Fibre optic detection of sodium plating in sodium-ion batteries

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

Introduction

Lithium-ion batteries (LIBs) have become a dominant storage medium for electrochemical energy thanks to their high specific energy and energy density as well as low self-discharge rate. However, lithium is both scarce and expensive. Therefore, sodium-ion batteries (SIBs) have recently begun to attract attention. Sodium is both cheap and plentiful. SIBs display many electrochemical similarities with LIBs, although SIBs have lower specific energy and energy density.

Hard carbon (HC) is one of the most attractive SIB anode materials. As much of its capacity is obtained very close to the equilibrium Na^+/Na potential, there is a risk of metallic Na (sodium) precipitating (plating) during cycling. Such depositions could lead to the formation of dendrites which run the risk of causing catastrophic failure by piercing of the separator. As such, it is of great importance to be able to detect metallic Na deposition (plating) to ensure safe battery operation.

In this study, EF (evanescent field) fibre optic sensors in conjunction with Insplorion's hardware were used to probe the anode of SIB cells, where plating was induced through aggressive electrochemical cycling conditions.

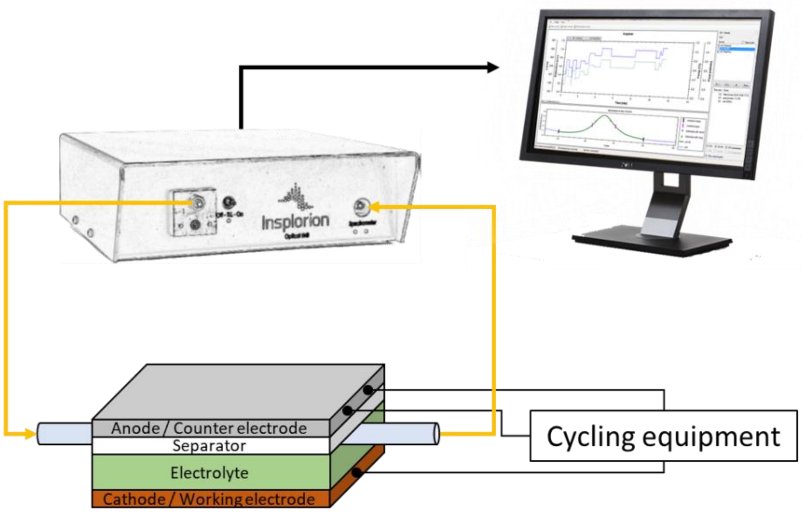

Figure 1: *Schematic illustration of the experimental setup used.*

Experimental procedure

Three-electrode pouch type cells were used either in half-cell or full-cell configuration. Two different half-cells were designed: one to plate Na on copper, Cu, and one to plate Na on HC. Sodium metal was used as both counter electrode and reference electrode. In the full cells (data not shown), Prussian white (PW) served as both cathode material and reference electrode, and HC as anode material.

The EF sensors were fixed onto the pouch material such that the sensing region was in contact with the active material where plating was expected. An Insplorion Optics Unit was used for optical readout.

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

The assembled cells were cycled such that the Cu or HC working electrodes (WEs) reached negative potentials relative to Na^+/Na, $E_{WE} - E_{CE} < 0$, triggering the precipitation of metallic Na.

Results

At the onset of Na plating on Cu, indicated by the WE potential, $E_{WE} - E_{CE}$, crossing over to negatives, the fibre optic sensor signal decreases. As is illustrated in **Figure 2**, light intensities across the spectrum decrease once plating has initiated and continue to decrease until a steady state is reached some 15 hours into the experiment.

An interesting phenomenon manifests in the form of

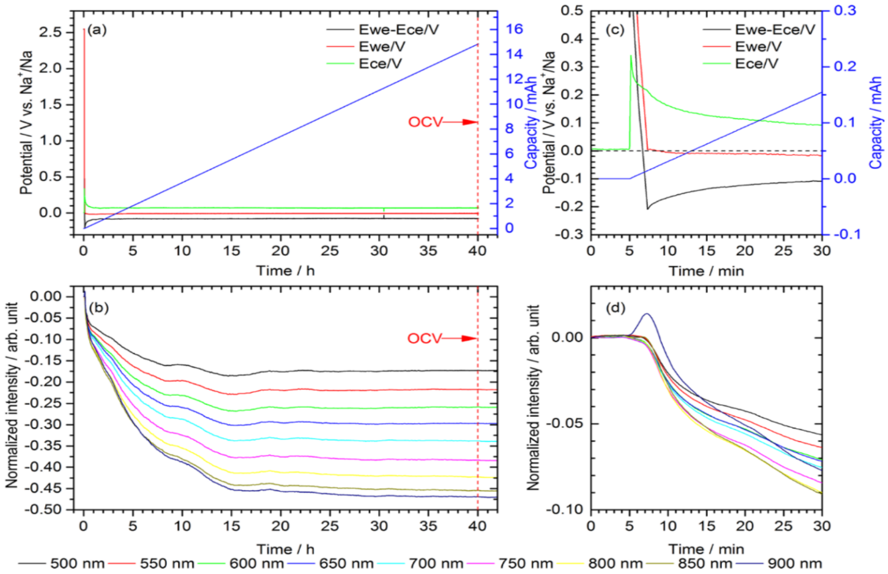

Figure 2: *Electrochemical and optical characteristics for plating on a Cu (WE) vs Na (CE) half-cell. The insets (c) and (d) highlight the start of Na precipitation.*

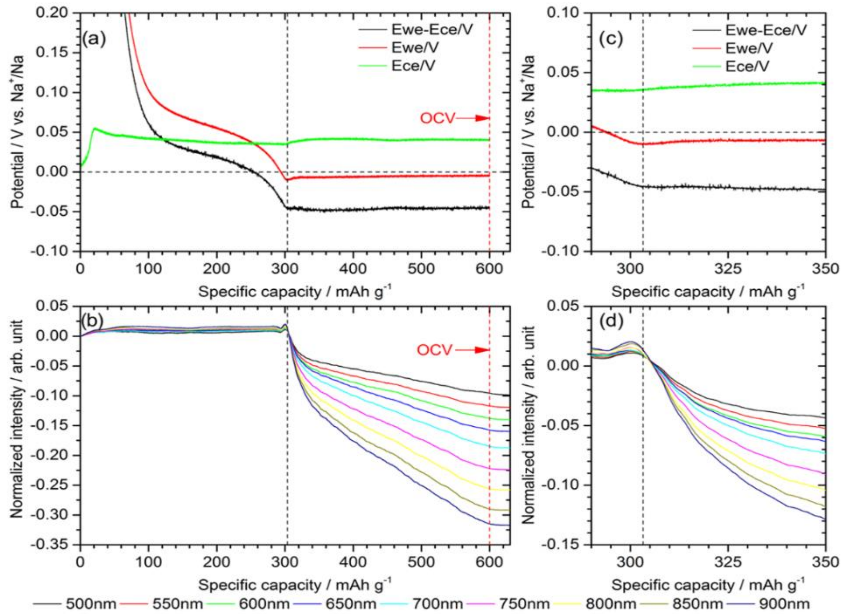

Figure 4: *Electrochemical and optical characteristics for sodiation of a hard carbon (WE) vs Na (CE) half-cell. The insets (c) and (d) highlight the start of Na plating.*

dispersion of the spectral components, suggesting the introduction of wavelength-dependent light scattering and/or absorption.

Similarly, at the onset of Na plating on HC, the EF sensor signal shifts. For this configuration, as is illustrated in **Figure 4**, there is a slight increase in the light intensity across the spectrum once the WE potential reaches < 0 vs Na^+/Na before decreasing. Plating continues for the duration of the experiment, accompanied by decreased optical signal intensities. Once the electrochemical cycling is interrupted and the plating process halted, the optical signal levels off.

Post-mortem analysis of the cells reveal that metallic Na has indeed precipitated across the cell, both on the Cu or HC working electrodes as well as on the separator, as shown in **Figure 3.**

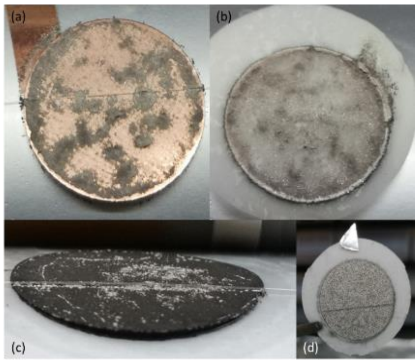

Figure 3: *Na plating on (a) Cu electrode and (b) separator from one half-cell, and (c) hard carbon and (d) separator from another half-cell.*

Conclusion

Insplorion technology enabled the fibre optic monitoring of Na plating in half and full cells, where plating was triggered both by the cell working electrode reaching negative potentials as well as by exposing the cells to high rates of sodiation. Through drastic intensity decrease, the optical signal clearly shows when plating has occurred, and the ability to monitor this phenomenon could hold great potential for both further research and applications where it is critical to ensure Na plating is contained.

This study was performed by Dr. Jonas Hedman and coworkers at Uppsala University.

References

[1] Hedman et al. (2022) *Fiber Optic Sensors for Detection of Sodium Plating in Sodium-Ion Batteries*. DOI: 10.1021/acsaem.2c 00595