Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A. This journal is © The Royal Society of Chemistry 2021

Supplementary Information

Decomposition pathways and mitigation strategies for highly-stable hydroxyphenazine flow battery anolytes

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Scheme S1. Proposed reaction pathways of charged DHPS.



Fig. S1. ¹H NMR spectrum of DHPS after cycling in 1M NaOH supporting electrolyte. The presence of two possible isomers of deoxygenated DHPS (monohydroxyphenazine sulfonic acid, MHPS) and the desulfonated derivative 2,3-DHP (along with it's downstream decomposition products) results in significant signal overlap of multiple species, and complicates absolute structural assignment.



Fig. S2. Low field zoom-in of the ¹H-NMR spectrum of DHPS after cycling in 1M NaOH supporting electrolyte.



Fig. S3. High field zoom-in of the ¹H-NMR spectrum of DHPS after cycling in 1M NaOH supporting electrolyte.



Fig. S4. ¹H NMR spectrum of DHPS after cycling in HPO_4^{2-}/PO_4^{3-} buffered electrolyte supporting electrolyte.



Fig. S5. Low field zoom-in of the ¹H NMR spectrum of DHPS after cycling in HPO_4^{2-}/PO_4^{3-} buffered electrolyte supporting electrolyte.



Fig. S6. High field zoom-in of the ¹H NMR spectrum of DHPS after cycling in HPO_4^{2-}/PO_4^{3-} buffered electrolyte supporting electrolyte.



Fig. S7. Mass spectrometry results of cycled DHPS in a buffered Na₂HPO₄/Na₃PO₄ electrolyte.

 Table S1. Energies of dihydroxyphenazine tautomers.







£250 250

Fig. S8. ¹H NMR spectrum of 1,3-dihydroxyphenazine in DMSO-*d*₆



Fig. S9. ¹³C{¹H} NMR spectrum of 1,3-dihydroxyphenazine in DMSO- d_6



Fig. S10. ¹H NMR spectrum of 1,4-dihydroxyphenazine in DMSO-*d*₆



Fig. S11. ¹³C{¹H} NMR spectrum of 1,4-dihydroxyphenazine in DMSO- d_6



Fig. S12. ¹H NMR spectrum of 1,8-dihydroxyphenazine in DMSO-*d*₆



Fig. S13. ¹³C $\{^{1}H\}$ NMR spectrum of 1,8-dihydroxyphenazine in DMSO- d_{6}



Fig. S14. ¹H NMR spectrum of 2,7-dihydroxyphenazine in DMSO-*d*₆



Fig. S15. ¹³C $\{^{1}H\}$ NMR spectrum of 2,7-dihydroxyphenazine in DMSO- d_{6}

Entry	Condition	Solubility (M)
1	1 M NaOH	0.07
2	1 M KOH	0.25
3	2 M KOH	0.60

Table S2. Solubility data of deprotonated 1,6-dihydroxyphenazine



Fig. S16. a) Cyclic voltammograms of DHP isomers. CV curves of all DHP isomers were recorded at a concentration of 5 mM in 10 mL of 1 M NaOH solution except 1,6- and 1,9-DHP which was recorded at concentration of 10 mM and 2 mM respectively. Signal of 1,6-DHP was reduced by a factor of 0.5 and signal of 1,9-DHP was increased by a factor of 5 to compare with other DHP isomers. All CV curves were run at scan rate of 100 mV/s under N₂ atmosphere. b) Electrochemistry of DHP.

Table S3. Experimental and calculated properties of DHP isomers. Calculated redox potentials are reported relative to the most positive phenazine, 1,4-DHP, to reflect the ability of DFT to predict the trend in electrochemical properties within this isomer family.

DHP Isomer	Potential (V vs. Hg/HgO)	Calc. Redox Potential Shift (V vs 1,4-DHP)	Peak-to-Peak Separation (mV)	Cell voltage (Fe(CN) ₆ ^{4-/3-})	D (cm ² s ⁻¹)	K ₀ (cm s ⁻¹)	Calc. Size (Å, LxWxH)
1,3-DHP	-0.88	-0.19	348	1.24	1.64 x 10 ⁻⁵	0.68 x10 ⁻³	10.31x6.25x1.42
1,4-DHP	-0.80	0	484	1.16	0.52 x 10 ⁻⁵	1.08 x10 ⁻³	9.66x6.90x1.42
1,6-DHP	-0.98	-0.03	673	1.34	2.10 x 10 ⁻⁵	6.33 x10 ⁻³	9.66x6.90x1.42
1,8-DHP	-1.09	-0.14	526	1.45	1.20 x 10 ⁻⁵	1.02 x10 ⁻³	10.64x6.25x1.42
1,9-DHP	-0.88	-0.07	530	1.24	0.12 x 10 ⁻⁵	0.36 x10 ⁻³	9.65x6.26x1,42
2,3-DHP	-1.14	-0.57	66	1.50	1.66 x 10 ⁻⁵	3.86 x10 ⁻³	10.63x5.64x1.42
2,7-DHP	-1.04	-0.24	561	1.40	1.36 x 10 ⁻⁵	0.48 x10 ⁻³	10.30x5.63x1.42

We calculated the redox potentials of DHP derivatives based on the Gibbs free energy change (ΔG) of the following two-electron redox reaction:¹

$$[DHP]^{2-} + 2H_2O + 2e^- \rightarrow [DHP-2H]^{2-} + 2OH^-$$

Since there's no continuum solvation model for alkaline water, the solvation energies are calculated in pure water solvent by using COSMO-RS method. The following equation is used to calculate the redox potential (U) vs standard hydrogen electrode:

$$U = -\frac{1}{ne}\Delta G - U_{SHE}$$

Where n is the number of electrons (in this case, n=2), $U_{SHE} = 4.44$ V as recommended by Trasatti.²



Fig. S17A RDE study of 1,3-DHP, solution containing 5 mM 1,3-DHP in 2 M KOH. a) LSV curves at a scan rate of 5 mV s⁻¹ with rotation rates from 300 to 2400 rpm, with increment of 300 rpm. b) Fitted linear Levich plots of the limiting current (i_L) versus the square root of rotation rate ($\omega^{1/2}$), R²=0.999999. c) Linearly fitted Koutecky-Levich plots of i^{-1} with respect to $\omega^{-1/2}$. d) Linearly fitted plots of log i_k at different overpotentials, R²=0.99711. The calculated diffusion coefficient is 1.64×10^{-5} cm²/s. The calculated kinetic reduction rate constant is 6.69×10^{-4} cm/s.



Fig. S17B RDE study of 1,4-DHP, solution containing 5 mM 1,4-DHP in 2 M KOH. a) LSV curves at a scan rate of 5 mV s⁻¹ with rotation rates from 300 to 2400 rpm, with increment of 300 rpm. b) Fitted linear Levich plots of the limiting current (i_L) versus the square root of rotation rate ($\omega^{1/2}$), R²=0.99909. c) Linearly fitted Koutecky-Levich plots of i^{-1} with respect to $\omega^{-1/2}$, the fitted data ranged from 1200 rpm to 2400 rpm, with increment of 300 rpm, at over potential from 60 mV to 100 mV. d) Linearly fitted plots of log i_k at different overpotentials, R²=0.99696. The calculated diffusion coefficient is 0.52×10^{-5} cm²/s. The calculated kinetic reduction rate constant is 1.08×10^{-3} cm/s.



Fig. S17B' RDE study of 1,4-DHP, solution containing 5 mM 1,4-DHP in 2 M KOH. a) Koutecky-Levich analysis full data range from 300 rpm to 2400 rpm, at over potential from 10 mV to 100 mV. The brown square indicates the linear fitted region as presented above for calculating D and k_0 . It was observed that at lower rpm (a) and lower overpotential (b), the data points were not in good linear relationship. This is suspected to arise from interference resulting from the small plateau that appears at ~ -0.6 V. This event occurs due to oxygen contamination which oxidizes the material and generates a new species. Despite best efforts to exclude oxygen from the experimental setup, minor contamination occurred with each attempt.



Fig. S17C RDE study of 1,6-DHP, solution containing 5 mM 1,6-DHP in 2 M KOH. a) LSV curves at a scan rate of 5 mV s⁻¹ with rotation rates from 300 to 2400 rpm, with increment of 300 rpm. b) Fitted linear Levich plots of the limiting current (i_L) versus the square root of rotation rate ($\omega^{1/2}$), R²=0.99962. c) Linearly fitted Koutecky-Levich plots of i^{-1} with respect to $\omega^{-1/2}$. d) Linearly fitted plots of log i_k at different overpotentials, R²=0.92622. The calculated diffusion coefficient is 2.1×10⁻⁵ cm²/s. The calculated kinetic reduction rate constant is 6.33×10⁻³ cm/s.



Fig. S17D RDE study of 1,8-DHP, solution containing 5 mM 1,8-DHP in 2 M KOH. a) LSV curves at a scan rate of 5 mV s⁻¹ with rotation rates from 300 to 2400 rpm, with increment of 300 rpm. b) Fitted linear Levich plots of the limiting current (i_L) versus the square root of rotation rate ($\omega^{1/2}$), R²=0.99987. c) Linearly fitted Koutecky-Levich plots of i^{-1} with respect to $\omega^{-1/2}$. d) Linearly fitted plots of log i_k at different overpotentials, R²=0.99636. The calculated diffusion coefficient is 1.2×10^{-5} cm²/s. The calculated kinetic reduction rate constant is 1.02×10^{-3} cm/s.



Fig. S17E RDE study of 1,9-DHP, solution containing 5 mM 1,9-DHP in 2 M KOH. a) LSV curves at a scan rate of 5 mV s⁻¹ with rotation rates from 300 to 2400 rpm, with increment of 300 rpm. b) Fitted linear Levich plots of the limiting current (i_L) versus the square root of rotation rate ($\omega^{1/2}$), R²=0.99993. c) Linearly fitted Koutecky-Levich plots of i^{-1} with respect to $\omega^{-1/2}$. d) Linearly fitted plots of log i_k at different overpotentials, R²=0.99965. The calculated diffusion coefficient is 1.18×10^{-6} cm²/s. The calculated kinetic reduction rate constant is 3.55×10^{-4} cm/s.



Fig. S17F RDE study of 2,3-DHP, solution containing 5 mM 2,3-DHP in 2 M KOH. a) LSV curves at a scan rate of 5 mV s⁻¹ with rotation rates from 300 to 2400 rpm, with increment of 300 rpm. b) Fitted linear Levich plots of the limiting current (i_L) versus the square root of rotation rate ($\omega^{1/2}$), R²=0.99986. c) Linearly fitted Koutecky-Levich plots of i^{-1} with respect to $\omega^{-1/2}$. d) Linearly fitted plots of log i_k at different overpotentials, R²=0.9944. The calculated diffusion coefficient is 1.66×10^{-5} cm²/s. The calculated kinetic reduction rate constant is 3.86×10^{-3} cm/s.



Fig. S17G RDE study of 2,7-DHP, solution containing 5 mM 2,7-DHP in 2 M KOH. a) LSV curves at a scan rate of 5 mV s⁻¹ with rotation rates from 300 to 2400 rpm, with increment of 300 rpm. b) Fitted linear Levich plots of the limiting current (i_L) versus the square root of rotation rate ($\omega^{1/2}$), R²=0.9992. c) Linearly fitted Koutecky-Levich plots of i^{-1} with respect to $\omega^{-1/2}$. d) Linearly fitted plots of log i_k at different overpotentials, R²=0.99633. The calculated diffusion coefficient is 1.36×10^{-5} cm²/s. The calculated kinetic reduction rate constant is 4.76×10^{-4} cm/s.

Fig. S17. RDE measurements were performed using a three-electrode configuration consisting of a glassy carbon working electrode (3 mm diameter), a glassy carbon counter electrode and an Hg/HgO reference electrode. The electrolytes of 5 mM redox-active materials in 2.0 M KOH were used. Data were collected using a CHI potentiostat at scan rates of 5mV/s in the potential range of $-1.5V \sim -0.4V vs$ Hg/HgO. The rotation rates were 300, 600, 900, 1200, 1500, 1800, 2100, 2400. The diffusion coefficient (D) was calculated according to Levich equation:

$$i_{Lim} = 0.62 n FAD^{2/3} \omega^{1/2} \upsilon^{-1/6} C$$

where i_{Lim} is limiting current, n is the number of electrons transferred (n=2), F is Faradaic constant (96485 C mol⁻¹), A is the surface area of the working electrode (0.0707 cm²), C is the concentration of redox species (5.0×10⁻⁶ mol cm⁻³), ω is the routing angular rotation rate (rad s⁻¹) and υ is the kinetic viscosity (0.0113 cm² s⁻¹ for 2M KOH in H₂O). The Koutecky-Levich plots at different overpotentials were extrapolated to get the kinetic current i_k according to the Koutecky-Levich equation:

$$\frac{1}{i} = \frac{1}{i_k} + \frac{1}{i_L} = \frac{1}{i_k} + \frac{1}{0.62nFAD^{2/3}\omega^{1/2}v^{-1/6}C}$$

The exchange current i_0 can be obtained by fitting i_k to the Tafel plot at the overpotential of zero, from which the reaction rate constant (k_0) was determined according to Butler-Volmer equation: $i_0 = nFACk_0$



Fig. S18. Low Concentration flow battery performance. Capacity and efficiency of cell composed of deprotonated 0.065 M 1,4-, 1,6- and 2,3-DHP in 1 M NaOH and excess $K_4Fe(CN)_6/K_3Fe(CN)_6$ dissolved in 1 M NaOH cycled at current density 20 mA/cm². a) 1,4-DHP, b) 1,6-DHP, c) 2,3-DHP. Inset: Galvanostatic charge-discharge voltage profile from selected cycles at 20 mA/cm².

Table S4. Summary of performances of low concentration flow batteries of 1,4-, 1,6- and 2,3-DHP coupled with K_4 Fe(CN)₆/ K_3 Fe(CN)₆.

	1,4-DHP	1,6-DHP	2,3-DHP
Solubility in 1 M NaOH (M)	0.36	0.07	1.6

Equivalent electrons concentration at	0.72	0.14	3.2
maximum solubility limit in 1 M NaOH			
Theoretical volumetric capacity at	19.30	3.75	85.76
maximum solubility limit in 1 M NaOH			
(Ah/L)			
Concentration of RFB (M)	0.065	0.065	0.065
Demonstrated volumetric capacity	3.48	3.48	3.48
(Ah/L)			
Material utilization (%)	97	92	86
Average CE (%)	100	100	99.99
Average VE (%)	85.26	66.40	92.97
Average EE (%)	85.27	66.45	92.96
No. of Cycles	2500	2500	2500
No. of Days	37	33	31
Overall capacity decay (%)	1.6	3.8	13.5*
Capacity decay/per cycle (%)	0.00064	0.00152	0.0054
Capacity decay/per day (%)	0.0432	0.115	0.435

*The initial, observed capacity gain due to precipitation was not considered.



Fig. S19. ¹H NMR spectra of 1,4-DHP from 0.065 M flow battery in 1 M NaOH after 2767 cycles. *tert*-butyl alcohol was used as the internal standard.



Fig. S20. ¹H NMR spectra of 1,6-DHP from 0.065 M flow battery in 1 M NaOH after 5000 cycles.



Fig. S21. ¹H NMR spectra of 2,3-DHP from 0.065 M flow battery in 1 M NaOH after 2777 cycles. *tert*-butyl alcohol was used as the internal standard.



Fig. S22. Thermolytic study of charged 2,3-DHP anolyte. An aliquot of 0.065 M charged 2,3-DHP in 1 M NaOH was diluted with D_2O (0.40 mL of anolyte was diluted with 0.10 mL of D_2O) and monitored via ¹H NMR spectroscopy. The sample was heated first at 50 °C, then at 75 °C and finally at 95 °C. Charged 2,3-DHP, discharged 2,3-DHP and aliphatic compounds are labeled with black, blue and green color asterisks. The overall time of heating is given in the parenthesis. Formation of precipitate was observed with heating and spectrum becomes broad when considerable amount of precipitate present in the solution.



Fig. S23. Low field zoom-in of the ¹H NMR spectrum of thermolytic study of charged 2,3-DHP anolyte.



Fig. S24. High field zoom-in of the ¹H NMR spectrum of thermolytic study of charged 2,3-DHP anolyte.



Fig. S25. Mass spectrometry results for cycled 2,3-DHP, indicating deoxygenation and subsequent tautomerization. a) full spectrum including the major peak for starting material and b) zoom-in showing deoxygenated and deoxygenated/hydrogenated species.



Fig. S26. Flow battery performance. Capacity and efficiency of cell composed of deprotonated DHPs in 2 M KOH and excess $K_4Fe(CN)_6/K_3Fe(CN)_6$ dissolved in 2 M KOH cycled at current density 20 mA cm⁻². a) 0.50 M 1,3-DHP, b) 0.42 M 1,4-DHP, c) 0.36 M 1,6-DHP, d) 0.60 M 1,8-DHP, e) 0.20 M 1,9-DHP, f) 0.10 M 2,7-DHP.

Table S5. Comparison of performances of flow batteries of 1,4-, 1,6-, 1,8-, 1,9- and 2,7-DHP isomers coupled with $K_4Fe(CN)_6/K_3Fe(CN)_6$.

	1,3-DHP	1,4-DHP	1,6-DHP	1,8-DHP	1,9-DHP	2,7-DHP
Theoretical cell voltage (V)	1.24	1.16	1.34	1.44	1.24	1.40
Solubility in 2 M KOH (M)	1.6	0.53	0.60	1.9	0.29	0.18
Equivalent electrons concentration at maximum solubility limit in 2 M KOH (M)	3.2	1.06	1.2	3.8	0.58	0.36
Theoretical volumetric capacity at maximum solubility limit in 2 M KOH (Ah/L)	85.8	28.4	32.2	101.8	15.5	9.6
Concentration of RFB (M)	0.50	0.42	0.36	0.60	0.20	0.10
Demonstrated volumetric capacity (Ah/L)	26.8	22.5	19.3	32.2	10.7	5.4
Material	85	89	90	92	76	Charged 38%

utilization (%)						more than theoretical capacity
Average CE (%)	100	99.91	99.86	99.93	99.93	99.68
Average VE (%)	63.78	69.99	68.39	63.47	56.77	46.38
Average EE (%)	63.80	69.92	68.29	63.42	56.74	46.19
No. of Cycles	277	1000	245	1200	3200	1000
No. of Days	17	107	16	86	50	2
Overall capacity decay (%)	3.0	3.1	2.6	37.3	20.2	89.2
Capacity decay (per cycle) (%)	0.0109	0.0031	0.0106	0.031	0.0063	0.0892
Capacity decay (per day) (%)	0.176	0.029	0.163	0.434	0.404	44.6



Fig. S27. ¹H NMR spectra of cycled 1,3-DHP from 0.50 M flow battery in 2 M KOH after cycle 1091.



Fig. S28. ¹H NMR spectra of 1,4-DHP from 0.42 M flow battery in 2 M KOH after 1524 cycles. *tert*-butyl alcohol was used as the internal standard.



Fig. S29. ¹H NMR spectra of cycled 1,6-DHP from 0.36 M flow battery in 2 M KOH after 647 cycles. *tert*-butyl alcohol was used as the internal standard.



Fig. S30. a) RFB of 0.50 M 1,3-DHP used for the galvanostatic-potentiostatic cycling. The anolyte contained 0.5 M 1,3-DHP combined with 2 equivalents of KOH in 6 mL of 2 M KOH and 0.16 M

 $K_4Fe(CN)_6/0.064$ M $K_3Fe(CN)_6$ catholyte in 125 mL of 2 M KOH. The cell was cycled galvanostatically at 20 mA cm⁻² between 1.9 V and 0.7 V. After every 50th galvanostatic cycle, three galvanostatic-potentiostatic (potential hold at 1.5 V after charge and at 0.9 V after discharge) cycles were performed until the magnitute of the current density fell to 2 mA cm⁻². Due to the difference in concentrations between anolyte and catholyte, volume transfer from catholyte to anolyte occurred which raised the solution height above the electrolyte return tube, causing poor electrolyte mixing and utilization (labeled with black asterisks). Once the return tube was elevated to above the anolyte solution level, proper mixing and full utilization of the solution was facilitated and capacity was restored.

	Only Galvanostatic	Galvanostatic with Potentiostatic Hold
Concentration of RFB (M)	0.50	0.50
Theoretical volumetric capacity (Ah/L)	26.8	26.8
Material utilization (%)	85	92
Average CE (%)	100	100
Average VE (%)	63.78	66.15
Average EE (%)	63.80	66.18
No. of Cycles	277	205
No. of Days	17	13
Overall capacity decay (%)	3.0	1.3
Capacity decay/per cycle (%)	0.0109	0.00634
Capacity decay/per day (%)	0.176	0.10

Table S6.	Comparison	of performan	ces of flow b	patteries of 1.	3-DHP batteries.



Fig. S31. RFB of 0.50 M 1,6-DHP used for the galvanostatic-potentiostatic cycling. The anolyte contained 0.5 M 1,6-DHP combined with 2 equivalents of KOH in 5 mL of 2 M KOH and 0.16 M $K_4Fe(CN)_6/0.064$ M $K_3Fe(CN)_6$ catholyte in 105 mL of 2 M KOH. The cell was cycled galvanostatically at 20 mA cm⁻² between 1.6 V and 0.7 V. After every 50th galvanostatic cycle, three galvanostatic-potentiostatic (potential hold at 1.5 V after charge and at 0.9 V after discharge) cycles were performed until the magnitute of the current density fell to 2 mA cm⁻².

	Only Galvanostatic	Galvanostatic with Potentiostatic Hold
Concentration of RFB (M)	0.36	0.50
Theoretical volumetric capacity (Ah/L)	19.3	26.8
Material utilization (%)	90	94
Average CE (%)	99.86	100
Average VE (%)	68.39	62.80
Average EE (%)	68.29	62.82
No. of Cycles	245	698
No. of Days	16	36
Overall capacity decay (%)	2.6	1.1
Capacity decay/per cycle (%)	0.0106	0.00158
Capacity decay/per day (%)	0.163	0.031

Table S7. Comparison of performances of flow batteries of 1,6-DHP batteries.

Table S8. Comparison of capacity retention of phenazine-based anolytes and the most stable anthraquinone-based anolyte.

Anolyte	Concentrat	Operating	Cycle	Capacity	Temporal	Reference
	ion of RFB	pH of	Number(n)/	Retentio	Capacity	
	(M)	RFB	Test Time	n (%)	Fade (%,	
			(days)		day-1)	
1,6-DHP	0.5	14	698/36	98.9	0.031	This work
1,4-DHP	0.42	14	1000/107	96.9	0.029	This work
1,3-DHP	0.5	14	205/13	98.7	0.10	This work
DHPS	1.4	14	500/14.3	90.25	0.68	3
BHPC	0.5	14	1300/23	98	0.08	4
1,6-DPAP	0.5	8	50/7	99.99	0.0015	5
DPivOHAQ	0.5	14	-/16	99.9712	0.0018	6



Fig. S32. Cyclic Voltammogram of 1,4-DHP with second oxidation. CV condition; 5 mM of 1,4-DHP in 10 mL of 1 M NaOH solution at scan rate of 100 mV/s under N_2 atmosphere.



Fig. S33. ¹H NMR spectra of 1,9-DHP from 0.20 M flow battery in 2 M KOH after 5000 cycles.



Fig. S34. Thermolytic study of charged 1,3-DHP anolyte. An aliquot of 0.50 M charged 1,3-DHP in 2 M KOH was diluted with D_2O (0.40 mL of anolyte was diluted with 0.10 mL of D_2O) and monitored via ¹H NMR spectroscopy. The sample was heated first at 50 °C, then at 75 °C and finally at 95 °C. The overall time of heating is given in the parenthesis. Formation of precipitate was observed at 75 °C and higher temperatures. Decomposed product is labeled with green color asterisks.



13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 f1 (ppm)

Fig. S35. Thermolytic study of charged 1,4-DHP anolyte. An aliquot of 0.42 M charged 1,4-DHP in 2 M KOH was diluted with D_2O (0.40 mL of anolyte was diluted with 0.10 mL of D_2O) and monitored via ¹H NMR spectroscopy. The sample was heated first at 50 °C, then at 75 °C and finally at 95 °C. The overall time of heating is given in the parenthesis. Formation of precipitate was observed at 75 °C and higher temperatures.



12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0 f1 (ppm)

Fig. S36. Thermolytic study of charged 1,6-DHP anolyte. An aliquot of 0.36 M charged 1,6-DHP in 2 M KOH was diluted with D_2O (0.40 mL of anolyte was diluted with 0.10 mL of D_2O) and monitored via ¹H NMR spectroscopy. The sample was heated first at 50 °C, then at 75 °C and finally at 95 °C. The overall time of heating is given in the parenthesis. Formation of precipitate was observed at 75 °C and higher temperatures and spectrum becomes broad due to the considerable amount of precipitate present in the solution at 95 °C. Charged and discharged anolytes are labeled with blue and black color asterisks, respectively.



Fig. S37. Thermolytic study of charged 1,9-DHP anolyte. An aliquot of 0.20 M charged 1,9-DHP in 2 M KOH was diluted with D_2O (0.40 mL of anolyte was diluted with 0.10 mL of D_2O) and monitored via ¹H NMR spectroscopy. The sample was heated first at 50 °C, then at 75 °C and finally at 95 °C. The overall time of heating is given in the parenthesis. Formation of precipitate was observed at 75 °C and higher temperatures. Charged and discharged anolytes are labeled with blue and black color asterisks, respectively.



Fig. S38. First 50 cycles of RFB of 0.60 M 1,8-DHP. Capacity and efficiency of cell composed of deprotonated DHPs in 2 M KOH and excess $K_4Fe(CN)_6/K_3Fe(CN)_6$ dissolved in 2 M KOH cycled at current density 20 mA/cm².



Fig. S39. Comparison of ¹H NMR spectra of cycled 2,7-DHP (cycle 352 and 5000) against uncycled anolyte. An aliquot of discharged anolyte from a 0.10 M RFB containing deprotonated 2,7-DHP in 2 M KOH was diluted with D_2O for the analysis. Internal standard; 1 M sodium methanesulfonate.



Fig. S40. *In-situ* ¹H NMR spectrum of discharged anolyte of cycle 5000 containing decomposed product of 2,7-DHP (3,4-DH-2,7-DHP) (labeled in red color asterisk) in D₂O. ¹H NMR (D₂O, 400 MHz): δ 7.39 (d, *J*_{H-H} = 9.0 Hz, Ar*H*, 1H), 6.99 (dd, *J*_{H-H} = 9.0 Hz, *J*_{H-H} = 2.7 Hz, Ar*H*, 1H), 6.78 (d, *J*_{H-H} = 2.7 Hz, Ar*H*, 1H), 3.06 (t, *J*_{H-H} = 7.5 Hz, C*H*₂, 2H), 2.51 (t, *J*_{H-H} = 7.6 Hz, C*H*₂, 2H).



Fig. S41. RFB of 0.60 M 1,8-DHP used for the decomposition study. The anolyte contained 0.60 M 1,8-DHP combined with 2 equivalents of KOH in 6 mL of 2 M KOH and 0.16 M K₄Fe(CN)₆/0.064 M K₃Fe(CN)₆ catholyte in 150 mL of 2 M KOH. An aliquot of anolyte (50 μ L) was taken out in Cycle 1, 3, 12, 15, and 34 during both charging and discharging steps and diluted with 450 μ L of D₂O for ¹H NMR analysis (given in Figure S8). The gap labelled with black color asterisk is due to the unplanned stopping of the Arbin system from a power outage.



Fig. S42. Comparison of ¹H NMR spectra of anolyte from 0.60 M 1,8-DHP RFB. Uncycled anolyte was compared with discharged anolyte of cycle 1, 3, 12, 15 and 34 in D_2O . Decomposed product was labeled with red color asterisks.

Cycle No.	Ratio between two species (%)			
	Discharged 1,8-DHP	DHDHP		
1	95	5		
3	87	13		
12	69	31		
15	64	36		
34	63	37		

Table S9. Distribution of discharged 1,8-DHP and DHDHP during cycle 1, 3, 12, 15, and 34.

Table S10. Distribution of charged 1,8-DHP and DHDHP during cycle 1, 3, 12, 15 and 34.

Cycle No.	Ratio between two species (%)				
	Charged 1,8-DHP	DHDHP			
1	97	3			
3	88	12			
12	65	35			
15	63	37			
34	61	39			



Fig. S43. *In-situ* ¹H NMR spectrum of discharged cycle 34 containing 1,8-DHP and DHDHP in D₂O. ¹H NMR (D₂O, 500 MHz): δ 7.19 (t, $J_{\text{H-H}}$ = 8.0 Hz, Ar*H*, 1H), 6.86 (d, $J_{\text{H-H}}$ = 7.8 Hz, Ar*H*, 1H), 6.67 (d, $J_{\text{H-H}}$ = 7.7 Hz, Ar*H*, 1H), 3.05 (t, $J_{\text{H-H}}$ = 7.6 Hz, C H_2 , 2H), 2.51 (t, $J_{\text{H-H}}$ = 7.6 Hz, C H_2 , 2H). Peaks corresponding to DHDHP are labeled with red color asterisks.



7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 f1 (ppm)



Fig. S44.A Comparison of ¹H NMR spectra of charged, 0.6 M 1,8-DHP held in an NMR tube under inert atmosphere and monitored at the indicated intervals between 3 and 621 hours after charging. DHDHP is discernible in the baseline at 3 hours and increases gradually over time until approximately 1:1 with charged DHP at hour 135. B) Time plot of mole % of charged 1,8-DHP in

the sample vs time. After rapid decay over the first 3 days, the ratio levels at approximately 1:1 with DHDHP, indicating that equilibrium has been reached.



Fig. S45. a) High Concentration RFB of 1,8-DHP. The anolyte contained 1.4 M 1,8-DHP combined with 2 equivalents of NaOH in 5 mL of 1 M NaOH and 0.30 M $K_4Fe(CN)_6/0.12$ M $K_3Fe(CN)_6$ catholyte in 156 mL of 1 M NaOH. Due to the difference in concentrations between anolyte and catholyte, a significant amount of volume transfer from catholyte to anolyte occurred, increasing the anolyte volume to 15 mL and raising the solution height above the electrolyte return tube. This caused poor electrolyte mixing and utilization. Once the return tube was elevated to above the anolyte solution level, proper mixing and full utilization of the solution was facilitated and capacity was partially restored. (labeled with black asterisk). Capacity of 1,8-DHP RFB decreases in both low and high concentrations. b) Galvanostatic charge-discharge voltage profiles from selected cycles at 20 mA/cm².



Fig. S46. *In-situ* ¹H NMR spectra of deprotonated 1,8-DHP and its decomposed products. An aliquot of anolyte in 2 M KOH was diluted with D_2O for the analysis. a) 0.60 M uncycled 1,8-DHP, b) discharged anolyte (at cycle 34) containing 1,8-DHP and DHDHP from 0.60 M RFB, c) discharged anolyte containing THDHP, and d) discharged anolyte (at cycle 332) containing DHDHP and THDHP along with 1,8-DHP from 1.4 M RFB. DHDHP and THDHP were labeled with red and blue asterisks respectively.



Fig. S47. RFB for the attempted electrochemical synthesis of DHDHP. The analyte contained 0.6 M 1,8-DHP combined with 2 equivalents of KOH in 6 mL of 2 M KOH and 0.16 M K_4 Fe(CN)₆/0.064

 $M K_3Fe(CN)_6$ catholyte in 150 mL of 2 M KOH. A; galvanostatic charging at 20 mA cm⁻¹, B; potential held at 1.6 V until current dropped to 0.4 mA cm⁻², C; potential held at 1.7 V until current dropped to 0.3 mA cm⁻², D; potential held at 1.8 V until current dropped to 0.2 mA cm⁻², E; galvanostatic discharging at 20 mA cm⁻² and then at 10 mA cm⁻¹.



Fig. S48. ¹H NMR spectrum of THDHP in D₂O (after step E in figure S46). ¹H NMR (D₂O, 400 MHz): δ 6.73 (t, $J_{\text{H-H}}$ = 8.0 Hz, Ar*H*, 1H), 6.22 (dd, $J_{\text{H-H}}$ = 8.2 Hz, $J_{\text{H-H}}$ = 1.0 Hz, Ar*H*, 1H), 6.05 (dd, $J_{\text{H-H}}$ = 7.8 Hz, $J_{\text{H-H}}$ = 1.1 Hz, Ar*H*, 1H), 5.44 (s, 1H), 3.98 (dd, $J_{\text{H-H}}$ = 11.6 Hz, $J_{\text{H-H}}$ = 4.9 Hz, 1H), 2.54-2.46 (m, 1H), 2.36-2.29 (m, 2H), 1.96-1.85 (m, 1H). Peaks corresponding to 1,8-DHP and DHDHP are marked with black and red color asterisks respectively. Little impurity coming from starting material is labeled in green color asterisks. MS (ESI⁻) m/z: 215.08 (M-H)⁻.

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