Forensic Analysis of Batteries for early Failure Modes (FAB-FM)

Analysing LFP Reference Electrodes for use in NMC/Graphite Pouch Cells

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Abstract

The study of battery degradation is an important topic nowadays, requiring a deep understanding of the inner mechanisms through various advanced scientific approaches.

One such method is the use of a reference electrode (RE) in the battery's components (Fig. 1). Doing this enables us to differentiate the electrochemical phenomena of the cathode and anode.

The aim of the project is the implementation of $LiFePO_4$ (LFP) based RE in single crystal $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ (NMC811)/graphite pouch cells. Scanning Electron Microscopy was used to determine the thickness correlated with the kinetic data from the Electrochemical Impedance Spectroscopy (EIS) (Fig. 2).

There were 2 pristine samples tested with the Scanning Electron Microscope: 20 µm and 220 µm blade gap calendered LFP coatings on Aluminium.

Moreover, X-Ray Diffraction and X-Ray Fluorescence were utilised on the NMC811 cathode and graphite anode of the pouch cell for quality control of the materials.

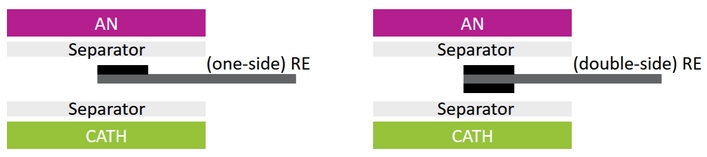

Fig. 1: Schematics of how the RE would be inserted in the pouch cells. The drawings show two initial designs of the RE, with LFP on one side and both sides, which would be tested.

Motivation

- To use LFP as reference electrodes in three electrode pouch cells.
- LFP was chosen as it provides stable potentials [1] and the possibility of high temperature operation [2].
- To design safer batteries by studying the degradation of electrodes beyond ambient conditions.

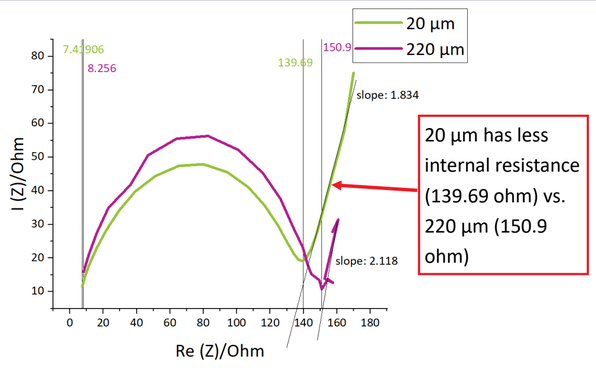

Fig. 2: Electron Impedance Spectroscopy (EIS) of the 20 and 220 µm LFP coatings.

Methods

- **Scanning Electron Microscopy (SEM):** analysis method for conductive materials which uses an electron beam to produce high magnification images of the surface of the sample.
- **Energy-Dispersive X-ray Spectroscopy (EDX):** surface analysis technique paired up with the SEM used for elemental investigation.
- **X-ray diffraction (XRD):** non-destructive technique used to identify the crystal and grain structure of a material.
- **X-ray fluorescence (XRF):** non-destructive analysis method used to study the chemical composition of a sample by scanning a large surface area.

SEM & EDX

- The following pictures are **SEM** and **EDX** images of cross-sections of the calendered RE with 20 µm (Fig. 3) and 220 µm blade gap (Fig. 4). These were used to determine their compositions (Table 1) and thicknesses.
- The pristine samples for the SEM and EDX imaging had been prepared with an ion miller which uses an ion beam to create a clean cross-section for the microscopes.
- For 20 µm blade gap, the thickness reduction after calendering was **50%**, whereas for 220 µm, the reduction was only **10%**.

20 Cal

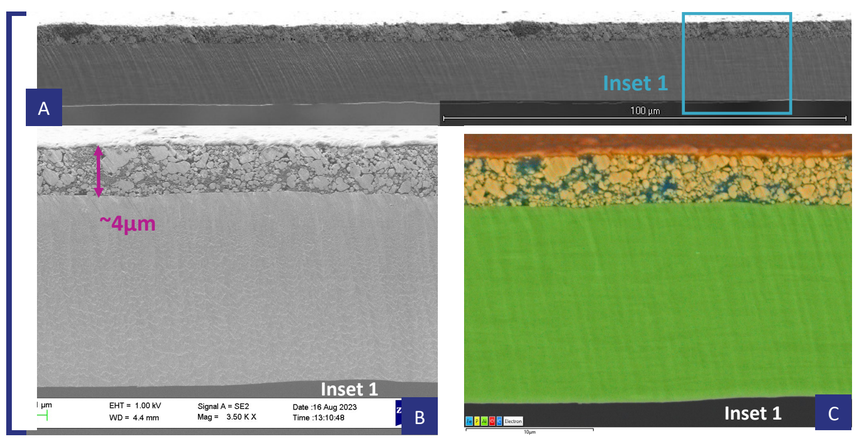

Fig. 3: Micrographs from 20 µm calendered sample: (A) SEM Image of the electrode, (B) SEM Image of the inset at 3500x magnification, (C) EDX map analysis of the inset.

220 Cal

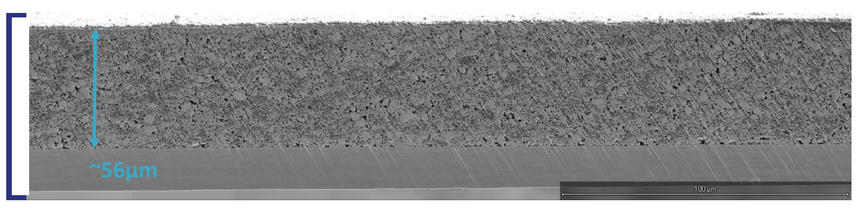

Fig. 4: Micrographs from 220 µm calendered sample. It can be seen the substantial difference in thickness of the LFP coating compared to the 20 µm calendered sample.

Sample	Al	O	C	Fe	P	Ag
20 cal	70.6	11.3	7.9	5.1	3.3	1.8
220 cal	32.4	20.0	13.3	23.5	10.2	0.6

Table 1: Chemical compositions in weight% of the RE samples determined by SEM-EDX analysis.

XRD

XRD spectrum of the pristine NMC811 cathode of the pouch cell (Fig. 5):

- The NMC811 sample preparation required an argon-filled glove box, as the Li would react if exposed to air.
- Prior into the project, **monocrystalline NMC811** was chosen for the cathode, rather than its polycrystalline counterpart [3].
- As such, the graph can show the single crystal nature of the NMC811 used.

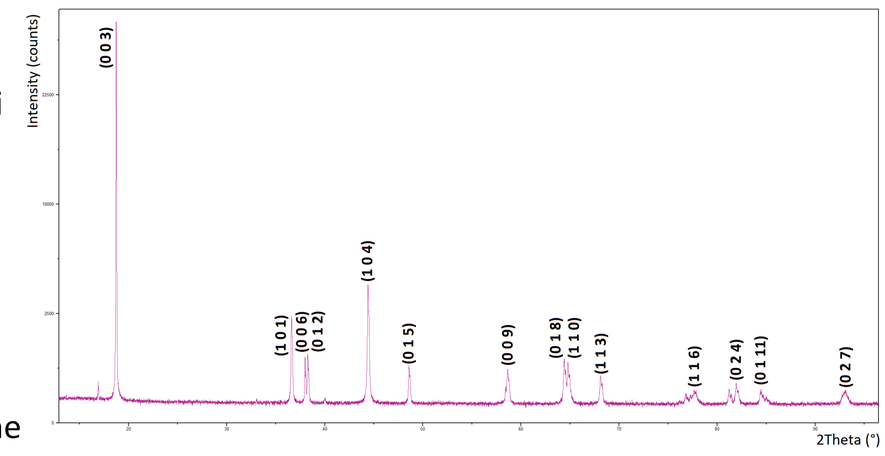

Fig. 5: XRD spectrum, each major peak has been labelled with the corresponding crystal plane of NMC811 as per the reference code 01-070-4314 [4].

XRF

XRF analysis of both the NMC811 cathode and the graphite anode (Fig. 6):

- By analysing the peaks, it can be calculated the atomic ratio between Ni and Mn in the cathode to be 8:1, confirming the material that has been utilised.
- **Advantage of XRF:** registering contaminants (Sulfur) and trace elements as a result of testing a large surface area.
- **Disadvantage of XRF:** the inability to capture light elements such as lithium, which is important when studying battery degradation and Li plating.

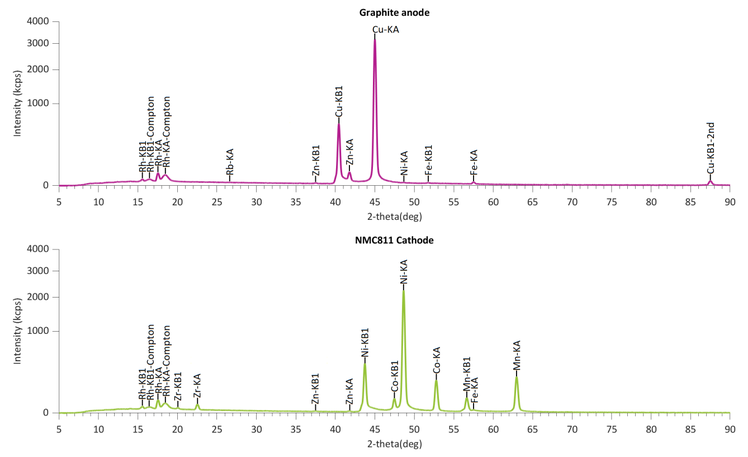

Fig. 6: The XRF spectra of the Graphite anode (above) and NMC811 Cathode (below). The Rh peaks in both of them is an artefact left from the XRF source used and not part of the anode and cathode.

Conclusions & Next Steps

- Together with the electrochemical data (EIS), the chosen coating for the continuation of the project is the **20 µm calendered coating**. Next steps include cycling the three electrode cells and refining the initial electrode designs.
- Analysis methods such as SEM, XRD, XRF and EDX offer important information in the research of battery degradation, but if the scope of the study is not just quality control but lithium plating or solid electrolyte interface (SEI) evolution, prominent problems in the battery field, these techniques offer limited data.
- As such, other methods like Secondary Ion Mass Spectrometry (SIMS) or Nuclear Magnetic Resonance (NMR) ought to be used [5].

References

[1] - la Mantia, F., Wessells, C. D., Deshazer, H. D., & Cui, Y. (2013). Reliable reference electrodes for lithium-ion batteries. Electrochemistry Communications, 31, 141–144. https://doi.org/10.1016/J.ELECOM.2013.03.015

[2] - Ahmed, Z., Roberts, A. J., & Amietszajew, T. (2022). Operando Thermo-Electrochemical Diagnostics with Au, TiO2, and LiFePO4 as Reference Electrodes in Li-Ion Pouch Cells. Energy Technology, 10(10), 2200248. https://doi.org/10.1002/ENTE.202200248

[3] - Saunders, L., Wang, J., & Stimming, U. (2022). Evaluating single-crystal and polycrystalline NMC811 electrodes in lithium-ion cells via non-destructive EIS alone. Journal of Applied Electrochemistry, 52, 1305–1316. https://doi.org/10.1007/s10800-022-01713-x

[4] - El Moutchou, S., Aziam, H., Mansori, M., & Saadoune, I. (2022). Thermal stability of Lithium-ion batteries: Case study of NMC811 and LFP cathode materials. Materials Today: Proceedings, 51, A1–A7. https://doi.org/10.1016/J.MATPR.2022.02.324

[5] - Waldmann, T., Iturrondobeitia, A., Kasper, M., Ghanbari, N., Aguesse, F., Bekaert, E., Daniel, L., Genies, S., Gordon, I. J., Löble, M. W., de Vito, E., & Wohlfahrt-Mehrens, M. (2016). Review—Post-Mortem Analysis of Aged Lithium-Ion Batteries: Disassembly Methodology and Physico-Chemical Analysis Techniques. Journal of The Electrochemical Society, 163(10), A2149–A2164. https://doi.org/10.1149/2.1211609JES

Intern bio

Andrei-Mircea Top is currently studying Materials Science and Engineering at the University of Sheffield. He has a deep passion for the sustainability field and is trying as many research fields as possible in order to find his path as a materials engineer.

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