

Application of Bruker EMXnano for *in operando* Analysis of Metallic Lithium Microstructure

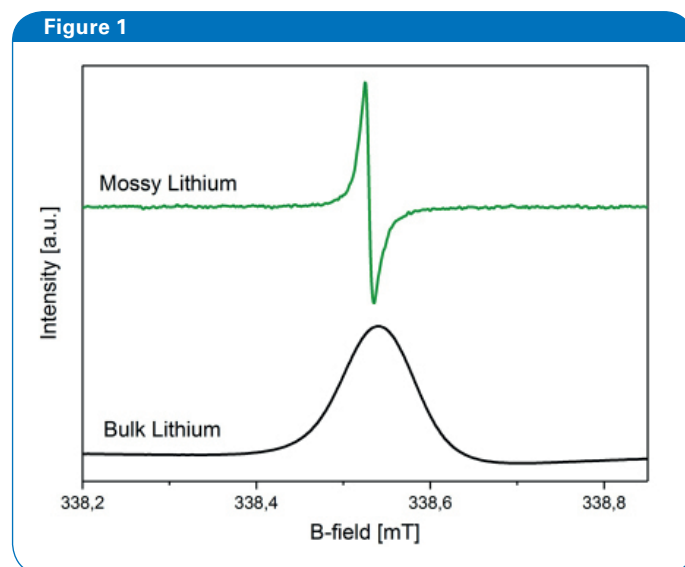
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To meet the growing demand for energy storage, substantial scientific efforts are undertaken to improve secondary battery performance.¹ Lithium-ion batteries are still state-of-the-art for commercial applications in the near future, but researchers are extensively investigating material improvements as well as alternative battery designs. Metallic lithium would be an ideal anode material due to its high specific capacity and low electric potential.² However, upon charging of a battery the formation of microstructured 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 shortening and reduces cell life due to increased electrolyte consumption. Measuring the build-up of these structures during cell operation is a challenging task but crucial for analyzing the cell behavior in operation mode.

Recently, magnetic resonance techniques have been introduced as appropriate non-invasive *in operando* methods to study the evolution of metallic Li species during battery cycling.^{3,4} Beside NMR, EPR is particularly suited to detecting the desired structural change with a simple setup, high sensitivity, and, in comparison to NMR, a higher surface

selectivity due to the low penetration depth of microwaves into the bulk. Therefore, a good differentiation between bulk and fine structured 'mossy' lithium can be made (Figure 1).



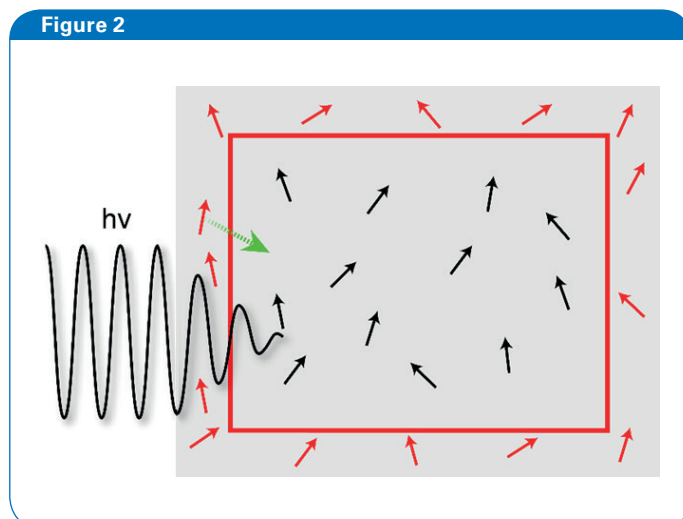
Different lithium morphologies detected with EPR spectroscopy. Top: mossy lithium (green). Bottom: bulk lithium (black).⁵

In this report, we demonstrate the applicability of the Bruker EMXnano benchtop setup for Li-microstructure detection during the charging process of a battery cell with metallic lithium as anode and LiCoO_2 as cathode material. We consider the affordable and easy-to-use benchtop instrumentation as a step closer to fast and batch-wise analysis of dendritic/mossy lithium in batteries and elsewhere. In addition to Li spectra analysis, crucial issues to set up an *in operando* measurement are presented herein, such as considerations of necessary hardware, internal referencing, and handling of metals and other conducting materials inside the EPR microwave cavity.

Concept of Conduction EPR

Similar to radicals or paramagnetic species, conduction electrons of metals exhibit a Zeemann splitting in an external magnetic field. Resonant microwaves induce transitions among these states. However, microwaves penetrate metals merely with a finite penetration/skin depth in the micrometer range at X-band frequency, i.e. at 9.8 GHz, known as the skin effect (Figure 2). This shrinks the examinable section to a surface layer of the material if the material is thick in comparison to the microwave skin depth. In the case of metallic lithium, the skin depth is ca. $1.1\mu\text{m}$.⁶ Therefore, the measured signal is sensitive to the surface, which would increase by formation of microstructured Li in the course of battery cycling.

The first EPR spectra of conduction electrons in Li were observed by Feher and Kip⁷ and further theoretically examined by Dyson in 1954.⁸ His theory states that the skin effect in combination with spin diffusion caused by self-diffusion of electrons in and out of the skin depth (Figure 1, green arrow) leads to a change in the signal phase and hence in the lineshape of the EPR signal. The resulting shape is known as Dysonian lineshape. Mathematically a Dysonian lineshape can be approximated by a phase shifted Lorentzian line, which is considerably simpler to handle for data analysis than the full Dysonian shape.⁴ If the dimensions of the metal structure are much smaller than the skin depth, a Lorentzian lineshape with zero phase shift is obtained. If the metal thickness is larger than the microwave skin depth (Figure 2), a phase shifted Lorentzian lineshape is recorded, i.e. the ratio of absorptive and dispersive parts changes towards a dispersive spectrum.



Schematic depiction of the skin effect of metallic species. Electromagnetic radiation such as microwaves for EPR experiments penetrates the material only at the skin. The skin depth (red bar) denotes the point where the radiation intensity decreases to $1/e$. In a first approximation, merely spins at the surface (red arrows) are excited. Diffusion of spins through the skin depth (green arrow) after excitation and before relaxation influences the signal lineshape.

Instrumentation

1. Ensuring stable and reliable acquisition

Long-term measurements require a certain degree of stability of the acquired spectra. In this respect, the necessity of an inert gas inlet for purging nitrogen gas through the cavity and cooling water for the electromagnet are evaluated. Changes in spectral parameters can be monitored by applying the implemented reference, which can be automatically moved into the cavity. Therefore, the signal intensity, the signal phase, and the B-field at resonance of the reference signal can be evaluated. The results over 18 h of acquisition reveal that drifts are minimized, though not eliminated entirely, with gas purging and cooling water. We note that particularly the intensity stays satisfyingly constant. The main reason for the parameter variations is expected to be the temperature as it changed significantly between day and night, causing a drift of the B-field up to 0.1 mT.

2. Internal referencing

Since the setup is still prone to drifts of phase and B_0 -field, it is advisable to include a reference sample during the whole experiment for quality control and potential data correction. The internal reference provided by the spectrometer is generally suitable but has an isotropic g -value of 1.98 (Figure 3b). Disadvantages are: (1) the signal separation with samples showing resonances close to that of the internal reference, though not a problem with metallic lithium (Figure 3b); and (2) a non-Lorentzian lineshape which complicates the fitting process. Accordingly, we decided to use a ruby single crystal that we placed directly below the sample within the electrochemical cell. It bears an adjustable resonance B_0 -field through orientation towards the magnetic field and a satisfying signal intensity. Figure 3a shows a possible field shift of the ruby reference signal. The variability of the reference field is also advantageous for reducing the spectral width in favor of shorter acquisition time and field sweep, hence improving the temporal resolution of the experiment.

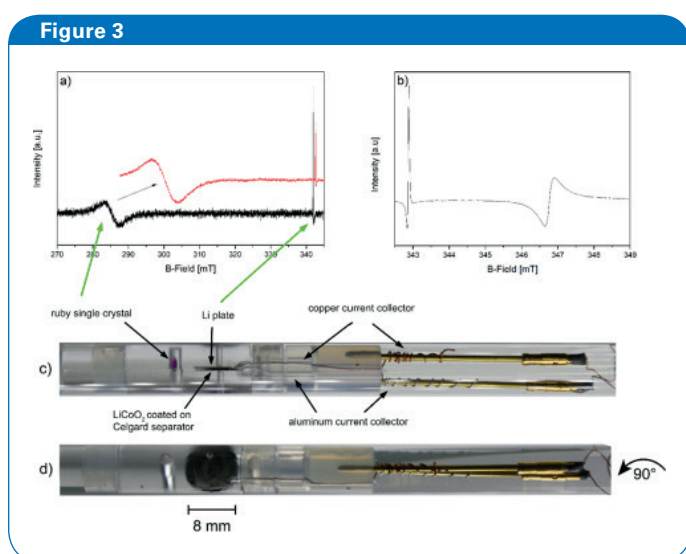


Figure 3 Comparison of internal references. Li-signal is observed at 343 mT. a) Ruby single crystal as internal reference, whose field position is adjustable by changing the orientation towards the external magnetic field. b) Non-adjustable, non-Lorentzian internal reference at a resonance field of ca. 346.8 mT that can be inserted into the cavity with the EMX Nano software. c) Side view of the quartz glass *in operando* cell. Two glass parts are pressed together with electrodes, separator and current collectors in between. d) *in operando* cell, emphasizing plate-like geometry of the electrodes.

Setting up an *in operando* Battery Cell Inside the Resonator

In order to acquire spectra with an EPR spectrometer, a standing microwave is generated in a cavity/resonator. Optimally tuned on resonance, there is only detectable reflection if spectroscopic transitions take place, otherwise the energy is stored inside the resonator. Generally, the sample and sample holder will alter the properties of the cavity and therefore change the resonance frequency, which is adjustable within a limited region. In the EMX Nano, normally a quartz glass inlet shifts the microwave frequency to the desired frequency range and enables measurements with e.g. 4 mm EPR sample tubes. Instead of this standard quartz glassware, we use a quartz glass tube of 0.5 mm wall thickness with a 10 mm outer diameter and a quartz glass support for the battery materials, whose design is reported elsewhere.⁹ The quartz glass components shift the microwave frequency similar to the original glass inlet of the spectrometer hardware. Figure 3c and 3d show photographs of the cell design. It consists of two glass parts with circular inlets of 8 mm diameter for anode, cathode, and separator and a channel for insertion of current collectors. They are pressed together with PFA (Perfluoroalkoxy) rings, which do not interact with microwaves. A second inlet contains the ruby single crystal as a reference.

As stated above, the microwaves do not fully penetrate the Li electrode, which is characterized by the skin depth. For explicit detection of deposited Li, the inner side of the Li electrode facing the counter electrode is of interest. Accordingly, we use a flat cell design, accessible by the microwave from both sides. We note that a signal from unaltered bulk Li will be detected since the electrode that is facing backwards should not be covered with mossy Li.

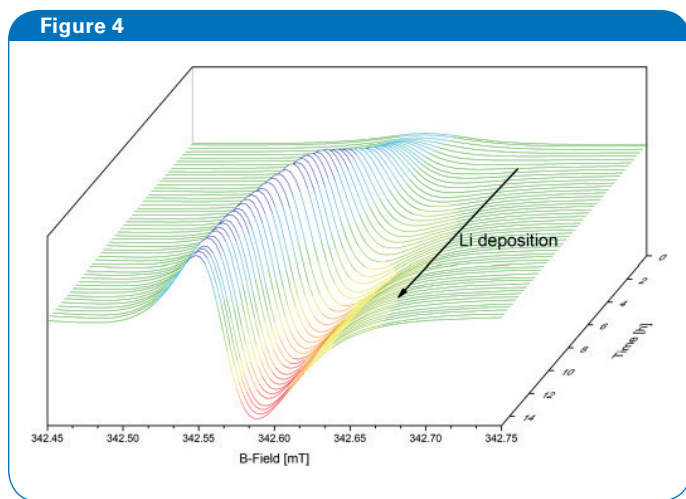
Lastly, positioning of the actual cell compartments in the resonator affects the microwave mode and can cause a lack of tunable resonance due to electrically conducting materials absorbing radiation. The overlap of the cell setup with the microwave electric field needs to be minimized while the interaction with the microwave B_1 field should be high. Positioning of the sample was performed by slowly inserting the sample into the resonator until a microwave mode was found, ensuring that the cell compartments were within the cavity. Although the cell is not centered in the resonator, spectra acquisition was satisfyingly feasible.

Li-microstructure Detection during Charging a Li-ion Battery

After successfully tuning the microwave frequency and connecting the battery to a potentiostat, EPR spectra were recorded with a TMHS resonator at 9.598 GHz with a microwave power of 0.316 mW. Field sweeps were conducted with 58.4 mT spectral width at a center field of 316.9 mT, accumulating 30 scans over 17.28 min for each spectrum. The field was modulated with a frequency of 100 kHz and an amplitude of 0.03 mT.

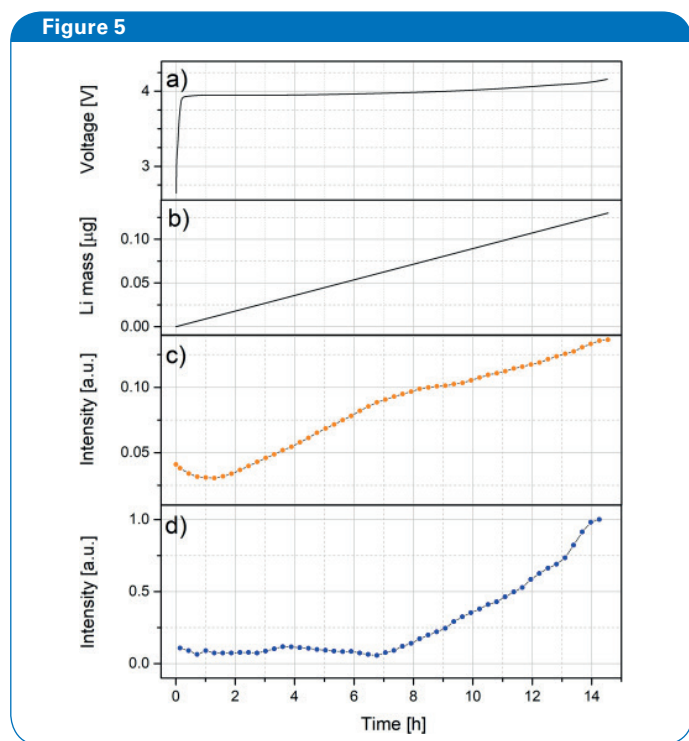
As a model system a Li/LiCoO₂ battery cell was used. A 380 μm thick, metallic Li plate with a copper current collector was pressed on LiCoO₂ ($t = 50 \mu\text{m}$) coated on a Celgard 3401 separator ($t = 25 \mu\text{m}$, $d = 8 \text{ mm}$), connected to an aluminum current collector. As electrolyte, 1 M lithium hexafluorophosphate (LiPF₆) in ethylene carbonate (EC) and dimethyl carbonate (DMC) in a ratio 1:1 was used (LP30, Sigma Aldrich). Electrochemical charging was conducted on a BioLogic potentiostat by applying a constant current of 34.5 μA, corresponding to a C-rate of 1/15.

Figure 4 displays all spectra during 14 h of the battery charging process. The reference signal at 300 mT was observed to be fairly constant, hence no spectra correction was necessary. Qualitatively, the amplitude of the signal rises continuously, indicating a growth of the Li surface area. The signal is dominated more and more by an absorptive lineshape. It arises from structures that are smaller than the skin depth, indicating that microstructured Li evolved.



Plot of Li EPR signal during 14 h of battery charging. For each spectrum 30 scans are accumulated.

Concerning the lithium signal, two components with different phase and width are distinguishable. For a semi-quantitative analysis, a superposition of two Dysonian lines was fitted. The first component with a phase of ca. $\pi/2$ originates from bulk Li; the second one with a phase of zero originates from microstructured Li evolving during the charge process.⁴ Figure 5 depicts the fit results along with the voltage profile (Figure 5a) and the deposited Li mass calculated by Faraday's law (Figure 5b). The intensity of the bulk Li signal (Figure 5c) gradually rises, caused by a roughening of the bulk surface. The intensity of the microstructured Li (Figure 5d), with structures smaller than the skin depth, appears from the early stages of charging, though not in the first spectrum before charging began. It starts rising continuously after 7 h of charging, indicating that formation of mossy lithium is suppressed initially. We note that *Wandt et al.*⁴ observed microstructure formation from the very beginning of their measurements; concluding that the flat and strained cell design herein is more robust than the concentrically wounded. The diminishing signal of bulk Li at the very start originates presumably from a change in conductivity of the cathode material (first-order Mott transition) from insulating to a metallic state,¹⁰ subsequently resulting in a change of shielding microwave radiation. A complete theoretical expression of conduction EPR signals for porous Li-metal structures with similar dimensions to the skin depth would permit a fully quantitative interpretation but is yet to be derived.



Results of the in operando measurement of a Li/LiCoO₂ battery. Fitting was carried out with a superposition of two Dysonian lines. a) Voltage profile of charging process. b) Deposited Li mass on anode, calculated by Faraday's law. c) Fitted intensity of first Dysonian, which is associated to a *narrow* Li component. d) Fitted intensity of second Dysonian which is linked to a *broader* Li species.

Conclusion

The benchtop EPR spectrometer EMXnano was used to perform *in operando* investigations of Li-microstructure formation in a Li/LiCoO₂ battery. Deposited Li metal was detected on the anode semi-quantitatively and differentiation between bulk and microstructured Li was feasible by a fit with two Dysonian lines. A quartz glass cell setup enables microwave tuning similar to the standardly used glass inlet. Considering instrumentation, flushing

nitrogen gas through the gas inlet and using cooling water for the magnet were found to minimize drift effects, especially in non-climatized environments. Advantages of an internal reference with an adjustable resonance field are outlined. In summary, the benchtop EPR spectrometer provides the potential of surface sensitive detection of metallic Li microstructures combined with a user-friendly and fast implementation.

References

- [1] Deng, D. Li-ion batteries: Basics, progress, and challenges. *Energy Sci. Eng.* 3, 385–418 (2015).
- [2] Xu, W. et al. Lithium metal anodes for rechargeable batteries. *Energy Environ. Sci.* 7, 513–537 (2014).
- [3] Bhattacharyya, R. et al. In situ NMR observation of the formation of metallic lithium microstructures in lithium batteries. *Nat. Mater.* 9, 504–510 (2010).
- [4] Wandt, J. et al. Operando electron paramagnetic resonance spectroscopy – formation of mossy lithium on lithium anodes during charge–discharge cycling. *Energy Environ. Sci.* 8, 1358–1367 (2015).
- [5] Niemöller, A., Jakes, P., Eichel, R.-A. & Granwehr, J. EPR Imaging of Metal Lithium. *arXiv:1802.00025* (2018).
- [6] Lewis, R. B. & Carver, T. R. Conduction electron spin transmission in lithium. *Phys. Rev. Lett.* 12, 693–694 (1964).
- [7] Feher, G. & Kip, A. F. Electron Spin Resonance Absorption in Metals. I. Experimental. *Phys. Rev.* 98, 337–348 (1955).
- [8] Dyson, F. J. Electron Spin Resonance Absorption in Metals. II. Theory of Electron Diffusion and the Skin Effect. *Phys. Rev.* 98, 349–359 (1955).
- [9] Niemöller, A. et al. Monitoring local redox processes in LiNi_{0.5}Mn_{1.5}O₄ battery cathode material by *in operando* EPR spectroscopy. *J. Chem. Phys.* 148, 014705 (2018).
- [10] Marianetti, C. A., Kotliar, G. & Ceder, G. A first-order Mott transition in Li_xCoO₂. *Nat. Mater.* 3, 627–631 (2004).



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