Thin-Film Ni-Rich Cathode Materials for Li-Ion Batteries

Enabling adoption of sustainable energy *via* cathode material research and development for high-performance Li-ion batteries

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Background of Research

- High-performance rechargeable Li-ion batteries could enable the widespread use of more environmentally friendly electric vehicles
- However, energy density and cycling stability need to be improved
- Over the past decade, **$LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ (NMC811)** has been used as a cathode material for electric vehicles by Mercedes, Kia, Ford etc.
- This is due to its high specific capacity ~200 $mAhg^{-1}$ and low content of costly Co

Issues With NMCs?

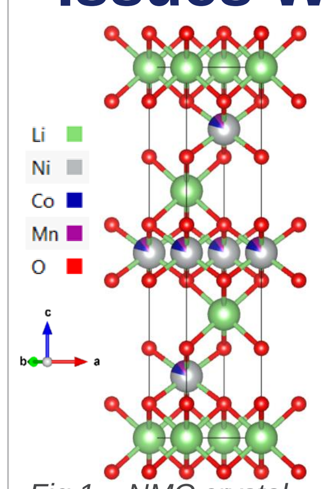


Fig 1 – NMC crystal structure [1]

- Electrode-electrolyte reactions and surface phase changes during battery charging/discharging cause capacity fading
- Ni^{4+} reacts with organic electrolytes to form resistive surface compounds
- Surface phase and anisotropic lattice volume changes create residual stresses causing polycrystalline material to crack which exposes additional surfaces to the electrolyte
- Thin-film NMC811 research can help us better understand surface degradation without the presence of carbon and binders found in polycrystalline cathodes

1 – Thin-Film NMC Deposition

- Deposited *via* RF magnetron sputtering with a $Li_{1.6}Ni_{0.8}Mn_{0.1}Ni_{0.1}O_2$ target in an Ar-O_2 atmosphere onto $SrTiO_3$ (100) substrates

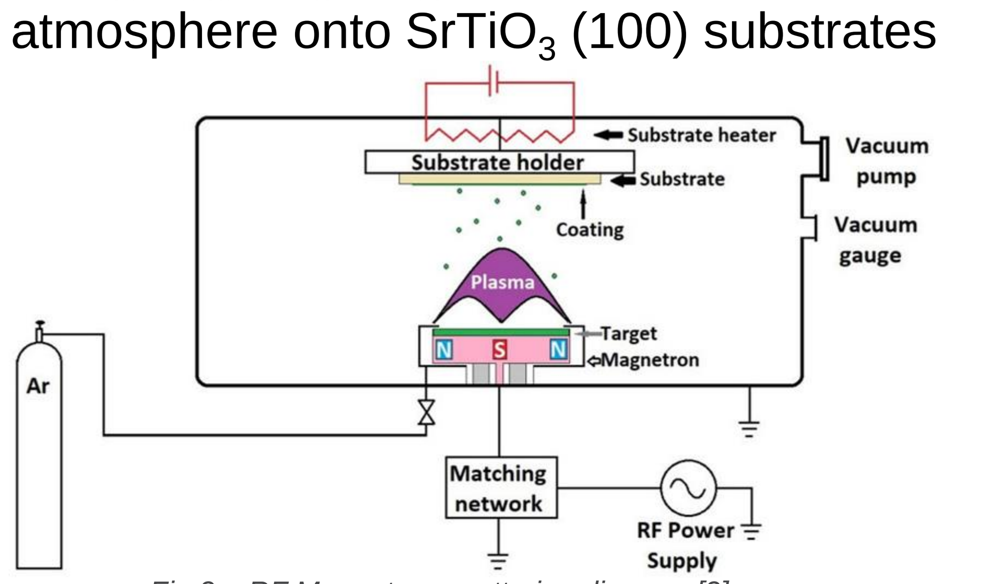


Fig 2 – RF Magnetron sputtering diagram [2]

- For electrochemical testing, $SrRuO_3$ was deposited using pulsed laser deposition onto conductive Nb-doped $SrTiO_3$ (100) substrates at 880ºC before the NMC
- $SrRuO_3$ acts as a current collector between the e^- conductive substrate and e^-/Li^+ conductive NMC

2 – Determining Optimum Deposition Condition

- RF power 100 W and rotations 10 RPM
- 10 min cleaning + 1hr deposition
- Different Ar:O_2 ratios at RT
- Post annealing in O_2 at 600ºC

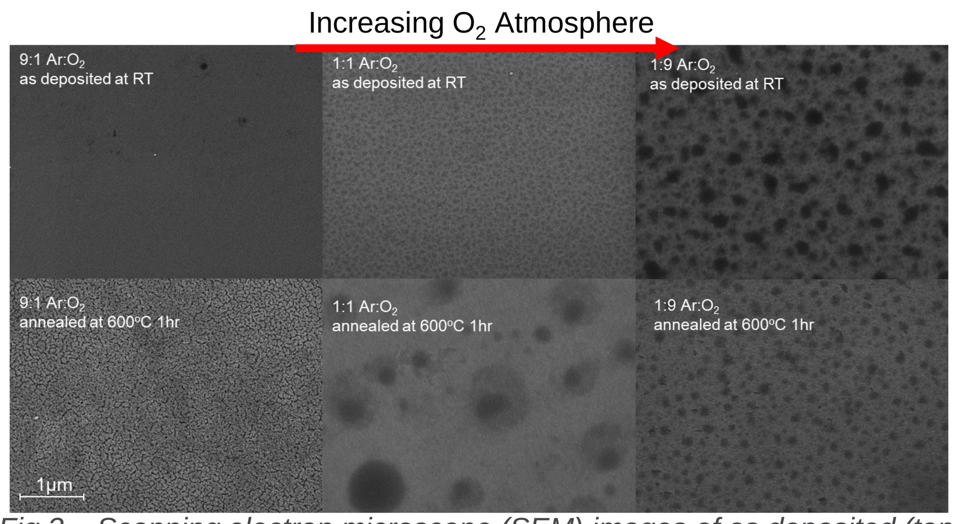


Fig 3 – Scanning electron microscope (SEM) images of as deposited (top) and annealed (bottom) NMC thin-films deposited in different atmospheres - (RT – room temperature)

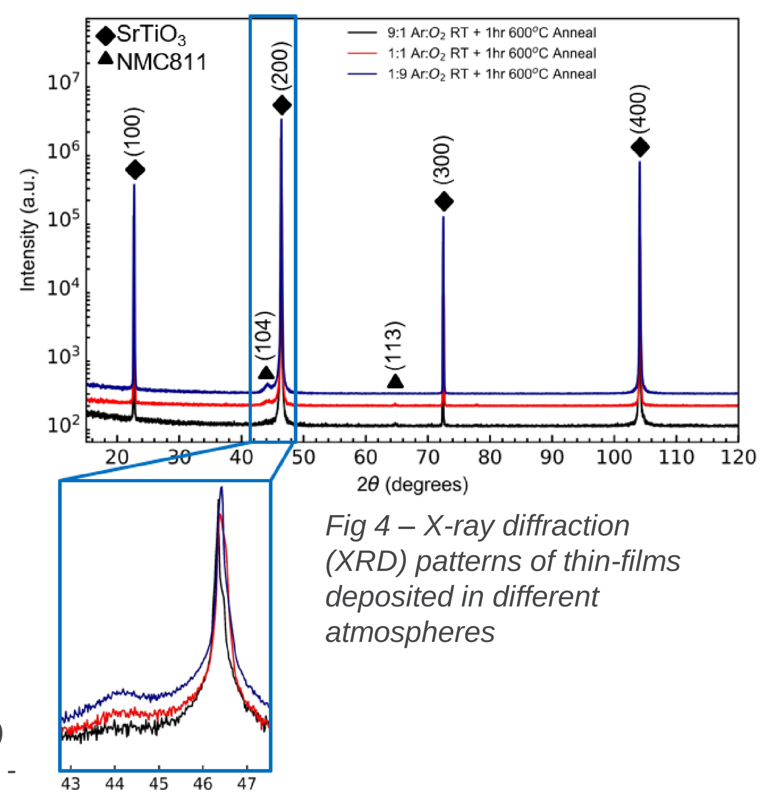


Fig 4 – X-ray diffraction (XRD) patterns of thin-films deposited in different atmospheres

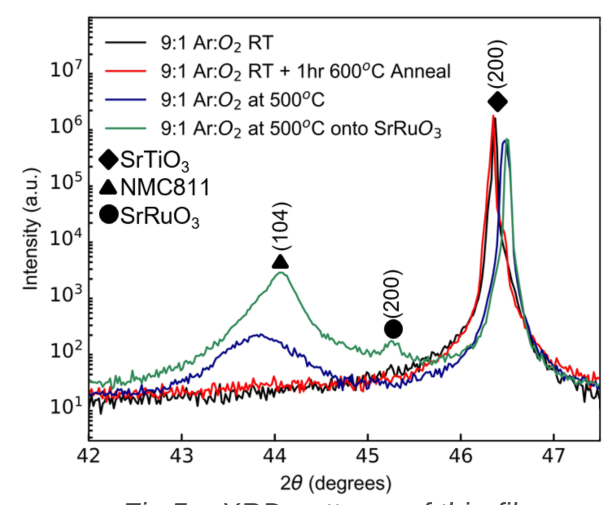


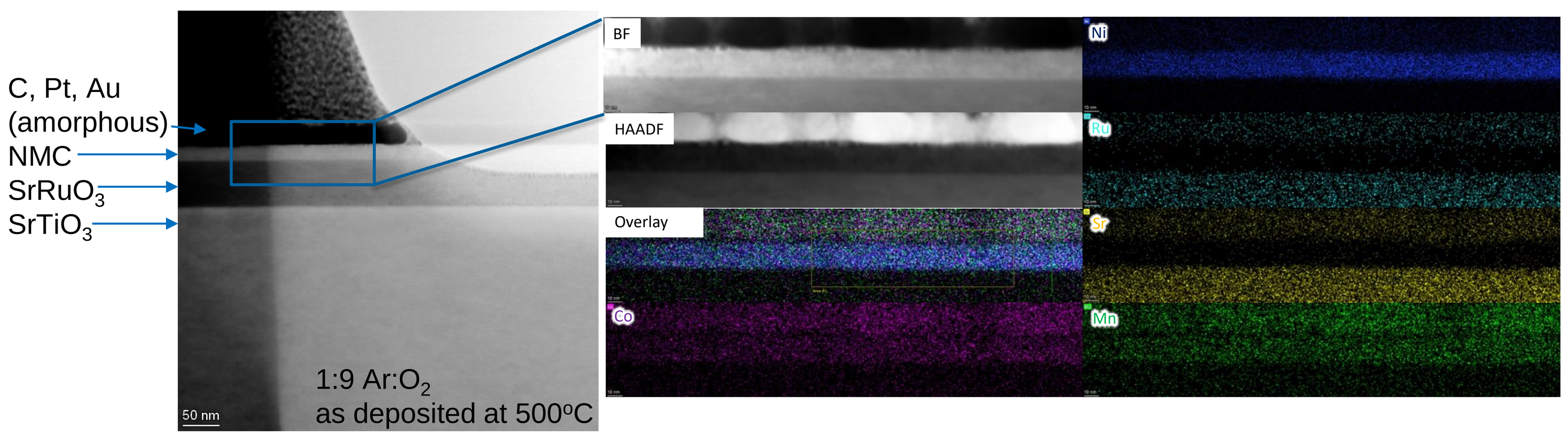
Fig 5 – XRD patterns of thin-films deposited at different temperatures

- $SrRuO_3$: growth of a highly aligned NMC layer
- Optimized condition: O-rich deposition + 500ºC deposition

- Inhomogeneity and porosity increased with O_2 fraction but was reduced by annealing (Fig 3)
- As deposited films were amorphous (revealed by XRD)
- Annealing increased the crystallinity: reflected by (104) NMC peak (Fig 4)

3 – Composition and thickness analysis using TEM

- Lamella of thin-film samples were prepared using focused ion beam (Ga-FIB)



Atomic Fraction (%)	
Mn	10.1
Co	11.5
Ni	78.5

Fig 6 – Bright field transmission electron microscope (BF-TEM) image of thin-film cross section, energy dispersive x-ray spectroscopy (EDX) was used to confirm elemental composition of each layer – Au was used to ensure the surface was conductive for SEM, Pt was used as a protective layer during FIB milling and C is a SEM by product

- BF-TEM was used to measure NMC thickness (20nm)
- EDX showed that the NMC layer was Ni-rich matching target composition of NMC811

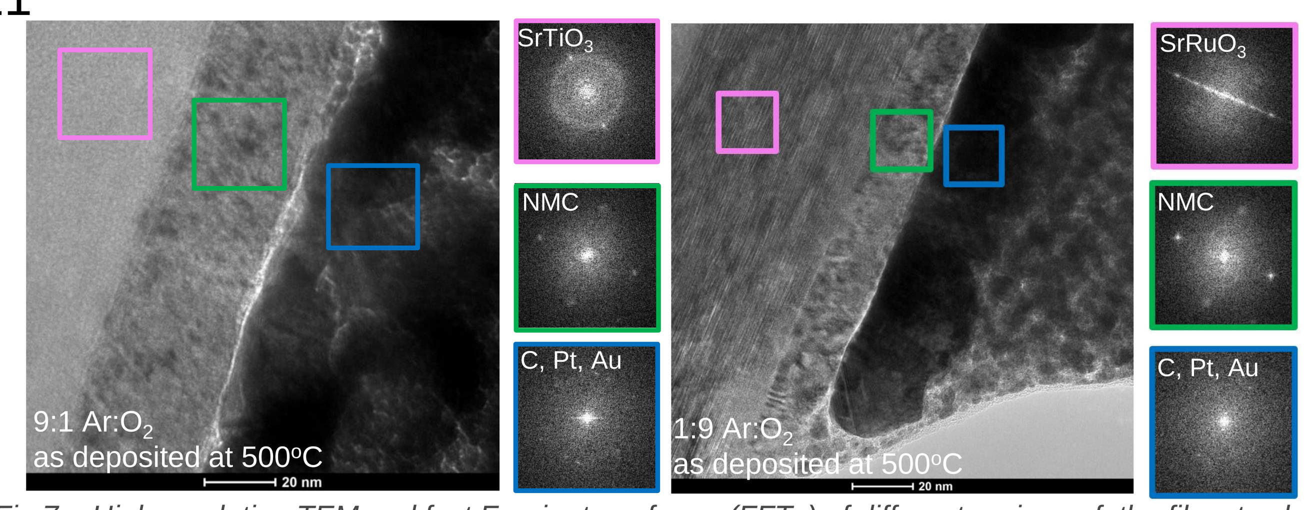


Fig 7 – High resolution TEM and fast Fourier transforms (FFTs) of different regions of the films to check the crystallinity and lattice plane orientation

- HR-TEM shows the $SrRuO_3$ layer to be highly orientated
- $SrRuO_3$ and O-rich deposition atmosphere also creates a more orientated NMC811 (003) layer as seen in the FFTs

4 – Electrochemical performance of thin-film *vs* polycrystalline NMC811

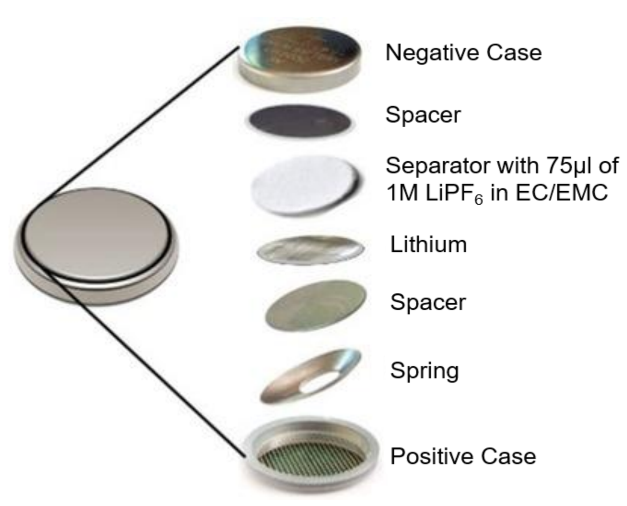


Fig 8 – Coin cell assembly – adapted from [3]

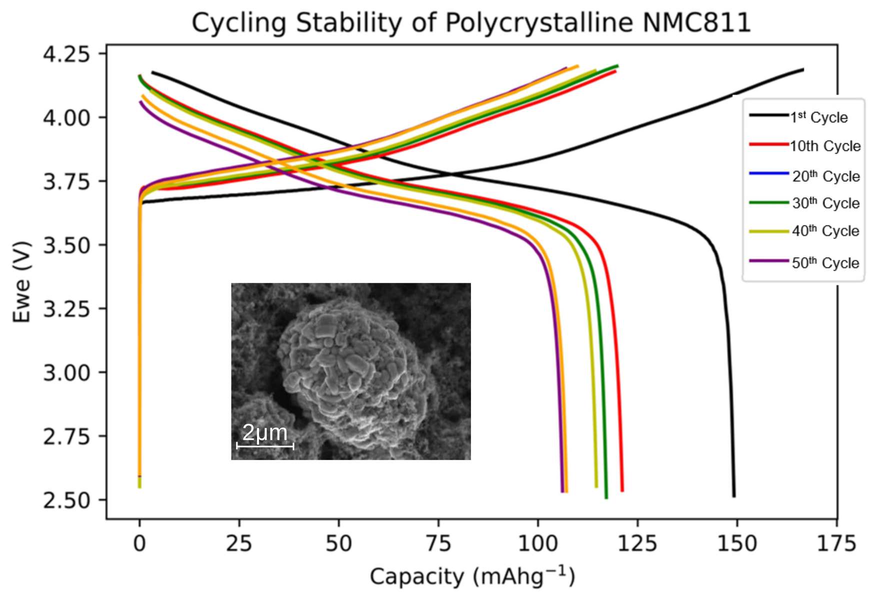


Fig 9 – Voltage vs capacity and an SEM Image of a secondary particle for polycrystalline NMC811

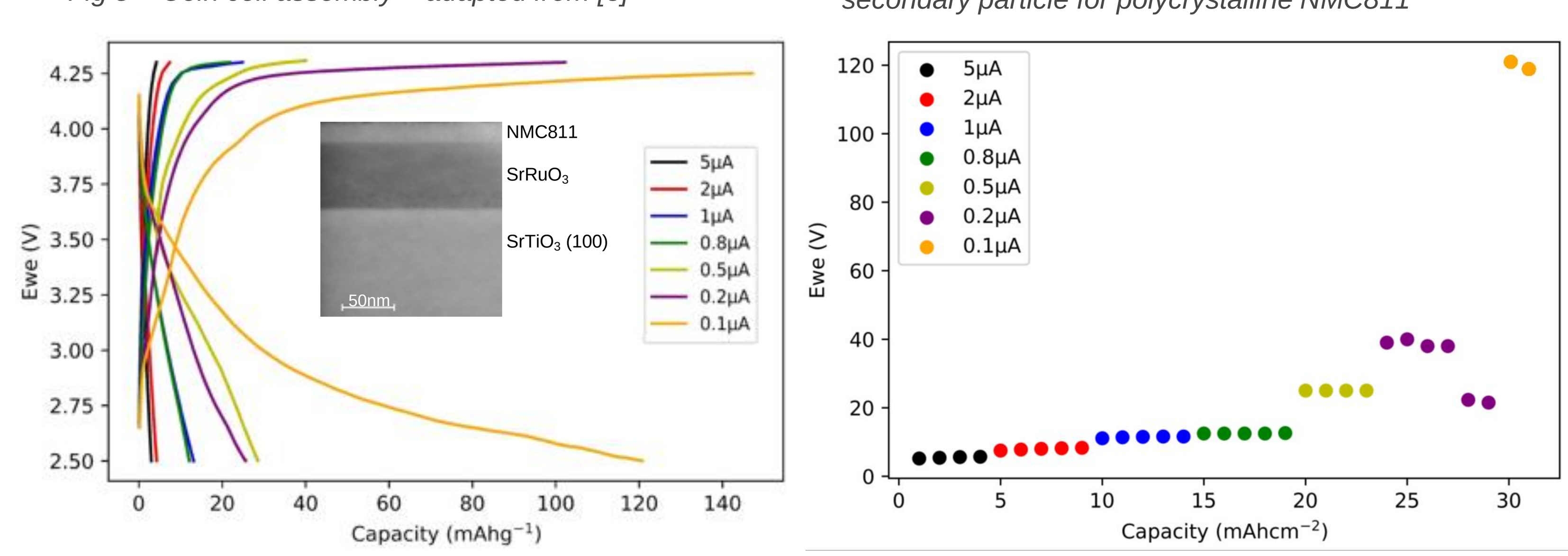


Fig 10 – Voltage vs capacity and BF-TEM image of thin film layers (left) and corresponding capacity vs cycle number for each current (right)

- For calculating capacity, thickness values from TEM were used
- Thin-film shows reasonably good electrochemical profile with initial discharge capacity being 121 $mAhg^{-1}$ with 0.1uA current

Impact

- Through RF sputtering, we have been able to fabricate high Ni content NMC thin-films verified *via* TEM-EDX
- We have shown these to have reasonable electrochemical performance.

Next Steps

- Reduce PLD deposition times to get thinner $SrRuO_3$
- Explore higher RF sputtering powers and longer deposition times to produce thicker films ~200nm
- Trial higher NMC deposition temperatures to increase thin film crystallinity whilst maintaining a high Ni content
- Use X-ray photoelectron spectroscopy (XPS) to explore the oxidation state of Ni ions in thin-film NMC811

References

[1] K. Momma and F. Izumi, "VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data," *J. Appl. Crystallogr.*, **44**, 1272-1276 (2011).
[2] M. Maximov (2021). Bioactive Glass—An Extensive Study of the Preparation and Coating Methods. Coatings. 11. 1386. 10.3390/coatings11111386.
[3] A. Zülke, Y. Li, P. Keil, R. Burrell, S. Belaisch, M. Nagarathinam, M. P. Mercer, H. E. Hoster, *Batteries & Supercaps* **2021**, *4*, 934.

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Intern bio

William is entering his 4th year studying Materials Science at the University of Oxford where he will be researching TEM sample damage from FIB preparation and comparing the effects of Ar, Ga and Xe ions

He has a keen interest in materials characterization, especially for enabling sustainable energy and is seeking related PhD opportunities and graduate roles in industry

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