Analytical Excellence in Battery Solutions

Electrolyte Reactions Studied by EPR

How to Probe Electrolyte Dynamics in Next-Generation Batteries

Innovation with Integrity

Introduction

Electron Paramagnetic Resonance (EPR) spectroscopy is a powerful analytical technique used to study materials with unpaired electrons. In the context of battery research, EPR has emerged as a valuable tool for investigating electrolyte reactions, particularly in lithium-ion batteries. This technique is highly sensitive to changes in the electronic environment of paramagnetic species, making it ideal for monitoring the redox processes that occur during battery operation.

EPR provides detailed insights into the mechanisms of electron transfer and the formation of free radicals within the electrolyte and is used to study electrolyte reactions in several ways:

- **Oxygen and peroxide species -** EPR detects and quantifies oxygen radicals in battery redox reactions, which helps engineers understand how these radicals affect battery performance and capacity [1]
- **Redox mechanisms –** EPR is used to analyze redox mechanisms in cathode materials during battery cycling. For example, in lithium cobalt oxide (LCO) batteries, EPR detects paramagnetic Co(II) that forms when the electrolyte first comes into contact with the LCO [2]
- **Electrolyte decomposition –** EPR can be used to study electrolyte decomposition in batteries. For example, EPR is used to follow the decomposition of 2,6-dihydroxyanthraquinone (DHAQ) and correlates it to the capacity fade in redox flow batteries [3]
- **Stability of the cathode/electrolyte interface –** EPR is used to study the chemical state of oxidized oxygen species in cathode materials. This helps to understand the stability of the cathode/electrolyte interface [4]

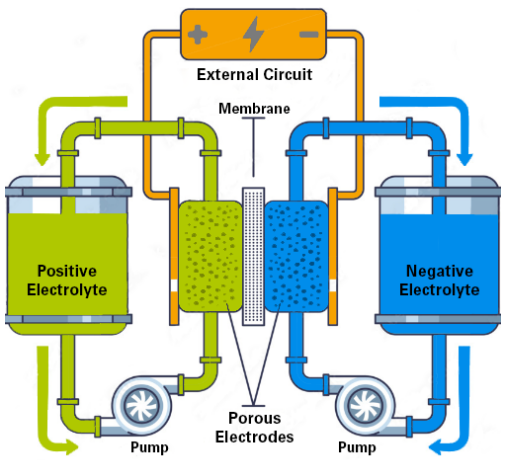

Figure 1: A flow battery diagram

Example 1: Impact of state of charge (SOC) on the physical properties of the VO^{2+}/VO_2^+ redox pair in all-vanadium redox flow batteries

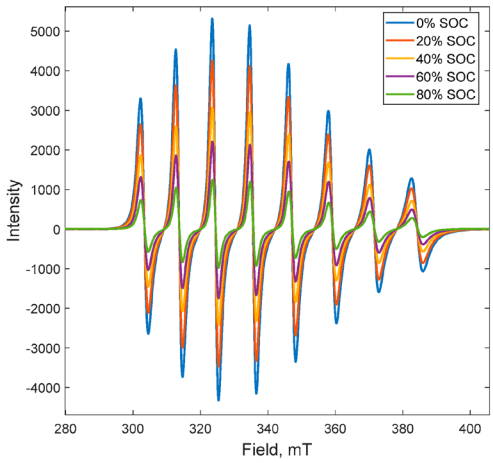

Figure 2: EPR spectra of vanadium electrolytes in 1M H_2SO_4 supporting electrolyte at 0%, 20%, 40%, 60%, and 80% state of charge. Note 100% state of charge is missing as VO_2^+ is EPR silent. Reproduced from reference [5] in accordance with Creative Commons Attribution 4.0 License.

- Similar to other redox flow batteries, the vanadium redox flow battery (VRFB) uses two circulating electrolyte tanks (Figure 1).
- The VO^{2+}/VO_2^+ redox pair, typically used at the positive terminal of a VRFB, was studied by EPR under different states of charge (SOC) and varying concentrations of H_2SO_4 supporting electrolyte
- EPR results indicate that SOC has little effect on the EPR line shape, primarily showing a reduction in signal intensity as VO^{2+} concentration decreases. Data fitting enabled the determination of translational and rotational diffusion coefficients (D_T, D_R) for VO^{2+} in both bulk solution and Nafion membranes

Example 2: LiI redox mediation in aprotic Li-O_2 batteries: solvation effects and singlet oxygen

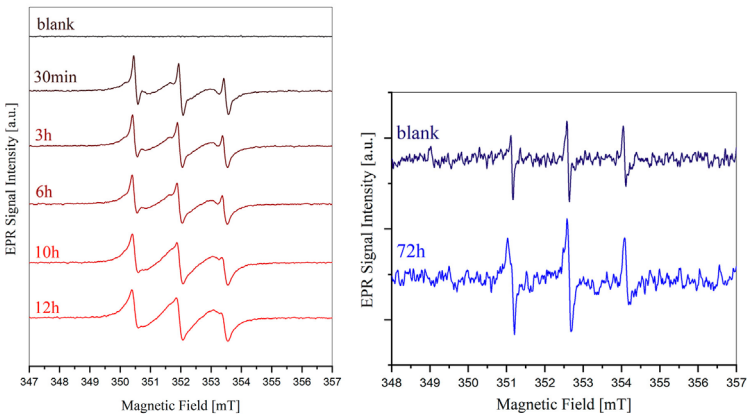

Figure 3: (Left) EPR spectra of a solution of 50 mM I_2 + 200 mM LiI + 80 mM 4-oxo-TEMP (spin probe specific for singlet oxygen) in DMSO reacting with excess Li_2O_2 for 12 h. (Right) EPR spectra of a reference solution of 80 mM 4-oxo-TEMP in G4 (top spectrum) and a solution of 50 mM I_2 + 200 mM LiI + 80 mM 4-oxo-TEMP with excess Li_2O_2 after 72 h of reaction (bottom spectrum). Reproduced from reference [6] in accordance with Creative Commons Attribution 4.0 License

- Lithium-oxygen aprotic batteries (aLOBs) promise high energy density but face challenges due to parasitic reactions affecting reversibility and cycle life
- The oxidation of Li_2O_2 requires large overpotentials without catalysis. Redox mediators (RMs), like lithium iodide (LiI), help reduce these overpotentials
- EPR was utilized to investigate LiI's role in degradation and singlet oxygen release in two different solvents: highly polar DMSO and low-polarity tetraglyme (G4)
- EPR data showed that LiI in DMSO-based electrolytes leads to extensive degradation and singlet oxygen release, while in G4-based electrolytes, it suppresses singlet oxygen release, improving cyclability

Conclusion

Parasitic reactions in battery electrolytes can lead to performance degradation and reduced lifespan. EPR spectroscopy is a valuable tool for studying these reactions, as it detects unpaired electrons and provides insights into the behavior of free radicals and transition metals during battery operation. This helps to understand and mitigate these reactions, ultimately improving battery efficiency and durability

References

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