

Testing the effect of conditions on lithium-ion batteries

Investigating the impact of nickel salts on lithium-ion battery degradation



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Abstract

Nickel rich NMC cathode materials have many limitations. Transition metal dissolution is one of the main issues that these cathodes cause. In this work, the effect of nickel ions have on batteries was investigated by intentionally adding Ni(TFSI)₂ into coin cells and then using cyclic voltammetry to assess the effects of the nickel salt on the battery performance. This was carried out on coin cells with graphite and copper anodes. Nickel reduction prevalent in the data recorded in the literature was not observed consistently in the results obtained in this experiment, however there are some similarities with the literature data.

Introduction

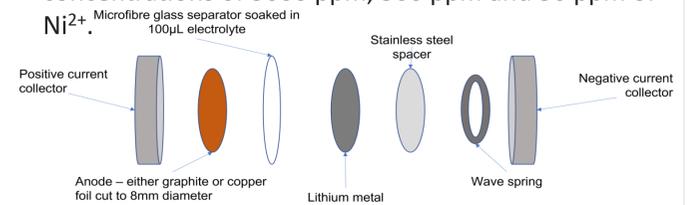
Nickel-rich NMC cathodes are now becoming common battery materials as they have increased capacity in comparison to previously used materials¹. However, using these can lead to capacity fade during the cycling process as a result of transition metal dissolution. The ions released are proposed to cause numerous side reactions² which can lead to electrolyte decomposition and deposition of these ions on the anode³ as well as causing a direct loss of active lithium¹.

Since nickel is the most abundant transition metal in these cathode materials it is important to understand the effects that this has on lithium-ion batteries. The literature⁴ suggests that reduction of the nickel occurs, and that metallic nickel starts to deposit at the anode and have determined this using cyclic voltammetry. This observation is confirmed in other experiments performed with a copper foil anode.² In this study similar procedures are carried out to determine the extent to which nickel reduction effects the performance of lithium-ion batteries.

Methods

The effects of deliberately adding Ni(TFSI)₂ into lithium/graphite half cells were explored:

- Solid Ni(TFSI)₂ was dissolved in 1M LiPF₆ in 3:7 EC-EMC electrolyte to make solutions with concentrations of 5000 ppm, 500 ppm and 50 ppm of Ni²⁺.



- The cells were then placed in a battery cycler to rest at OCV for 6 hours and then cycled 10 times at a scan rate of 0.1 mV/s.

Lithium/copper half cells were subsequently constructed tested to attempt to make the nickel reduction peaks more visible by reducing the effects of intercalation.

Results

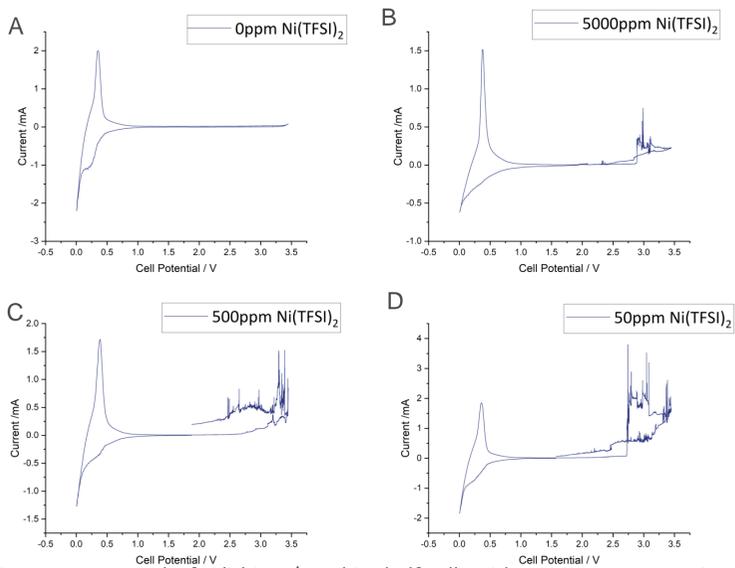


Figure 1 – CV graphs for lithium/graphite half cells with varying concentrations of Nickel

The first cyclic voltammogram for four half cells with different nickel concentrations are shown in Figure 1:

- As the nickel concentration increased the magnitude of the current produced decreased.
- The oxidation peaks at voltages greater than 2.5 V are due to the presence of nickel as no peak appears in Figure 1.A.
- There is no evidence of the nickel reduction that is visible in the cyclic voltammograms published by Jung et al⁴.

Discussion / Conclusions

Carrying out the experiments showed that it was very difficult to reproduce results similar to those seen in the literature:

- While the oxidation that is observed in the lithium/graphite coin cells with different concentrations of nickel was observed again in repeats of the experiment, this observation is not mirrored in any of the literature. These oxidations could have happened due to the nickel salt not being heated up during the drying process and instead just being left overnight under vacuum in the glovebox antechamber. This could mean residual moisture was left in the nickel salt which leads to reactions causing these oxidation peaks.

- Several other coin cells with a copper foil anode were tested in addition to the ones whose graphs are shown. Very few of the batteries cycled yielded CVs that were like those seen in the literature. Many of these batteries showed signs of copper degradation at higher voltages (large currents at potentials about 3 V) and others appeared to show small amounts of intercalation, however, this could also just be lithium deposition and stripping above 0 V because the lithium is destabilised by the addition of the nickel salt.

Cyclic voltammograms of lithium/copper coin cells with 500 ppm of Ni(TFSI)₂ are presented in Figure 2:

- The red line on both graphs represents data digitally extracted from the literature².
- In Figure 2.A, a clear reduction peak can be seen at a similar potential to the nickel reduction potential seen in the literature data.
- In Figure 2.B a very similar shape to the literature data is observed however a prominent nickel reduction peak is not seen.

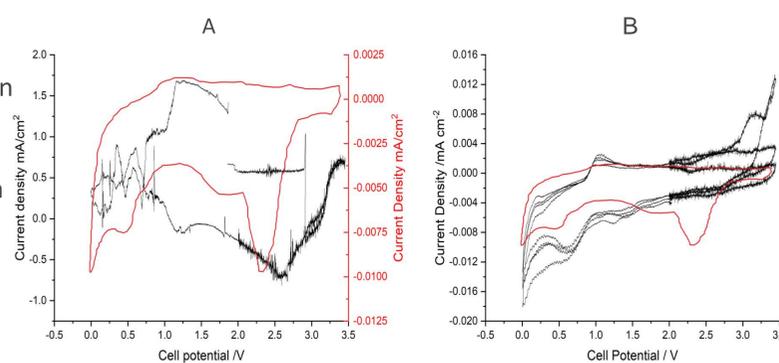


Figure 2 – CV graphs of the lithium/copper half cells

Next steps

- Dry the nickel at a higher temperature to evaporate as much moisture as possible and rerun the same experiments to see if the oxidation peaks at higher voltages disappear
- Run the same experiment with LiTFSI, to verify claims^{2,4} that the TFSI⁻ anion does not have an impact on the battery performance
- Perform experiments with Mn(TFSI)₂ and Co(TFSI)₂ to see how different metals affect the batteries.
- Perform experiments with full cells to observe the differences in the behaviour in comparison to half cells

References

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Intern bio

Louis Jones is studying Joint Honours Chemistry and Physics at Durham University. Interested in the intersection between these two subjects. Aspiring to go on to complete a PhD and have a career in scientific research.

