

EPR EPR for Energy: Conversion and Storage

Application Note

Innovation with Integrity

Introduction

Energy systems across the globe are undergoing a fundamental transformation. As we continue to decrease dependence on fossil fuels, the world is demanding more diverse power solutions for our energy needs. Batteries convert chemical energy to electrical energy, with all or most of the reactants stored within the battery.

Lithium-ion batteries are an important and quickly developing part of portable electronics due to their high working voltage and capacity in comparison with other types of batteries.

The finding of novel electrode and electrolyte materials for high-power and high-density batteries is one of the most widely investigated topics in materials chemistry in the last few decades.

- Paramagnetic imperfections such as defects, impurities, amorphous components, deficiencies, domains of varying stoichiometry affect the electrochemical energy storage properties of batteries. Prevention of non-uniform deposition of metallic Li is very important to avoid internal short-circuits.
- Transition metal ions present in the cathode material (LiMO_2 , where $M = \text{Co}, \text{Ni}, \text{Mn}, \text{V}, \text{Fe}$) determine the operating voltage of the batteries and have significant influence on the electrochemical characteristics of the cathode materials. These facts indicate that studying the transition metal ions and their local environment is essential to evaluate electrodes performance.
- Reactive intermediate radical species are formed in many decomposition mechanisms of electrolyte solution on the electrodes which is one of the major causes of battery self-discharge.

Challenge: Some of the main challenges in developing new Li-ion batteries are:

- Lower capacity is achieved due to spin defects leading to power fading
- Poor reversibility caused by radical degradation reactions which mainly occur during battery charging and are still not understood

EPR solution:

- Detecting and quantifying spin defects and lattice imperfections that affect the battery capacity and performance
- Directly monitoring radical reactions of electrolyte solutions in contact with electrodes
- Evaluating the rate of radical formation and decay in order to investigate self-discharge and capacity fade during storage

EPR for Energy

I. Batteries

- Degradation of electrode material
- Oxidation of electrolyte components
- Structural changes during cycling
- Parasitic chemistry

II. Solar cells

- Evaluation of defect density and level of impurities (dangling bonds, E⁻, Pb-centers, vacancies, etc.)

III. Fuel cells

- Accelerated aging tests
- Short-lived radical degradation reactions

IV. Catalysis

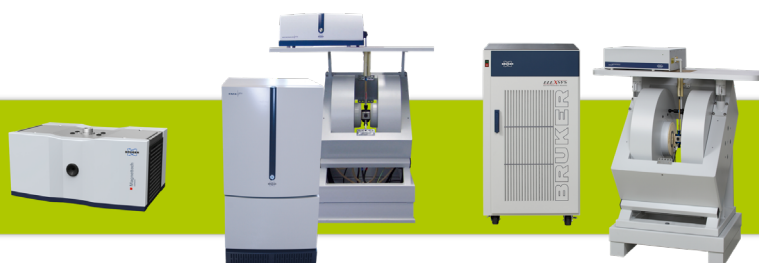
- H₂/H⁺ interconversion reactions
- Evaluation of biohybrids and biomimetics for artificial photosynthesis and solar fuel production

Effect:

Free radicals and EPR active metals

Detection:

EPR Spectroscopy



Li dendrites – *in operando* EPR and *in situ* EPR imaging and localization of lithium dendrites

Metallic lithium is an ideal anode material for Li-ion batteries due to its high specific capacity and low electric potential. However, upon charging of a battery the formation of micro-structured Li, e.g. in the form of dendrites or mossy species, when deposited on Li-metal surfaces prevented the use as metallic anodes in commercial products so far. It can cause severe safety problems due to internal cell shorting and reduces cell life due to increased electrolyte consumption. Measuring the build-up of these structures by *in operando* EPR is a challenging task but crucial for analyzing the cell behavior in operation mode. Moreover, *in situ* EPR imaging (EPRI) allows identification (spectral) and localization (spatial) of micro-structured lithium particles created by plating (deposition) or stripping (altered bulk lithium surface).

Figure 1. Different lithium morphologies detected by *in operando* EPR. The peak-to-peak linewidth is minimal for dendritic lithium with ca. 0.005 mT (green), showing a Lorentzian lineshape. For mossy lithium it increases to 0.03 mT (blue). It reaches a maximum for bulk lithium with ca. 0.15 mT (red), showing a Dysonian lineshape. Inset: Plot of Li EPR signal during 14 h of battery charging. Reproduced from reference [1] in accordance with Creative Commons Attribution 4.0 License.

Figure 2. EPR image of lithium dendrites grown in a glass fiber separator with a diameter of 8 mm. The appearance of dendrites is preferably found at the edge of the separator. In addition, an intense dendrite signal is found in its center. The inset shows a photograph of the separator. The same main features are visible, yet low intensity contributions are more apparent in the EPR image due to the selectivity of the method to lithium metal only. Reproduced from reference [1] in accordance with Creative Commons Attribution 4.0 License.

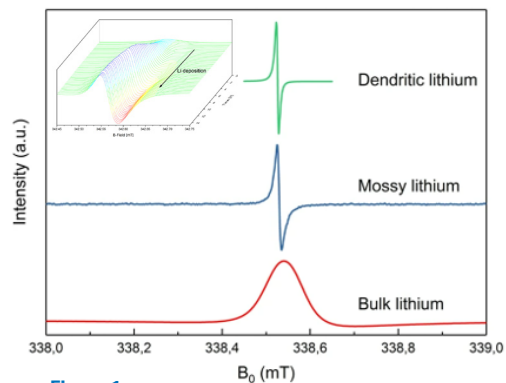


Figure 1

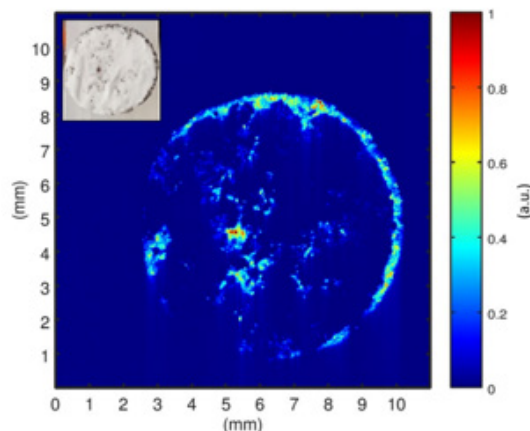


Figure 2

Structural changes in electrode materials

Example: NaCrO₂ cathode

- NaCrO₂ is a potential cathode material for Na-ion batteries with a good cycle stability and rate performance within a range of 2.2 – 3.6 V with an EPR signal at $g = 1.962$ due to Cr³⁺
- EPR confirms that the electrochemical process is irreversible when voltage above 3.7 V is applied, and the electron remains delocalized
- A new EPR signal is observed at $g = 1.976$ after charging to 4.5 V. The new phenomenon is attributed to a new species, Cr⁵⁺, dissolved in the electrolyte

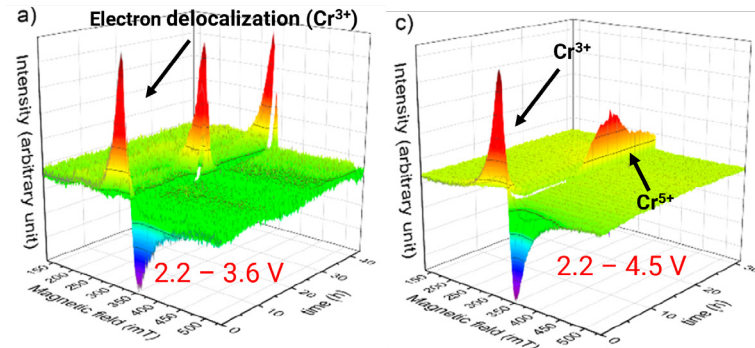


Figure 3. In operando EPR spectra of a NaCrO₂/Na-ion cell cycled at 10 mA g⁻¹ between (a) 2.2 - 3.6 V and (b) 2.2 - 4.5 V. Reproduced from reference [2] in accordance with Creative Commons Attribution 4.0 License.

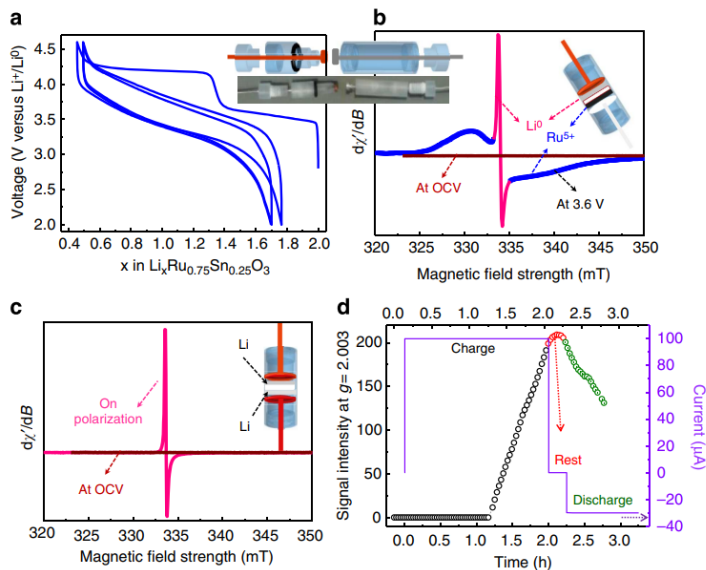


Figure 4. (a) Electrochemical cycling performance of the cell (inset in a,b) designed for in situ EPR measurements. (b) In operando EPR spectra of the Li₂Ru_{0.75}Sn_{0.25}O₃ versus Li half cell at OCV and after charging to 3.6 V. (c) EPR spectra of the Li versus Li symmetric cell. Bulk lithium did not show any EPR signal because of skin depth effect and a sharp signal because of deposited lithium particles is observed on polarization of the cell. (d) Change in intensity of Li metal signal on cycling the Li versus Li symmetric cell. Reproduced from reference [3] in accordance with Creative Commons Attribution 4.0 License.

Example: Li-rich layered cathode

- Li₂Ru_{0.75}Sn_{0.25}O₃, a high-capacity (4270 mAh g⁻¹) Li-rich layered oxide, as positive electrode was used in a locally designed and built EPR electrochemical cell
- At open-circuit voltage (OCV), no EPR signal was detected (Ru⁴⁺ is EPR silent)
- At 3.6 V an EPR signal with $g = 2.0002$ was observed due to Ru⁵⁺ and a sharp narrow signal with $g = 2.0023$ due to Li aggregates deposited on the negative lithium foil during the charging process

Parasitic chemistry

Example: Li-O₂ battery degradation

- Aprotic lithium-oxygen (Li-O₂) batteries have attracted attention in the past few years due to their outstanding theoretical energy density (3460 Wh/kg)
- Parasitic reactions with electrolyte and electrode materials involve highly reactive oxygen species (ROS) that lead to poor reversibility and battery degradation
- Singlet oxygen is formed upon Li₂O₂ oxidation at potentials above 3.5 V and detected by EPR using a spin trap 4-oxo-TEMP

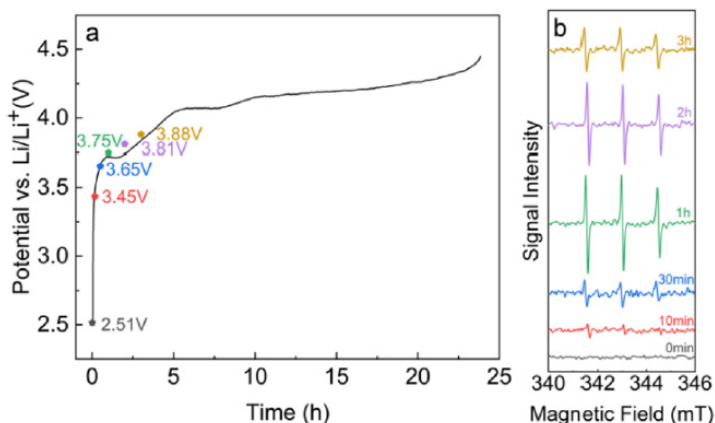
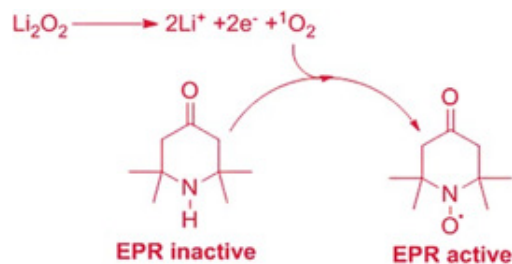


Figure 5. Charge profiles of the carbon nanotube cathode in electrolyte (1 M LiTFSI/TEGDME) and the corresponding ex-situ EPR spectra using a spin trap (0.1 M 4-Oxo-TEMP) at 60 mA g⁻¹. Reproduced from reference [4] in accordance with Creative Commons Attribution 4.0 License.

Example: Structural defects of layered cathode materials LiMO₂ (M = Co, Ni, Mn) for Li-ion batteries

- EPR has been applied as a tool to identify and quantify impurities and deficiencies in layered structured cathode LiCoO₂ materials
- It is found that the final structures of materials are strongly influenced by their synthetic temperatures, and oxygen and/or Li-deficient sites often exist in synthesized materials
- EPR confirms that the number of defects decreases as the synthetic temperature increases

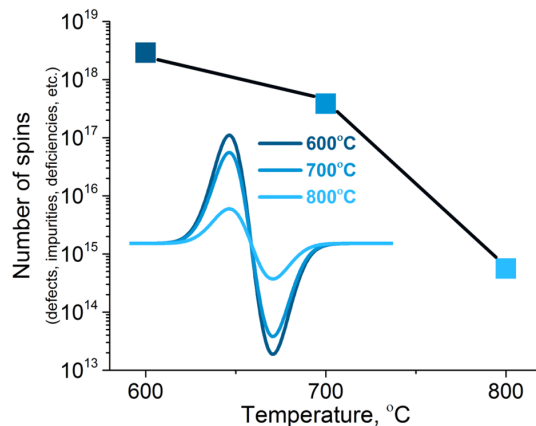


Figure 6. Correlation between structural paramagnetic imperfections of cathode materials detected by EPR and synthetic temperatures.

Conclusion

Battery aging, power fading, and capacity decay originate from multiple and complex mechanisms quite often involving transition metal ions and free radicals. Surface chemistry, phase transitions and structural changes are monitored and investigated non-destructively by the use of EPR spectroscopy.

References:

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