A New Michael-Reaction-Resistant Benzoquinone for Aqueous Organic Redox Flow Batteries

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As intermittent renewable energy sources based on solar photovoltaics and wind turbines are installed worldwide, electrical energy storage facilities will be of paramount importance to maintain the stability of the electricity grid and to meet the growing demand for clean energy. Rechargeable batteries have shown promise in meeting this large energy storage demand, because of their high efficiency and scalability.1–3 Redox flow batteries (RFBs) are especially attractive for stationary applications due to their scalability and their inherent ability to address the power and energy requirements independently.4,5 However, none of today’s battery technologies can meet the demands of robustness, low-cost, and environmental-friendliness simultaneously.6 Recently, flow batteries based on aqueous solutions of simple water-soluble organic redox couples, or ORBAT, have become the subject of great interest because of their prospect of offering such a grid-scale energy storage solution. Thus, the investigation into simple organic molecules that can be readily synthesized or procured for use in ORBAT has grown significantly.7–12

Specifically, we and others have found that quinone- and anthraquinone-based molecules have the essential electrochemical characteristics for the design of ORBAT.13–19 We first reported the properties of an “all-quinone” organic redox flow battery in 2014 in which the positive electrode was supplied with a solution of 4,5-dihydroxybenzene-1,3-disulfonic acid (BQDS), while the negative electrode used a solution of either anthraquinone-2-sulfonic acid (AQS) or anthraquinone-2,6-disulfonic acid (AQDS).20 The positive and negative electrode compartments were separated by a proton-conducting polymer electrolyte membrane (Figure 1). We showed that these organic redox couples undergo rapid proton-coupled electron transfer to store or release electrical energy without any expensive precious metal electrocatalysts. Furthermore, ORBAT avoids toxic and expensive heavy metals such as vanadium and chromium, and does not use volatile or flammable organic solvents that add to environmental and safety challenges. We have shown that ORBAT can be charged and discharged repeatedly with a round-trip energy efficiency of 70% at 100 mA/cm2 and 100% coulombic efficiency for 100 cycles, and achieved a power density of 100 mW/cm2, when operating the cell at high concentrations of reactants.21

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The issues arising from the Michael reaction of water with BQDS.—In our most recent publication, we presented a challenge that arose from the use of BQDS as the positive side material.21 In this cell with BQDS as the positive electrolyte and AQDS as the negative electrolyte, undesired chemical transformations of BQDS occur in addition to the necessary redox reactions. While AQDS is stable and does not undergo such chemical transformations, BQDS undergoes the Michael reaction with water. In this reaction, BQDS transforms through sequential steps of water addition and electrochemical

Figure 1. Operating principle of the Organic Redox Flow Battery (ORBAT) using aqueous solutions of 4,5-dihydroxybenzene-1,3-disulfonic acid (BQDS) at the positive electrode and anthraquinone-2,6-disulfonic acid (AQDS) at the negative electrode and the corresponding electrochemical reactions.
oxidation to eventually form 1,2,4,6-tetrahydroxybenzene-3,5-disulfonic acid – a fully substituted benzoquinone (Figure 2). Thus, although we may start with BQDS, it is the fully-substituted 1,2,4,6-tetrahydroxybenzene-3,5-disulfonic acid that undergoes charge and discharge during subsequent cycling of the cell. The Michael reaction leads to at least three technical issues:

1) Three equivalents of the negative side material (AQDS) are needed to convert every equivalent BQDS into a stable and rechargeable positive side material. However, only one equivalent of the AQDS is actually used during discharge and charge. Thus, this excess requirement of AQDS adds to the overall cost of the system, as two-thirds of the negative side material remains unutilized beyond the first charge.

2) The substituted products of the Michael reaction decrease the cell voltage of this system. The reduction potential of the molecule decreases by 100 mV for every electron-donating -OH group substitution.22

3) Incomplete utilization of AQDS results in a reduced concentration of the discharged form of AQDS, which reduces the maximum current density during subsequent charging.

The approach to design a Michael-reaction resistant benzoquinone.—To overcome the disadvantages resulting from the Michael reaction, a molecule that is resistant to this reaction is needed. To this end, we present here the design, synthesis, and properties of a new redox couple based on 3,6-dihydroxy-2,4-dimethylbenzenesulfonic acid, (DHDMBS).23 To reduce the susceptibility of the molecule to the Michael reaction it was essential to design a molecule with the minimum number of unsubstituted positions on the benzoquinone. Sulfonic acid groups were still desirable substituents, as they increased the reduction potential and the solubility of the molecule in water. To limit the number of open positions on the phenyl ring, methyl groups were used as substituents. Though the disulfonic acid molecule was desirable, adding a second sulfonic acid group to DHDMBS proved to be a challenge for synthesis. Furthermore, we speculated that the one open position on the DHDMBS in the quinone form is less prone to nucleophilic attack by water compared to BQDS as the two methyl groups, being electron-donating, lower the nucleophilicity of the open position.

Experimental

Synthesis and chemical characterization of DHDMBS.—We have synthesized DHDMBS with a product yield of 85%. Our synthetic method uses benign conditions and provides a higher yield compared to a previously reported method.24 The reaction steps for the synthesis of DHDMBS are summarized in Figure 3. 2, 6-dimethylbenzene-1,4-diol (50 g) was added in small portions to vigorously stirred concentrated sulfuric acid (100 mL) over a period of 15 minutes to form a pale yellow solution that solidified in about 20 min. After leaving the resulting mixture standing at room temperature for 24 h, it was added to a vessel with sufficient ice. We needed sufficient ice to avoid excessive heating during the exothermic dilution of sulfuric acid; insufficient heat removal could lead to polymer formation. The resulting aqueous solution was neutralized with a stoichiometric amount of solid potassium carbonate. The resulting solid, at neutral pH, was filtered and washed with water. Acetone was added to precipitate out the potassium sulfate, and the filtered solution was concentrated by rotary evaporation and left overnight in a refrigerator for crystallization. The resulting crystals were filtered and washed...
with cold 10% water/acetone and acetone, and dried overnight under high vacuum. The crystallization procedure was repeated to obtain 78.8 g (85% yield) of a beige crystalline solid.

The structure and purity of compound was confirmed by $^1$H NMR (400 MHz with D$_2$O), $^{13}$C-NMR and Electron-spray-ionization high-resolution mass spectrometry (ESI-HRMS). $^1$H and $^{13}$C NMR spectra were recorded on Varian 500 MHz or 400 MHz NMR spectrometers. $^1$H NMR chemical shifts were determined relative to the signal of a residual protonated solvent, D$_2$O ($\delta$ 4.79 ppm). $^{13}$C NMR chemical shifts were determined relative to the $^{13}$C signal of solvent, DMSO-d$_6$ ($\delta$ 39.52 ppm). ESI-HRMS analysis was conducted at the University of Illinois–Urbana Champagne Mass Spectrometry Facility. The chemical shift values in ppm of the $^1$H NMR (400 MHz, D$_2$O) were 6.70 (singlet, 1H), 2.47 (singlet, 3H), and 2.22 (singlet, 3H). The chemical shift values in ppm of the $^{13}$C NMR (126 MHz, DMSO-d$_6$) were 147.1, 145.1, 128.2, 126.8, 124.1, 115.2, 16.9, 13.6. ESI-HRMS calculated for C$_8$H$_9$O$_5$S, 217.0171; found [M$^+$].

NMR samples for the crossover analysis were typically prepared by diluting 150 microliters of electrolyte sample with 350 microliters of deuterated water (D$_2$O) and $^1$H NMR spectra were obtained on Varian 500 MHz NMR instruments with 128 scans.

In our previous publication, we demonstrated that changing the starting material from an alkali metal salt to an acid greatly increased its solubility. The acid-form allowed us to reach higher concentration values – as high as 3 M for BQDS and 2 M for AQDS. In turn, this increase in concentration yielded higher operating current densities and improved the overall performance of the cell. Therefore, the potassium salt solution of DHDMBS was passed through a proton exchange column, to convert the potassium salt to the acid form of DHDMBS. The concentration of the acid solution of DHDMBS was then increased to the required value by rotary evaporation of water.

**Electrochemical characterization.**—The kinetic parameters and diffusion coefficients were determined by conducting experiments with a three-electrode glass cell using a rotating glassy-carbon disk working electrode, a platinum wire counter electrode, and a mercury/merccurous sulfate (MSE) reference electrode ($E^{\mathrm{rev}}$ = +0.65 V). DHDMBS was dissolved in 1 M sulfuric acid to a concentration of 1 mM. The solution was de-aerated and kept under a blanket of argon gas throughout all the electrochemical experiments. Linear-sweep voltammetry measurements were conducted at a scan rate of 5 or 50 mV s$^{-1}$ (Versastat 300 potentiostat) over a potential range of −1.5 V to +1.5 V. Cyclic voltammetry measurements were performed on a static glassy carbon electrode at a scan rate of 50 mV s$^{-1}$ over a potential range of −1.0 to 0.8 V vs MSE.

**Charge/discharge cycling of ORBAT flow cells.**—For the flow cell experiments, we adapted fuel cell test hardware (Electrochem Inc.) fabricated with densified graphite flow field plates and with an electrode active area of 25 cm$^2$. The reactants were circulated at flow rates in the range of 0.1–0.2 liter min$^{-1}$ using centrifugal pumps (March Pump Model #: BC-2CP-MD 12 VOLT DC) (Figure 4). We used an interdigitated flow field and graphite felt electrodes (3 mm thick). This type of flow field arrangement allowed for pressure drops to be high enough to utilize the entire volume of the porous electrode. To increase their wettability, the graphite felt electrodes (PAN Graphite Felt, Graphite Store) were treated with concentrated sulfuric acid for three hours. The acid treatment increased the electroactive and wetted surface area of the graphite felts by making them more hydrophilic. To address impregnation of the single sulfonic acid group (Figure S3, Supplementary Information).

The structure and purity of compound was confirmed by $^1$H NMR (400 MHz with D$_2$O), $^{13}$C-NMR and Electron-spray-ionization high-resolution mass spectrometry (ESI-HRMS). $^1$H and $^{13}$C NMR spectra were recorded on Varian 500 MHz or 400 MHz NMR spectrometers. $^1$H NMR chemical shifts were determined relative to the signal of a residual protonated solvent, D$_2$O ($\delta$ 4.79 ppm). ESI-HRMS analysis was conducted at the University of Illinois–Urbana Champagne Mass Spectrometry Facility. The chemical shift values in ppm of the $^1$H NMR (400 MHz, D$_2$O) were 6.70 (singlet, 1H), 2.47 (singlet, 3H), and 2.22 (singlet, 3H). The chemical shift values in ppm of the $^{13}$C NMR (126 MHz, DMSO-d$_6$) were 147.1, 145.1, 128.2, 126.8, 124.1, 115.2, 16.9, 13.6. ESI-HRMS calculated for C$_8$H$_9$O$_5$S, 217.0171; found [M$^+$].

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**Charge/discharge cycling of ORBAT flow cells.**—For the flow cell experiments, we adapted fuel cell test hardware (Electrochem Inc.) fabricated with densified graphite flow field plates and with an electrode active area of 25 cm$^2$. The reactants were circulated at flow rates in the range of 0.1–0.2 liter min$^{-1}$ using centrifugal pumps (March Pump Model #: BC-2CP-MD 12 VOLT DC) (Figure 4). We used an interdigitated flow field and graphite felt electrodes (3 mm thick). This type of flow field arrangement allowed for pressure drops to be high enough to utilize the entire volume of the porous electrode. To increase their wettability, the graphite felt electrodes (PAN Graphite Felt, Graphite Store) were treated with concentrated sulfuric acid for three hours. The acid treatment increased the electroactive and wetted surface area of the graphite felts by making them more hydrophilic. The treated felts were repeatedly washed with DI water to remove excess acid and then introduced into the cell. A Nafion 117 membrane was used as a proton-exchange membrane.

All flow cell experiments were carried out at 23 °C with the acid form of the redox couples dissolved in 1 M sulfuric acid. Two glass containers served as reservoirs for the solutions of the redox couples

![Figure 4. Photograph of the test set-up used for the flow cell studies.](image-url)
electrochemical studies (Table I). However, the reduction potential was still sufficiently positive to that of AQDS to be tested in a flow cell.

Quinones with a sulfonic acid group in an ortho-position to a hydroxyl group allows for intramolecular hydrogen bonds to form that reduce the rate constant for the kinetics of proton-coupled electron transfer in the molecule. This aspect of the molecular design was discussed at length in our earlier paper. Methyl groups in DHDMBS cannot slow down the kinetics of charge transfer through this mechanism.

We determined the rate constant and the exchange current density for the charge transfer process from the linear-sweep voltammetry measurements made on the rotating disk electrode (Figure 6a). We made a plot of the logarithm of the kinetic current (i.e., after correcting for mass-transport polarization) vs. the electrode potential, for values made on the rotating disk electrode (Figure 6a). We applied the Levich equation (Figure 6b, Eq. 3).

\[ I_{\text{lim}} = 0.62 n F A D^{2/3} \omega^{1/2} v^{-1/6} C^* \]

Where \( D \) is the diffusion coefficient, \( \omega \) is the angular rotation rate in radians s\(^{-1}\), and \( v \) is the kinematic viscosity of the solution. Other constants are the same as defined before in Eq. 1.

The half-wave potential, \( E_{1/2} \) was determined from the electrode potential corresponding to half the limiting current. For a reversible electrochemical reaction, \( E_{1/2} \) can be approximated to the standard reduction potential.

The half-wave potential for DHDMBS was approximately 0.28 V lower than that of BQDS, in line with our predictions based on known substituent effects (Table I). Although the \( E_{1/2} \) for DHDMBS is less positive to that of BQDS, the transformations that occur with BQDS, through the two Michael reactions leading to 1, 2, 4, 6-tetrahydroxy-3, 5-disulphonic acid, also results in lowering of the reduction potential. Thus, we do not expect to be at any disadvantage in this respect with DHDMBS.

The rate constant for the electrochemical redox reaction of DHDMBS was found to be comparable to that of BQDS (Table I). We must emphasize that this value of rate constant significantly exceeds that of the well-known \( \text{VO}^{2+}/\text{VO}^{4+} \) couple that is utilized in vanadium redox flow batteries. The diffusion coefficient of DHDMBS was also comparable to that of BQDS (Table I), and thus we expect the mass-transport-limited currents to be as high as that observed for BQDS. The cyclic voltammetric scans for over 50 times did not show any hysteresis in the current-voltage curves (Figure 6c), suggesting that DHDMBS does not form any irreversible products or films on the surface of the electrode. With these electrochemical properties, we are confident that DHDMBS meets all the essential criteria for being a positive electrode material for an aqueous organic redox flow battery.

Table I. Electrochemical Properties of BQDS and DHDMBS.

| Name and Source | Molecular Weight (g/mol) | Half Wave Potential, \( E_{1/2} \) vs NHE (Volt) | Diffusion Coefficient, \( D \) \((\text{cm}^2 \text{s}^{-1})\) | Rate Constant, \( k_o \) \((\text{cm}^s^{-1})\) | Solubility (M) | Reference |
|-----------------|--------------------------|-----------------------------------|-----------------|-----------------|--------------------|----------|
| 3,6-dihydroxy-2,4-dimethylbenzene sulfonic acid (DHDMBS) | 218 | 0.82 | 4.12E-6 | 1.30E-4 | ∼2 | This work |
| Synthesized in house | | | | | | |
| 4,5-dihydroxybenzene-1,3-disulfonic acid (BQDS) Purchased from Alfa Aesar | 332 | 1.10 | 3.80E-6 | 1.55E-4 | ∼3 | 20 |
Charge/discharge studies in flow cell.—We combined 1 M DHDMBS in 1 M aqueous sulfuric acid on the positive side of the flow cell with 1 M anthraquinone-2,7-disulfonic acid (2,7-AQDS) in 1 M aqueous sulfuric acid on the negative side. We used 2,7-AQDS instead of 2,6-AQDS, because of inadequate supply and the high cost of obtaining 2,6-AQDS. Earlier we had tested the electrochemical and kinetic parameters of both 2,6-AQDS and 2,7-AQDS and found that all properties were comparable (see Table S1 for details).

In these flow cell experiments, we ensured that the same number of equivalents of DHDMBS and 2,7-AQDS were used on both sides. The charge and discharge curves at 100 mA/cm² showed a single plateau (Figure 7), which is markedly different from that of the BQDS where multiple plateaus were observed from the very first cycle.21 Furthermore, with BQDS the first discharge only returned one-third of the first charge capacity, consistent with the transformations caused by the Michael reaction, needing three times the amount of charge to reach the final charged state. When DHDMBS was used, the first charge and discharge capacities were almost equal, proving that there was no Michael transformation occurring with DHDMBS.22

Upon continuing the cycling of the cell with DHDMBS and 2,7-AQDS, we were able to achieve 100% coulombic efficiency repeatedly during charge and discharge cycles (Figure 8a) indicating that all the charged DHDMBS was being returned to the discharge state. The 100% coulombic efficiency was yet further proof that the Michael reaction was not occurring with the DHDMBS electrolyte.

During the 25th cycle the current-voltage curve was obtained in the fully charged state. The cell was able to achieve 500 mA/cm² of current density (Figure 8b). The flatness of the curve at high current densities suggested that the mass-transport limitations were not significant even at such high current densities. However, the ohmic resistance arising from the graphite felt electrodes with 1 M sulfuric acid as measured by impedance spectroscopy contributed 0.020 Ohm. At a discharge current of 12.5 A (500 mA/cm²), the voltage drop due to this series ohmic resistance was 0.25 V, a very significant number. This ohmic resistance can be lowered with the choice of thinner electrodes combined with modifications to the contact area of the flow field plate.24 To remove this passive contribution to the voltage loss, we have corrected the value of cell voltage for this ohmic resistance in Figure 8b.

The relatively low cell voltage of the system could lead to an increase in costs for the scaled-up system as more cell units would be necessary; more cell units entail the use of more flow field plates, electrodes, and membranes. However, the lower cost of the electrolyte and active material, especially when compared to vanadium, still makes this system worthy of consideration for a grid-storage RFB. Therefore, cell and electrode design optimization would be an essential part of the scale up of this system. Further, we can design molecules with electron-withdrawing substituents to achieve a higher reduction potential that would raise the cell voltage while preserving the resistance of the redox molecule to the Michael reaction, just as demonstrated here with DHDMBS.

After 25 cycles, even though the cell maintained close to 100% coulombic efficiency, the discharge capacity showed about a 0.05% decrease in every cycle (Figure 9). We removed 500 microliters from each side of the cell at the end of the 25th discharge to determine the state of the materials using electrochemical and spectroscopic techniques. This sample was compared with the sample prior to the commencement of cycling.1H NMR analysis confirmed that DHDMBS was still in its original state and had not undergone any significant chemical transformation (Figure 10). The continued presence of the aromatic proton signal after 25 cycles showed that the Michael reaction had not occurred on DHDMBS, unlike BQDS. The minor peaks in the aliphatic region of the 1H NMR potentially corresponded to the oxidized form of DHDMBS present even in the discharged state. Therefore, it was clear from the NMR results that the DHDMBS had remained unchanged during the 25 cycles.

Further confirmation of the absence of any chemical transformation of DHDMBS was evident from electrochemical tests. Linear-sweep voltammograms of the DHDMBS before cycling and after 25 cycles showed no change in the onset potential and no noticeable change in the limiting current for both samples (Figure 11). These observations further confirmed that there had been no chemical transformation of the molecule over the 25 cycles. Thus, the electrochemical and spectroscopic analysis confirmed that the capacity decrease with cycling was not due to any chemical transformations. These results

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Figure 6. a) Linear-sweep voltammetry at the rotating disk electrode for 1 mM DHDMBS in 1 M sulfuric acid at various rotation rates in rpm shown on the plot; b) Levich plot based on data in Figure 6a; c) Cyclic voltammetric measurements at 50 mV s⁻¹ showing the overlay of the data for 50 scans.
Figure 7. Charge and discharge curves for 1 M DHDMBS as the positive electrolyte and 1 M 2,7-AQDS as the negative electrolyte, each dissolved in 100 mL of 1 M sulfuric acid. The cell used interdigitated flow fields and graphite felt electrodes. The membrane was Nafion 117. Charge and discharge currents were 2.5 Amperes, and the cut off voltage was 1.0 V during charge, and 0.005 V during discharge. The dashed lines represent the IR-corrected voltages; the solid lines the non-corrected voltage values.

Figure 8. Cycling studies of 1 M DHDMBS and 1 M 2,7-AQDS when charged and discharged at 100 mA/cm². (a) Coulombic efficiency of flow cell; (b) Current-voltage curve at the end of charge in the 25th cycle.

Figure 9. Capacity of flow cell operating with 1 M DHDMBS and 1 M 2,7-AQDS when charged and discharged at 100 mA/cm².

attested to the robustness of DHDMBS to the Michael reaction with water, and confirmed the suitability of using DHDMBS as a positive electrolyte. Thus, DHDMBS had overcome the principal issue encountered with BQDS.

Crossover through Nafion membrane.—While continuing the search for explanations for the slow capacity decrease with cycling, we found that the crossover of DHDMBS from the positive side of the cell to the negative side of the cell could be a possibility. We had expected that the sulfonic acid molecules would be fully ionized and the anionic molecular species would therefore be excluded by the Nafion membrane. However, when we determined the pKₐ of DHDMBS to be 2.46, we concluded that in a 1 M solution of sulfuric acid (at a pH close to zero) much of the DHDMBS would be in the unionized form as the sulfonic acid. Thus, permeation and electro-osmotic drag could allow DHDMBS to be transported across the membrane. On analyzing the negative electrolyte compartment by ¹H NMR, it was determined that small amounts of DHDMBS had indeed crossed over through the Nafion 117 membrane (Figure 12). The concentration of DHDMBS in the AQDS electrolyte had slowly increased with time. Since the cells were being cycled at 100 mA/cm², the impact of concentration changes on the capacity was even more significant than it would have been at lower current densities. From studies of the limiting current on the rotating disk electrode, we determined that the concentration of DHDMBS had reduced by about 10% through the 25 cycles, consistent with the decrease in capacity observed. Similar investigations of the positive electrolyte (Figure 10) did not show any AQDS crossover into the positive electrolyte even after 25 cycles. It was surprising that although AQDS is also not expected to be fully ionized, we did not...
Figure 10. $^1$H- NMR studies on samples of DHDMBS before and after 25 cycles. Imidazole was added deliberately as an internal standard for estimating concentration. Electrolyte solutions were diluted with deuterated-water (D$_2$O).

see its crossover to the positive side. We concluded that in addition to the state of ionization, the molecular size has a significant effect on the permeability of the molecule through the membrane. Thus, the slow decrease in capacity of the cell could be attributed largely to the slow fall in concentration of DHDMBS in the positive electrolyte due to crossover. We are now focusing on conducting further studies to determine the rate of crossover and separating the contributions to crossover from simple permeation and electro-osmotic drag. 29,30

We also need to focus future efforts on approaches to limit or eliminate crossover of the redox species, using other proton exchange membranes.

Figure 11. Linear-sweep voltammogram of DHDMBS samples before and after 25 cycles. Both samples were at a 1 mM concentration. The scan rate was 50 mV/sec and the rotation rate was 1500 rpm. The working electrode was a glassy carbon rotating disk electrode, the counter electrode was a platinum wire, and the reference electrode was mercury sulfate (MSE, $E^{0} = 0.65$ V vs. NHE).

We were able to synthesize, characterize and demonstrate the properties of a new positive electrolyte material, DHDMBS, for aqueous organic redox flow batteries. We have determined that the standard reduction potential, the rate constant of the redox reaction, and the diffusion coefficient are ideally suited for use in ORBAT. Specifically, DHDMBS overcomes the issue faced with BQDS that underwent multiple chemical transformations through the Michael reaction. We have demonstrated the chemical stability of DHDMBS to repeated electrochemical cycling and the absence of the Michael reaction products through NMR and electrochemical studies. The flow cell with DHDMBS and 2,7-AQDS has now been shown to operate at close to 100% coulombic efficiency for over 25 cycles. This cell could sustain current densities as high as 500 mA/cm$^2$ without any noticeable chemical degradation. DHDMBS can be synthesized relatively inexpensively. Thus, the electrochemical and chemical properties of DHDMBS are particularly well-suited for use in organic redox flow batteries. We have found that over several days of cycling that DHDMBS crosses over gradually to the negative side of the cell through the Nafion membrane. Such a loss of material from the positive side to the negative side had led to a slow yet gradual decrease in capacity of the cell. Thus, although the present study has shown DHDMBS as a promising candidate for the positive side material for an all-organic aqueous redox flow battery in acidic media, our future efforts will focus on effects of long-term cycling and understanding the crossover of DHDMBS through the membrane.

Conclusions

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Acknowledgments
Figure 12. $^1$H-NMR studies on samples of 2,7-AQDS before and after 25 cycles. Imidazole was added deliberately as an internal standard for estimating concentration. Electrolyte solutions were diluted with deuterated-water (D$_2$O).

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