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Electrosynthesis of hydrogen peroxide by phase transfer catalysis

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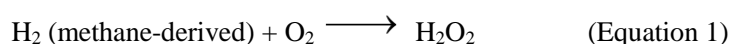
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Summary

The portable electrochemical generation of hydrogen peroxide from air and water would enable greater utilization of this versatile green oxidant in applications ranging from environmental remediation to portable sanitation. Currently, electrochemical H₂O₂ synthesis is hampered by the lack of low-cost, non-toxic catalysts that selectively reduce O₂ to H₂O₂ and the lack of low-energy methods for separating the produced H₂O₂ from the electrolyte media. Herein, we show that a disulfonated anthraquinone can simultaneously catalyze the selective conversion of O₂ to H₂O₂ and shuttle between immiscible aqueous and organic phases *via* ion exchange. We exploit both of these properties in a flow system to assemble an all Earth-abundant prototype device for the continuous generation and separation of H₂O₂ into an electrolyte-free water stream. The combination of molecular redox mediation and phase transfer catalysis demonstrated here has broad implications for the electrochemical synthesis and isolation of value-added chemicals and fuels.

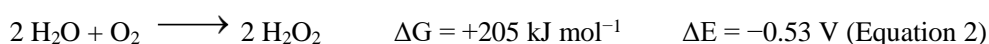
Introduction

Hydrogen peroxide (H₂O₂) is a strong, environmentally benign, atom-economical oxidant that is employed in a wide variety of applications. In particular, it can be used directly at low concentrations for the disinfection of drinking water and for routine domestic sanitation needs.¹ In addition, H₂O₂ is used in *advanced oxidation processes*, where strongly oxidizing hydroxyl radicals (OH•), generated by the ultraviolet (UV)-light induced decomposition of hydrogen peroxide, are employed for purification of waste water from industrial and agricultural sources.^{2,3} Indeed, lack of access to clean water and sanitation has been linked to 2.4 million annual deaths in the developing world, and contributes to childhood mortality at a rate higher than HIV, malaria and tuberculosis combined.⁴ In principle, environment sustainability and global human health could be advanced by greater access to hydrogen peroxide at the point of greatest need. The legacy method for large-scale peroxide production is the anthraquinone or Riedl-Pfleiderer process, which involves O₂ hydrogenation via a homogeneous proton/electron carrier.⁵ The net reaction for this process is:

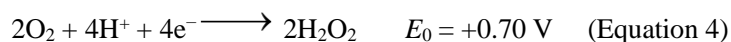
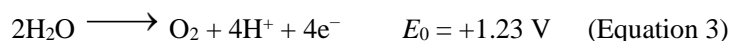


The H₂ required for this reaction is typically sourced from steam methane reforming (SMR), a high-temperature, capital intensive process that is challenging to down-scale.⁶ In 2015, close to 4.3 Mt of H₂O₂ was produced *via* the anthraquinone process, which consumes 17.6 kWh/kg H₂O₂, leading to an aggregate energy consumption of ~ 8.6 GWyr annually.⁷ This energy is mainly supplied via fossil fuel combustion, which adds to the already substantial carbon footprint of the SMR process that precedes H₂O₂ production. The SMR process alone contributes 0.25 equivalents of CO₂ per equivalent of H₂O₂, leading to a carbon footprint for H₂O₂ production of >2.8 Mt in 2015 (see SI, p S10). Clearly, methods for driving the synthesis of H₂O₂ with renewable electricity have the potential to substantially reduce the carbon footprint associated with producing this important oxidizer.

In addition to the energy considerations described above, many application of H₂O₂, including distributed water treatment, disinfection, and sanitation, increasingly demand portable generation of H₂O₂ at the point-of-use.⁴⁻⁶ For these applications, a portable alternative to the legacy anthraquinone process is the direct synthesis of hydrogen peroxide from water and oxygen:



This net reaction (Equation 2) is endergonic, but can be driven electrochemically via two countervailing half-reactions; the oxidation of H₂O to O₂ (Equation 3) and the two-electron, two-proton partial reduction of O₂ to H₂O₂ (Equation 4):



Direct electrochemical H₂O₂ synthesis suffers from a variety of challenges. In particular, since H₂O₂ is a highly water-soluble liquid, separating the H₂O₂ product from the strongly acidic or alkaline electrolyte medium can be challenging. This separation could, in principle, be achieved via either distillation or reverse osmosis. However, distillation leads to an exorbitant energy cost for separation that is comparable to the anthraquinone process itself; reverse osmosis should have a lower input of heat (see SI, page S10), but requires expensive membranes that are susceptible to oxidative degradation and parasitic loss of H₂O₂ in the rejected brine.

Current electrochemical methods for H₂O₂ production can be divided into two categories. Firstly, established methods exist using carbon or modified carbon catalysts,⁸⁻¹³ which often are used to produce hydroperoxide anion in strongly alkaline media. This method is general employed for the on-site generation of the hydroperoxide anion for wood pulping applications. Alternatively, metal-based electrocatalysts can be used to generate H₂O₂ in acidic media¹⁴⁻¹⁷ and have been integrated into PEM electrolysis devices, which can facilitate H₂O₂ production in electrolyte-free water.^{18,19}

Despite these advances, challenges in electrochemical hydrogen peroxide synthesis remain. Many hydrogen-peroxide forming catalysts are also active for the direct reduction of O₂ to H₂O, and the parasitic disproportionation of the synthesized hydrogen peroxide to O₂ and H₂O, leading to low selectivity.¹⁸⁻²² Additionally, many state-of-the art electrocatalysts for direct H₂O₂ synthesis employ precious metals with toxic metal additives such as Hg and Pb.²² Finally, the rate of H₂O₂ production is typically limited by diffusion of poorly soluble O₂ to the electrode, making it hard to access high production rates.^{14,18,19} We acknowledge that peroxide solutions typically include stabilizers and one could, in principle, obviate the need for downstream separation by using a benign electrolyte that also served as the stabilizer. However, fulfilling these multiple requirements with a high conductivity electrolyte remains challenging.

Anthraquinones themselves have been used in various electrochemical systems to produce hydrogen peroxide, including immobilized on electrodes,²³⁻²⁵ in emulsion-type systems in conjunction with an alkaline aqueous phase,^{26,27} and in aqueous solution under photoelectrochemical conditions.²⁸ However, to the best

of our knowledge there are no examples of electrolyte-free H₂O₂ production using homogeneous electrochemical mediation.

We envisioned that all of the above challenges could be overcome simultaneously by integrating anthraquinone-mediated H₂O₂ generation with phase transfer catalysis. In particular, we postulated that the following three step sequence could allow for rapid, continuous H₂O₂ production *and* separation without the use of precious metal catalysts (Figure 1):

- (1) The electrochemical reduction of a quinone to a hydroquinone in aqueous electrolyte.
- (2) Phase transfer of the hydroquinone into an immiscible solvent phase
- (3) Contact of the hydroquinone with an oxygenated pure water stream to generate H₂O₂ and regenerate the original quinone for recycling to the electrochemical cell.

In this process, the quinone serves both as an electrochemical redox mediator *and* phase transfer agent for shuttling electron/proton equivalents between the electrolyte medium and pure water streams. As a result, this process substitutes the high energy and membrane costs of distillation or reverse osmosis with low-cost, low-energy, extraction-based separation steps.²⁹ While molecular redox mediation has been applied to a variety of electrochemical transformations including water splitting,^{30–33} and oxygen reduction in fuel cells,^{34,35} to best of our knowledge, it has never been applied in combination with phase transfer catalysis to enable *in situ* product generation *and* separation.

Herein, we establish the feasibility of redox-mediated phase-transfer (RMPT) electrocatalysis and demonstrate that the approach enables continuous H₂O₂ electrosynthesis from H₂O and O₂ with simultaneous separation into an electrolyte-free aqueous product stream. We assemble an all earth-abundant proof of concept device that displays superior selectivity and H₂O₂ flux relative to reported direct electrosynthetic methods.

Electrochemistry of the Electron-Proton Transfer Mediator

The success of the proposed electrochemical phase-transfer scheme requires a molecular redox mediator with the following properties: (a) high solubility in water *and* an immiscible organic media, (b) tunable phase transfer properties, (c) reversible two-electron, two-proton redox chemistry, and (d) high activity for the selective conversion of O₂ to H₂O₂. Given the known activity and selectivity of dihydroanthraquinones used in industrial peroxide synthesis,⁵ we adapted this core motif to the requirements of electrochemical RMPT H₂O₂ synthesis. To fulfill the requirement of selective transfer of quinone from the aqueous to an immiscible organic phase and vice-versa, we sought an anionic anthraquinone derivative that could pair with hydrophilic and lipophilic cations in each respective phase. Specifically, we selected a dianionic anthraquinone with sulfonyl groups, 2,7-disulfonyl anthraquinone (AQDS²⁻, Figure 2).³⁶

The electrochemistry of AQDS²⁻ is ideal for mediating peroxide synthesis and our data establish that AQDS²⁻ indeed undergoes selective two-electron, two-proton electroreduction to generate dihydroanthraquinone disulfonate (AQDSH₂²⁻, Figure 2). In aqueous 0.1 M HClO₄, 20 mM AQDS²⁻ displays a reversible redox wave at $E_{1/2} = 0.13$ V vs the reversible hydrogen electrode (RHE) on glassy carbon electrodes (Figure 3a). This potential corresponds to a modest 0.55 V overpotential relative to the thermodynamic value for the O₂/H₂O₂ couple, providing ample driving force for the two-electron reduction of O₂ to hydrogen peroxide. We observe a peak-to-peak separation of 90 mV indicative of electrochemical

quasireversibility, possibly due to quinone partial dimerization as previously reported.³⁷ Indeed, at higher concentrations still it is likely that anthraquinones decompose in a bimolecular fashion³⁸. Nonetheless, the ratio of peak integrations, q_c/q_a , is 1.00, pointing to the chemical reversibility of this two-electron, two-proton process. In line with literature reports,³⁶ preparative electrolysis at 0 V vs RHE leads to clean conversion of the quinone to AQDSH₂²⁻ as judged by UV-Vis spectroscopy (Figure S1).³⁹ Since the carbon electrode does not catalyze hydrogen evolution or other reduction reactions at 0.0 V, we observe a high Faradaic efficiency, >95%, for the electrochemical conversion of AQDS²⁻ to AQDSH₂²⁻. Together, these observations establish that AQDS²⁻ undergoes selective, high-yield, electrochemical reduction in acidic aqueous electrolytes.

Phase Transfer of the Mediator

Subsequently, we investigated the phase transfer of AQDS²⁻/AQDSH₂²⁻ from the aqueous HClO₄ electrolyte into an organic phase (Figure 4). We chose 1-hexanol as the organic phase for our application because of its low cost, low toxicity, and low miscibility with water as determined by ¹H NMR spectroscopy (Figure S2). Indeed, current pharmaceutical industry best practice considers 1-hexanol a sustainable solvent for large-scale industrial use.⁴⁰ By controlling the cation composition of the aqueous and organic phases, we are able to systematically tune the phase transfer equilibrium constant for both the oxidized and reduced forms of the mediator. For a 0.1 M HClO₄ aqueous phase in contact with 0.1 M tetrabutylammonium chloride (TBACl) in 1-hexanol, we observe a phase transfer partition coefficient, X_{aq} , of 0.44 and 0.66 for AQDS²⁻ and AQDSH₂²⁻, respectively. The similar partition coefficients for the reduced and oxidized mediator suggest that the protonation/redox state of the quinone core does not dramatically alter the thermodynamics of phase transfer. Indeed, for this solvent mixture, we posit that the dominant driving force for phase transfer is the transfer of Cl⁻ ions from the organic phase to the aqueous phase. In line with this postulate, increasing the concentration of TBACl from 50 mM to 300 mM leads to a roughly linear decrease in X_{aq} from 0.61/0.84 to 0.16/0.22 respectively (Figure 3b). Additionally, over the entire range of TBACl electrolyte strengths, we observe a similar ratio of phase transfer coefficients for AQDS²⁻ and AQDSH₂²⁻ of ~2:3. These partition coefficients are strongly dependent on the hydrogen bonding properties of the organic phase – when hexanol is substituted with dichloromethane, we observe partition coefficients, X_{aq} , of 0.64 and 0.95 for AQDS²⁻ and AQDSH₂²⁻, respectively in the presence of 0.1 M TBACl (Figure S3). This suggests that a hydrogen bonding organic solvent is required to facilitate efficient transfer of AQDSH₂²⁻ into the organic phase. These studies highlight the interplay between mediator charge, solvent, and ionic strength, all of which can be readily tuned to optimize the phase transfer equilibria. Together, the data establish that both AQDS²⁻ and AQDSH₂²⁻ are able to reversibly transfer between HClO₄/water and TBACl/hexanol phases to facilitate RMPT H₂O₂ synthesis.

Synthesis of H₂O₂

Our data establish that the reduced anthraquinone, AQDSH₂²⁻, promotes hydrogen peroxide production at the water/hexanol boundary, separating this reaction from the site of quinone reduction at the aqueous electrode. AQDSH₂²⁻ rapidly converts O₂ to H₂O₂ in both the organic and aqueous phases. Following exposure of a 20 μM solution of AQDSH₂(TBA)₂ in 1-hexanol to bubbling O₂, we observe an isosbestic point at 355 nm in the UV-Vis spectra, that is indicative of clean conversion of AQDSH₂²⁻ to AQDS²⁻ (Figure 3c). In the organic phase alone, this reaction is concluded in ~25 minutes, but its rate can be substantially accelerated by shaking with water, which leads to complete conversion in less than 15 seconds. Analysis of the water layer indicates quantitative generation of one equivalent of H₂O₂ per AQDSH₂²⁻

mediator. Importantly, we also observe complete retention of the AQDS²⁻ in the hexanol phase, with no transfer of reduced or oxidized quinone species to electrolyte-free water (Figure S4), as well as clean regeneration of AQDS²⁻ upon H₂O₂ generation, with no detectable mediator degradation (Figure S5). We attribute this to a low concentration of phase-transfer promoting ions in the aqueous phase and highlight the importance of this finding: Indeed, *phase transfer electrosynthesis of H₂O₂ results in a product stream which consists only of peroxide and water, overcoming a key limitation of direct electrochemical H₂O₂ synthesis.* While the complete mechanistic picture for hydrogen peroxide generation by AQDSH₂²⁻ remains uncertain in this system, our data provide basic insight. The apparent rate acceleration in the presence of water suggests that proton transfer is key to the overall reaction. It is therefore possible that H₂O₂ forms via an endoperoxide-bridged species in analogy to the prevailing mechanistic model for H₂O₂ production in the anthraquinone process.^{41,42} If this is the case, however, the intermediate appears to be in minor equilibrium, as indicated by our observation of an isosbestic point in the UV-Vis data. Irrespective of the specific mechanism, the data establish that AQDSH₂²⁻ rapidly generates aqueous H₂O₂ while regenerating AQDS²⁻ in the organic phase for continuous recycling.

Proof-of-Concept Process for Continuous H₂O₂ Synthesis

Taking advantage of the combined electrochemical, catalytic, and phase transfer properties of AQDS²⁻ / AQDSH₂²⁻, we designed a proof-of-concept process for continuous hydrogen peroxide generation (Figure 5). In this process, an acidic aqueous solution of AQDS²⁻ is pumped past a carbon cathode to generate AQDSH₂²⁻. This cathodic half-reaction is paired with anodic water oxidation to O₂, thereby enabling the complete conversion of water to O₂ and H₂O₂. With the goal of achieving an all Earth-abundant device, we employed a commercially-available nickel foam as the anode material and oxygen evolving catalyst.⁴³ Nickel oxide performs oxygen evolution most effectively and durably in an alkaline environment, while AQDS²⁻ reduction is most efficient in an acidic environment. To satisfy the disparate pH requirements of the anode and cathode reactions, we employed a bipolar membrane to effectively separate the cathodic and anodic environments within our cell. Upon polarization, the electric field across this bipolar membrane promotes the dissociation of water into H⁺ and OH⁻, thereby generating a pH gradient across the cell that serves to replenish the protons consumed during AQDS²⁻ reduction and the OH⁻ ions consumed during oxygen evolution.⁴⁴ We note that this bipolar membrane also serves to inhibit cross-over of the redox mediator between anode and cathode compartments, ensuring a sustained pool of the mediator available for continuous H₂O₂ generation.

Following electrochemical reduction of AQDS²⁻, the resulting aqueous AQDSH₂²⁻ stream is contacted with the hexanol phase. The two phases are vigorously mixed and subsequently separated using a ‘mixer-settler’ (Figure S7 & S8) apparatus commonly employed for phase-transfer separations.⁴⁵ This first mixer-settler partitions the reduced and oxidized quinones between the two phases. The aqueous stream is fed back into the electrochemical cell, whereas the organic stream, now containing AQDSH₂²⁻, is contacted with O₂ and water in a second mixer-settler (Figure S8). In this second step, O₂ is rapidly converted to H₂O₂, regenerating the AQDS²⁻ mediator. As described above, the AQDS²⁻ remains in the hexanol phase and is recycled to the first mixer-settler, while pure H₂O₂ partitions preferentially into the water phase for isolation. Importantly, this continuous process generates H₂O₂ remote from the membrane and the electrolytic cell. In addition to producing electrolyte-free H₂O₂, this process eliminates the possibility of oxidative damage to the polymer membrane and catalytic disproportionation of H₂O₂ to water and O₂ by the cathode material. Thus, through the simple combination of a pump and two mixer-settlers, this phase transfer system achieves the electrosynthesis of pure aqueous H₂O₂ with the quinone mediator acting as a proton and electron transfer agent.

Efficient H₂O₂ production in this mediated system relies on efficient gas transport into the reacting phases. Indeed, if O₂-saturated water is contacted with the organic phase in MS-2, the maximum single pass H₂O₂ concentration is limited to the 1 mM O₂ solubility in water. However, we found that this limit could be easily exceeded by continuously bubbling O₂ into the mixing zone of MS-2. In this configuration, shrinking gas bubbles provide a constant supply of dissolved oxygen in the aqueous phase to match the rapid rate of H₂O₂ production at the water/hexanol interface.³⁶ While the studies reported here were conducted with a 1.0 atm O₂ feed, we stress that AQDSH₂²⁻ also reacts rapidly with air (see above and Figure 2c). Thus, the process can be readily adapted to an air stream by matching the flux of mediator and gas streams to the lower atmospheric O₂ partial pressure. Irrespective of the O₂ source, matching the fluxes of O₂ and AQDSH₂²⁻ mediator is critical for preventing O₂ permeation throughout the rest of the system.

Our proof-of-concept device is effective for continuous, long-term H₂O₂ production. We observe stable current densities between 8 and 10 mA cm⁻² (relative to the geometric area of the electrochemical cell, see Figure S9) over the course of 7 hours of continuous operation at an applied cell voltage of 2.25 V. This cell voltage includes significant contributions from parasitic resistive losses in the 26 cm² prototype cell we employed. From current-voltage data (Figure S10), we estimate a lower bound of the effective cell resistance of ~4.5 Ω, leading to an estimated iR-free cell voltage of ~ 1.4 V. We envision that further cell engineering and/or increased aqueous electrolyte strength should be able to minimize these resistive losses and reduce the operating voltage.⁴⁶ The H₂O₂ concentration in the final output water stream was periodically quantified by iodometric titration, revealing that the H₂O₂ production rate (Figure 6a, blue) corresponds to near quantitative Faradaic efficiency for H₂O₂ production (Figure 6a, red). This efficiency decreases slightly to ~80% over many hours of operation, an effect which we attribute to parasitic H₂ evolution at the cathode and/or adventitious disproportionation of the produced H₂O₂. These challenges can be addressed by optimizing the flow field in the electrochemical cell and minimizing trace metal impurities on the side walls of the mixer-settlers (particularly in the gas-mixing zone of MS-2 where local H₂O₂ concentrations are high) respectively. Notwithstanding, the partial current density contributing to mediated H₂O₂ production in this system remains in excess of 8 mA cm⁻² over long term operation. This value greatly exceeds the diffusion-limited rate of direct O₂ reduction to H₂O₂ of < 3 mA cm⁻² on an electrode rotated at 2000 RPM, highlighting the value of this approach for high flux H₂O₂ production.⁴⁷ Additionally, our H₂O₂ production rate (3 μmol min⁻¹ cm⁻²) rivals optimized values for polymer electrolyte devices that operate at significantly higher temperature and oxygen flux with lower Faradaic efficiencies (30%).¹⁸

Importantly, the current density and flow rate ratios can be independently controlled to set the desired concentration of peroxide in the aqueous output stream. Varying the current density of mediator regeneration over a range of 2 to 10 mA cm⁻² leads to a roughly linear increase in H₂O₂ production rate (Figure 6b, blue), consistent with the high Faradaic efficiency of the process (Figure 6b, red). Likewise, varying the flow rate of aqueous product stream, **3**, relative to the mediator recycle loop, **2**, permits *selection* of the concentration of H₂O₂ in the product stream. Indeed, by reducing the flow ratio we obtain a higher H₂O₂ concentration and can access a more dilute H₂O₂ stream by increasing the flow ratio (Figure 6c, blue), all while maintaining a high Faradaic efficiency (Figure 6c, red). Over all of these conditions, we observe a continuous production rate of H₂O₂ of 2-3 μmol min⁻¹ cm⁻² for many hours and have been able to access H₂O₂ concentrations of 33 mM (Figure S11).

The device consumes a modest amount of power, $<10 \text{ mW cm}^{-2}$, suitable for distributed or remote operation. Furthermore, since in situ product separation proceeds passively via phase transfer, the system only draw power to drive the electrochemical cell and pump the non-viscous solutions. Thus, the overall energy efficiency of the process, neglecting pumping costs, can be calculated based on the cell voltage. Excluding resistivity losses, the process displays an energetic efficiency of $\sim 40\%$ across a wide range of current densities (Figure 6d, S12). Together, these observations highlight the inherent advantages of mediated electrolysis, particularly for the production of H_2O_2 .

Conclusion and Outlook

In summary, we have employed a redox mediator phase-transfer, RMPT, approach to produce *and* isolate aqueous H_2O_2 from the electrolysis of H_2O and O_2 . Generally, the development of electrochemical processes often ignores the energy and capital costs associated with the separation and purification of the value-added product. Particularly for liquid products, these separation costs cannot be ignored. By employing a redox mediator that can be easily phase separated, we showcase the power of the RMPT approach to facilitate simultaneous production and separation of a liquid product within an integrated electrochemical/phase-transfer process for the first time. This concept has broad implications because the functionality of the mediator can also be purposefully designed to deliver redox equivalents to reaction/separation environments that would be incompatible with their generation. Indeed, there is growing evidence that the uncontrolled proton donor environment of aqueous electrolytes, combined with the nucleophilicity of hydroxide, compromises the efficiency and selectivity of more complex reactions including CO_2 reduction,^{48,49} N_2 reduction,^{50,51} and NH_3 oxidation⁵². Additionally, in the context of organic electrosynthesis, many substrates are simply not soluble in aqueous media. In all of these electrochemical processes, our RMPT approach could be used to drive difficult redox transformations in non-aqueous environments that are incompatible with electrochemistry but are ideal for maximizing substrate solubility, and enhancing reaction selectivity and efficiency. Thus, by decoupling the conditions of electrochemistry from the conditions ideal for substrate turnover and separation, the RMPT approach established here enables a vast expansion of the utility of electrochemical processes.

Experimental Procedures

Batch Electrochemical Characterization. Cyclic voltammetry (CV) and chronoamperometry (CA) were recorded using a Biologic VSP 16-channel potentiostat, a glassy carbon (GC) working electrode, platinum counter electrode, and a Ag/AgCl reference electrode (see Supplementary Methods for further details)

Determination of Partition Coefficients. Two phases (20 mM AQDSNa₂ in 0.1 M HClO₄ and TBACl in 1-hexanol) were shaken in a vial and allowed to separate for 5 minutes. Subsequently, the amount of quinone remaining in the aqueous layer was measured by UV-Vis spectroscopy.²² The same procedure was use for AQDSH₂Na₂ which was prepared by bulk electrolysis of AQDSNa₂.

Quinone Autooxidation. 20 mM AQDSNa₂ in 0.1 M HClO₄ aqueous electrolyte was fully reduced in a flow cell, under N_2 . The reduced quinone AQDSH₂²⁻ was then extracted into 0.1 M TBACl in 1-hexanol under N_2 . The organic hexanol phase was transferred into a UV-Vis cuvette that was purged with N_2 and the first spectrum of the fully reduced quinone was recorded. The cap of the cuvette was then

removed to allow oxygen dissolution and diffusion into 1-hexanol for the slow oxidation of the reduced quinone. Spectra were recorded periodically every 2 minutes. The full oxidation was achieved within 25 minutes.

Flow electrochemical cell fabrication. The electrochemical cell was fabricated using 3" × 3", 1/8" thick, 316 stainless steel sheet current collectors. Silicone rubber sheets (50A Durometer) containing 2" × 2" cavities served as gaskets. Four overlapping 2" × 2" graphite felt pieces were used as the cathode and three overlapping 2" × 2" nickel foam sheets were used as the anode. Polypropylene inlet and outlet fittings were inserted into the sides of the silicone sheets to allow for anolyte and catholyte circulation flows. The two half-cells were separated by a 3" × 3" bipolar membrane. The exposed electrode area of the cell was 2" × 2" (25.8 cm²).

Mixer settler fabrication. MS-1 was machined from polypropylene. The mixing zone was a cylindrical cup, with liquid inlets on both sides at the bottom, and was separated from the settling zone by an emulsion overflow and a baffle. The settling zone had three coalescence plates, to enhance phase separation, and a light phase weir to allow for level fluctuations. The volumes of the mixing and settling zones was ~ 100 mL each, resulting in a total holdup volume of ~ 200 mL. MS-2 was custom fabricated from glass by James Glass inc. and was of similar intrinsic design with the additional ability to bubble gas streams into the mixing zone. See Supplementary Methods for full details.

Device operation. Surge tanks in the flow system (Figure 5/S6) were charged with the appropriate solutions, (Table S2). The first mixer-settler, in M-S 1, was primed by syringe addition of 100 mL each of 20 mM AQDS²⁻ / 0.1 M HClO₄ and 20 mM AQDS²⁻ / 0.1 M TBACl/hexanol. The second mixer-settler, M-S 2, was primed with 110 mL each of water, stabilized with 1 mM Na₂EDTA and 3 mM citric acid, and 0.1 M TBACl/hexanol. The pumps (Cole-Parmer, Masterflex) were run at 10 mL/min for 20 mins to allow the system to reach equilibrium before electrochemistry or O₂ sparging were commenced. Tanks S-2, S-3 and S-4 (Figure S6) were constantly bubbled with nitrogen to prevent oxygen from M-S 2, carried by the organic phase, from entering the electrochemical cell during the operation of the system. The flow system was operated at ambient temperature, 20 – 22°C. The system was operated at constant potential or current depending on the experiment.

H₂O₂ quantification. H₂O₂ was quantified by iodometric titration according to a standard procedure.¹¹ An aliquot of KI in H₂SO₄ was added to the test sample to generate I₂, which was titrated by quenching with a standard solution of 0.1 M Na₂S₂O₃ until the color disappeared. Peroxide titrations were periodically cross-checked using peroxidase-based semi-quantitative test strips (Millipore MQuant™, 0-100 ppm / 100-1000 ppm, LaMotte InstaTest™ 0-90 ppm, 1 mM = 34 ppm).

Supplementary Information

Supplementary Information includes full experimental details, 13 figures, and 2 tables.

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Author Contributions

A.T.M. and S.V. are co-first authors. Y.S., T.A.H, A.M., S.V., and M.S. conceived of and designed the experimental investigations. A.T.M. and S.V. performed experiments. Y.S., T.A.H, A.T.M., S.V., and M.S. analyzed the data and wrote the paper.

Declaration of Interest Statement

The authors declare the following financial interest(s): Y.S., T.A.H, A.T.M., and S.V. are inventors on provisional patent application 62/718,745 filed by the Massachusetts Institute of Technology that covers the electrochemical peroxide production method reported in this work.

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References

1. McDonnell, G. (2014). The Use of Hydrogen Peroxide for Disinfection and Sterilization Applications. In PATAI'S Chemistry of Functional Groups (American Cancer Society), pp. 1–34.
2. Oller, I., Malato, S., and Sánchez-Pérez, J.A. (2011). Combination of Advanced Oxidation Processes and biological treatments for wastewater decontamination—A review. *Sci. Total Environ.* *409*, 4141–4166.
3. Butkovskiy, A., Bruning, H., Kools, S.A.E., Rijnaarts, H.H.M., and Van Wezel, A.P. (2017). Organic Pollutants in Shale Gas Flowback and Produced Waters: Identification, Potential Ecological Impact, and Implications for Treatment Strategies. *Environ. Sci. Technol.* *51*, 4740–4754.
4. Bartram, J., and Cairncross, S. (2010). Hygiene, Sanitation, and Water: Forgotten Foundations of Health. *PLOS Med.* *7*, e1000367.
5. Riedl, H.-J.; Pfeleiderer, G. (1939). Production of Hydrogen Peroxide. U.S. Patent US 2,158,525, 1939.
6. Campos-Martin, J.M., Blanco-Brieva, G., and Fierro, J.L.G. (2006). Hydrogen Peroxide Synthesis: An Outlook beyond the Anthraquinone Process. *Angew. Chem. Int. Ed.* *45*, 6962–6984.
7. Merchant Research and Consulting Ltd., Hydrogen Peroxide (HP): 2015 World Market Outlook (2015). (Merchant Research and Consulting Ltd.,).
8. McIntyre, J.A., and Phillips, R.F. (1984). Method for electrolytic production of alkaline peroxide solutions. US Patent US 4,431,494 A.

9. Liu, Y., Quan, X., Fan, X., Wang, H., and Chen, S. (2015). High-Yield Electrosynthesis of Hydrogen Peroxide from Oxygen Reduction by Hierarchically Porous Carbon. *Angew. Chem. Int. Ed.* *54*, 6837–6841.
10. Thostenson, J.O., Ngaboyamahina, E., Sellgren, K.L., Hawkins, B.T., Piascik, J.R., Klem, E.J.D., Parker, C.B., Deshusses, M.A., Stoner, B.R., and Glass, J.T. (2017). Enhanced H₂O₂ Production at Reductive Potentials from Oxidized Boron-Doped Ultrananocrystalline Diamond Electrodes. *ACS Appl. Mater. Interfaces* *9*, 16610–16619.
11. Chen, Z., Chen, S., Siahrostami, S., Chakthranont, P., Hahn, C., Nordlund, D., Dimosthenis, S., Nørskov, J.K., Bao, Z., and Jaramillo, T.F. (2017). Development of a reactor with carbon catalysts for modular-scale, low-cost electrochemical generation of H₂O₂. *React. Chem. Eng.* *2*, 239–245.
12. Iglesias, D., Giuliani, A., Melchionna, M., Marchesan, S., Criado, A., Nasi, L., Bevilacqua, M., Tavagnacco, C., Vizza, F., Prato, M., *et al.* (2018). N-Doped Graphitized Carbon Nanohorns as a Forefront Electrocatalyst in Highly Selective O₂ Reduction to H₂O₂. *Chem* *4*, 106–123.
13. Lu, Z., Chen, G., Siahrostami, S., Chen, Z., Liu, K., Xie, J., Liao, L., Wu, T., Lin, D., Liu, Y., *et al.* (2018). High-efficiency oxygen reduction to hydrogen peroxide catalysed by oxidized carbon materials. *Nat. Catal.* *1*, 156.
14. Siahrostami, S., Verdaguer-Casadevall, A., Karamad, M., Deiana, D., Malacrida, P., Wickman, B., Escudero-Escribano, M., Paoli, E.A., Frydendal, R., Hansen, T.W., *et al.* (2013). Enabling direct H₂O₂ production through rational electrocatalyst design. *Nat. Mater.* *12*, 1137–1143.
15. Jirkovský, J.S., Panas, I., Ahlberg, E., Halasa, M., Romani, S., and Schiffrin, D.J. (2011). Single Atom Hot-Spots at Au–Pd Nanoalloys for Electrocatalytic H₂O₂ Production. *J. Am. Chem. Soc.* *133*, 19432–19441.
16. Verdaguer-Casadevall, A., Deiana, D., Karamad, M., Siahrostami, S., Malacrida, P., Hansen, T.W., Rossmeisl, J., Chorkendorff, I., and Stephens, I.E.L. (2014). Trends in the Electrochemical Synthesis of H₂O₂: Enhancing Activity and Selectivity by Electrocatalytic Site Engineering. *Nano Lett.* *14*, 1603–1608.
17. Pizzutilo, E., Freakley, S.J., Cherevko, S., Venkatesan, S., Hutchings, G.J., Liebscher, C.H., Dehm, G., and Mayrhofer, K.J.J. (2017). Gold–Palladium Bimetallic Catalyst Stability: Consequences for Hydrogen Peroxide Selectivity. *ACS Catal.* *7*, 5699–5705.
18. Li, W., Bonakdarpour, A., Gyenge, E., and Wilkinson, D.P. (2013). Drinking Water Purification by Electrosynthesis of Hydrogen Peroxide in a Power-Producing PEM Fuel Cell. *ChemSusChem* *6*, 2137–2143.
19. Yang, S., Verdaguer-Casadevall, A., Arnarson, L., Silvioli, L., Čolić, V., Frydendal, R., Rossmeisl, J., Chorkendorff, I., and Stephens, I.E.L. (2018). Toward the Decentralized Electrochemical Production of H₂O₂: A Focus on the Catalysis. *ACS Catal.* *8*, 4064–4081.
20. Otsuka, K., and Yamanaka, I. (1990). One step synthesis of hydrogen peroxide through fuel cell reaction. *Electrochimica Acta* *35*, 319–322.
21. Yamanaka, I., and Murayama, T. (2008). Neutral H₂O₂ Synthesis by Electrolysis of Water and O₂. *Angew. Chem. Int. Ed.* *47*, 1900–1902.

22. Siahrostami, S., Verdaguer-Casadevall, A., Karamad, M., Deiana, D., Malacrida, P., Wickman, B., Escudero-Escribano, M., Paoli, E.A., Frydendal, R., Hansen, T.W., *et al.* (2013). Enabling direct H₂O₂ production through rational electrocatalyst design. *Nat. Mater.* *12*, 1137–1143.
23. Vaik, K., Mäeorg, U., Maschion, F.C., Maia, G., Schiffrin, D.J., and Tammeveski, K. (2005). Electrocatalytic oxygen reduction on glassy carbon grafted with anthraquinone by anodic oxidation of a carboxylate substituent. *Electrochimica Acta* *50*, 5126–5131.
24. Forti, J.C., Rocha, R.S., Lanza, M.R.V., and Bertazzoli, R. (2007). Electrochemical synthesis of hydrogen peroxide on oxygen-fed graphite/PTFE electrodes modified by 2-ethylanthraquinone. *J. Electroanal. Chem.* *601*, 63–67.
25. Valim, R.B., Reis, R.M., Castro, P.S., Lima, A.S., Rocha, R.S., Bertotti, M., and Lanza, M.R.V. (2013). Electrogeneration of hydrogen peroxide in gas diffusion electrodes modified with tert-butyl-anthraquinone on carbon black support. *Carbon* *61*, 236–244.
26. Huissoud, A., and Tissot, P. (1999). Electrochemical reduction of 2-ethyl-9,10-anthraquinone (EAQ) and mediated formation of hydrogen peroxide in a two-phase medium Part I: Electrochemical behaviour of EAQ on a vitreous carbon rotating disc electrode (RDE) in the two-phase medium. *J. Appl. Electrochem.* *29*, 11–16.
27. Huissoud, A., and Tissot, P. (1999). Electrochemical reduction of 2-ethyl-9,10-anthraquinone (EAQ) and mediated formation of hydrogen peroxide in a two-phase medium Part II: Production of alkaline hydrogen peroxide by the intermediate electroreduction of EAQ in a flow-by porous electrode in two-phase liquid–liquid flow. *J. Appl. Electrochem.* *29*, 17–25.
28. Keita, B., and Nadjo, L. (1984). Electrochemistry and photoelectrochemistry of sodium 9,10-anthraquinone-2,6-disulfonate in aqueous media: Application to rechargeable solar cells and to the synthesis of hydrogen peroxide. *J. Electroanal. Chem. Interfacial Electrochem.* *163*, 171–188.
29. Fair, J.R., and Humphrey, J.L. (1984). Liquid-Liquid Extraction: Possible Alternative to Distillation. *Solvent Extr. Ion Exch.* *2*, 323–352.
30. Symes, M.D., and Cronin, L. (2013). Decoupling hydrogen and oxygen evolution during electrolytic water splitting using an electron-coupled-proton buffer. *Nat. Chem.* *5*, 403–409.
31. Rausch, B., Symes, M.D., and Cronin, L. (2013). A Bio-Inspired, Small Molecule Electron-Coupled-Proton Buffer for Decoupling the Half-Reactions of Electrolytic Water Splitting. *J. Am. Chem. Soc.* *135*, 13656–13659.
32. Rausch, B., Symes, M.D., Chisholm, G., and Cronin, L. (2014). Decoupled catalytic hydrogen evolution from a molecular metal oxide redox mediator in water splitting. *Science* *345*, 1326–1330.
33. Kirkaldy, N., Chisholm, G., Chen, J.-J., and Cronin, L. (2018). A practical, organic-mediated, hybrid electrolyser that decouples hydrogen production at high current densities. *Chem. Sci.* *9*, 1621–1626.
34. Anson, C.W., and Stahl, S.S. (2017). Cooperative Electrocatalytic O₂ Reduction Involving Co(salophen) with p-Hydroquinone as an Electron–Proton Transfer Mediator. *J. Am. Chem. Soc.* *139*, 18472–18475.
35. Preger, Y., Gerken, J.B., Biswas, S., Anson, C.W., Johnson, M.R., Root, T.W., and Stahl, S.S. (2018). Quinone-Mediated Electrochemical O₂ Reduction Accessing High Power Density with an Off-Electrode Co-N/C Catalyst. *Joule* *2*, 2722–2731.

36. Huskinson, B., Marshak, M.P., Suh, C., Er, S., Gerhardt, M.R., Galvin, C.J., Chen, X., Aspuru-Guzik, A., Gordon, R.G., and Aziz, M.J. (2014). A metal-free organic–inorganic aqueous flow battery. *Nature* 505, 195–198.
37. Carney, T.J., Collins, S.J., Moore, J.S., and Brushett, F.R. (2017). Concentration-Dependent Dimerization of Anthraquinone Disulfonic Acid and Its Impact on Charge Storage. *Chem. Mater.* 29, 4801–4810.
38. Wermeckes, B.; Beck, F. (1994). Acid-Catalyzed Disproportionation of Anthrahydroquinone to Anthraquinone and Anthrone. *Denki Kagaku* 62, 1202–1205.
39. Gamage, R.S.K.A., McQuillan, A.J., and Peake, B.M. (1991). Ultraviolet–visible and electron paramagnetic resonance spectroelectrochemical studies of the reduction products of some anthraquinone sulphonates in aqueous solutions. *J. Chem. Soc. Faraday Trans.* 87, 3653–3660.
40. Alder, C.M., Hayler, J.D., Henderson, R.K., Redman, A.M., Shukla, L., Shuster, L.E., and Sneddon, H.F. (2016). Updating and further expanding GSK’s solvent sustainability guide. *Green Chem.* 18, 3879–3890.
41. Arpe, H.J., Weissermel, K. (2003). In *Industrial Organic Chemistry*, pp. 329–330.
42. Nishimi, T., Kamachi, T., Kato, K., Kato, T., and Yoshizawa, K. (2011). Mechanistic Study on the Production of Hydrogen Peroxide in the Anthraquinone Process. *Eur. J. Org. Chem.* 2011, 4113–4120.
43. Trotochaud, L., Young, S.L., Ranney, J.K., and Boettcher, S.W. (2014). Nickel–Iron Oxyhydroxide Oxygen-Evolution Electrocatalysts: The Role of Intentional and Incidental Iron Incorporation. *J. Am. Chem. Soc.* 136, 6744–6753.
44. Schreier, M., Héroguel, F., Steier, L., Ahmad, S., Luterbacher, J.S., Mayer, M.T., Luo, J., and Grätzel, M. (2017). Solar conversion of CO₂ to CO using Earth-abundant electrocatalysts prepared by atomic layer modification of CuO. *Nat. Energy* 2, 17087.
45. Alter, H.W., Coddling, J.W., and Jennings, A.S. (1954). Miniature Mixer Settler for Continuous Countercurrent Solvent Extraction. *Anal. Chem.* 26, 1357–1361.
46. Ke, X., Prah, J.M., Alexander, J.I.D., Wainright, J.S., Zawodzinski, T.A., and Savinell, R.F. (2018). Rechargeable redox flow batteries: flow fields, stacks and design considerations. *Chem. Soc. Rev.* 47, 8721–8743.
47. Treimer, S., Tang, A., and Johnson, D.C. (2002). A Consideration of the Application of Koutecký-Levich Plots in the Diagnoses of Charge-Transfer Mechanisms at Rotated Disk Electrodes. *Electroanalysis* 14, 165–171.
48. Zhang, B.A., Ozel, T., Elias, J.S., Costentin, C., and Nocera, D.G. (2019). Interplay of Homogeneous Reactions, Mass Transport, and Kinetics in Determining Selectivity of the Reduction of CO₂ on Gold Electrodes. *ACS Cent. Sci.* 5, 1097–1105.
49. Zhang, B.A., Costentin, C., and Nocera, D.G. (2019). On the Conversion Efficiency of CO₂ Electroreduction on Gold. *Joule* 3, 1565–1568.
50. Deng, J., Iñiguez, J.A., and Liu, C. (2018). Electrocatalytic Nitrogen Reduction at Low Temperature. *Joule* 2, 846–856.

51. Andersen, S.Z., Čolić, V., Yang, S., Schwalbe, J.A., Nielander, A.C., McEnaney, J.M., Enemark-Rasmussen, K., Baker, J.G., Singh, A.R., Rohr, B.A., *et al.* (2019). A rigorous electrochemical ammonia synthesis protocol with quantitative isotope measurements. *Nature* 570, 504–508.
52. Bunce, N.J., and Bejan, D. (2011). Mechanism of electrochemical oxidation of ammonia. *Electrochimica Acta* 56, 8085–8093.

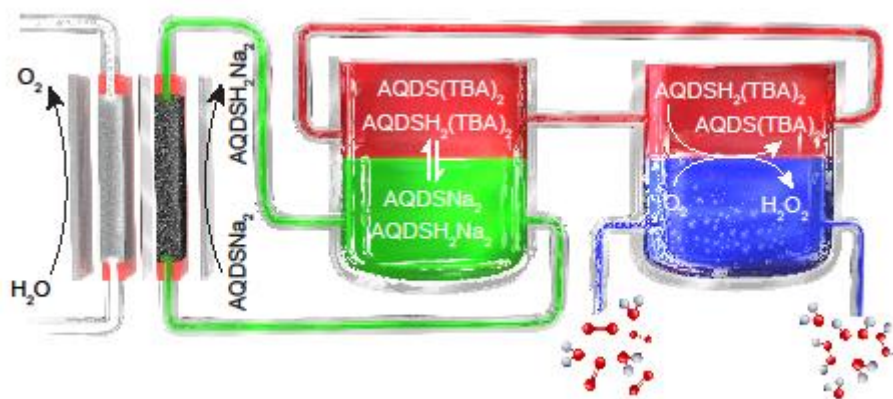


Figure 1. Schematic of overall phase transfer approach to electrochemical H_2O_2 production. The scheme depicts the electrochemical cell (left) carrying out mediator reduction and water oxidation, phase transfer of the mediator (middle) between the electrolyte (green) and organic (red) phase, and H_2O_2 production and extraction (right) from the organic phase to generate a pure aqueous H_2O_2 stream (blue).

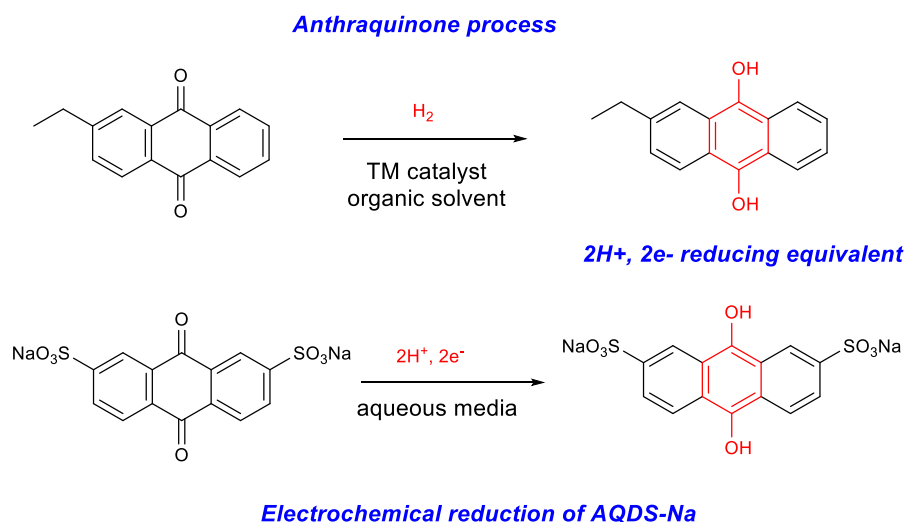


Figure 2. Anthraquinone process (top) and electrochemical reduction of AQDS^{2-} to AQDSH_2^{2-} (bottom)

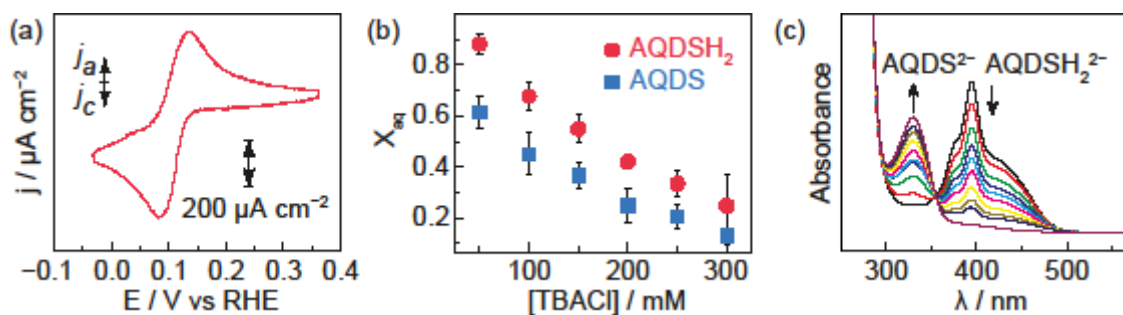


Figure 3. (a) Cyclic voltammogram of 5 mM anthraquinone 2,7-disulfonic acid disodium salt (AQDSNa₂) in 0.1 M HClO₄. (b) Water/hexanol partition coefficient, X_{aq} , for AQDS²⁻ (blue squares) and AQDSH₂²⁻ (red circles) in 0.1 M HClO₄ vs TBACl concentration in the hexanol phase. (c) UV-Vis time course over 25 minutes of the air oxidation of AQDSH₂(TBA)₂ in 1-hexanol.

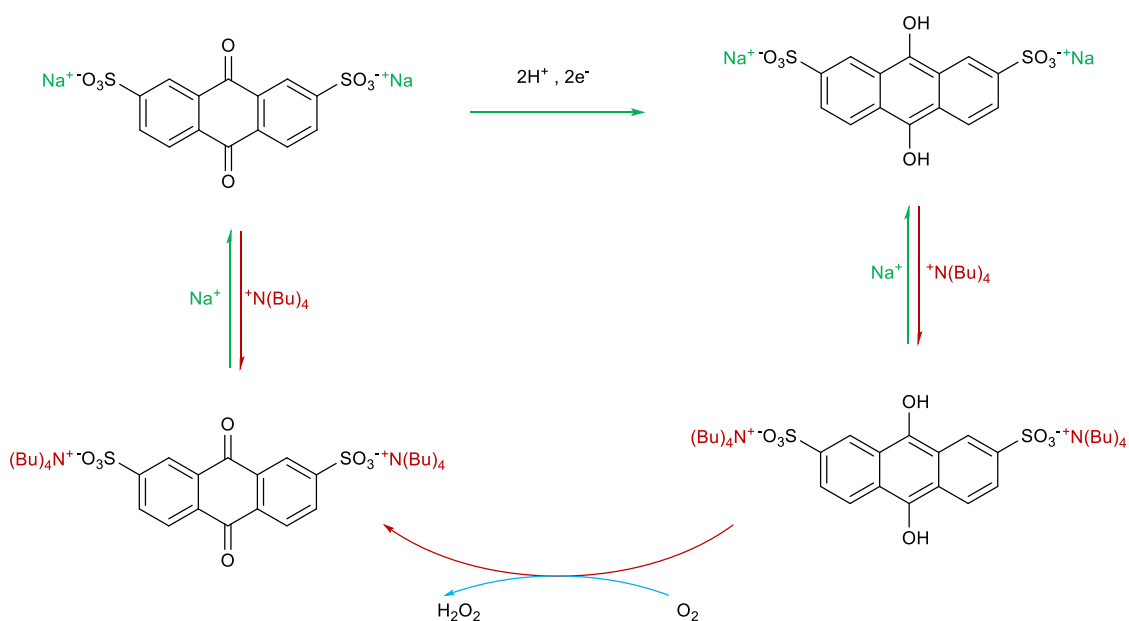


Figure 4. Schematic depicting the electrochemical reduction of AQDSNa₂ to AQDSH₂Na₂ (top arrow), phase transfer equilibration between AQDSNa₂ and AQDS(TBA)₂ (left), phase transfer equilibration between AQDSH₂(TBA)₂ and AQDSH₂Na₂ (right), and mediated O₂ reduction to H₂O₂ (bottom arrows).

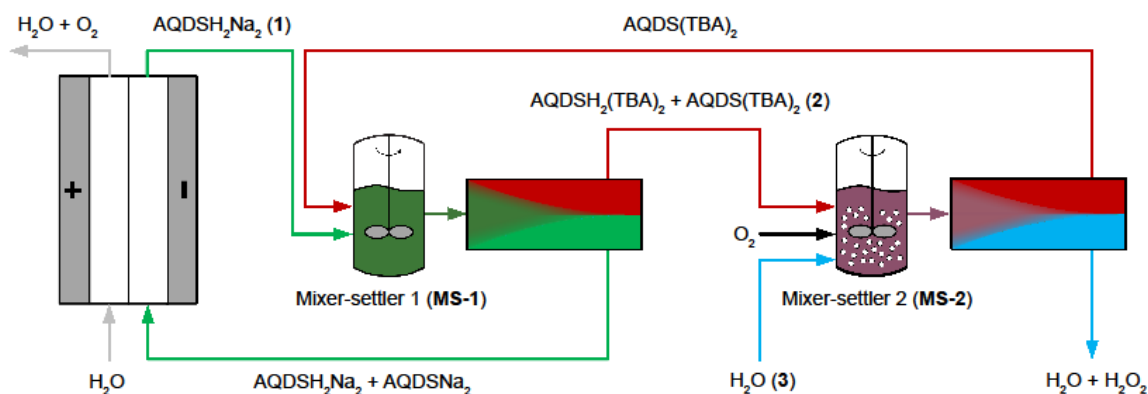


Figure 5. Detailed scheme for the proof-of-concept H_2O_2 synthesis/separation device. The scheme depicts the electrochemical cell (left), mixer-settler 1, MS-1 (middle), and mixer-settler 2, MS-2 (right). See Figure S6 for additional detail.

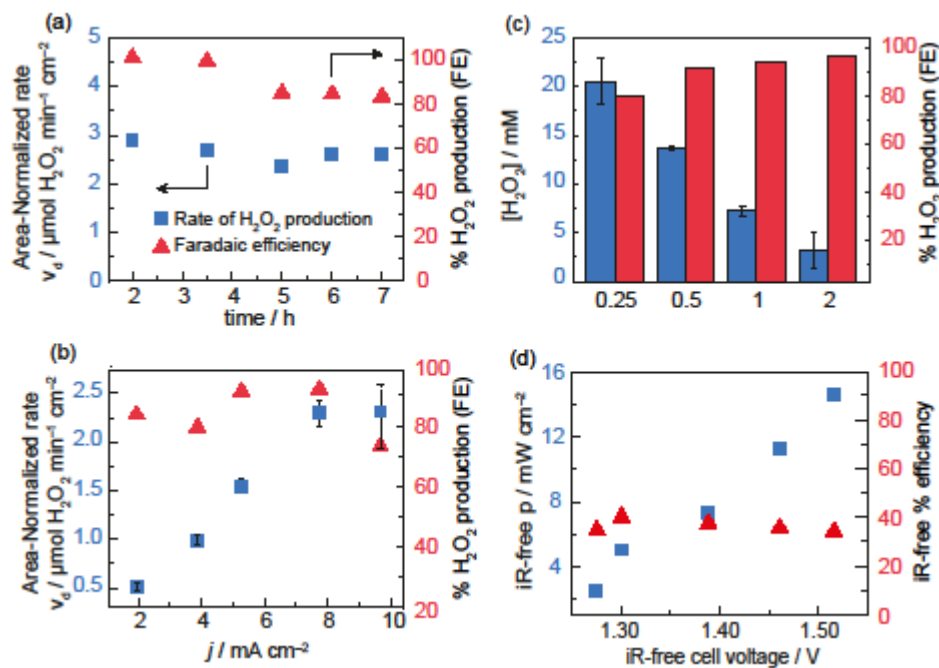


Figure 6. (a) Area-normalized rate of H_2O_2 production, v_a (left axis, blue squares), and Faradaic efficiency (right axis, red triangles) vs time. (b) H_2O_2 production rate (left axis, blue squares) and Faradaic efficiency (right axis, red triangles) vs the applied current density, j . (c) Steady state H_2O_2 concentration in the product stream (left axis, blue bars) and Faradaic efficiency (right axis, red bars) vs the ratio of flow rates of streams **2** and **3** (see Figure 3) (d) Power density consumed by the device (left axis, blue squares), and iR-free % efficiency for H_2O_2 production (right axis, red triangles), as a function of the iR-free cell voltage. Error bars show standard deviation of the mean from average of three runs.