (red line and circles). However, when no ECPB* was used (black line and triangles), the current density only reached 0.5 A cm^{-2} when the cell bias was >2.5 V *and* a large-area Pt mesh was used in place of the carbon felt/ECPB* combination. The use of a Pt mesh was essential when no ECPB* was present to oxidize, as when carbon felt is polarized anodically in the absence of easily oxidized species the reaction that occurs is oxidation of the carbon anode and not oxidation of water to O_2.[18] When the ECPB/ECPB* mixture was oxidized with a carbon felt electrode and 1.8 M H_3PO_4 was reduced concomitantly at a Pt mesh in an airtight cell (see Figure S12), gas chromatography headspace analysis (GCHA) indicated that the amount of hydrogen produced corresponded to a Faradaic efficiency of 98% ± 7% for the HER (Figure 3b). The amount of O_2 originating from water splitting under these conditions was determined to be <2% of that which would be expected if the HER and OER were occurring concurrently (see Supporting Information for details of the determination of percentages of gases in the cell headspace). The pH changes that might be expected when the HER is decoupled from the OER were significantly diminished by using hydroquinone sulfonate as an electron mediator (see Supporting Information, Table S1), supporting the hypothesis that the 1,4-hydroquinone sulfonate/*p*-benzoquinone sulfonate system accepts and donates both protons and electrons during the decoupled half-reactions of water splitting and thus acts as an ECPB.

Figure 4a shows current densities for O_2 evolution and simultaneous ECPB reduction. Current densities of 0.5 A cm^{-2} could be achieved when an *iR*-corrected voltage of 1.90 V was applied across a cell using a Pt anode and a carbon cathode/ECPB combination (red line and circles), but 2.78 V had to be applied across this cell to obtain a current density of 0.5 A cm^{-2} when no ECPB was present (black line and circles). The O_2 headspace concentration found by GCHA indicated a Faradaic yield of 91 ± 5% for the production of O_2. No H_2 was detected, again suggesting that the ECPB/ECPB* mixture allowed the OER and HER to be fully decoupled.

In order to test the stability of this ECPB to repeated cycling, a 10 mM solution of potassium hydroquinone sulfonate was alternately fully oxidized and fully reduced in a two-electrode, two-compartment H-cell. Figure S13b shows the resulting plot of charge passed vs cycle number, which shows that the ability to re-reduce the oxidized form of the ECPB decreased by around 1% per cycle (over 20 cycles). This decrease in charge storage capacity was matched by a color change to red, which was recorded at regular intervals during electrochemical cycling of the solution by UV/vis spectroscopy (Figures S13a and

S14). Exclusion of O_2 made little difference to the rate of discoloration, but less concentrated solutions were observed to suffer slower degradation than more concentrated solutions. Taken together, these results suggest that the oxidized form of the ECPB is somewhat unstable with respect to oligomerization, as previously observed with benzoquinone derivatives under highly acidic conditions.[19] In contrast, the reduced hydroquinone form (ECPB*) could be stored for several days in the dark without significant aerial oxidation or degradation, as gauged by UV/vis (see Figure S15) and coulometry (after 8 days under air in the dark, >98% of the charge stored in a 0.5 M sample of ECPB* could be recovered for H_2 production).

The use of larger or more sterically hindered quinone derivatives would be expected to significantly retard oligomerization of the oxidized form of the ECPB, and should thus extend the cyclability of the system. Larger ECPB molecules could also be beneficial with regard to ECPB permeation through the membrane. Nafion was chosen as the membrane in these studies because it hinders the movement of anions while remaining freely permeable to protons. However, we found that the Nafion membrane was not entirely impermeable to this ECPB/ECPB* couple, which was able to cross the Nafion membrane at a rate of $\sim 2.7 \times 10^{-6}$ mol h^{-1} (determined by UV/vis spectroscopy, see Supporting Information and Figure S16). This could potentially lead to nonproductive cycling of the ECPB, which could be reduced and protonated on one electrode, cross the membrane, and become reoxidized at the other electrode. Larger quinone derivatives would be expected to cross the membrane less readily, boosting overall efficiency.

In conclusion, we have shown that the hydroquinone/benzoquinone redox couple has potential as the basis for a system of low MW, organic ECPBs that can effectively decouple the OER from the HER during electrolytic water splitting. This work not only extends the ECPB concept to include organic molecules as redox mediators, but also highlights parallels with the role of quinones in photosynthetic water splitting. Work to improve the stability and cyclability of such organic ECPBs is ongoing in our laboratories.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental protocols for electrochemistry, gas analysis, operation of the ECPB in alternative electrolytes, and stability tests. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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