Analytical Excellence in Battery Solutions

Characterization of Anode Materials by EPR

How to Investigate Lithium Depositions with CW-EPR

Innovation with Integrity

Introduction

Electron Paramagnetic Resonance (EPR) spectroscopy is a powerful technique in battery research, especially for analyzing anode materials. Its sensitivity to unpaired electrons makes it ideal for:

- **Detection of paramagnetic species:** EPR is highly sensitive to unpaired electrons, making it ideal for studying paramagnetic species that are often present in anode materials. This includes defects, radical species, and transition metal ions.
- **Understanding Electronic Environments:** EPR provides detailed information about the electronic environments of atoms within the anode material. This helps researchers understand how these environments change during processes like lithiation and sodiation.
- **Characterizing Structural Changes:** EPR can detect changes in the local structure of anode materials as they undergo intercalation and deintercalation of lithium or sodium ions. This is crucial for understanding the mechanisms that affect battery performance and longevity.
- **Investigating Solid-Electrolyte Interphases (SEI):** The formation and evolution of SEI layers are critical for the stability and efficiency of batteries. EPR helps in studying these layers by identifying and characterizing the paramagnetic species involved.
- **Identifying Defects and Impurities:** EPR is effective in detecting and characterizing defects and impurities within anode materials, which can significantly impact the performance and safety of batteries.
- **Monitoring Degradation Processes:** By providing insights into the degradation mechanisms of anode materials, EPR helps in developing strategies to enhance the durability and lifespan of batteries.

Role of EPR in Studying Lithium Depositions

Graphite is widely used as an anode material in lithium-ion batteries due to its ability to reversibly intercalate lithium ions. During the charging process, lithium ions move from the cathode to the anode and insert themselves between the layers of graphite. This process is known as lithium intercalation. During discharge, the lithium ions move back to the cathode, releasing energy. Graphite's low-voltage open-circuit potential makes it prone to metallic lithium deposition during charging, especially at low temperatures, high charge rates, and high states of charge. Normally, lithium plating is minimal but contributes to capacity loss due to lithium consumption and additional solid electrolyte interphase (SEI) formation. Under severe conditions, lithium can form dendrites, posing safety risks like internal short circuits.

EPR is ideal for ex-situ, in situ, and in operando measurements, allowing detailed probing of Li-metal deposits such as bulk, dendrites, or metallic filaments. Its high sensitivity to conduction electrons results in a distinctive Dysonian EPR lineshape with an asymmetric ratio (*A/B*), where (*A*) and (*B*) are the intensities of the positive and negative peaks, respectively (Figure 1). The asymmetric lineshape results from the fast movement of electrons and the skin effect, with electrons moving in and out of the skin depth region during microwave irradiation in an EPR experiment.

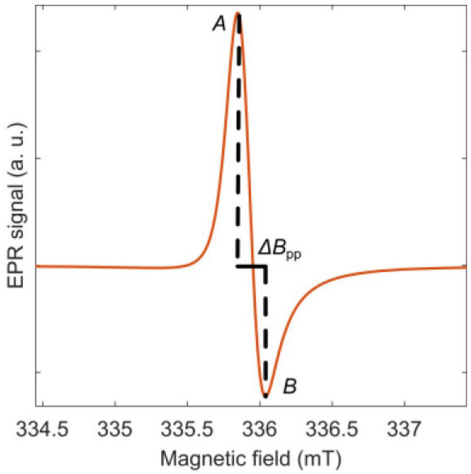

Figure 1: Typical EPR lineshape of conduction electrons in a metallic system. The intensity of the positive peak, *A*, is larger than the intensity of the negative peak, *B*, resulting in a Dysonian lineshape. The peak-to-peak linewidth, ΔB_{pp}, is also defined. Reproduced from reference [1] in accordance with CC BY 4.0 License.

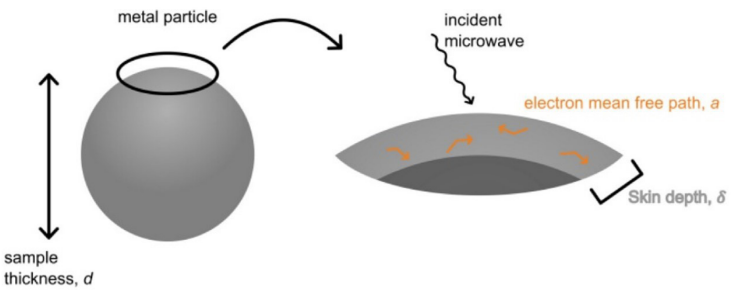

Figure 2: Illustration of the skin depth δ of a generic metal particle with diameter *d* upon incoming microwave radiation. Reproduced from reference [1] in accordance with CC BY 4.0 License.

- The thickness/skin depth ratio, d/δ, determines the (*A/B*) ratio and the contribution of absorptive and dispersive components to the EPR lineshape
- Thin metallic films ($d << \delta$) have a dominant absorptive component and are more symmetric with a Lorentzian lineshape and an asymmetric ratio $A/B = 1$
- Thick films ($d >> \delta$) have a dominant dispersive component with a Dysonian line and asymmetric ratio $A/B >> 1$

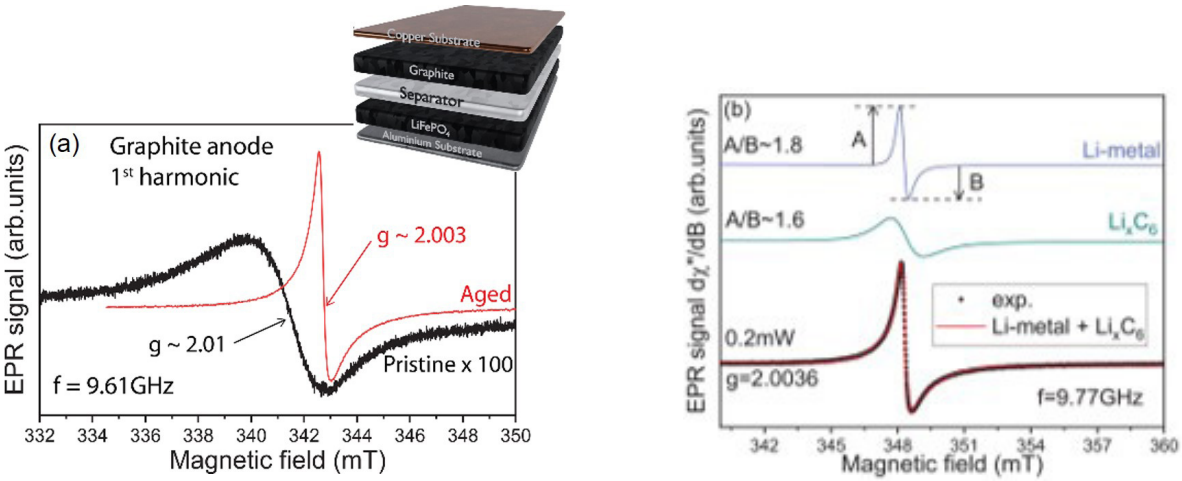

Figure 3: (a) EPR spectra of the pristine (black) and aged (red) electrodes using the first-harmonic detection scheme. (b) Simulation of the lithiated graphite anode aged signal recorded at room temperature using two Dysonian contributions. The green line represents the lithiated graphite spectrum (Li_xC_6), and the blue line is indicative of Li metal. Reproduced from reference [3] in accordance with CC BY 4.0 License.

- EPR spectrum of pristine graphite contains a single line at g ~ 2.01 (Figure 3a, black trace), attributed to oxygen-centered radicals and/or defect spins from surface dangling bonds
- *Ex situ* EPR data of the graphite anode after battery cycling showed a new EPR signal with g ~ 2.0036 and a Dysonian lineshape (Figure 3a, red trace)
- Simulation of this new EPR signal revealed a mixture of two overlapping contributions: (i) lithuated graphite species Li_xC_6 ($0 < x < 1$) with A/B ~ 1.6 and linewidth ΔB_{pp} ~ 1 mT (Figure 3b, green trace); (ii) traces of micrometallic lithium aggregates with A/B ~ 1.8 and ΔB_{pp} ~ 0.2 mT (Figure 3b, blue trace)
- Based on calculations, these micrometallic lithium aggregates were assigned to a non-dendritic Li particles with a size of about 1.6 µm (Figure 3b, blue trace)

Conclusion

EPR is a powerful tool for studying lithium-metal elements in battery anodes. Its ability to detect unpaired electrons and provide real-time analysis helps researchers understand complex processes such as lithium intercalation, leading to the development of more efficient and durable batteries, which advances energy storage solutions.

References

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2. Wang B. et al. *Nat. Commun.* 2024, 15, 3013–3027
3. Dutoit C. et al. *Magn. Reason.* 2024, 5, 87-93

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