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# A Long Lifetime All-Organic Aqueous Flow Battery Utilizing TMAP-TEMPO Radical



TMAP-TEMPO represents an extremely stable redox-active radical organic for an AORFB posolyte. An all-organic AORFB based on TMAP-TEMPO and BTMAP-Vi exhibits an OCV of 1.1 V and a long lifetime, featuring a concentration-independent temporal capacity retention rate of >99.974% per h, or a capacity retention rate of 99.993% per cycle over 1,000 consecutive cycles.

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### HIGHLIGHTS

Highly soluble and long lifetime TMAP-TEMPO for pH 7 aqueous flow batteries

The posolyte features a concentration-independent capacity retention rate

Temporal capacity retention rate of >99.974% per h for over 1,000 cycles

Rational molecular design leads to improved stability



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# A Long Lifetime All-Organic Aqueous Flow Battery Utilizing TMAP-TEMPO Radical

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### SUMMARY

The massive-scale integration of renewable electricity into the power grid is impeded by its intrinsic intermittency. The aqueous organic redox flow battery (AORFB) rises as a potential storage solution; however, the choice of positive electrolytes is limited, and the aqueous-soluble organic positive redox-active species reported to date have short lifetimes. Here we report a stable organic molecule for the positive terminal, 4-[3-(trimethylammonio)propoxy]-2,2,6,6-tetramethylpiperidine-1-oxyl (TMAP-TEMPO) chloride, exhibiting high (4.62 M) aqueous solubility. When operated in a practical AORFB against a negative electrolyte comprising BTMAP-viologen at neutral pH, the flow cell displayed an open-circuit voltage of 1.1 volts and a Coulombic efficiency of >99.73%. The capacity retention rate is among the highest of all-organic AORFBs reported to date, at 99.993% per cycle over 1,000 consecutive cycles; the temporal capacity fade rate of 0.026% per h is independent of concentration.

### **INTRODUCTION**

Because of the emissions from fossil fuel combustion, efforts have been devoted to creating a sustainable supply of energy for our modern lifestyle with a minimum carbon footprint.<sup>1,2</sup> Facilitated by technological breakthroughs, more electricity is generated from sunlight and wind with ever-increasing efficiencies and rapidly falling cost;<sup>3-6</sup> the massive-scale integration of energy from these renewable resources into the power grid becomes inevitable. However, if directly connected to the grid, the intrinsically intermittent nature of solar and wind energy will cause undesirable power fluctuations, which could potentially be solved by energy storage systems. To this end, numerous methods have been proposed to store electrical energy, among which flow batteries are garnering interest for longer discharge duration applications.<sup>7-10</sup> The energy content of flow batteries is stored externally in their electrolytes (the posolyte, i.e., the positive electrolyte, and the negolyte, i.e., the negative electrolyte). Therefore, their capital cost approaches the cost of these electrolytes at sufficiently long discharge duration. If sufficiently inexpensive electrolytes can be developed, flow batteries may reach costs below those of conventional battery technologies, such as lead-acid and lithium-ion. Within this framework, AORFBs, which store energy in water-soluble redox-active organic compounds composed of earth-abundant elements, may enable low electrolyte costs.<sup>11–13</sup>

Nevertheless, the lifetime of current AORFBs cannot currently meet the expected 20 years of service life for widespread market penetration.<sup>9,14</sup> Capacity fade of AORFBs is often the result of molecular decomposition of the organic reactants.<sup>14</sup>

#### **The Bigger Picture**

With the rapidly falling cost of photovoltaic and wind energy generation, grid-scale integration of renewable energy becomes inevitable. This, however, is impeded by the intrinsic intermittency of these renewable energy resources. Safe, costeffective storage could solve this problem. Aqueous organic redox flow batteries (AORFBs), which store energy externally in low-cost electroactive water-soluble organic molecules, have emerged as promising for this application. Current AORFBs are limited by short lifetimes and the limited choices for redox-active material for the positive electrolyte. We report a long lifetime TMAP-TEMPO/BTMAP-Vi all-organic aqueous flow battery, the capacity retention rate of which is among the highest of all-organic AORFBs. We discuss the potential cause of the stabilization of the free radical posolyte molecule. The results we report here constitute an important step toward massive-scale intermittent renewable energy penetration into the future electric grid.

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Progress has been made in recent years, especially for the negolyte. For the particular case of neutral-pH systems, the focus of the current work, the first neutral-pH AORFB employed a negolyte based on methyl viologen (MV).<sup>15</sup> MV was later shown to have a low capacity retention rate due to bimolecular annihilation.<sup>16</sup> By introducing positively charged functional groups to enhance Coulombic repulsion, the lifetime of an MV derivative, bis-(trimethylammonio) propyl viologen (BTMAP-Vi), was extended to a multi-year timescale (for more details on the stability of MV-derivatives see Supplemental Information).<sup>16</sup> An example of an MV derivative with intermediate stability is the 4,4'-(thiazolo[5,4-*d*]thiazole-2,5-diyl)bis(1-(3-(trime-thylammonio) propyl)pyridin-1-ium).<sup>11</sup>

Despite the advancements achieved for synthesizing stable organic molecules for aqueous negolytes, little progress has been made in designing stable organic high-potential posolytes. In addition, the concentration-dependent cycling stability of electrolyte in AORFBs remains a long-standing obstacle,<sup>11,15–18</sup> and only a few studies conducted rigorous long-term cycling experiments (e.g., >500 cycles and >1 week).<sup>19–21</sup>

Here, we report an extremely stable variant of the radical posolyte molecule 4-[3-(trimethylammonio)propoxy]-2,2,6,6-tetramethylpiperidine-1-oxyl (TMAP-TEMPO) chloride (Figures 1A, S1, and S2) synthesized from low-cost (\$5–6 kg<sup>-1</sup>)<sup>9</sup> 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl (4-OH-TEMPO) by adding Coulombic repulsion to suppress bimolecular interactions and by eliminating functionalities that could potentially lead to molecular decomposition. TMAP-TEMPO chloride features a solubility of 4.62 M in water and a highly reversible single-electron oxidation potential at 0.81 (V) versus the standard hydrogen electrode (SHE), approaching the thermodynamic limit of water stability at neutral pH. When paired with BTMAP-Vi (Figures S3–S5), the TMAP-TEMPO/BTMAP-Vi battery has an open-circuit voltage (OCV) of 1.1 V and exhibits an extremely high capacity retention rate, at 99.993% per cycle over 1,000 consecutive cycles; the temporal capacity fade rate of 0.026% per h is independent of concentration.

#### **RESULTS AND DISCUSSION**

A cyclic voltammetry (CV) study of TMAP-TEMPO at a scan rate of 100 mV s<sup>-1</sup> gave a reversible oxidation peak at 0.81 V versus SHE ( $E_{1/2}$ ) in 1 M NaCl (Figure 1B). A peak separation of 58 mV was observed in good accordance with the theoretical value of a reversible single-electron redox reaction at pH 7 (59 mV), and the oxidation peak does not shift when the scan rate varies (Figure S5). Regardless of the electrode overpotential, the oxidation potential of TMAP-TEMPO, 0.81 V versus SHE, approaches the thermodynamic upper limit of water stability at pH 7 (oxygen evolution reaction, 0.816 V versus SHE). No oxygen generation was detected with a ppm-level sensitive oxygen detector when the experiment was conducted in a properly sealed environment.

Rotating disk electrode measurements of TMAP-TEMPO gave an oxidation rate constant ( $k_0$ ) of 1.02 × 10<sup>-2</sup> cm s<sup>-1</sup> (Figure S6). The rate constants of both TMAP-TEMPO and BTMAP-Vi (Table 1) are much faster than those of most other inorganic, organic, or organometallic species (Table S1).

The promising electrochemical characteristics suggest that TMAP-TEMPO might make a suitable posolyte for an AORFB. We then assembled a neutral-pH AORFB, with a posolyte comprising TMAP-TEMPO chloride and a negolyte comprising

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Figure 1. Syntheses of TMAP-TEMPO and BTMAP-Vi and Their Potential Use as Electrolytes in AORFB (A) Synthetic routes for TMAP-TEMPO and BTMAP-Vi.

(B) Cyclic voltammograms of TMAP-TEMPO (solid red trace), 4-OH-TEMPO (dashed light red trace), and BTMAP-Vi (solid blue trace). The electroactive compounds were tested at 1 mM in 1 M NaCl solution at a scan rate of 100 mV s<sup>-1</sup>, on a glassy carbon working electrode.

(C) Schematic of a neutral flow battery assembled with TMAP-TEMPO in the posolyte and BTMAP-Vi in the negolyte, with chloride ions passing through a Selemion AMV anion-selective membrane.

BTMAP-Vi tetrachloride, separated by a Selemion<sup>®</sup> AMV anion-exchange membrane. In a typical charge process, electrons are withdrawn from the TMAP-TEMPO, flow along the external circuit, and combine with the negolyte, BTMAP-Vi, while Cl<sup>-</sup> ions serve as the internal charge carrier, migrating across the Selemion<sup>®</sup> AMV membrane (Figure 1C). TMAP-TEMPO (the posolyte side) is the capacity-limiting side, and as a reference, the 4-OH-TEMPO/BTMAP-Vi cell with the same electrolyte concentration was also assembled (Figure 2, for details see the Supplemental Information).

The total discharge capacity was 25.7 mAh, which corresponded to 95.9% of the theoretical capacity (26.8 mAh). The deviation between the theoretical and the measured value is attributed to the loss during material transfer and the electrode overpotential during the charge-discharge process. We then stepwise charged the cell at constant voltage (1.5 V) with a 10% increment in the state-of-charge (SOC) and measured the polarizations of the cell. The OCV at 50% SOC rests at around 1.10 V (Figure S7), which is slightly lower than expected from CV studies (1.19 V, Figure 1B).

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Electrolyte	$D ({\rm cm}^2{\rm s}^{-1})$	$k_0$ (cm s <sup>-1</sup> )	E <sub>1/2</sub> (V versus SHE)	Water Solubility (mol L <sup>-1</sup> )	Permeability (cm <sup>2</sup> s <sup>-1</sup> ) <sup>a</sup>	Reference
TMAP-TEMPO	3.48 × 10 <sup>-6</sup>	1.02 × 10 <sup>-2</sup>	0.81	4.62	6.40 × 10 <sup>-10</sup> (AMV)	This work
4-OH-TEMPO	2.95 × 10 <sup>-5</sup>	$2.60 \times 10^{-4}$	0.80	2.1	1.34 × 10 <sup>-9</sup> (AMV)	6
BTMAP-Vi	3.60 × 10 <sup>-6</sup>	2.20 × 10 <sup>-2</sup>	-0.36	2.0	6.70 × 10 <sup>-10</sup> (DSV)	7
			-0.38		5.20 × 10 <sup>-11</sup> (AMV)	This work

#### Table 1. Electrochemical and Physicochemical Properties of TMAP-TEMPO, 4-OH-TEMPO, and BTMAP-Vi

<sup>a</sup>Membrane names are included in the parentheses. Abbreviations are as follows: D, diffusion coefficient;  $k_0$ , electron-transfer rate constant; and  $E_{1/2}$ , redox potential.

At ~100% SOC, the peak galvanic power density of the cell reaches 99.03 mW cm<sup>-2</sup> at a current density of 162.7 mA cm<sup>-2</sup> (Figure 2D), which is nearly the same as that of the neutral FcNCl/MV cell (100 mW cm<sup>-2</sup>) with comparable OCV (1.05 V).<sup>17</sup> The modest peak power density of the TMAP-TEMPO/BTMAP-Vi cell is due to high membrane resistance. The polarization area specific resistance of the entire cell at 50% SOC is 3.17  $\Omega$  cm<sup>2</sup>, while high-frequency area specific resistance is 2.20  $\Omega$  cm<sup>2</sup> (Figure S8). The high contribution from the membrane is expected to decrease as highly anion-conductive membranes become available.

The TMAP-TEMPO/BTMAP-Vi cell was initially cycled at constant current densities of 10, 20, 40, and 60 mA cm<sup>-2</sup> (Figure 2E). For each current density, 20 consecutive galvanostatic cycles were performed and we observed almost 100% Coulombic efficiency during 20 consecutive cycles. A capacity utilization of 97% and a round-trip energy efficiency of 93.41% were reached at the current density of 10 mA cm<sup>-2</sup>.

Prolonged galvanostatic cycling was performed to probe the cycling lifetime of the cell and the stability of the posolyte. Both the TMAP-TEMPO/BTMAP-Vi cell and the reference cell were cycled at 40 mA cm<sup>-2</sup> for 1,000 cycles (Figures 2B and 2F). The TMAP-TEMPO/BTMAP-Vi cell displayed a Coulombic efficiency of >99.73% and a significantly long cycling lifetime. The cell retained 94% of the initial capacity after 1,000 cycles, projecting a capacity retention rate of 99.993% per cycle or a temporal capacity retention rate of 99.974% per h (Figure 2F) or a loss rate of roughly 0.026% per h. In contrast, the reference cell lost 41% of its original capacity over 1,000 cycles (Figures 2B and S9–S12), projecting a temporal capacity loss rate of 0.22% per h, which is almost one order of magnitude higher than that of the TMAP-TEMPO/BTMAP-Vi cell.

The extended cycling lifetime of a flow battery could be the result of less membrane crossover of electroactive species or higher stability of the electroactive molecules. To understand the possible contribution from crossover, the permeabilities of 4-OH-TEMPO, TMAP-TEMPO, and BTMAP-Vi across a Selemion<sup>®</sup> AMV membrane were measured using a two-compartment diffusion cell (for details see the Supplemental Information; Figures S13–S15) and were determined to be  $1.34 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ ,  $6.40 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$ , and  $5.20 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$ , respectively (Table 1). The lowered permeability for TMAP-TEMPO is consistent with its larger molecular radius and positive charge. The capacity-limiting TEMPO species show higher membrane permeabilities than that of the BTMAP-Vi. A CV study of the electrolyte after 1,000 consecutive cycles confirms the crossover of TMAP-TEMPO to the negolyte solution and BTMAP-Vi to the posolyte solution (Figure S16), even though the membrane crossover rate of either is very low.

Based on these measurements, we estimate that crossover contributed 39.6% of capacity lost in the TMAP-TEMPO cell, and only 9.4% of the capacity lost in the

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Figure 2. Performance of a Neutral-pH AORFB Assembled with Either 4-OH-TEMPO (0.1 M, A–B) or the Chloride Salt of TMAP-TEMPO (0.1 M, C–F) in Posolyte (10 mL) and BTMAP-VI Tetrachloride (0.1 M) in Negolyte (15 mL, 1.5 Times e<sup>-</sup> Excess)

(A) Structures of 4-OH-TEMPO and BTMAP-Vi.

(B) Galvanostatic cycling of the reference 4-OH-TEMPO/BTMAP-Vi cell at 40 mA cm<sup>-2</sup> for 1,000 consecutive cycles. Charge-discharge capacity, round-trip energy efficiency, and Coulombic efficiency (EE and CE, respectively) were plotted as functions of the cycle number. The entire 1,000 cycles occurred over a period of 191 h.

(C) Structures of TMAP-TEMPO and BTMAP-Vi.

(D) Polarization curves of the TMAP-TEMPO/BTMAP-Vi cell at varied SOC.

(E) Charge-discharge capacity, CE, and EE of the cell when galvanostatically cycled at current densities of 10, 20, 40, and 60 mA cm<sup>-2</sup>, respectively. (F) Galvanostatic cycling of the TMAP-TEMPO/BTMAP-Vi cell at 40 mA cm<sup>-2</sup> for 1,000 consecutive cycles. Charge-discharge capacity, EE and CE were plotted as functions of the cycle number. The entire 1,000 cycles occurred over a period of 220 h. (Insets in (B) and (F): the normalized discharge capacity of the cell at the 1st, the 100th, the 200th, and the 1,000th cycle, respectively.)

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reference cell because the capacity loss of 4-OH-TEMPO is so obvious. Hence, the slower crossover of TMAP-TEMPO accounts for merely a small fraction of the  $\sim$ 10× slower capacity fade rate, namely 5.12% of the total savings of capacity loss (see the Supplemental Information, "Calculation of capacity loss due to electrolyte crossover"). This indicates that TMAP-TEMPO is structurally more stable than 4-OH-TEMPO.

The rest of the capacity loss is attributed to the chemical decomposition of TMAP-TEMPO. We hypothesize that the ring-opening side reactions on the nitroxide radicals of TMAP-TEMPO during galvanostatic charging or discharging is responsible for the loss of redox-active material.<sup>22</sup> The attack of water on the oxidized nitroxide radicals would open the ring but would not change the aliphatic hydrogens; this is consistent with the absence of new proton peaks in the <sup>1</sup>HNMR spectrum of the TMAP-TEMPO after cycling for 1,000 consecutive cycles (Figure S17).

To further investigate the source of capacity loss and eliminate the effect of crossover, we employed the unbalanced compositionally symmetric-cell cycling method by putting the same 50% SOC TMAP-TEMPO on both sides.<sup>14</sup> Over 25 days, 1,850 cycles, the cell lost roughly 14% of its initial capacity, equating to roughly 0.023% per h (Figures S18–S20), which is in reasonable agreement with the fade rate observed in the previously mentioned full-cell data.

Permeability analysis and the symmetric-cell results combine to establish the low fade rate of TMAP-TEMPO. Encouraged by the high capacity retention rate of TMAP-TEMPO/BTMAP-Vi at 0.1 M and the high water solubility of the electrolytes, we constructed a cell with a higher active concentration of 0.5 M for both sides. The concentrated TMAP-TEMPO/BTMAP-Vi cell showed a peak galvanic power density of 134 mW cm<sup>-2</sup> (Figure 3A, EIS of the cell is presented in Figure S21) and exhibited Coulombic efficiencies of >99.9% at all current densities (Figure 3B). The cell was cycled continuously for 200 cycles at 100 mA cm<sup>-2</sup> (Figures 3C and S22). After 200 cycles, the cell retained 95% of its original capacity, projecting a temporal capacity retention rate of 99.973% per h or a temporal capacity loss rate of 0.027% per h. The temporal capacity loss rate is nearly the same as that obtained from the TMAP-TEMPO/BTMAP-Vi cell at 0.1 M concentration, indicating a concentration-independent temporal capacity loss rate, which is in contrast to the results obtained for other radical posolytes.<sup>11,15,18</sup> Even at a higher electrolyte concentration of 1.5 M, the cell manifested a capacity retention rate of 99.985% per cycle, projecting a temporal capacity retention rate of 99.977% per h or a temporal capacity loss rate of 0.023% per h (Figure 4).

TMAP-TEMPO has a water solubility of 4.62 M (Supplemental Experimental Procedures), which corresponds to a theoretical posolyte capacity of 120 Ah L<sup>-1</sup>. We expect the solubility of the oxidized form to be even higher because when oxidized, the molecule will bear one more positive charge and the molecular weight or motif remains unchanged. The solution has a viscosity of ~580 mPa·s at 4.5 M (a homogeneous solution as shown in Figure S23), which is higher than that of a polymeric electrolyte<sup>12</sup> and would compromise the overall efficiency of the system because of pumping loss. The viscosity at 0.5 M is only 3.58 mPa·s (Figure S21B).

When taken together, the long-term galvanostatic cycling results, symmetriccell cycling results, and permeability measurements suggest that TMAP-TEMPO is exceptionally stable. This stability might be due to any of several possible causes,

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# Figure 3. Performance of Concentrated TMAP-TEMPO/BTMAP-Vi Cell Assembled with TMAP-TEMPO Chloride (0.5 M) in Posolyte (10 mL) and BTMAP-Vi Tetrachloride (0.5 M) in Negolyte (15 mL)

(A) Polarizations of the cell at varied SOC.

(B) Charge-discharge capacity, CE and EE of the cell when galvanostatically cycled at current densities of 100, 80, 60, and 40 mA cm $^{-2}$ , respectively.

(C) Galvanostatic cycling of the cell at 100 mA cm<sup>-2</sup> for 200 consecutive cycles. Charge-discharge capacity, EE, and CE are plotted as functions of the cycle number. Inset: the normalized discharge capacity of the cell at the 1st, the 50th, the 100th, the 150th, and the 200th cycle, respectively. Total discharge capacity of the cell on the first discharge is 446.1 C, which is 93% of the theoretical value. The entire 200 cycles occurred over a period of 80.6 h.

namely steric hindrance, Coulombic repulsion, and electronic isolation of the charged functional groups. The plausible mechanisms are provided as follows. The four peripheral methyl groups provide steric hindrance, which could suppress possible interactions between the free radicals. Additionally, the Coulombic repulsion between the positively charged TMAP-TEMPO molecules might also reduce bimolecular or multi-molecular interaction. Prior work with 4-OH-TEMPO<sup>15</sup> and TEMPO-4-ammonium (TEMPTMA,<sup>18</sup> also known as N<sup>Me</sup>-TEMPO<sup>11</sup>) and TEMPO-4sulfate<sup>23</sup> exhibited lifetimes that decreased with increasing concentration, whereas in our system, concentration-independent lifetime with TMAP-TEMPO was observed. This suggests that the TMAP-TEMPO has suppressed bimolecular or multi-molecular annihilation and may follow a decomposition mechanism that is only first order on TMAP-TEMPO concentration. Finally, attaching a charge directly to the 6-membered ring might compromise the stability of the molecules because the electronic effect, especially a strong one, could make the joint weak and susceptible to ring-opening side reactions. This is more consistent with the longer lifetime of TMAP-TEMPO than with that of TEMPTMA,<sup>18</sup> to which the positively charged ammonium is directly attached, or with that of TEMPO-4-sulfate,<sup>23</sup> to which the negatively charge sulfate is directly attached. The use of aliphatic spacers may mitigate ring-opening side reactions caused by the electronic effect of the charged functionalities.

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# Figure 4. Performance of High Concentration TMAP-TEMPO/BTMAP-Vi Cell Assembled with TMAP-TEMPO Chloride (1.5 M) in Posolyte and BTMAP-Vi Tetrachloride (1.5 M) in Negolyte. (A) Polarizations of the cell at varied SOC.

(B) Representative cell voltage and charge-discharge current density versus time during cycling at 100 mA  $\rm cm^{-2}.$ 

(C) Galvanostatic cycling of the cell at 100 mA cm<sup>-2</sup> for 250 consecutive cycles. Charge-discharge capacity, EE, and CE are plotted as functions of the cycle number. Inset: the normalized discharge capacity of the cell at the 1st, the 50th, the 100th, the 150th, the 200th, and the 250th cycle, respectively. Total discharge capacity of the cell on the first discharge is 625.0 C. The entire 250 cycles occurred over a period of 171.7 h.

TMAP-TEMPO/BTMAP-Vi is among the most stable all-organic AORFB chemistry to date, but we note that there are longer-lifetime AORFBs at high pH in which the posolyte utilizes the inorganic redox couple ferricyanide-ferrocyanide,<sup>21</sup> and at neutral pH in which the posolyte comprises the organometallic redox couple FcNCI,<sup>17</sup> and an even longer-lifetime functionalization, BTMAP-Fc.<sup>16</sup> A critical question is whether there is a fundamental reason that voltage trades off against lifetime, or whether it is possible to enhance both. This question is apparent if one examines OCVs and lifetimes among ferrocene-based batteries and does the same for TEMPO-based ones. The FcNCI/MV cell (OCV 1.06 V) has a temporal capacity fade rate of 0.078% per h, while the low-OCV version, BTMAP-Fc/BTMAP-Vi (OCV 0.75 V) shows greatly enhanced lifetime with a temporal capacity fade rate of 0.0042% per h. Similarly, TMAP-TEMPO/BTMAP-Vi (OCV 1.19 V) has a temporal capacity fade rate that is half that of TEMPTMA/MV (OCV 1.42 V) and is less than one-fourth that of N<sup>Me</sup>-TEMPO/[(NPr)<sub>2</sub>TTz]Cl<sub>4</sub> (OCV 1.44 V) (Table S2). Better understanding of capacity fade mechanisms will likely be necessary before this question can be answered.

In summary, we have synthesized an extremely stable redox-active radical organic for an AORFB posolyte, TMAP-TEMPO, which has >4.5 M solubility in water. An all-organic AORFB based on TMAP-TEMPO and BTMAP-Vi exhibits an OCV of 1.1 V and exhibits exceptionally long lifetime. It features a concentration-independent temporal capacity retention rate of >99.974% per h, or a capacity retention rate of 99.993% per cycle over 1,000 consecutive cycles. Symmetric-cell testing

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established the low fade rate of TMAP-TEMPO. We anticipate that by improving the ion selective membrane, the entire cell resistance might be greatly reduced, thereby increasing the power density, and the membrane crossover rate of electroactive species might be reduced, thereby further increasing the capacity retention rate. Our results constitute an important step toward massive-scale intermittent renewable energy penetration into the future electric grid.

#### SUPPLEMENTAL INFORMATION

Supplemental Information can be found online at https://doi.org/10.1016/j.chempr. 2019.04.021.

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#### **AUTHOR CONTRIBUTIONS**

Z.Y., M.J A., and T.X. designed the project. Y.L., Y.J., L.T., and Z.Y. synthesized the compounds. Y.L. and M.-A.G. collected the experimental data. Z.Y., Y.L., M.-A.G., L.T., R.G.G., M.J.A., L.W., Y.L., and T.X. analyzed the experimental results and helped with discussions. Z.Y., Y.L., M.-A.G., T.X., and M.J.A. wrote the paper, and all authors contributed to revising the paper.

#### **DECLARATION OF INTERESTS**

The authors declare no competing interests.

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#### **REFERENCES AND NOTES**

- 1. Armand, M., and Tarascon, J.M. (2008). Building better batteries. Nature 451, 652–657.
- 2. Obama, B. (2017). The irreversible momentum of clean energy. Science 355, 126–129.
- Arora, N., Dar, M.I., Hinderhofer, A., Pellet, N., Schreiber, F., Zakeeruddin, S.M., and Grätzel, M. (2017). Perovskite solar cells with CuSCN hole extraction layers yield stabilized efficiencies greater than 20%. Science 358, 768–771.
- Hou, Y., Du, X., Scheiner, S., McMeekin, D.P., Wang, Z., Li, N., Killian, M.S., Chen, H., Richter, M., Levchuk, I., et al. (2017). A generic interface to reduce the efficiency-stabilitycost gap of perovskite solar cells. Science 358, 1192–1197.
- 5. Yang, W.S., Park, B.W., Jung, E.H., Jeon, N.J., Kim, Y.C., Lee, D.U., Shin, S.S., Seo, J., Kim, E.K., Noh, J.H., et al. (2017). Iodide

management in formamidinium-lead-halidebased perovskite layers for efficient solar cells. Science 356, 1376–1379.

- Bush, K.A., Palmstrom, A.F., Yu, Z.J., Boccard, M., Cheacharoen, R., Mailoa, J.P., McMeekin, D.P., Hoye, R.L.Z., Bailie, C.D., Leijtens, T., et al. (2017). .23.6%-efficient monolithic perovskite/ silicon tandem solar cells with improved stability. Nat. Energy 2, 17009.
- Wang, W., Luo, Q.T., Li, B., Wei, X.L., Li, L.Y., and Yang, Z.G. (2013). Recent progress in redox flow battery research and development. Adv. Funct. Mater 23, 970–986.
- Soloveichik, G.L. (2015). Flow batteries: current status and trends. Chem. Rev. 115, 11533– 11558.
- Winsberg, J., Hagemann, T., Janoschka, T., Hager, M.D., and Schubert, U.S. (2017). Redoxflow batteries: from metals to organic redox-

active materials. Angew. Chem. Int. Ed. 56, 686–711.

- Noack, J., Roznyatovskaya, N., Herr, T., and Fischer, P. (2015). The chemistry of redox-flow batteries. Angew. Chem. Int. Ed. 54, 9776– 9809.
- Luo, J., Hu, B., Debruler, C., and Liu, T.L. (2018). A pi-conjugation extended viologen as a twoelectron storage anolyte for total organic aqueous redox flow batteries. Angew. Chem. Int. Ed. 57, 231–235.
- Janoschka, T., Martin, N., Martin, U., Friebe, C., Morgenstern, S., Hiller, H., Hager, M.D., and Schubert, U.S. (2015). An aqueous, polymerbased redox-flow battery using non-corrosive, safe, and low-cost materials. Nature 527, 78–81.
- Lin, K., Chen, Q., Gerhardt, M.R., Tong, L., Kim, S.B., Eisenach, L., Valle, A.W., Hardee, D., Gordon, R.G., Aziz, M.J., et al. (2015).

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Alkaline quinone flow battery. Science 349, 1529–1532.

- Goulet, M.A., and Aziz, M.J. (2018). Flow battery molecular reactant stability determined by symmetric cell cycling methods. J. Electrochem. Soc. 165, A1466–A1477.
- Liu, T.B., Wei, X.L., Nie, Z.M., Sprenkle, V., and Wang, W. (2016). A total organic aqueous redox flow battery employing a low cost and sustainable methyl viologen anolyte and 4-HO-TEMPO catholyte. Adv. Energy Mater 6.
- Beh, E.S., De Porcellinis, D., Gracia, R.L., Xia, K.T., Gordon, R.G., and Aziz, M.J. (2017). A neutral pH aqueous organic–organometallic redox flow battery with extremely high capacity retention. ACS Energy Lett. 2, 639–644.
- 17. Hu, B., DeBruler, C., Rhodes, Z., and Liu, T.L. (2017). Long-cycling aqueous organic redox

flow battery (AORFB) toward sustainable and safe energy storage. J. Am. Chem. Soc. 139, 1207–1214.

- Janoschka, T., Martin, N., Hager, M.D., and Schubert, U.S. (2016). An aqueous redox-flow battery with high capacity and power: the TEMPTMA/MV system. Angew. Chem. Int. Ed. 55, 14427–14430.
- Murali, A., Nirmalchandar, A., Krishnamoorthy, S., Hoober-Burkhardt, L., Yang, B., Soloveichik, G., Prakash, G.K.S., and Narayanan, S.R. (2018). Understanding and mitigating capacity fade in aqueous organic redox flow batteries. J. Electrochem. Soc. 165, A1193–A1203.
- Ji, Y., Goulet, M.A., Pollack, D.A., Kwabi, D.G., Jin, S., Porcellinis, D., Kerr, E.F., Gordon, R.G., and Aziz, M.J. (2019). A phosphonatefunctionalized quinone redox flow battery at

near-neutral pH with record capacity retention rate. Adv. Energy Mater. *9*.

- Ma, Y., Loyns, C., Price, P., and Chechik, V. (2011). Thermal decay of TEMPO in acidic media via an N-oxoammonium salt intermediate. Org. Biomol. Chem. 9, 5573– 5578.
- Winsberg, J., Stolze, C., Schwenke, A., Muench, S., Hager, M.D., and Schubert, U.S. (2017). Aqueous 2,2,6,6-Tetramethylpiperidine-N-oxyl catholytes for a high-capacity and high current density oxygen-insensitive hybrid-flow battery. ACS Energy Lett. 2, 411–416.
- Kwabi, D.G., Lin, K., Ji, Y., Kerr, E.F., Goulet, M.-A., DePorcellinis, D., Tabor, D.P., Pollack, D.A., Aspuru-Guzik, A., Gordon, R.G., et al. (2018). Alkaline quinone flow battery with long lifetime at pH 12. Joule 2, 1894–1906.