Analytical Excellence in Battery Solutions

Characterization of Cathode Materials by EPR

Degradation and Structural Studies of Lithium Transition-Metal Oxides in Batteries

Innovation with Integrity

Introduction

The main components of metal-ion batteries include cathode, anode, separator, and electrolyte. During charging and discharging, the anode and cathode materials undergo complex structural changes that impact the cells' electrochemical performance. Notably, the cathode material is the primary factor limiting cell performance, and advancements in cathode research can significantly drive battery evolution.

Electron Paramagnetic Resonance is a powerful technique for characterizing cathode materials in batteries. It provides valuable information that can help improve the performance, stability, and efficiency of cathode materials in batteries by:

- **Detection of unpaired electrons:** EPR is highly sensitive to unpaired electrons, which are often present in transition metals used in cathode materials. This sensitivity allows researchers to study the electronic environment and oxidation states of these ions.
- **Identifying defects and impurities:** EPR can detect defects and impurities in cathode materials, which can affect battery performance. Identifying and understanding these defects can lead to the development of more efficient and stable cathode materials.
- **Monitoring redox processes:** EPR can be used to observe redox processes in real-time. This is crucial for understanding how cathode materials behave during charge and discharge cycles. By combining EPR with other techniques like nuclear magnetic resonance (NMR), X-ray diffraction (XRD), scanning electron microscopy (SEM), etc. researchers can visualize these processes and gain insights into the material's performance.
- **In operando studies:** EPR can be used in operando (under operating conditions) to study the behavior of cathode materials in real-time. This helps in understanding the dynamic changes that occur during battery operation and can lead to the design of better materials and battery systems.

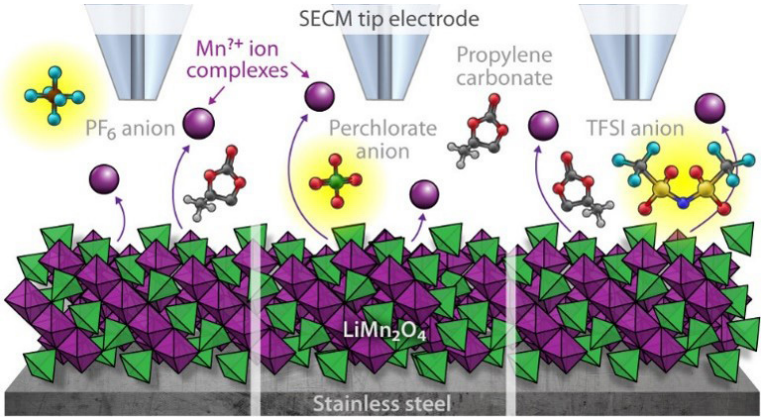

Figure 1: Dissolution processes in $LiMn_2O_4$ cathode. Reproduced from reference [1] in accordance with CC BY 4.0 License.

Example 1: Understanding degradation at the lithium-ion battery cathode/electrolyte interface

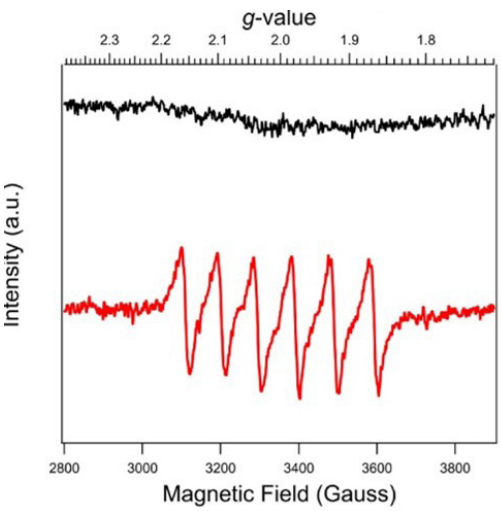

Figure 2: EPR signals of fresh electrolyte $LiClO_4$/propylene carbonate (black) and post-voltage hold (red). Reproduced from reference [1] in accordance with CC BY 4.0 License.

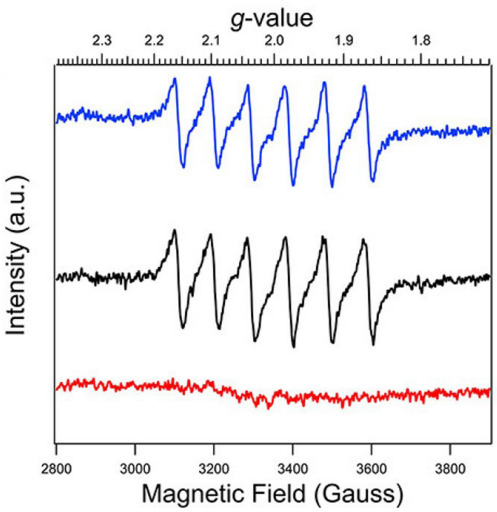

Figure 3: EPR signals of various electrolyte solutions [$LiPF_6$/PC (blue), $LiClO_4$/propylene carbonate (black), and LiTFSI/PC (red)] after voltage hold. Reproduced from reference [1] in accordance with CC BY 4.0 License.

- Lithium transition-metal oxides, such as $LiMn_2O_4$, are commonly used as cathode materials in lithium-ion batteries due to their significant capacity and energy density
- However, various processes at the cathode/electrolyte interface can degrade overall performance (Figure 1)
- One key failure mechanism is the dissolution of Mn from the cathode, which can be directly measured by EPR (Figure 2)
- EPR has also been utilized to better understand the properties of Mn(II) complexes formed after metal dissolution. The mechanism for Mn dissolution depends on the lithium salt anion in the electrolyte systems (Figure 3)

Example 2: Structural studies of $LiCoO_2$ obtained by combustion synthesis

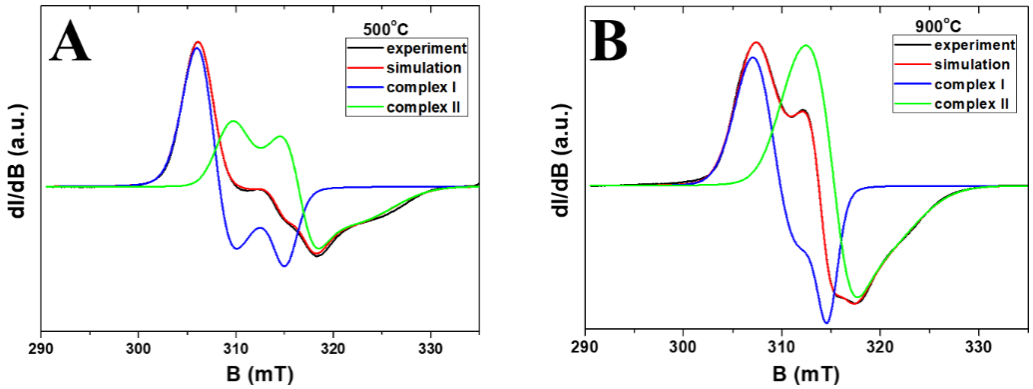

Figure 4: Experimental and simulated spectra for samples prepared at 500 °C (a) and 900 °C (b) and recorded at 5 K.
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- Lithium cobalt oxide ($LiCoO_2$ or LCO) is the most prevalent cathode material for lithium-ion batteries. It is extensively used in a variety of applications, such as mobile phones, tablets, laptops, and cameras, due to its high energy density and stable performance
- EPR was used to investigate the structure and composition of a single-phase nanocrystalline layered LCO synthesized via a novel combustion method. The data indicated the presence of low concentrations of Ni(III) impurities, regardless of the synthesis temperature
- Low temperature EPR at 5K revealed the existence of two types of Ni(III) complexes with distinct symmetries, as confirmed by spectral simulations (Figure 4)

Conclusion

EPR offers detailed insights into electronic structures, oxidation states, and local environments of paramagnetic species, aiding in understanding battery performance and degradation. This sensitivity is especially useful for studying transition metal-based cathodes and reactive oxygen species in Li-rich cathodes. As battery technology advances, EPR remains crucial for developing more efficient, durable, and high-capacity energy storage systems.

References

1. Huang D. et al., ACS Appl. Mater. Interfaces 2021, 13, 11930-11939
2. Michalska M. Et al., Beilstein J. Nanotechnol. 2022, 13, 1473–1482

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