Investigating the performance and surface reactivity of the high voltage cathode Li_2MnO_2F with different electrolytes in Li-ion batteries

Exploring cycling and electrolyte degradation for a range of electrolyte compositions

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Abstract

Li_2MnO_2F is a promising next generation DRX cathode [1] suffering from poor cycling performance, partly due to incompatibilities with the electrolyte. The purpose of this project is to explore the stability of Li_2MnO_2F with different electrolyte formulations to find a more stable combination and to investigate the reasons behind the reactivity.

Background

- It has been suggested that LiFSI contributes to forming a more stable SEI, reducing Mn dissolution, as well as preferentially oxidizing carbonate solvents and reducing reactivity of $LiPF_6$ to suppress HF formation. [2]
- FTIR and DFT calculations have suggested cyanide groups in LiTDI form hydrogen bonds with residual water, trapping it and reducing reactivity with the electrolyte. [3]

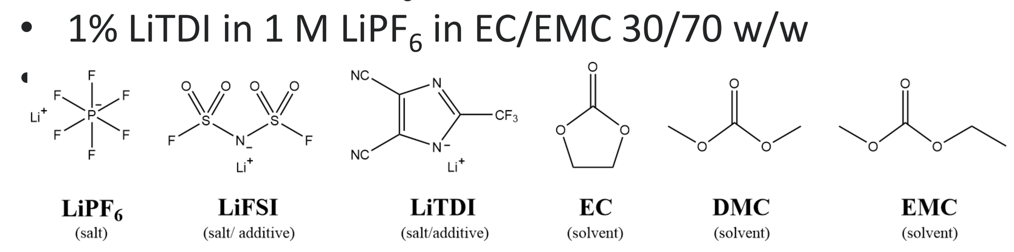
This is important in degradation mechanisms [4] such as:

$$LiPF_6 + H_2O \rightarrow OPF_2(OH) + HF$$

Methods

The active material was prepared by ball milling, then combined with carbon and PTFE (8:1:1) to make the cathode. Coin cells were then prepared using a range of different commercial electrolyte compositions available:

- 1 M $LiPF_6$ in EC/DMC 50/50 v/v
- 1 M $LiPF_6$ in EC/EMC 30/70 w/w
- 1% LiFSI in 1 M $LiPF_6$ in EC/EMC 30/70 w/w
- 1% LiTDI in 1 M $LiPF_6$ in EC/EMC 30/70 w/w

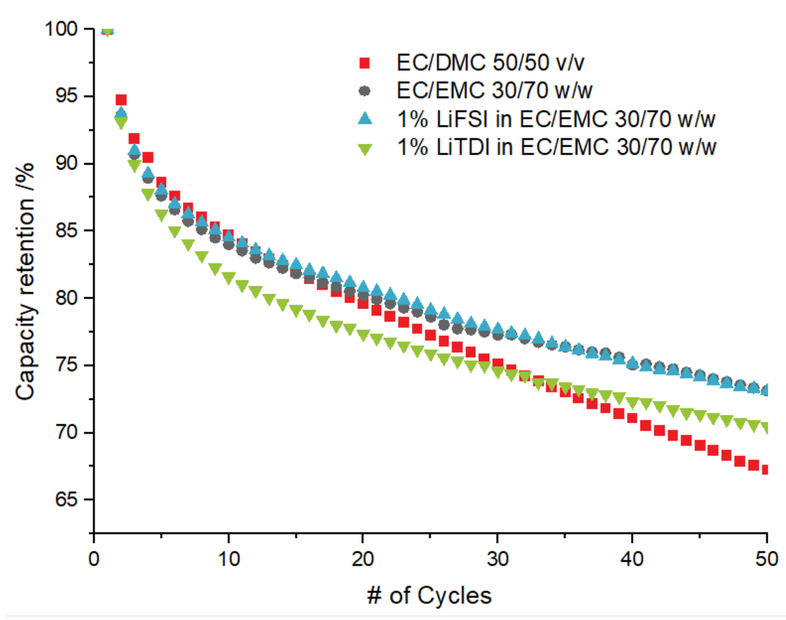


These cells were cycled at 100 mA g-1 for 50 cycles.

Impedance spectroscopy, ^{19}F and ^{1}H NMR, and GCMS were used.

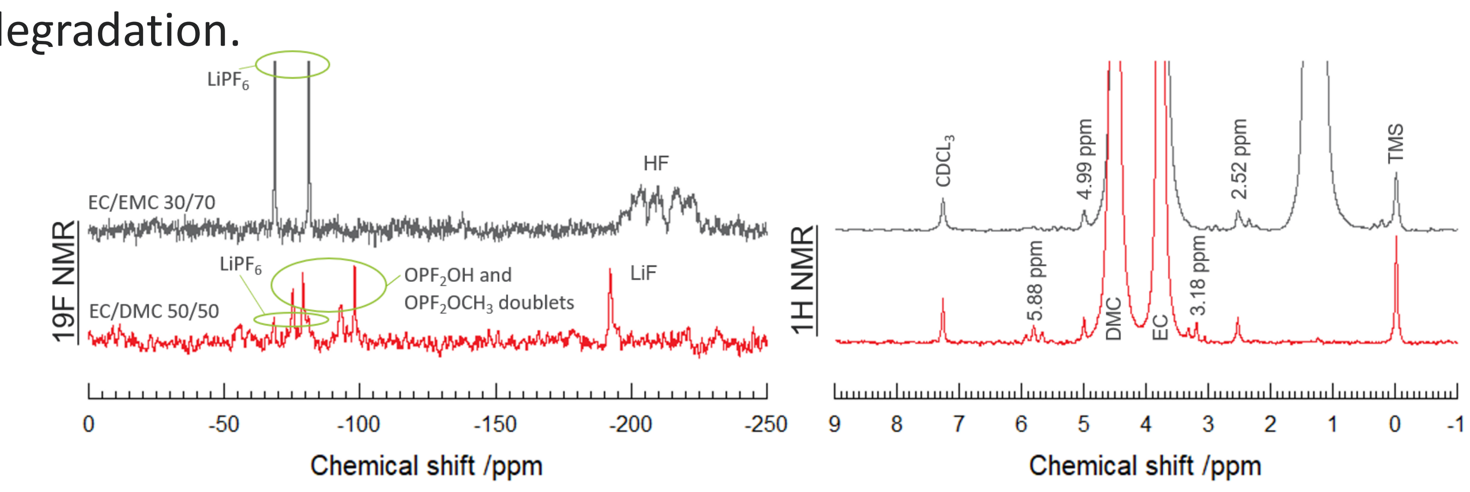
Cycling Performance

- 6% improvement in overall capacity retention seen by using EC/EMC 30/70 instead of EC/DMC 50/50
- EC/EMC 30/70 with and without 1% LiFSI additive performed very similarly
- Using 1% LiTDI gave worse performance compared to the same composition without the additive



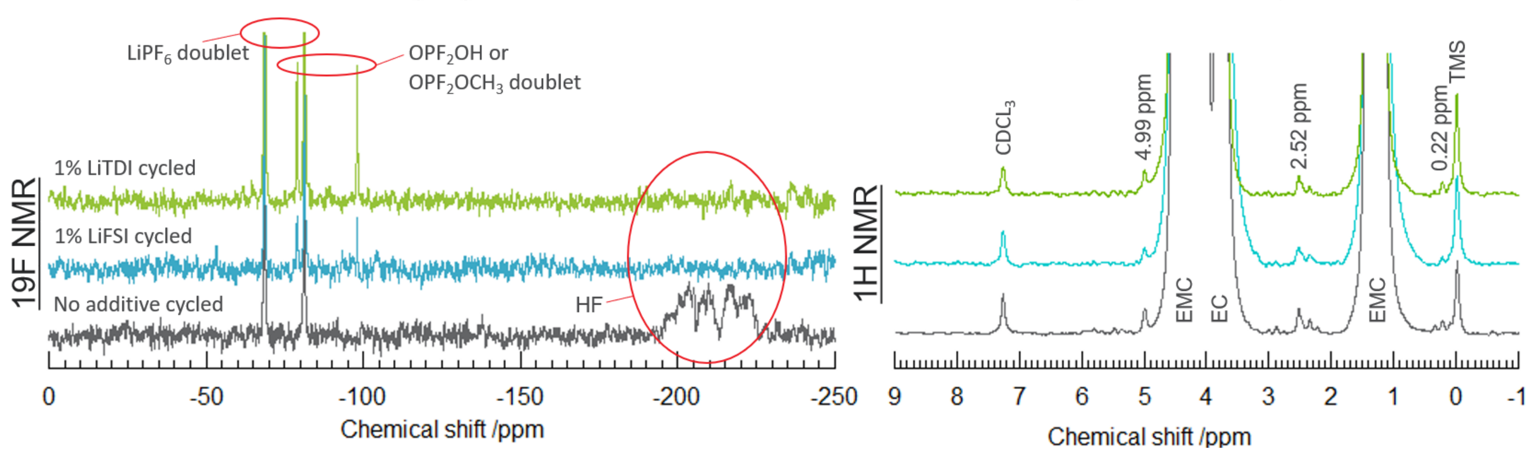
The Effect of Different Solvents

- After 50 cycles, the EC/DMC 50/50 electrolyte had degraded substantially, with the $LiPF_6$ salt degrading to form OPF_2OH and OPF_2OCH_3 anions.
- A substantial amount of LiF (-195 ppm, EC/DMC) and HF (-205 ppm, EC/EMC) are seen in the ^{19}F NMR spectra, which are both byproducts of $LiPF_6$ degradation.



Do Additives Improve Capacity Retention?

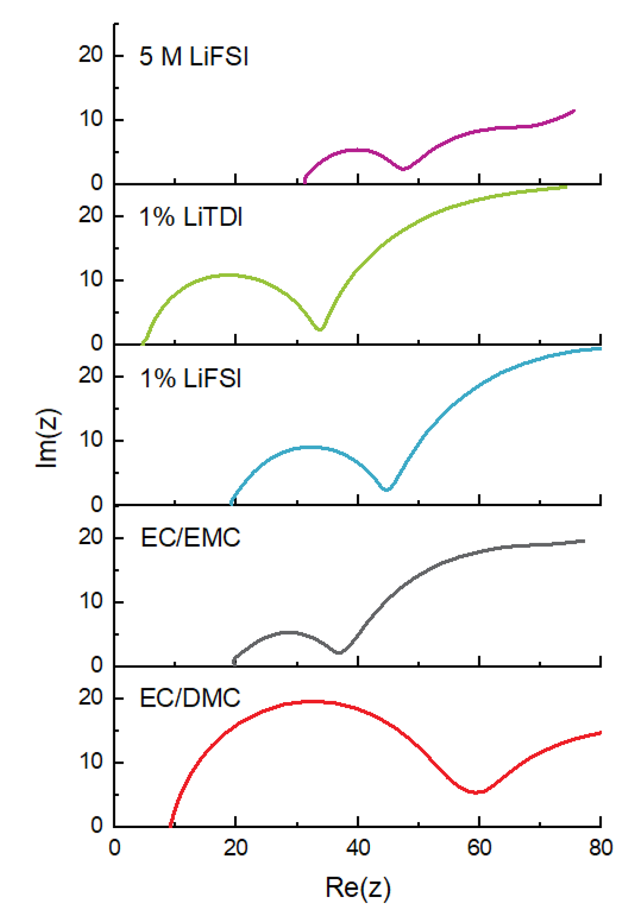
- A large amount of HF formed when using EC/EMC without additive, but HF was not evident in ^{19}F NMR when LiTDI or LiFSI additives were used. Despite this, performance was nearly identical with and without LiFSI and LiTDI worsened performance.
- The OPF_2OCH_3 or OPF_2OH doublet at -88.5 ppm had greatest relative peak area (relative to $LiPF_6$ peak) for 1% LiTDI which performed worst of these three formulations. None of this fluorinated side product was seen for EC/EMC without additive, which performed best.
- ^{1}H NMR showed negligible differences in solvent degradation products.



Impedance Spectroscopy

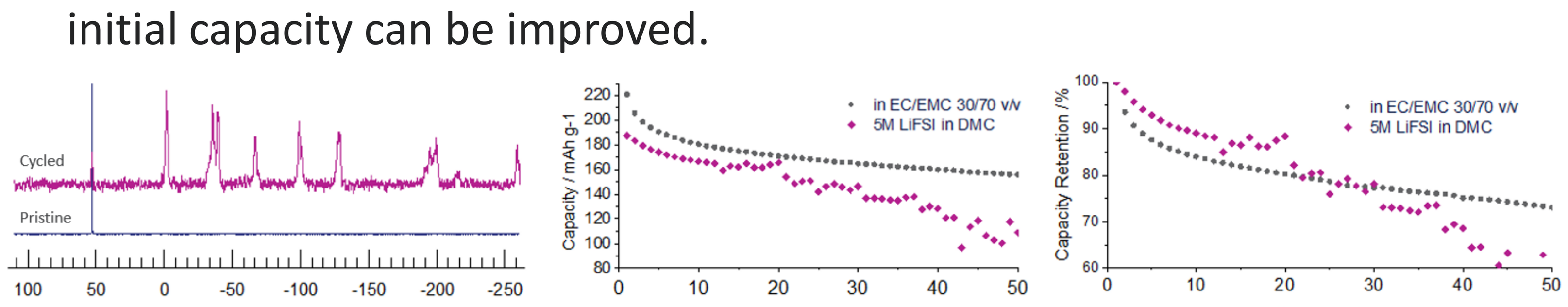
This technique can help quantify resistance in different parts of the cell. The Re(z) value at which the first semicircle begins indicates the impedance contribution from the electrolyte. The horizontal Re(z) span of each semicircle indicates resistance of different components of the cell (likely the CEI and the cathode).

- Impedance of the first discharge shows a much larger first semicircle for the EC/DMC cell compared with the EC/EMC cell, indicating a more resistive CEI. This greater resistance correlates with worse cycling performance (we can similarly compare the two additives; LiTDI has a more resistive CEI).
- There is also a large electrolyte resistance for 5 M LiFSI due to its high viscosity.



High Concentration Electrolyte; 5 M LiFSI

- The 5 M electrolyte was very viscous and cells did not achieve an initial capacity that was comparable with cells with 1M electrolyte solutions, even with a 12-hour rest time before cycling.
- ^{19}F NMR shows a complicated degradation of LiFSI with many products.
- Percentage capacity retention for the first 10 cycles is still promising if the initial capacity can be improved.



Conclusion

- The EC/EMC 30/70 solvent composition outperformed EC/DMC 50/50 with a 6% improvement in capacity retention over 50 cycles.
- ^{19}F NMR showed LiFSI and LiTDI additives dramatically suppressed formation of HF, giving evidence of their role in trapping water and altering reactivity.
- HF is not the major reason for capacity fade, as seen by the almost identical capacity retention with and without LiFSI (both in EC/EMC 30/70).
- More fluorinated side products from $LiPF_6$ degradation observed in NMR correlated with a more resistive CEI observed in impedance and a greater capacity fade, suggesting deposition of the fluorinated side products. Very little solvent degradation was seen.

Impact / Next steps

- More work is needed to determine whether the benefit of EC/EMC 30/70 over EC/DMC 50/50 or is due to the ratio of carbonates or the choice of carbonate.
- Different carbonate ratios and longer chain carbonates such as DEC should be investigated.
- More analysis of electrolytes in DRX cells is needed to understand their degradation mechanisms and surface reactivity.

References

[1] Click *here* for a paper on Li_2MnO_2F

[2] Click *here* for a paper on LiFSI

[3] Click *here* for a paper on LiTDI

[4] Click *here* for a paper on $LiPF_6$ degradation

Intern bio

Esmé is entering her 3rd year of studying Chemistry at the University of Oxford. Interested in how chemistry can be applied to problems surrounding energy and the environment, she plans to continue to study for a PhD.

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