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Supplementary Information for

Hydrogen/functionalized benzoquinone for a high-performance regenerative fuel cell as a potential large-scale energy storage platform

Javier Rubio-Garcia,[a] Anthony Kucernak,*[a] Rutao Liu [a] and Barun Chakrabarti [b,c]

a) *Department of Chemistry, Imperial College London, SW7 2AZ, UK.*
b) *RFC Power, 52 Princes Gate, Exhibition Road, London, SW7 2PG, United Kingdom*
c) *Current address: Warwick Manufacturing Group, University of Warwick, Coventry, CV4 7AL, United Kingdom.*

(*corresponding author e-mail: anthony@imperial.ac.uk)

Discussion on NMR

As seen in Figure S1 (inset), the first battery charge, involves 2-3 times higher charge than expected via a 2-electron process. This might be due to the hydroxylation of the BQDS to 2,4,5-trihydroxybenzene-1,3-disulfonic acid (THBQDS). Hence, nuclear magnetic resonance (NMR) spectroscopy was conducted on the BQDS prior to and after cycling at 100 mA cm^{-2}.

To analyse the chemical transformations of the BQDS electrolyte, proton NMR is conducted. The chemical shifts are given relative to D_2O at δH=4.79 ppm. The two aromatic protons of 4,5-dihydroxybenzene-1,3-disulfonic acid produce two singlets at 7.20 ppm and 7.50 ppm with a mostly equal ratio as Figure S1 shows. After the cycling test, the two proton peaks of dihydroxy compound **a** are absent, and at the same time, a new aromatic proton peak with a quarter ratio of the other two peaks occurs at 7.20 ppm, which might be generated by the trihydroxy compound **b** (Figure S1). From the charge and discharge curve analysis, it is possible to conclude that a Michael addition of **a** and **b** produces the tetrahydroxy compound **c**, which is a fully-substituted molecule and has no aromatic protons [1–3]. In the NMR spectra, we cannot prove that there is compound **c** in the electrolyte directly. However, the functionalisation of BQ with hydroxyl groups would lead to a lower redox potential [1–3]. As a result we hypothesise that the formation of **c** would correspond to the redox peak found at 0.65 V in Figure 3B (in the main text) whereas the trihydroxy compound **b** would offer similar redox potential to the dihydroxy compound **a** but with lower ΔE which means better reversibility.

Fig. S1. ^{1}H NMR of 4,5-dihydroxybenzene-1,3-disulfonic acid (red peaks) after being cycled at 100 mA cm^{-2} 200 times in the RFC. δH=4.79 ppm (singlet, D_2O); δH=7. 20 ppm (singlet, aromatic proton); δH=7.50 ppm (singlet, aromatic proton). ^{1}H NMR of BQDS electrolyte after cycling 200 times (blue peaks). δH=4.79 ppm (singlet, D_2O); δH=7.20 ppm (singlet, aromatic proton); δH=7.27 ppm (singlet, aromatic proton); δH=7.50 ppm (singlet, aromatic proton). Electrolyte is 1 mM BQDS in 1 M H_2SO_4.

References

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