



MAGNETIC RESONANCE FOR BATTERIES RESEARCH AND MANUFACTURING

Multi-Modal Characterization and Analysis of Organic Redox-Flow Batteries by EPR and NMR

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Innovation with Integrity

Introduction

Researchers across the globe, both in industry and academia, are working together to discover new resources to build a more sustainable future. A large effort is being poured into the pursuit of new battery materials and systems in order to achieve cleaner, efficient energy conversion devices. Organic redox-flow batteries (RFB) have emerged as a newer player in the field of flow batteries. RFB's make use of organic redox active molecules, termed catholyte and anolyte, to generate chemical potential differences in an electrochemical cell. These potentials provide the electromotive force to generate power.

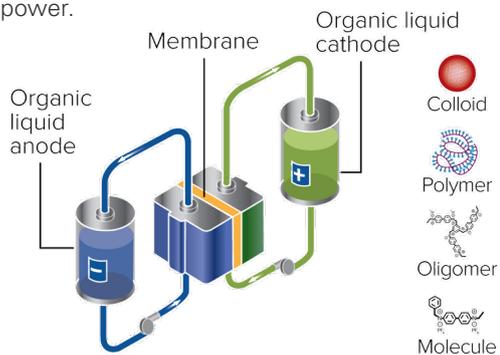


Figure 1: Schematic of a redox-flow battery system, showing organic liquid anode (anolyte) reservoir (left), electrochemical cell (center) and organic liquid cathode (catholyte), reservoir (right). On the right are examples of compounds suitable for redox-active electrolyte solutions.

The main advantage of RFB cells are their intrinsic ability to decouple power generation and energy storage. Power is generated in the electrochemical cell only when electrolyte solutions are provided whilst system energy is stored in the volume of the liquid electrolyte.

Additionally, they are composed of naturally abundant elements and making them more cost-efficient.

1 H Hydrogen 1.008	6 C Carbon 12.011	7 N Nitrogen 14.007	8 O Oxygen 15.999
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Challenges: While RFB's show promise, there are remain certain challenges :

Capacity fade/loss resulting in low cycle life caused by:

- Molecule/electrolyte decomposition
- Electrode passivation
- Self-discharge
- Side reactions between components
- Lower energy density compared to Li-ion
- Membrane issues

EPR Solution:

- Detection and quantification of radical intermediates involved in electrolyte decomposition and side reactions
- Determination of mechanism of electrolyte decomposition
- Determination of rates of radical formation

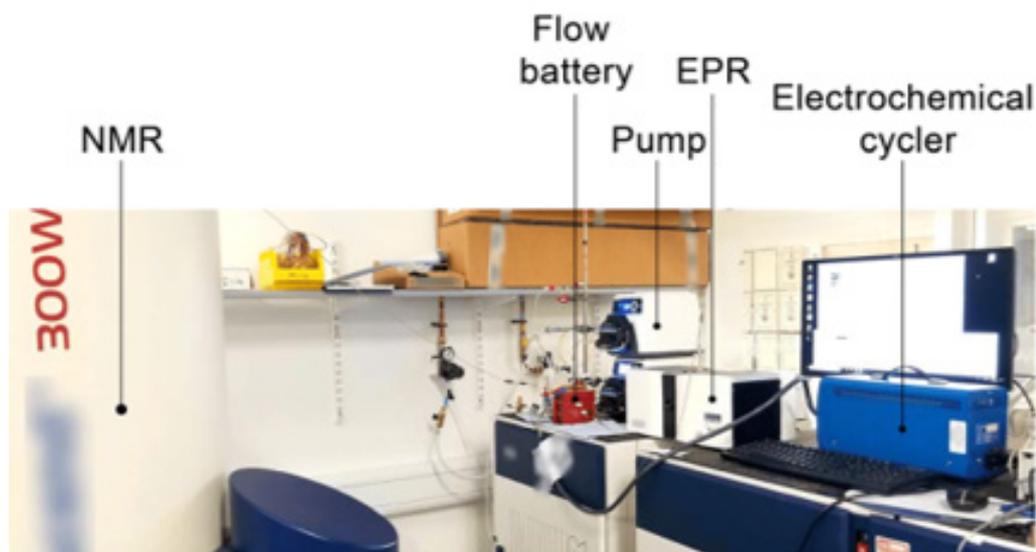


Figure 2: Online EPR-NMR set up for studying of Organic RFB's. Involved is an electrochemical cycler, two peristaltic pumps, RFB, benchtop Magnetech ESR5000 EPR (Bruker), and 300 MHz NMR (Bruker).¹

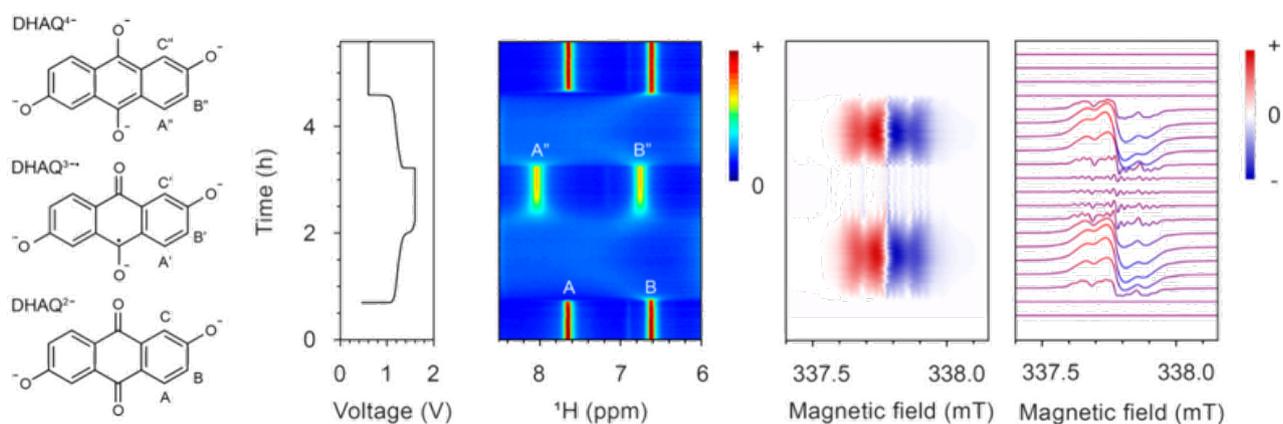


Figure 3: Structure of electrolyte molecule, 2,6-dihydroxyanthraquinone (DHAQ), states and charge cycle (left) used in RFB cell and respective ¹H NMR contour plot (center) and EPR spectra and contour plot (right).¹

Quinone molecules have garnered interest as potential anolyte solutions for organic RFB's. Zhao and co-workers developed an RFB cell that employs 2,6-dihydroxyanthraquinone (DHAQ) at a concentration of 10 mM and studied it with an online EPR and NMR setup (Figure 2). During electrochemical cell cycling, it can be observed that NMR signals of aromatic protons A and B (Figure 3) from DHAQ begin to disappear as the voltage is increased past 1.15 V. Simultaneously, the EPR spectrum shows no signal until after the 1.15 V threshold is surpassed, and then a radical species is observed belonging to the DHAQ^{3•-} radical anion. The radical intensity increases as the voltage increases. Upon charging to the cutoff voltage of 1.6 V, the EPR signal begins to diminish and a new set of proton NMR peaks are visible, belonging to the doubly reduced DHAQ⁴⁻ anion (A'' and B''). The process is shown to be reversible when the cell is discharged, with reformation and disappearance of the radical in the EPR spectrum and reappearance of the proton resonances from A and B.

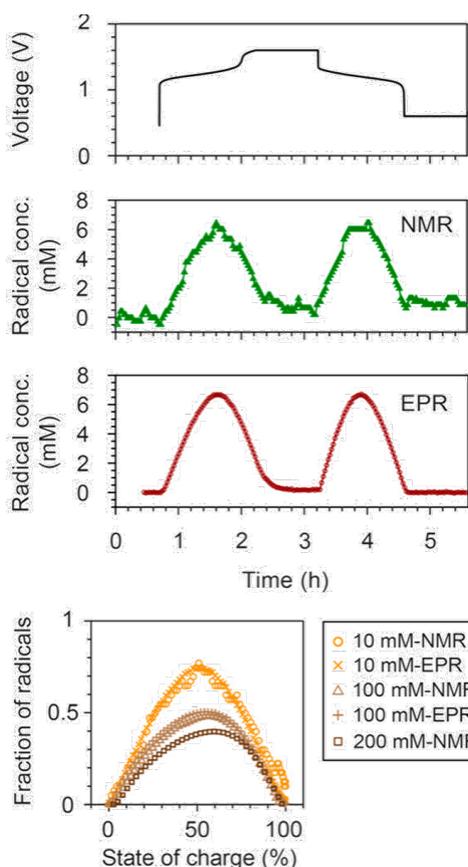


Figure 4: Concentration of $\text{DHAQ}^{3\bullet}$ radical over time measured by bulk magnetic susceptibility shift of water in NMR and by spin counting in EPR. Both methods show agreement across state of charge of the battery cell.¹

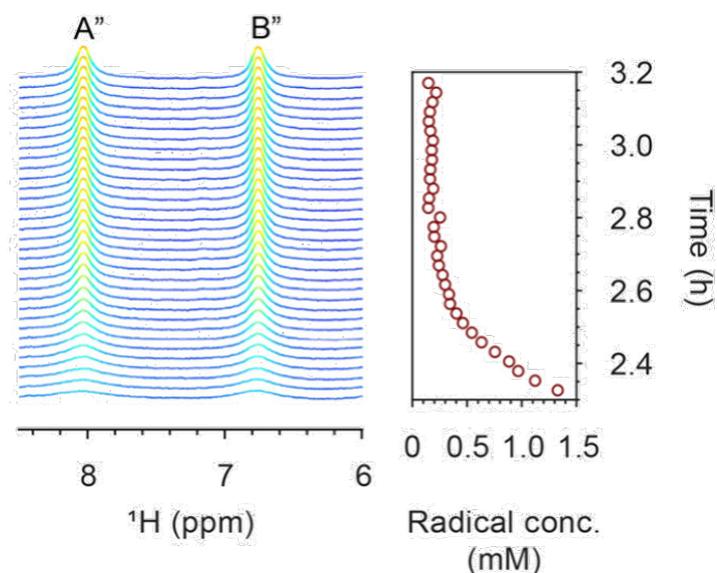


Figure 5: ^1H NMR spectra of DHAQ^{4-} as a function of time with corresponding radical concentrations from EPR data.

The amount of radical molecules generated during cell cycling was accomplished via two methods: bulk magnetization changes from water resonance in NMR, and by spin counting with EPR. In Figure 4, it can be observed that the radical concentration by both methods are consistent during cell cycling. This was then tested at a higher concentrations, 100 and 200 mM, and similar results were achieved by both techniques. It is also observed that the radical concentrations differ with varying concentrations of anolyte, suggesting reaction equilibria that are separate from the formation of the $\text{DHAQ}^{3\bullet}$ radical anion and thus. The rate of electron transfer between $\text{DHAQ}^{3\bullet}$ and DHAQ^{4-} were enabled by EPR where the concentration of radical species can be reliably detected even at higher states of charge. Proton resonances for A'' and B'' in the NMR spectra were observed to decrease as the radical concentration also decreased (Figure 5). The EPR and NMR analysis reveal an average electron transfer rate of $2.0 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$.

Summary

- The ^1H NMR spectra show chemical shifts for aromatic protons, A and B, in DHAQ^{2-} that disappear upon cell cycling coinciding with the appearance of a radical species, $\text{DHAQ}^{3\bullet}$, in the EPR spectrum. The EPR spectrum diminishes at max. voltage and new ^1H peaks appear corresponding to DHAQ^{4-} . The process is reversible during discharge.¹
- EPR spin quantification of radical species is verified by bulk magnetic susceptibility shifts of water in NMR spectra, showing excellent agreement between the two methods¹ and shows how EPR combined with NMR efficiently tracks the formation of multiple species during cell cycling.
- EPR was able to reliably detect $\text{DHAQ}^{3\bullet}$ at high voltages, where decomposition processes often take place and enabled calculation of an electron transfer rate from $\text{DHAQ}^{3\bullet}$ to DHAQ^{4-} . This provides insights into the redox mechanism inside the battery cell.¹
- EPR and NMR are a powerful duo for analysis and characterization of organic RFB's, but additionally can be applied in studies of degradation, a common issue in organic RFB's.² The same principle can be applied for many other battery types as well.

References:

1. Zhao, E. et al., J. Amer. Chem. Soc., (2021), **143(4)**, 1885-1895
2. Museveni, S. K. et al., *Mat. Sci. for Ener. Tech.*, (2023), **6**, 561-566.



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