Supplementary Information

Use of voltage for recomposing degraded redox active molecules for flow battery applications

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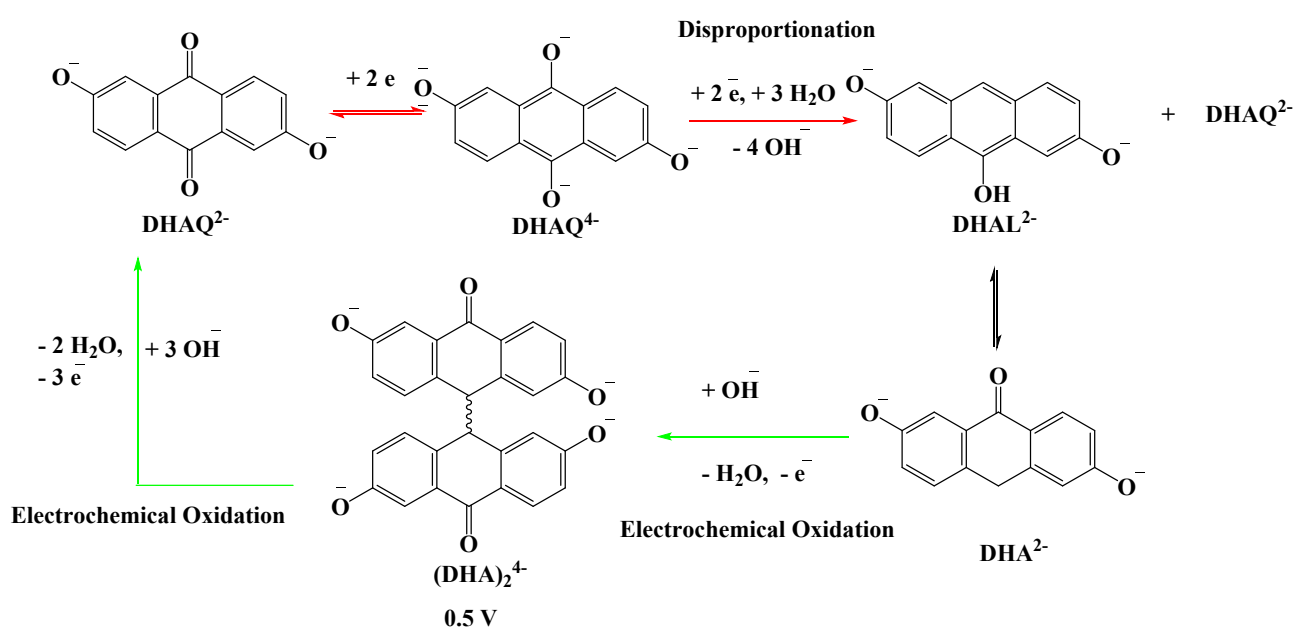
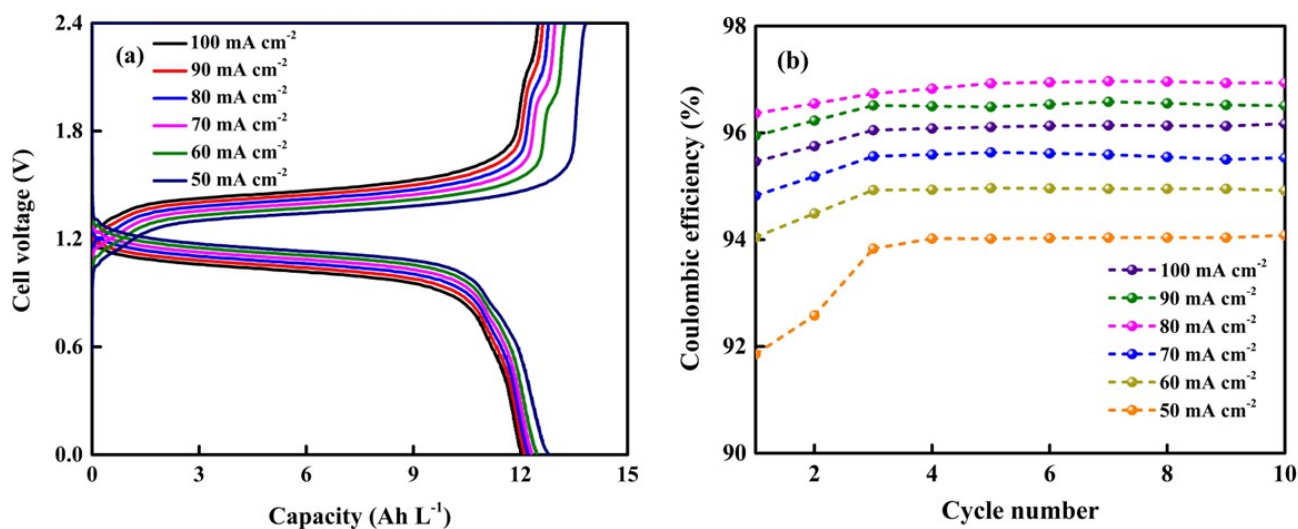**Scheme S1.** Electrochemical re-composition of $DHAQ^{2-}$.

Fig. S1. (a) Rate capability study with 0.25 M anolyte and 0.5 M catholyte at 50, 60, 70, 80, 90 and 100 mA cm^{-2}) (b) Coulombic efficiency at different scan rate.
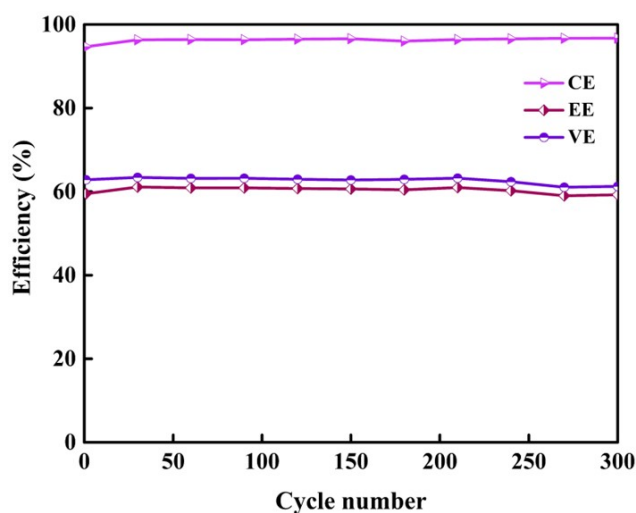

Fig. S2. Coulombic efficiency (CE), Voltage efficiency (VE) and Energy efficiency (EE) of DHAQ - K$_4$ [Fe(CN)$_6$] system at 80 mA cm^{-2} current density.
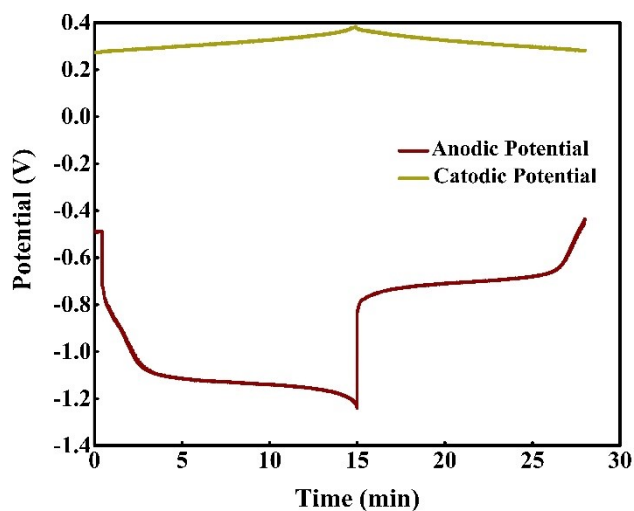
Fig. S3. Single electrode potential study of DHAQ - K_4 [Fe (CN)$_6$] system charged up to 2.4 V cut-off cell voltage.
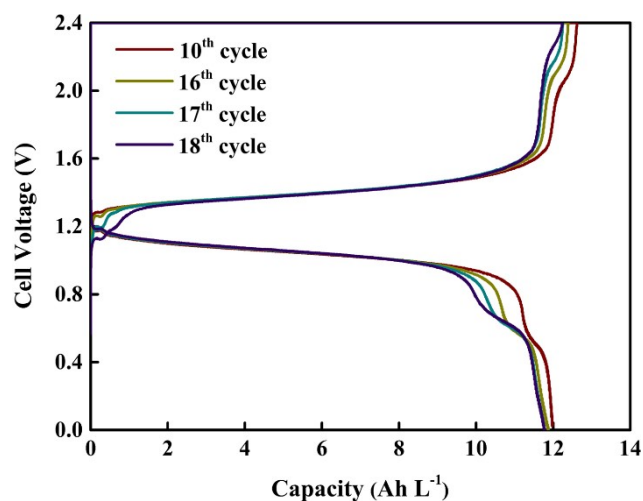

Fig. S4. 10th, 16th, 17th and 18th GCD cycles.

To determine the equilibrium constant of dimerization, the sample after the 120th discharge cycle was subjected to a CV study. First, the anolyte was cycled in a potential range of -1.4 V to 0.6 V to see the oxidation of the dimer. Subsequently, CV was performed only up to 0.15 V to prove the species correspond to the peak at -0.8 V is unrelated with peroxo dimer oxidation observed at ~ 0.4 V. As can be seen from Fig. S5, the peak current of DHAQ^{2-}/DHAQ^{4-} redox couple at ~ -0.9 V has increased while using a shorter potential window, without affecting the small plateau observed at -0.8 V. So, the increment in the peak current (due to the peroxo

dimer reduction into DHAQ^{4-}) can be directly correlated with the species responsible for 0.4 V peak, i.e., dimer. Therefore, the difference in the area of the reduction peaks (the peak spanning from -0.66 V to -1.4 V) obtained from the CVs recorded up to 0.15 V and 0.6 V is proportional to the concentration of the dimer formed. The area under the reduction peak of the CV carried out up to 0.6 V is proportional to the equilibrium concentration of DHAQ^{2-}. To precisely calculate the concentration of the DHAQ^{2-} in the GCD cycled solution, we have performed CV of 0.075, 0.1, 0.125 and 0.15 M DHAQ^{2-} solutions to generate a calibration graph (Fig. S6). The concentration of DHAQ^{2-} species is 0.081 M in the GCD cycled solution as obtained from the peak spanning from -0.66 V to -1.4 V. The difference in area corresponds to the concentration of DHAQ^{2-} lost in the form of (DHAQ)$_2$$^{6-}$, therefore the estimated concentration of (DHAQ)$_2$$^{6-}$ is 0.009 M. Using equations (1) and (2), the calculated equilibrium constant is 1.3.

$$2DHAQ^{2-} + 2e^- \rightleftharpoons (DHAQ)^{6-}_2 \qquad (1)$$
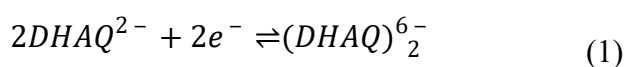
$$\text{Equilibrium constant} = \frac{[(DHAQ)^{6-}_2]}{[DHAQ^{2-}]^2} \qquad (2)$$
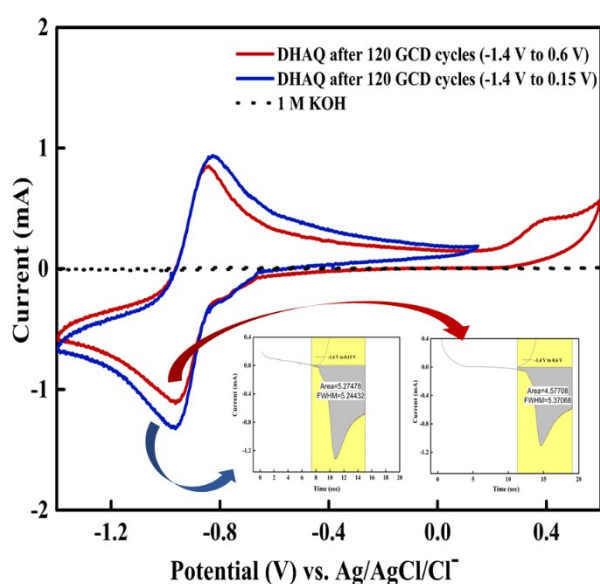
Fig. S5. Cyclic voltammograms of 0.1 M 2,6-DHAQ in 1 M KOH before and after 120 GCD cycles (the cell was run with 0.25 M 2,6-DHAQ and diluted later with 1 M KOH to obtain nominal concentration of 0.1 M) along with the CV of 1M KOH solution (inset shows the integrated area of cathodic peaks).
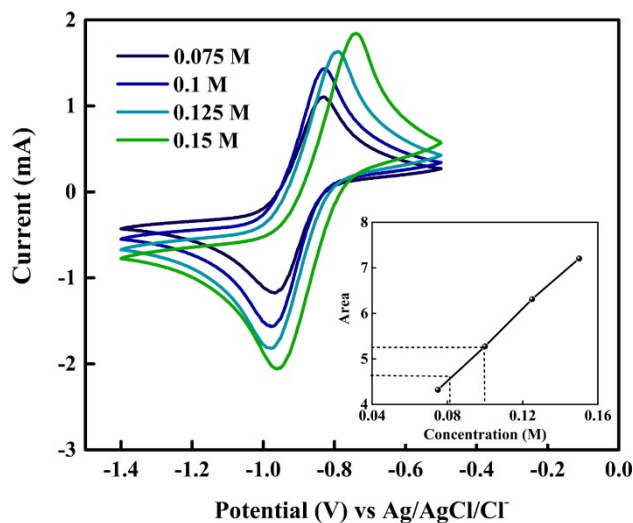

Fig. S6. Cyclic voltammogram of 0.075 M, 0.1 M, 0.125 M and 0.15 M DHAQ in 1 M KOH (inset shows the area under cathodic peak vs. concentration of DHAQ).
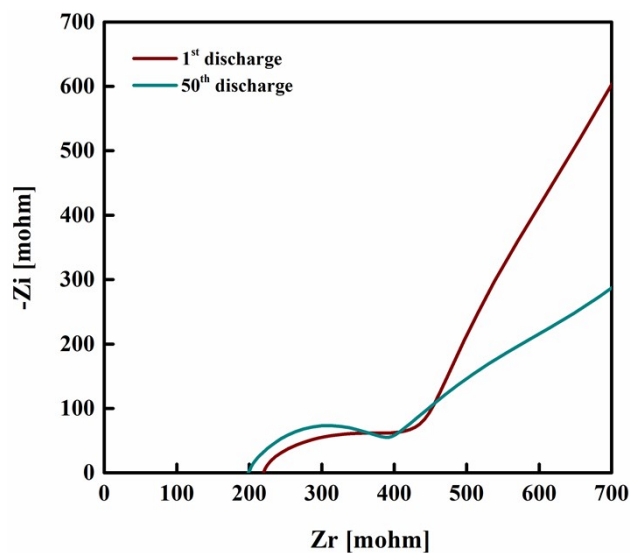

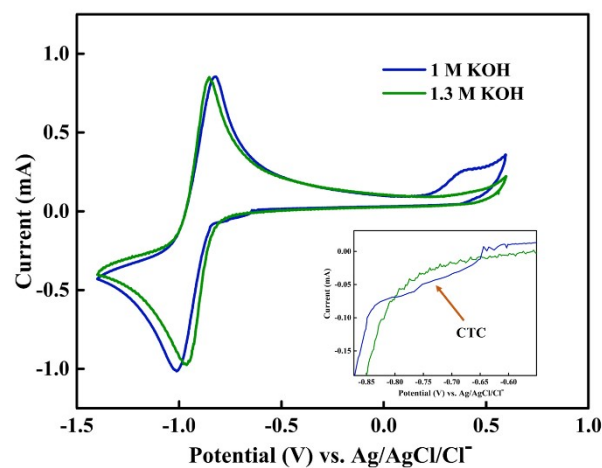**Fig. S7.** EIS data of the cell after 1st and 50th discharge.

Fig. S8. Cyclic voltammogram of 0.1 M DHAQ in 1 M KOH after 300 GCD cycles and 0.1 M DHAQ in 1.3 M KOH after 150 GCD cycles (inset shows the peak due to CTC)
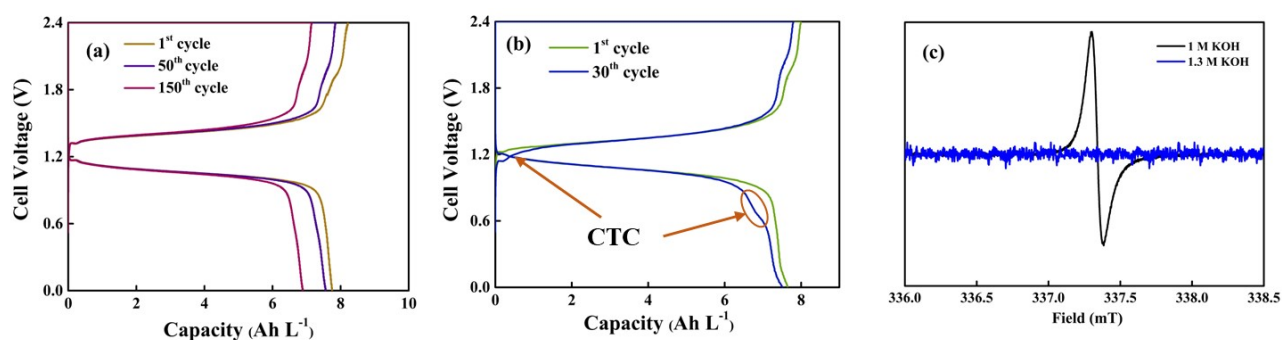

Fig. S9. GCD profile of 0.16 M 2,6-DHAQ anolyte in (a) 1.3 M KOH for 1st, 50th and 150th cycles, and (b) in 1 M KOH for 1st and 30th cycles (current density of 80 mA cm^{-2}), (c) The EPR spectra of anolyte at different KOH concentrations, which were charged up to 2.4 V, confirming absence of CTC in 1.3 M KOH based electrolyte.

Reference

1   Y. Jing, E. W. Zhao, M. A. Goulet, M. Bahari, E. M. Fell, S. Jin, A. Davoodi, E. Jónsson, M. Wu, C. P. Grey, R. G. Gordon and M. J. Aziz, *Nature Chemistry* 2022, **14**, 1103–1109.