

***In-operando* EPR**

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Electron-paramagnetic resonance (EPR) is a very sensitive and non-destructive method to detect paramagnetic centers. The sensitivity ranges down to 10^{11} electrons per sample. The sensitivity to the local chemical environment of unpaired electrons in transition metal oxides can be applied to study electrode materials as post-test experiment¹, or as an ‘*in-operando*’ experiment to investigate full electrochemical cells.²⁻⁴ In addition, the susceptibility can be used to distinguish between paramagnetic systems and exchange-coupled systems. These include ferromagnetic or anti-ferromagnetic as well as ferrimagnetic interactions and changes in electrical conductivity.

Due to its metallic conductivity and the resulting skin effect, lithium EPR is surface-sensitive down to 1 μm . This makes it possible to observe processes during lithium plating as well as lithium stripping. The formation of mossy lithium but also the formation of dendrites can be distinguished. Less conductive materials, e.g. cathode materials can be indirectly observed without contact by the change in the quality-factor of the resonator. No additional electrodes need to be applied.

The challenge for EPR spectroscopy of electrochemical systems is the maximum outer diameter of 10 mm for X-band. All electrochemical constructions must be realized within this dimension. A second requirement is the right choice of materials. The materials must not be magnetic and do not have their own EPR signal, but at the same time resist the chemical environment of an ‘*in-operando*’ experiment.

References

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