The integration of electrical energy generated from solar and wind power into the grid is faced with the challenge of intermittent electricity output from these sources. This challenge can be effectively met by storing the electricity during times of excess production and releasing the electrical energy to the grid during times of peak demand. Rechargeable batteries are very attractive for energy storage because of their high energy efficiency and scalability. Since grid-scale electrical energy storage requires hundreds of gigawatt-hours to be stored, the batteries for this application must be inexpensive, robust, safe and sustainable. None of today’s mature battery technologies meet all of these requirements. The vanadium redox flow battery is one such battery technology that has reached an advanced level of development for grid-scale applications. However, the limited resources of vanadium, the high expense associated with the cell materials, and the toxicity hazard of using large quantities of soluble vanadium, have been the major challenges to the widespread adoption of the vanadium redox flow battery. Aiming to overcome these disadvantages, we have demonstrated for the first time an aqueous redox flow battery that uses water-soluble organic redox couples at both electrodes that are metal-free. Such a battery has the potential to meet the demanding cost, durability, eco-friendliness, and sustainability requirements for grid-scale electrical energy storage. We have termed this battery an Organic Redox Flow Battery (ORBAT).

In ORBAT, two different aqueous solutions of water-soluble organic redox substances such as quinones are circulated past electrodes. The positive and negative electrodes are separated by a proton-conducting polymer electrolyte membrane (Figure 1). In the schematic, the positive electrode uses a solution of 1,2-benzquinone-3,5-disulfonic acid (BQDS) and the negative electrode uses a solution of 1,2- dihydrobenzoquinone-3,5-disulfonic acid (AQDS). By choosing the appropriate organic redox couples for the positive and negative electrodes, we project that a cell voltage as high as 1.0 V can be achieved. The quinones have a charge capacity in the range of 200–490 Ah/kg, and cost about $5–10/kg or $10–20/kWh, leaving ample scope for achieving the US Department of Energy’s target of $100/kWh for the entire battery system. ORBAT is unique in that it does not use any heavy metals such as vanadium, chromium or zinc, and also avoids volatile organic solvents such as those used in lithium batteries. Additionally, the redox reactions will not require any expensive precious metal catalysts or metallic electrodes. With the potential of being simultaneously inexpensive and environmentally-friendly such a battery presents an attractive solution for grid-scale energy storage.

While oxidation-reduction properties of organic compounds such as quinones have been known to electrochemists for many years, hardly a handful of these material pairs have been exploited for energy storage, especially as rechargeable batteries. Furthermore, to our knowledge none of these compounds have been studied for a large-scale energy storage system. In 2009, Xu and Wen studied a battery that uses 1,2-benzquinone disulfonic acid as a positive electrode solution and combined it with a conventional lead sulfate negative electrode. We made a public announcement of the idea of a battery with a dual-aqueous feed of water soluble organic redox couples as part of the ARPA-E project press release in March 2013 and presented technical results on the operation of such a battery at the Electrochemical Society Meeting in October 2013. More recently, in January 2014, Aziz et al. reported the use of aqueous solutions of anthraquinone-2,7-disulfonic acid at the negative electrode in a redox flow battery with a bromine flow electrode on the positive side and highlighted the possibility of avoiding heavy metals. These quinone/bromine flow cells perform at high current densities of 1 A/cm² demonstrating the possibility of using the organic redox cou-
amples for achieving high power densities. However, the bromine-based positive electrode presents some challenges with respect to handling and use of bromine, and also bromine crossover from the positive to the negative electrode. The use of a water-soluble organic redox couple at the positive electrode that we have studied here has the clear prospect of overcoming the foregoing problems. Non-aqueous solutions of organic redox substances have been considered by Rasmussen and Brusheft.\textsuperscript{14,15} In this publication, we focus on understanding the performance characteristics of a dual-aqueous feed organic flow battery and discuss the materials, challenges, and directions for further research in this area.

Factors Governing the Operation of ORBAT

Charge-transfer processes.— The principal basis of an efficient rechargeable redox flow battery is the rapid kinetics of charge-transfer at the positive and negative electrodes. Many organic redox couples, especially from the quinone family, undergo rapid proton-coupled electron transfer without the need for dissociating high energy bonds. Consequently, these redox couples have relatively high rate constants for the charge-transfer process. In general, we expect molecules with conjugated carbon-carbon bonds and keto- and enol groups that allow for the delocalization and rearrangement of the pi-electrons to undergo these redox transformations with extraordinary facility.\textsuperscript{16} Typical organic redox couples are 1,2-benzoquinone-3,5-disulfonic acid (BQDS) and anthraquinone-2-sulfonic acid (AQS) (Eqs. 1 and 2).

\begin{equation}
\text{HO}_3\text{SS SO}_3\text{H} + 2e^- + 2\text{H}^+ \rightleftharpoons \text{HO}_3\text{SS SO}_3\text{H} \quad E^0 = +0.85 \text{ V}
\end{equation}

\begin{equation}
\text{O} \rightleftharpoons \text{SO}_3\text{H} + 2e^- + 2\text{H}^+ \quad E^0 = +0.09 \text{ V}
\end{equation}

Such quinone-based redox couples have rate constants that are 2–3 orders of magnitude higher than that of the vanadium ions in the commercial vanadium redox system.\textsuperscript{17,18} Overpotential losses from charge-transfer are expected to be low with these organic redox couples. As dissociation and rearrangement of C-C and C-H bonds do not occur in these electrochemical reactions, high-surface area conductive metal-free electrode surfaces, such as those based on carbon black, are sufficient to support the charge-transfer process. No precious metal electro-catalyst is required. Selecting the appropriate compounds with fast rate constants (on the order of $10^{-3}$ to $10^{-4}$ cm s$^{-1}$) is necessary when considering the technical viability of ORBAT.

Cell voltage.— The standard reduction potential of the redox couple is characteristic of the molecule and its specific substituent groups. Since the standard reduction potential is also related to the electronic energy of the molecular orbitals, the voltage of a redox flow cell is determined by the difference in energy of the highest occupied molecular orbital (HOMO) of redox couple used as the negative electrode material and the lowest unoccupied molecular orbital (LUMO) of the redox couple used as the positive electrode material. Previous experimental studies on quinones show that electron-withdrawing substituent groups lower the energy levels of the HOMO and LUMO, while electron-donating substituents raise the levels.\textsuperscript{19} Thus, we can use substituent groups to selectively tune the standard reduction potential of the quinone compounds to achieve the desired cell voltage. We may use the Gibbs free-energy change for the reduction of the redox couple with hydrogen, as estimated from quantum mechanical calculations, to determine the standard reduction potential of the redox couples.

Being an aqueous battery, the voltage range for ORBAT is limited by the oxygen evolution reaction at the positive electrode and the hydrogen evolution reaction at the negative electrode. Consequently, a maximum cell voltage of 1.23 V is to be expected at room temperature. However, by inhibiting the kinetics of the hydrogen evolution and oxygen evolution reactions, we may achieve higher cell voltages. In this respect, the non-aqueous systems have an advantage of being able to provide a wider range of cell voltage. However, the inherent advantage of lower cost and higher level of safety presented by aqueous systems is particularly attractive for large-scale energy storage applications.

Mass transport processes.— To realize a low-cost battery, we must be able to operate at high current densities without compromising voltage efficiency. With the rapid charge transfer processes in quinones, the current density will be limited by mass transport of the reactants and products. If a current density of 100 mA cm$^{-2}$ is required at a reactant concentration of 1 M, we may use the steady-state Nernst diffusion layer model to estimate the mass transport coefficients to be approximately $5 \times 10^{-4}$ cm s$^{-1}$.\textsuperscript{20} Consequently, to maintain a current density of 100 mA cm$^{-2}$ with a redox couple that has a solubility of 1 M and a diffusion coefficient of about $1 \times 10^{-6}$ cm$^2$ s$^{-1}$, the solutions must be circulated past the electrodes so as to maintain a thin diffusion layer of approximately 2 $\times 10^{-3}$ cm. Such a diffusion layer thickness is in the practical range of values observed with rapid circulation. Flow-through electrodes can lead to further reduction in diffusion layer thickness.\textsuperscript{21,22} Thus, the diffusion coefficient and solubility of the redox couple are principal properties for which the values must be as high as possible for reaching the performance and cost targets for large-scale energy storage applications.

In general, the un-substituted quinones exhibit limited solubility in water. However, the solubility of the quinones can be increased substantially by the incorporation of sulfonic acid and hydroxyl substituents. For example, benzoquinone has a solubility of 0.1 M, while BQDS has a solubility of approximately 1.7 M at 25°C. Further increases in solubility can be achieved by raising the temperature. Therefore, achieving solubility values as high as 2 M is practical even within the quinone family of compounds. Other organic redox couples with high aqueous solubility include carboxylic acids and aromatic heterocyclic compounds.\textsuperscript{8}

Reactivity and long-term cycling.— Under acidic conditions, the electro-reduction of quinones occurs often by a concerted proton transfer and electron transfer process and no radical species are produced as part of this redox process. Sometimes, the mechanisms could involve sequential steps of protonation and electron transfer.\textsuperscript{23} Additionally, alkaline environments favor the formation of anion radicals that tend to be reactive. Such formation of radicals in alkaline medium is commonly encountered at about a pH of 9 and have lifetimes long enough to be studied by electron spin resonance spectroscopy.\textsuperscript{10,23–25} Another significant benefit of acidic over alkaline systems arises from the absence of free cations besides the proton (or hydronium ion) in the solutions. Thus, a proton exchange membrane electrolyte with high ionic conductivity can be used. Inexpensive hydrocarbon membranes such as polysulfonoresulfonic acid, sulfonated polyetheretherketone and sulfonated polyethersulfone can also be used instead of Nafion.\textsuperscript{26,27} Furthermore, the proton exchange membrane will inhibit the transport of any anionic chemical species across the membrane avoiding crossover of reactants from one side of the cell to another, thereby avoiding self-discharge. Consequently, the long-cycle life requirement of large-scale energy storage systems is more likely to be realized with acidic systems.

For continuous operation at temperatures as high as 60°C the selected organic compounds must have sufficient hydrolytic stability. The quinones are generally quite stable in contact with oxygen. However, when the reduced form of the quinones (hydroquinones) in solution come in contact with oxygen from air, the reduced form can be re-oxidized to the quinone form. No permanent loss of material prop-
Faradaic efficiency.— The potential for faradaic efficiency losses are generally associated with the negative electrode in these types of systems due to the proximity of the hydrogen evolution potential. In the case of AQDS, the standard reduction potential is about 100 mV, where the Tafel equation is applicable (Eq.4 and Figure3e). To determine the kinetic parameters for the charge-transfer process occurring on a glassy carbon electrode in the oxidized form for BQDS suggested a possible slow chemical step following electron transfer. Such a slow step is consistent with the self-discharge process can be prevented by allowing the proximity of the redox couple. The calculations were performed at the B3LYP/6-31+G(d,p) level of theory with thermal correction and implicit consideration of water-solvation. The free energy correction for the standard state of 1 atm in the gas phase and 1 M solution was applied, i.e., $\Delta G_{\text{solute}} = \Delta G_{\text{gas}} + 1.9$ kcal·mol$^{-1}$ at 298 K. Considering the lower $pK_w$ value of benzenesulfonic acid ($pK_w$ of benzenesulfonic acid) = $-2.8$), the quinone sulfonic acid derivatives are expected to dissociate to sulfonates in 1 M sulfonic acid aqueous solution. $\Delta G^*$ was calculated based on the reduction of quinone derivatives with $H_2$. The standard electrode potential for the redox couple was deduced from $E^* = \Delta G^*/nF$, where $n$ is the number of protons involved in the reaction and $F$ is the Faraday constant.

Results and Discussion

Cyclic voltammetric measurements on AQS and AQDS show a single step electrochemical reaction involving two electrons (Figures 2a and 2b). Peak separations suggested AQDS was less kinetically reversible than AQS. The cyclic voltammograms for BQDS showed a rapid oxidation step, but a slower reduction step (Figure 2c). The shape of the reduction peak for BQDS suggested a possible slow chemical step following electron transfer. Such a slow step is consistent with the hydration process leading to the conversion of the hydroquinone to 1,4-benzoquinone-2-hydroxy-3,5-disulfonic acid, as reported by Xu and Wen.10 The reversible potentials estimated from the anodic and cathodic scans for the three compounds were in agreement with the quantum mechanical calculations (Table I). The facile proton and electron transfer processes occurring on a glassy carbon electrode in the absence of any catalyst confirmed an outer-sphere type of mechanism.

Linear sweep voltammetric measurements at a rotating disk electrode at various rotation rates (Figure 3a–3c) showed that the limiting current, $I_{\text{lim}}$, was found to depend linearly on the square root of the rotation rate, $\omega$, as per the Levich equation (Eq. 3).

$$ I_{\text{lim}} = 0.62n F A D_a^{1/2} \omega^{1/6} v^{-1/6} C^* $$

where $n$ is the number of electrons transferred, $F$, the Faraday constant, $A$, the electrode area, $D_a$, the diffusion coefficient, $v$, the kinematic viscosity of the solution and $C^*$, the bulk concentration of the reactants. For $n = 2$, an active electrode area of 0.1925 cm$^2$, and a kinematic viscosity of the electrolyte of 0.01 cm$^2$·s$^{-1}$, we were able to evaluate the diffusion coefficient from the slope of the straight line plots in Figure 3d.

To determine the kinetic parameters for the charge-transfer process, namely the rate constant and the apparent transfer coefficient, the logarithm of the kinetic current (after correction for mass-transport losses) was plotted against the observed overpotentials greater than 100 mV, where the Tafel equation is applicable (Eq. 4 and Figure 3e).

$$ \left( \frac{I}{1 - \frac{I}{I_{\text{lim}}}} \right) = I_{\text{ex}} \left( \frac{C_O}{C_P} \right) \exp \left( \frac{-anF(E - E_{\text{rev}})}{RT} \right) $$

$$ = \frac{C_R}{C_P} \exp \left( \frac{(1 - \alpha)nF(E - E_{\text{rev}})}{RT} \right) $$

$$ \frac{1}{1 - \frac{I}{I_{\text{lim}}}} = \frac{I_{\text{ex}}}{C_O} \exp \left( \frac{-anF(E - E_{\text{rev}})}{RT} \right) \left( \frac{C_R}{C_P} \right) $$

$$ = \frac{C_R}{C_P} \exp \left( \frac{(1 - \alpha)nF(E - E_{\text{rev}})}{RT} \right) $$

Where $I$ is the current, $I_{\text{lim}}$ is the limiting current, $I_{\text{ex}}$ is the exchange current density, $C_O$ and $C_P$ are the concentration of the oxidized and reduced species at the surface of the electrode, $C_O^*$ and $C_P^*$ are the bulk concentrations of the oxidized and reduced species, $\alpha$ is the transfer coefficient, $n$ is the number of electrons transferred, $F$ is the Faraday constant, $E_{\text{rev}}$ is the overpotential, $R$ is the gas constant, and $T$ is the temperature.

The rate constant, $k_{\text{ex}}$, was obtained from the exchange current density (Eq. 5).

$$ k_{\text{ex}} = I_{\text{ex}}/nFAC^* $$
Figure 2. Cyclic voltammograms at a scan rate of 5 mV s\(^{-1}\) on a glassy carbon electrode in 1 M sulfuric acid containing (a) 1 mM anthraquinone-2-sulfonic acid, (b) 1 mM anthraquinone-2,6-disulfonic acid and (c) 1 mM 1,2-benzoquinone-3,5-disulfonic acid.

Besides BQDS, AQS and AQDS, we have also measured the current-overpotential curves for hydroquinone and hydroquinone sulfonic acid (see supplementary material). Solubility of anthraquinone in 1 M sulfuric acid was too low to obtain any reliable data.

The half-wave potential values (Table I) are consistent with the values reported in the literature for the various compounds tested.\textsuperscript{29,31} It is clear that the addition of aromatic rings has a marked effect of lowering the standard reduction potential and half-wave potential.

The addition of sulfonic acid groups tends to increase the standard reduction potential, which is consistent with the lowering of molecular orbital energies by electro-withdrawing groups.

To understand the changes in the standard reduction potentials we have used quantum mechanics to calculate the free-energy change in the reaction of the oxidized form of the redox couple with hydrogen. If \(\Delta G^\circ\) is the Gibbs free energy change under standard conditions, then

\[
-\frac{\Delta G^\circ}{nF} \text{ is the standard electrode potential for the redox couple,}
\]

### Table I. Standard reduction potentials for selected quinones.

<table>
<thead>
<tr>
<th>Redox Couple</th>
<th>Experimental ((E_{1/2}) values) vs. NHE</th>
<th>(E_0) (formal)</th>
<th>Theoretical</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydroquinone</td>
<td>0.67</td>
<td>0.68</td>
<td>0.70</td>
</tr>
<tr>
<td>Hydroquinone sulfonic acid</td>
<td>0.82</td>
<td>0.70</td>
<td>0.77</td>
</tr>
<tr>
<td>1,2-benzoquinone -3,5-disulfonic acid</td>
<td>1.1</td>
<td>0.87</td>
<td>0.85</td>
</tr>
<tr>
<td>Anthraquinone</td>
<td>Insoluble</td>
<td>Insoluble</td>
<td></td>
</tr>
<tr>
<td>Anthraquinone-2-sulfonic acid</td>
<td>0.13</td>
<td>0.15</td>
<td>0.09</td>
</tr>
<tr>
<td>Anthraquinone-2,6-sulfonic acid</td>
<td>0.05</td>
<td>0.19</td>
<td>0.12</td>
</tr>
</tbody>
</table>
Figure 3. Linear sweep voltammetric data (scan rate of 5 mV s\(^{-1}\)) at a glassy carbon rotating disk electrode for 1 mM concentration of BQDS (a), AQS (b) and AQDS (c) at the rotation rates indicated. Electrode potentials are versus a mercury sulfate reference electrode (\(E_0 = +0.65\)). (d) Levich plot of the square root of rotation rate vs the limiting current for AQS (♦), BQDS (Δ), and AQDS (○). (e) Mass transport-corrected current-voltage plot for BQDS, AQS, and AQDS.

where \(n\) is the number of protons involved in the reaction and the \(F\) is the Faraday constant. The values of \(E_{1/2}\) from experiments follow the trends predicted by the theoretical calculations (Table I). The strong correlation between experimental and theoretical predictions suggest that such free energy calculations can be used to predict the trends in \(E_{1/2}\) values of the redox compounds prior to experimental testing, potentially enabling the discovery of new redox couples by this computational approach.

The values of diffusion coefficients (Table II) are about an order of magnitude smaller in aqueous solutions than in non-aqueous...
solvents such as acetonitrile. In aqueous solutions, the observed extent of decrease in the values of diffusion coefficients with increase in molecular mass is about $6 \times 10^{-9}$ cm$^2$ s$^{-1}$ per unit of molecular mass. This coefficient is an order of magnitude lower than that observed in acetonitrile. Thus, besides the effect of molecular mass, the molecular diameters resulting from the solvation and the interaction of ionic groups with water through hydrogen bonding have a significant effect on the diffusion coefficient values in aqueous solutions.

Rate constants are within the range of values found widely in the literature for quinones. As sulfonic acid groups are added to the ring, the intra-molecular hydrogen bonding interactions in the quinone molecules increase. This intra-molecular hydrogen bonding plays a critical role in the rate limiting step of proton-coupled electron transfer, due to the increased stability of the compound and increased cleavage energy required for concerted proton and electron transfer. This stability provides a competition between the resident hydrogen atom and the incoming proton for interaction with the carbonyl oxygen. According to our calculations, hydroquinone sulfonic acid preferentially adopts a conformation allowing the formation of intra-molecular hydrogen bonding, which leads to a stabilization energy of 1.6 kcal mol$^{-1}$. Similarly, intra-molecular hydrogen bonding provides extra stabilization of other hydroquinone sulfonic acid derivatives (Eq. 6 and Eq. 7). Thus, the intra-molecular hydrogen bonding could explain the lowering of the rate constants observed with the addition of sulfonic acid groups.

The quinone-based redox systems have been extensively reported in the literature and it is well known that these systems undergo proton-coupled electron transfer. The rate constants for charge transfer were generally quite high, at least an order of magnitude higher than that observed for the vanadium redox couples. The value of the transfer coefficients being close to 0.5 and the high values of rate constants suggest an “outer-sphere” process.

While the rate constants for the various compounds were at least one order of magnitude greater than that of vanadium system, the diffusion coefficients were comparable to that of vanadium, making the quinone redox couples very attractive from the standpoint of electrode kinetics compared to the vanadium redox flow battery system.

The Nernst diffusion layer model allows us to estimate the limiting current for the oxidation and reduction processes (Eq. 8).

$$I_{\text{lim}} = n F C^\ast D \delta$$

Where $I_{\text{lim}}$ is the limiting current density, $n$ is the number of moles of electrons transferred per mole of reactants, $F$ is the Faraday constant (96485 C mole$^{-1}$), $C^\ast$ is the concentration, $D$ is the diffusion coefficient, and $\delta$ is the diffusion layer thickness.

For a diffusion layer thickness of 50 microns, a diffusion coefficient of $3.8 \times 10^{-6}$ cm$^2$ s$^{-1}$, and a bulk concentration of 0.2 M, we predict from Eq. 8 a limiting current density of 30 mA cm$^{-2}$. Further increase in limiting current density can be achieved by increasing the concentration of reactants, reducing the diffusion layer thickness, and by increasing the diffusion coefficient. Higher concentrations and diffusion coefficients are achieved by raising the operating temperature while a lower diffusion layer thickness can be achieved by increased convective mass transport to the surface of the electrode.

We have operated flow cells with aqueous solutions of 0.2 M BQDS at the positive electrode and 0.2 M AQDS or 0.2M AQDS at the negative electrode. In these cells the electrodes consisted of Toray paper coated with high-surface area carbon black bonded to the Nafion membrane. These cells did not show any noticeable change in capacity over at least 12 cycles of repeated charge and discharge (Figure 4). This result confirmed that the quinones in aqueous acid solution are chemically stable to repeated cycling. The capacity realized at a current density of 10 mA cm$^{-2}$ was over 90% of the capacity contained in the solutions. The use of Toray paper electrodes on either side of the cell as current collecting surfaces presented a barrier to convective transport, setting the diffusion layer thickness to as high as 150 microns, reducing the limiting current density and lowering the cell voltage.

Increasing the mass transport of reactants and products improved the current density and cell voltage significantly. In one configuration of the electrodes, the increase in mass transport was achieved by punching nine equally-spaced holes 1 cm in diameter in the Toray paper electrodes to allow the flow of redox active materials to shear directly past the carbon black layer bonded to the membrane. The increased current and voltage observed as a result of the change in the access of the redox materials to the electrode (Figure 5) confirmed that the kinetics of the electrode reactions are largely controlled by the mass transport of the reactants and products.

The dependency of cell voltage on current density when measured as a function of the state of charge of ORBAT confirmed that the mass transport of reactants had a significant impact on the operating cell voltage (Figure 6a). The power density of the cell decreased significantly below 50% state-of-charge. The alternating current impedance of the cells measured as a function of frequency also confirmed that the mass transport limitations increased as the state-of-charge decreased. The slopes of the Nyquist plot at low frequencies were found to steadily increase with decreasing state-of-charge, while the rest of the impedance spectrum remained almost unaffected (Figure 6b), suggesting an increasing thickness of the diffusion layers with a decrease in the state-of-charge. Therefore, it is clear from

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**Table II. Electrochemical properties of the redox couples determined from rotating disk electrode experiments. MSE refers to the mercury sulfate reference electrode ($E^\circ = +0.65$ V).**

<table>
<thead>
<tr>
<th>Redox Couple</th>
<th>$E^\circ$ vs. MSE, (Volt)</th>
<th>Exchange Current Density, (A cm$^{-2}$)</th>
<th>Diffusion Coefficient, (cm$^2$ s$^{-1}$)</th>
<th>Transfer Coefficient, (cm$^2$ s$^{-1}$)</th>
<th>Solubility, (cm$^2$ s$^{-1}$)</th>
<th>Constant, (cm$^2$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydroquinone</td>
<td>0.02</td>
<td>5.09E-5</td>
<td>5.03E-6</td>
<td>0.508</td>
<td>0.53 M</td>
<td>2.36E-3</td>
</tr>
<tr>
<td>Hydroquinone sulfonic acid</td>
<td>0.17</td>
<td>1.10E-5</td>
<td>4.28E-6</td>
<td>0.418</td>
<td>0.8 M</td>
<td>5.52E-4</td>
</tr>
<tr>
<td>1,2-benzquinone-3,5-disulfonic acid</td>
<td>0.45</td>
<td>3.00E-6</td>
<td>3.80E-6</td>
<td>0.582</td>
<td>1 M</td>
<td>1.55E-4</td>
</tr>
<tr>
<td>Anthraquinone-2-sulfonic acid</td>
<td>-0.52</td>
<td>1.96E-5</td>
<td>3.71E-6</td>
<td>0.677</td>
<td>0.2 M</td>
<td>2.25E-4</td>
</tr>
<tr>
<td>Anthraquinone 2,6-disulfonic acid</td>
<td>-0.60</td>
<td>2.97E-6</td>
<td>3.40E-6</td>
<td>0.426</td>
<td>0.5 M</td>
<td>1.52E-4</td>
</tr>
</tbody>
</table>

---

[6]  The quinone-based redox systems have been extensively reported in the literature and it is well known that these systems undergo proton-coupled electron transfer. The rate constants for charge transfer were generally quite high.

[7]  While the rate constants for the various compounds were at least one order of magnitude greater than that of vanadium system, the diffusion coefficients were comparable to that of vanadium.
the results in Figure 6 that at all current densities, mass transport limitations made a significant contribution to the overpotential losses.

In an effort to understand the results presented in Figure 6, we have analysed the effect of state-of-charge on the current-voltage characteristics using a simplified one-dimensional model (see Appendix). The assumptions in this analysis are based on experimental findings from RDE studies and flow cell studies that show that the charge-transfer reactions are facile and that mass transport processes determine the cell voltage during operation.

The analysis yields the following relationship between the observed cell voltage and the discharge current as a function of state-of-charge.

\[
V_{\text{cell}} = E^0_c - E^0_a + \frac{RT}{nF} \ln \left( \frac{Q^2}{(1-Q)^2} \right) - 2I_d \left( \frac{RT}{nF} \right) \left[ \frac{1}{nFm_lAQc_i - I_d} \right] + \frac{1}{nFm_lA(1-Q)c_i + I_d} - I_d R_{\text{ohm cell}} \]

[9]

Where \( V_{\text{cell}} \) is the cell voltage during discharge and \( E^0_{\text{c/n cath}} \) and \( E^0_{\text{a/anode}} \) are the standard reduction potentials for the two redox couples used at the cathode and anode, respectively. \( I_d \) is the discharge current and \( Q \) is the state-of-charge with values between 0 to 1. \( C_{\text{initial}} \) is the starting concentration of the reactants at 100% state-of-charge; \( C_{\text{initial}} \) is assumed in this analysis to be the same at both electrodes. \( A \) is the area of the electrode, and \( m_l \) is the mass transport coefficient defined as the diffusion coefficient divided by the diffusion layer thickness. \( R \) is the universal gas constant, \( F \) is the Faraday constant, \( T \) is the temperature, and \( n \) is the number of electrons in the redox reaction.

Eq. 9 has been graphed (Figure 7) for various states-of-charge using experimentally determined parameters for the BQDS and AQS system (Table III). Comparison of Figure 7 with the experimental data in Figure 6 shows general agreement of the trend predicted by the analysis with the observed experimental results; decrease in state-of-charge resulted in a decrease of discharge current at any particular voltage, leading to a significant reduction in discharge rate capability at low states-of-charge. However, the experimental current-voltage curves were nearly linear at the high states of charge and the experimental values of cell voltage at low current values decreased substantially with decreasing state-of-charge. These deviations from the analytical expression suggest that there are additional resistance elements under dynamic operating conditions that are not captured in the simplified analysis. We list at least two other effects that can cause substantial changes to the observed voltage:

1. Electro-osmotic drag of water molecules (estimated to be about 3 molecules per proton) occurs across the membrane during passage of current. These water molecules either appear at or are removed from the diffusion layer at each electrode causing changes to the pH and concentration of reactants and products. These concentration changes at the interface will contribute to a reduction in cell voltage. For example, at the cathode during discharge, water molecules could be added to the diffusion layer causing the pH to increase and, consequently, the electrode potential to decrease. Correspondingly, water molecules will be removed from
Figure 6. 25 cm² redox flow cell, 0.2 M BQDS, 0.2 M AQS, 1 M sulfuric acid (a) Cell voltage-current density curves as a function of state-of-charge (5% difference each run). (b) Impedance spectroscopy data from 10 kHz to 10 mHz on the cells at various states-of-charge.

Table III. Parameters used in the analysis of current-voltage curves as a function of state-of-charge.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard Reduction Potential of Cathode (E_{cath}), V</td>
<td>+0.45</td>
</tr>
<tr>
<td>Standard Reduction Potential of Anode (E_{anod}), V</td>
<td>−0.52</td>
</tr>
<tr>
<td>Initial concentration of reactants (C_{initial}) moles cm⁻³</td>
<td>2 E-4</td>
</tr>
<tr>
<td>Diffusion coefficient of cathode and anode reactants and products (D) cm² s⁻¹</td>
<td>4E-6</td>
</tr>
<tr>
<td>Diffusion layer thickness (δ) cm</td>
<td>4E-3</td>
</tr>
<tr>
<td>Geometric Area of the Electrode (A), cm²</td>
<td>25</td>
</tr>
<tr>
<td>Number of electrons in the reaction (n)</td>
<td>2</td>
</tr>
<tr>
<td>Series equivalent resistance at impedance at 10 kHz (R_{ohmcell}), Ohm</td>
<td>0.05</td>
</tr>
</tbody>
</table>

the anode, causing the pH to decrease, the electrode potential to increase, and the cell voltage to decrease.

2. At the anode, we use a solution of AQS at concentrations close to the solubility limit (0.2 M). Consequently, at a low state-of-charge when the oxidized form of AQS at the negative electrode is present in high concentrations in the bulk of the solution, the high rates of discharge would cause the solubility limits to be exceeded at the surface of the negative electrode. This would result in the precipitation of redox materials at the surface of the electrode and with a significant reduction of the current. To avoid such an abrupt drop in cell voltage at high current densities and low states-of-charge, the solubility of the redox materials must be high. Additionally, reducing the thickness of the diffusion layer by using a flow-through electrode will increase the “saturation-limited” current density.

The analysis helps us to quantify the variations in performance that can result from changes to local mass-transport conditions at any state-of-charge. The observed differences between the experimental data and the predictions of simple analysis of the cell performance also help us to identify the phenomena that are important to consider for further design and modeling of redox flow cells.

When an aqueous solution of 0.2 M AQDS was used on the negative side of the flow battery, the tests showed charge-discharge cycling...
At various states-of-charge. Such findings motivate us to investigate AQS highlights the role of solubility limits on the rate capability of AQS. The aqueous solubility limit of AQDS is about 0.5 M while higher concentrations and temperatures with AQDS in future studies. Thus, higher solubility allows the cell voltage to be maintained at a higher value with AQDS compared to AQS especially with AQS. Consequently, even at very low states-of-charge, the solubility limit was less likely to be exceeded with AQDS than with AQS. Therefore, higher solubility allows the cell voltage to be maintained at a higher value with AQDS compared to AQS especially at low states-of-charge. This difference in performance of AQDS and AQS highlights the role of solubility limits on the rate capability at various states-of-charge. Such findings motivate us to investigate higher concentrations and temperatures with AQDS in future studies.

Conclusions

For the first time, we have demonstrated the feasibility of operating an aqueous redox flow cell with reversible water-soluble organic redox couples (we have termed ORBAT). This type of metal-free flow battery opens up a new area of research for realizing inexpensive and robust electrochemical systems for large-scale energy storage. The cells were successfully operated with 1,2-benzoquinone disulfonic acid at the cathode and anthraquinone-2-sulfonic acid or anthraquinone-2,6-disulfonic acid at the anode. The cell used a membrane-electrode assembly configuration similar to that used in the direct methanol fuel cell. 39 We have shown that no precious metal catalyst is needed because these redox couples undergo fast proton-coupled electron transfer.

We have determined the critical electrochemical parameters and various other factors governing the performance of the cells. The standard reduction potentials calculated using density functional theory were consistent with the experimentally determined values. This type of agreement suggested that quantum mechanical methods for prediction of the reduction potentials could be used reliably for screening various redox compounds. The experimental values of the diffusion coefficients of the various quinones in aqueous sulfuric acid suggested that strong interaction of the ionized quinones with water resulted in lower diffusion coefficients compared to those in non-aqueous media. Further, we found that significant stabilization by intra-molecular hydrogen bonding occurred with the sulfonic acid substituted molecules. These differences will be important to consider in interpreting the changes in the rate of proton-coupled electron transfer in these molecules.

Our experiments also demonstrated that the organic redox flow cells could be charged and discharged multiple times at high faradaic efficiency without any sign of degradation. Our analysis of cell performance shows that the mass transport of reactants and products and their solubilities are critical to achieving high current densities.

Further testing and analysis is underway to understand the behavior of other redox couples in the quinone family, assess the impact of solubility on full cell performance, and optimize the structure of the membrane-electrode assemblies. Solubility is still a challenge for this type of redox flow battery. Choosing a substituent such as sulfonic acid to modify both positive and negative electrode materials appears to be the most promising approach at this time to meet the challenge of solubility in water. However, understanding the effect of substituent group type and placement on the standard reduction potential and kinetic reversibility are also important areas for further study.

Acknowledgment

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Appendix

Analysis of Current-voltage Curves at Various States of Charge

The following analysis is aimed at deriving a relationship between cell voltage and discharge current for a flow battery using electrochemically reversible redox couples. For any cell undergoing discharge, the cell voltage and current are related by Eq. A1.

\[
V_{\text{cell}} = E_o - E_a - \frac{R T}{n F} \ln \left( \frac{C_o}{C_a} \right) \quad [A1]
\]

Where \( V_{\text{cell}} \) is the cell voltage, \( E_o \) is the electrode potential of the cathode, \( E_a \) is the electrode potential of the anode, \( I \) is the discharge current, and \( R_{\text{el}} \) is the series equivalent resistance of the electrolyte and current collectors.

For electrodes with reactions involving with rapid charge transfer kinetics relative to mass transport processes (usually termed as kinetically reversible reactions), the electrode potentials are given by the Nernst equation.

\[
E_c = E^\circ_c + \frac{R T}{n F} \ln \left( \frac{C_o}{C_a} \right) \quad [A2]
\]

\[
E_a = E^\circ_a + \frac{R T}{n F} \ln \left( \frac{C_o}{C_a} \right) \quad [A3]
\]

In Eqs. A2 and A3, and in subsequent equations, the subscripts \( c \) and \( a \) refer to the cathode and anode, respectively. \( C_o \) and \( C_a \) are the concentrations of the oxidized and reduced species at the surface of the electrode. Let \( C_o^*, C_a^*, C_o^{\circ*}, C_a^{\circ*} \) be the concentration of the species in the bulk of the solution at the respective electrodes, and the asterisk will always refer to the values in the bulk of the solution. When the flow rate is high relative to the consumption rate at the electrodes, we expect the concentrations to be uniform in the plane of the electrode. Under these conditions, we may describe the variation in concentration due to mass transport limitations only in one-dimension, i.e., perpendicular to the surface of the electrode.

In the steady-state, the discharge current \( I_{\text{disch}} \) can be related to the diffusion coefficient, \( D \), concentration of reactants and products, and the diffusion layer thickness, \( h \) by

\[
I_{\text{disch}} = n F D C_d h \rho \quad [A4]
\]
We also define the mass transfer coefficient, \( m \), as equal to \( \Delta F / \Delta \Omega \) for the oxidized and reduced species. The values of \( m \) for the cathode and anode will be assumed to be same in the analysis because we are considering a case of symmetrical electrode structures and same flow rates, and molecules with very similar diffusion coefficients. \( A \) is the area of the electrode.

Re-arranging Eqs. A4 and A5 we obtain,

\[
C_{x,0} = \frac{I_{\text{disch}}}{n F A m} \times C_{x,0} + \frac{I_{\text{disch}}}{n F A m} + C_{x,0}
\]

Similarly, at the anode, the discharge current and surface concentration are given by,

\[
C_{x,0} = \frac{I_{\text{disch}}}{n F A m} + C_{x,0} \quad C_{x,0} = \frac{I_{\text{disch}}}{n F A m}
\]

The change in concentration resulting from changes at the anode and cathode is given by

\[
dC_{x,0} = \frac{dI_{\text{disch}}}{n F A m}
\]

\[
dC_{x,0} = \frac{dI_{\text{disch}}}{n F A m}
\]

From the Nernst equation, we can obtain the change in potential resulting from such changes in concentration.

\[
de_E = \frac{RT}{n F} \left[ C_{x,0} \frac{dC_{x,0}}{dI_{\text{disch}}} \right] \frac{Q_{\text{initial}}}{Q_{\text{initial}}}
\]

\[
de_E = \frac{RT}{n F} \left[ C_{x,0} \frac{dC_{x,0}}{dI_{\text{disch}}} \right] \frac{Q_{\text{initial}}}{Q_{\text{initial}}}
\]

From Eqs. A8, A9 and A10 we obtain,

\[
dE - E_0 = -\frac{RT}{n F} \left[ C_{x,0} \frac{dC_{x,0}}{dI_{\text{disch}}} \right]
\]

\[
dE - E_0 = -\frac{RT}{n F} \left[ C_{x,0} \frac{dC_{x,0}}{dI_{\text{disch}}} \right]
\]

Let \( C_{\text{initial}} \) be the concentration in both reservoirs of equal volume at the start of the experiment. Then, even at various states of charge, the sum of the bulk concentrations of the oxidized and reduced species on both sides will equal \( C_{\text{initial}} \).

\[
C_{\text{initial}} = C_{x,0} + C_{x,0}
\]

Since \( C_{\text{initial}} \) can now be used to define the state-of-charge, \( Q \), as follows:

\[
C_{x,0} = \frac{Q_{\text{initial}}}{Q_{\text{initial}}}
\]

\[
C_{x,0} = \frac{Q_{\text{initial}}}{Q_{\text{initial}}}
\]

The anode,

\[
C_{x,0} = \frac{Q_{\text{initial}}}{Q_{\text{initial}}}
\]

\[
C_{x,0} = \frac{Q_{\text{initial}}}{Q_{\text{initial}}}
\]

Combining Eqs. A6, A7, A11, and A12–A15, we obtain

\[
de_E - E_0 = \frac{R T}{n F} \left[ \frac{Q_{\text{initial}}}{Q_{\text{initial}}} - \frac{Q_{\text{initial}}}{Q_{\text{initial}}} \right]
\]

\[
de_E - E_0 = \frac{R T}{n F} \left[ \frac{Q_{\text{initial}}}{Q_{\text{initial}}} - \frac{Q_{\text{initial}}}{Q_{\text{initial}}} \right]
\]

At any state of charge, the electrode potential is related to the state of charge by

\[
e_{E,0} = e_{E,0} + \frac{R T}{n F} \ln \left[ \frac{Q_{\text{initial}}}{Q_{\text{initial}}} - \frac{Q_{\text{initial}}}{Q_{\text{initial}}} \right]
\]

\[
e_{E,0} = e_{E,0} + \frac{R T}{n F} \ln \left[ \frac{Q_{\text{initial}}}{Q_{\text{initial}}} - \frac{Q_{\text{initial}}}{Q_{\text{initial}}} \right]
\]

The cell voltage in Eq. A1 can then be expressed as,

\[
V_{\text{cell}} = e_{E,0} - \frac{R T}{n F} \ln \left[ \frac{Q_{\text{initial}}}{Q_{\text{initial}}} - \frac{Q_{\text{initial}}}{Q_{\text{initial}}} \right] - I_{\text{Ranbucci}}
\]

Substituting for the various terms in Eq. A19 from above, we have an expression for the cell voltage as a function of discharge current and state of charge, when the initial concentration of the active materials are the same on both sides.

\[
V_{\text{cell}} = \frac{e_{E,0} - \frac{R T}{n F} \ln \left[ \frac{Q_{\text{initial}}}{Q_{\text{initial}}} - \frac{Q_{\text{initial}}}{Q_{\text{initial}}} \right] - 2 \frac{I_{\text{Ranbucci}}}{n F A m} \left[ \frac{Q_{\text{initial}}}{Q_{\text{initial}}} - \frac{Q_{\text{initial}}}{Q_{\text{initial}}} \right] + \frac{1}{n F A m} \left[ A \left( \frac{Q_{\text{initial}}}{Q_{\text{initial}}} - \frac{Q_{\text{initial}}}{Q_{\text{initial}}} \right) - \frac{I_{\text{Ranbucci}}}{n F A m} \right]
\]