Effect of Nickel Content on Lithium Diffusion in NMC Cathode Materials

Using GITT to estimate Lithium Diffusion constants in NMC622 and NMC811 cathode materials.

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Abstract

The Galvanostatic Intermittent Titration Technique (GITT) was carried out on coin cells using NMC622 ($LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$) and NMC811 ($LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$) cathodes. The potential and current versus time data was used to fit a model giving diffusion coefficient versus State of Charge (SOC), y in $Li_{1-y}Ni_aMn_bCo_cO_2$.

Lithium transport in the two NMCs was then compared.

Motivation

Nickel-rich NMCs suffer large dimensional change during cycling which leads to fracture, reducing the lifetime of the cell. [1] A finite element model, requiring Li diffusion coefficients, could be used to better understand the interplay of chemical and mechanical properties. Single crystal NMCs are studied to better reflect the single crystal nature of the model.

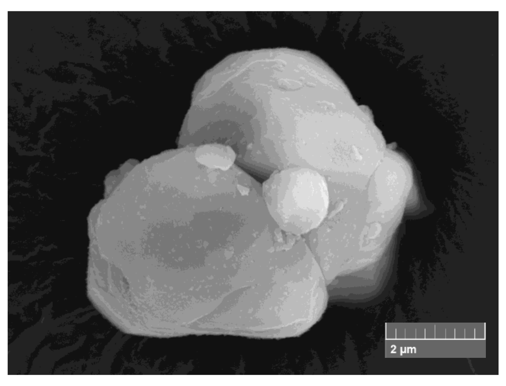

Figure 1: SEM image of NMC622 single crystal powder.

Sample Preparation

Cathodes were cast onto Al foil with 90% NMC622 powder provided by Umicore, 5% PVdF polymer binder, 5% TIMCAL Super P carbon and 0.75ml of NMP solvent. This was dried at 70°C in a nitrogen purge box for 1 hour before cutting into 12.7mm diameter discs. Premade NMC811 cathodes from LiFUN were cut to the same size to be used as a comparison.

The cathodes were put into 2032-coin cells against Li metal with LP57 + 2%VC electrolyte.

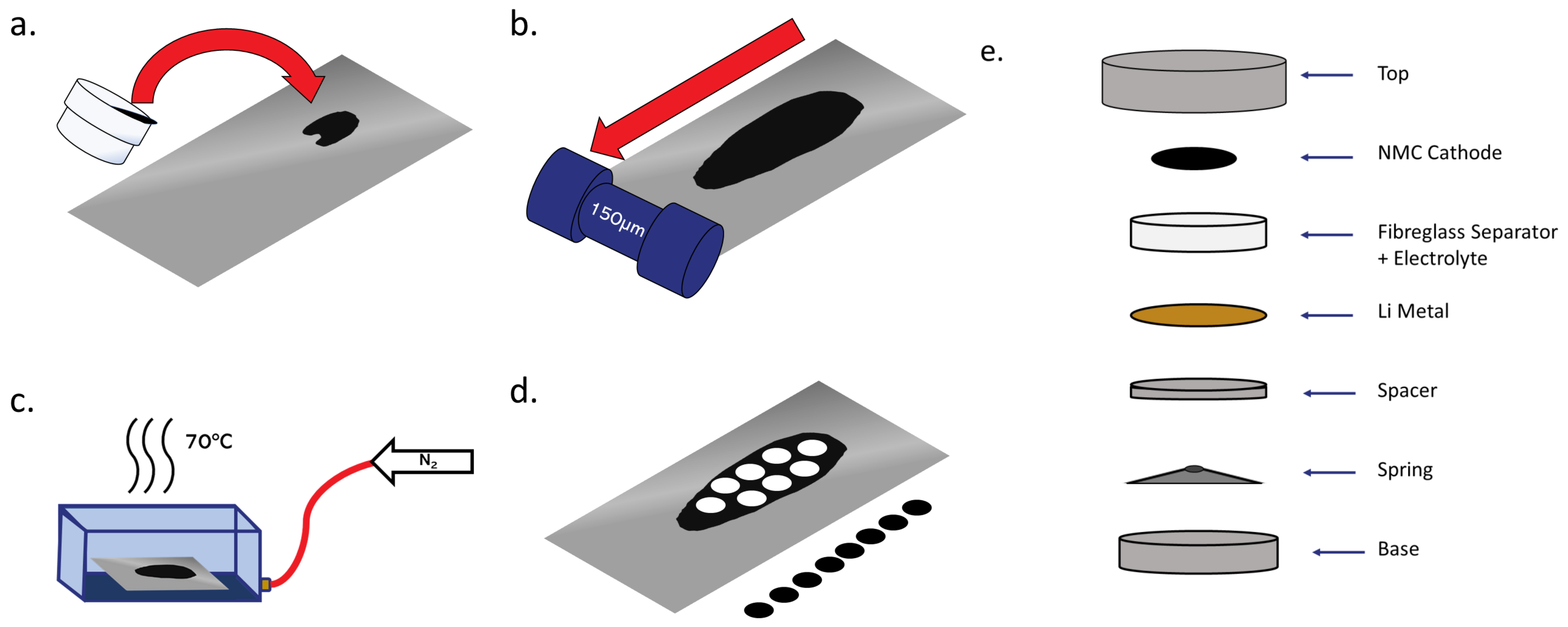

Figure 2: Electrode casting steps (a-d) and coin cell configuration (e).

GITT and Data Analysis

The GITT procedure chosen was a current of $10 mAg^{-1}$ of active material (equivalent to C/20) being applied for 30 minutes followed by a 2-hour rest. This was done until the potential reached 4.4V. Equivalent discharge pulses were applied until potential dropped to 3.2V. Two of these cycles were carried out on each NMC.

A diffusion coefficient data point can be found for each overall pulse and rest period as shown in Equation 1. U_o is the Open Circuit Voltage (OCV) that the cell rests to after each pulse. Corresponding y, State of Charge (SOC) values were found using data from a separate constant current C/20 cycle on identical cells.

$dV/d\sqrt{t}$ was found by looking only at data points after the sharp increase from the sudden current pulse shown in red on Figure 4.

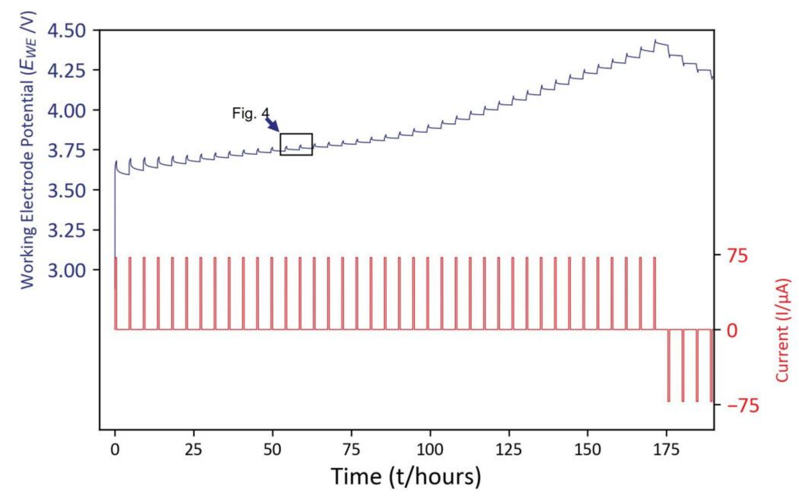

Figure 3: Working electrode potential and current in first 180 hours of NMC622 GITT cycle.

$$\frac{D_S S^2}{V_m^2} = \frac{4}{\pi}\left(\frac{I}{F}\right)^2 \left(\frac{dU_o/dy}{dV/d\sqrt{t}}\right)^2$$

Equation 1:Relationship between normalised diffusion constant (left) and values obtained from GITT plot. [2]

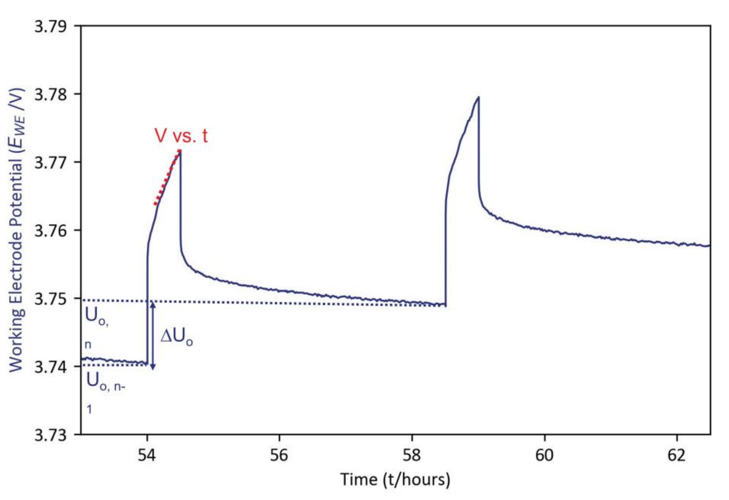

Figure 4: Zoom in on potential/time GITT plot showing a single pulse and relaxation with how the open circuit voltage U_o was obtained.

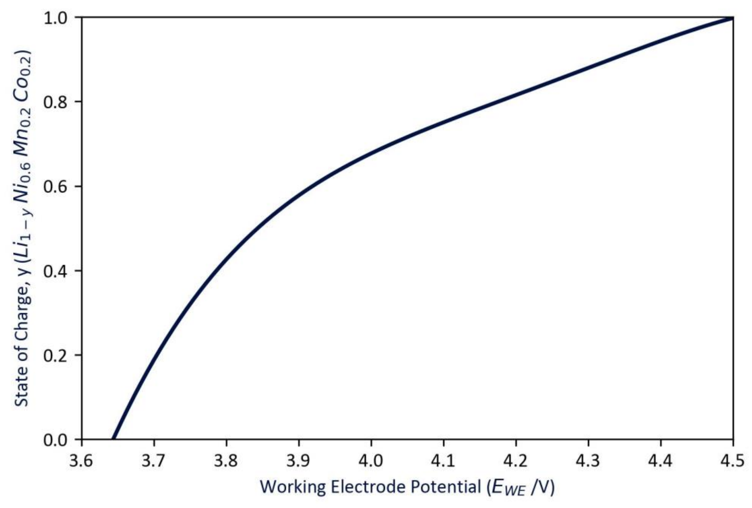

Figure 5: Curve fitting working electrode potential to state of charge for NMC622 based on data from a previous C/20 cycle.

Results

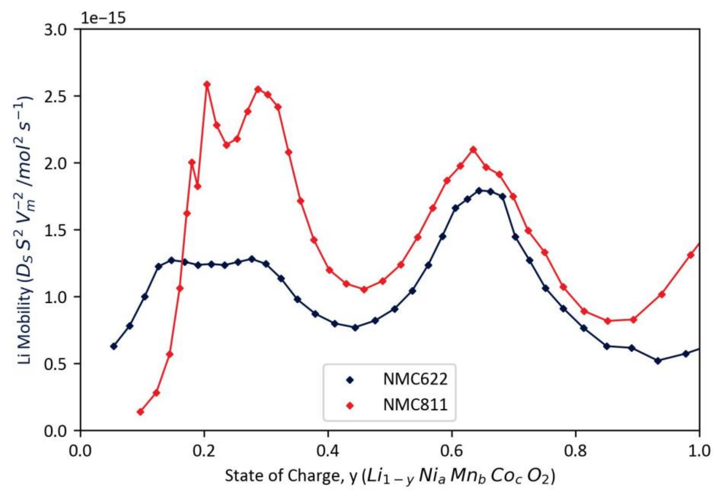

Figure 6: Calculated Li mobility versus state of charge for NMC622 and NMC811

A similar pattern in how Li mobility varies with SOC for both NMC622 and NMC811 is observed. However, the NMC811 values are generally greater than NMC622.

Conclusions

- A method for determining the diffusion coefficients of NMCs with different Ni content has been demonstrated.
- The similar pattern of Li mobility against SOC between NMC622 and NMC811 indicates Li diffusion occurs in a similar way.
- The generally higher diffusion constants of NMC811 suggests greater Li mobility may be linked to shortened lifetime of Ni-rich NMCs .

Impact / Next steps

- The GITT method shown could be used to develop the finite element model for prediction of stress/strain fracture modes of NMCs.
- The method shown here could be repeated over more cycles, with longer rest times to ensure the actual OCV is reached and to a lower upper voltage limit to gather a greater amount of data and investigate how the diffusion constants might change over many cycles.
- The shear strain calculation proposed by Stallard et. al. [3] could be repeated for NMC622 and NMC811 for further comparison.

References

[1] Ryu, H.-H.; *et al. Capacity Fading of Ni-Rich Li[NixCoyMn1–x–y]O2 (0.6 ≤ x ≤ 0.95) Cathodes for High-Energy-Density Lithium-Ion Batteries: Bulk or Surface Degradation?.* Chem. Mater. 2018, 30 (3), 1155–1163.

[2] Märker, K.; *et. al. Evolution of Structure and Lithium Dynamics in LiNi0.8Mn0.1Co0.1O2 (NMC811) Cathodes during Electrochemical Cycling.* Chem. Mater. 2019, 31 (7), 2545-2554

[3] Stallard, J. C.; *et al. Effect of Lithiation upon the Shear Strength of NMC811 Single Crystals,* J. Electrochem. Soc. 2022, 169 040511

Intern bio

Jack Ginnis is a third-year undergraduate studying Materials Science at the University of Oxford. His primary interests are in the mechanical properties of materials for the energy industry specifically for rechargeable batteries and nuclear fission/fusion. He is aspiring towards a career in research focusing on the design and testing of materials to improve the lifetimes of energy systems.

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