Fibre Optical Detection of Lithium Plating

Insplorion's sensing technology enables *in operando* probing inside battery cells. Using Insplorion's fibre optic sensors, it is possible to glimpse the progression of internal precipitation processes without the need of expensive and bulky equipment.

Introduction

Lithium plating is known to have an adverse effect on the lifetime, performance and safe operation of lithium-ion batteries. The plating is observed as the lithium ions are deposited as metallic lithium on the anode material instead of intercalating in the crystal structure of the anode. Lithium plating might lead to the formation of dendrites that can pierce through the separator and cause a short circuit in the cell.

Since lithium-ion batteries are currently the go-to option for sustainable transportation, assuring long-term and safe operation is crucial. Therefore, it is important to know under which conditions plating occurs. Ideally, plating is monitored using sensors inside the battery cells. Sensors based on optical fibres are particularly well suited as they can be very thin, enabling precise positioning in different parts of the battery cell.

In this study, evanescent field (EF) fibre optic sensors coupled with Insplorion's optics unit were used for *in operando* detection of lithium plating in pouch cells [1].

Experimental Section

Three electrode pouch cells were prepared in a half-cell configuration. Metallic lithium was used as both counter electrode (CE) and reference electrode, whereas copper or graphite was used as working electrode (WE). The EF sensors were positioned on the surface of the WE, where the plating was expected to occur. The battery assembly was conducted in an argon-filled glovebox. Galvanostatic cycling was performed for lithium plating and stripping experiments. Subsequently, the electrochemical data was coupled with the optical read-out obtained from Insplorion's optics unit.

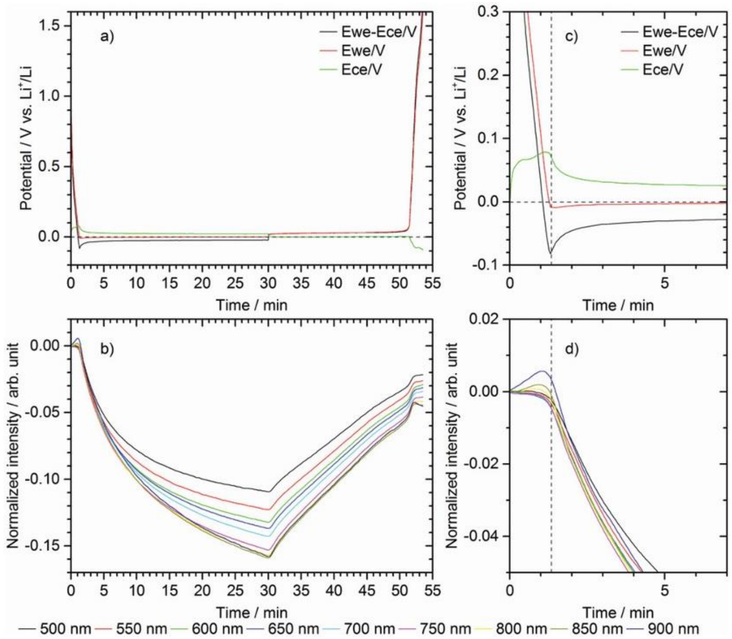

Figure 1: *Potential profile of lithium plating and stripping in a Cu (WE) and Li (CE) half-cell (a) and corresponding intensity of the optical signal (b). The zoomed-in figures (c) and (d) present Li plating.*

Results

The first lithium plating demonstration was done on Cu, functioning as the WE in a half-cell. Plating and stripping steps were limited to 30 min each. A negative current was applied to induce the plating (**Figure 1a**). As Li metal was electrochemically deposited on the Cu, a sharp decrease was observed in the intensity of the collected optical signal, at all wavelengths (**Figure 1b**). **Figure 1c,d** reveals a detailed observation for both potential and optical data during the first few minutes of the experiment. Following the initial reduction of the electrolyte at the start of the experiment, the potential of the WE rapidly dropped below 0 V versus Li+/Li and there was also a clear sign of a

Tip! The Insplorion M8: 8-Channel Analyzer can be used to measure on up to eight fibre optic sensors simultaneously!

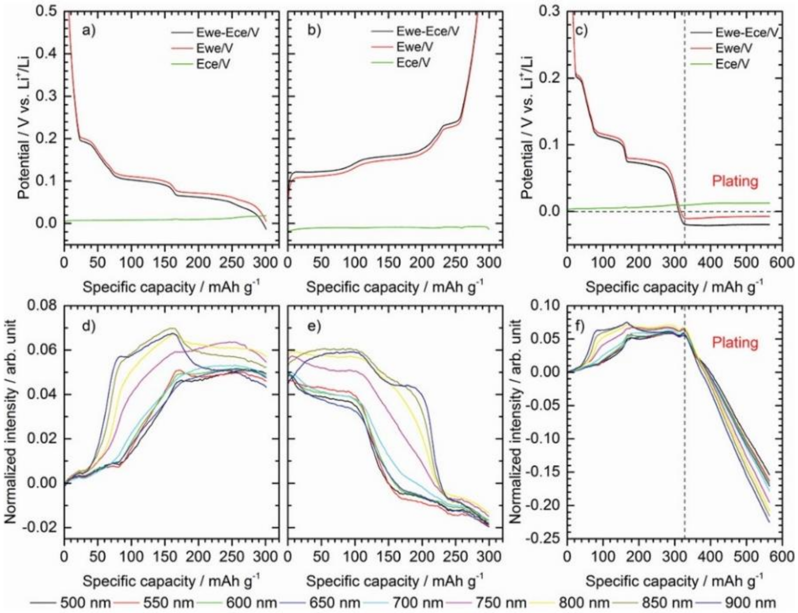

Figure 2: *Potential profile of lithiation and delithiation of graphite (WE) and Li (CE) half-cell are presented in (a) and (b), respectively. The corresponding intensity of the optical signal is shown in (d) and (e). The zoomed-in figures (c) and (d) present the Li plating region.*

nucleation dip, indicating lithium plating (dashed line in **Figure 1c**). As plating started, the intensity of the optical signal was observed to decrease. In addition, the optical signal intensity was observed to increase directly before the onset of lithium plating, giving an early indication that plating was about to occur. After 30 minutes, a positive current was applied to oxidize the deposited lithium. Both the voltage and optical signals reversed, but did not reach their initial values, indicating that some lithium remained passivated.

A similar experiment was conducted using graphite as WE. **Figure 2** shows the potential profiles and corresponding optical signals during constant current lithiation (2a,d) and delithiation (2c,e) of graphite. The steps clearly seen in **Figure 2a,b** represent the lithium staging in graphite. The staging was also visible in the optical data. After the formation cycles, the cell was slowly (c/20) over-lithiated beyond the maximum intercalation capacity of graphite (**Figure2c,f**). Once the number of intercalation sites became limited, the potential of the WE dropped below zero and a nucleation dip was observed (dashed lines in **Figure 2c**). A clear distinct drop in the optical signal intensity was observed at the initiation of plating. At the later stages of plating, the wavelength dependency of the optical signal became more evident. These observations align with the ones from lithium plating on Cu presented above, as well as the authors' previous study on sodium plating on Cu and hard carbon electrodes [2].

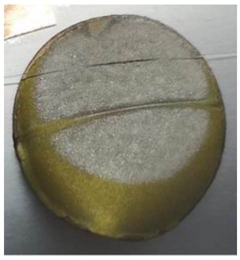

Figure 3: *Post-mortem image of the graphite electrode that was over-lithiated.*

Post-mortem analysis of the graphite after over-lithiation showed that lithium had plated on the surface of the electrode (**Figure 3**), apart from the regions where the optical fibre was located. The outer region of the graphite had a golden colour, indicating full lithiation.

Conclusion

This study reveals that the EF fibre optic sensors have great potential to be used in operando detection of lithium plating. The optical signal showed drastic intensity changes both right before the onset of plating and during the plating. The flexibility of EF fibre optic sensors in positioning inside of the cell and the optical signal's properties enable gathering of broad and detailed data about the battery chemistry and performance.

This study was performed by Dr. Jonas Hedman and co-workers at Uppsala University.

References

[1] Hedman, J. *et al.* (2022). Fiber Optical Detection of Lithium Plating at Graphite Anodes. *Advanced Materials Interfaces*, 2201665.

[2] Hedman, J. *et al.* (2022). Fiber Optic Sensors for Detection of Sodium Plating in Sodium-Ion Batteries. *ACS Applied Energy Materials*, 5(5), 6219-6227.