Using *in operando* pulse EPR to investigate metallic lithium anodes in rechargeable batteries

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Li-ion battery technology is key for the mobility reorientation towards electric vehicles in upcoming years.[1] Two main factors of battery performance are the capacity, which determines range, and the charging time. To enhance both, various electrode materials, cell characteristics, and charging protocols have to be tested under realistic operating conditions. A tenfold increase in specific capacity might be achieved by using lithium metal anodes instead of commercially used graphite.[2] However, irregularly deposited lithium upon charging still poses a safety issue leading to degradation or short-circuiting. Here, we demonstrate the application of pulse electron paramagnetic resonance (EPR) as a non-invasive technique to monitor electrochemically deposited lithium metal.[3] *In operando* pulse EPR is shown to be capable of monitoring batteries under fast-charging conditions with sampling intervals of 100 ms. This sampling rate is sufficient to observe dynamic effects of deposited lithium. When using an electrochemical pulse charging scheme, dynamic morphology changes are detected that evolve for several seconds after fresh lithium was deposited.

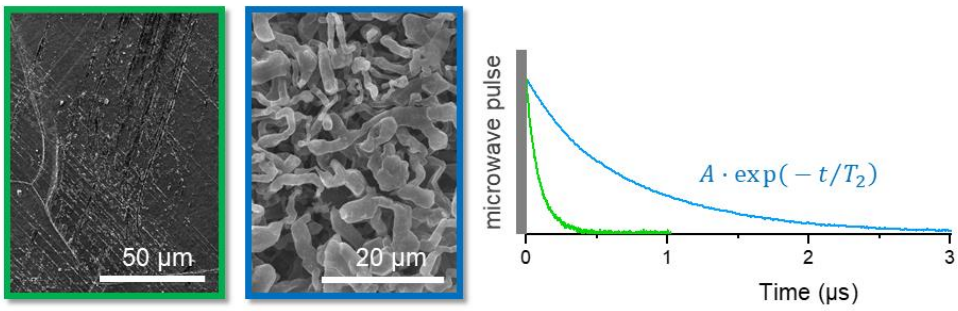

Figure: Electron microscopy images of pristine lithium metal anode (green frame) and electrochemically deposited microstructured lithium (blue frame). The lithium metal morphology gives rise to pulse EPR responses with characteristic relaxation times, which can be used to monitor transient morphology changes.

References

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We demonstrate the importance of using operando/in-situ techniques in examining the microstructural changes of the electrodes under various operating conditions, in both macro and micro-scales. These techniques also reveal the working and the degradation mechanisms of the electrodes and the possible side reactions involved.Â Rechargeable batteries are the main energy source for electric vehicles (EV), consumer electronics, and promising candidates for renewable energy storage, owing to their relative high energy and power densities, light weight, long cycle life and environmental acceptability (Tarascon and Armand, 2001; PalacÃn, 2009; Dunn et al., 2011; Budde-Meiwes et al., 2013).Â Operando XRD is used to investigate the phase transformation and crystal structure... Lithium (Li) metal is an ideal anode material for rechargeable batteries due to its extremely high theoretical speciï¬c capacity (3860 mAh gâˆ’1), the lowest negative electrochemical potential (âˆ’3.040 V versus standard hydrogen electrode), and low density (0.534 g cmâˆ’3); thus rechargeable Li metal batteries have been investigated extensively during the last 40 years.Â (1998, 1999) ï¬rst reported using in situ SEM to observe the cross section of plastic rechargeable Li batteries using solid polymer electrolytes. They observed the accumulation of mossy Li and growth of dendritic Li at the Li/polymer electrolyte (Fig. 2.1), which was the origin of rapid interface deterio- ration and capacity fading. Neudecker et al. Lithium-ion batteries are a portable power source with a high energy density and stable electrochemistry that have changed our daily lives. Thanks to technological developments in areas such as smartphones and electric vehicles, there is an increased demand for high energy density and fast-charging lithium-ion batteries that can provide greater power capacity.Â Figure 1a shows the anode materials of lithium rechargeable batteries categorized into four main groups based on electrochemical reactions. The first group is that of insertion (or intercalation) anode materials.Â Graphite has been widely used in various applications thanks to its theoretical capacity of 372 mAh/g and low average working potential of ca. 0.2 V [36].