Advanced Characterization of Sodium Layered Oxide Cathodes

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Sodium-Ion Batteries (SIBs)

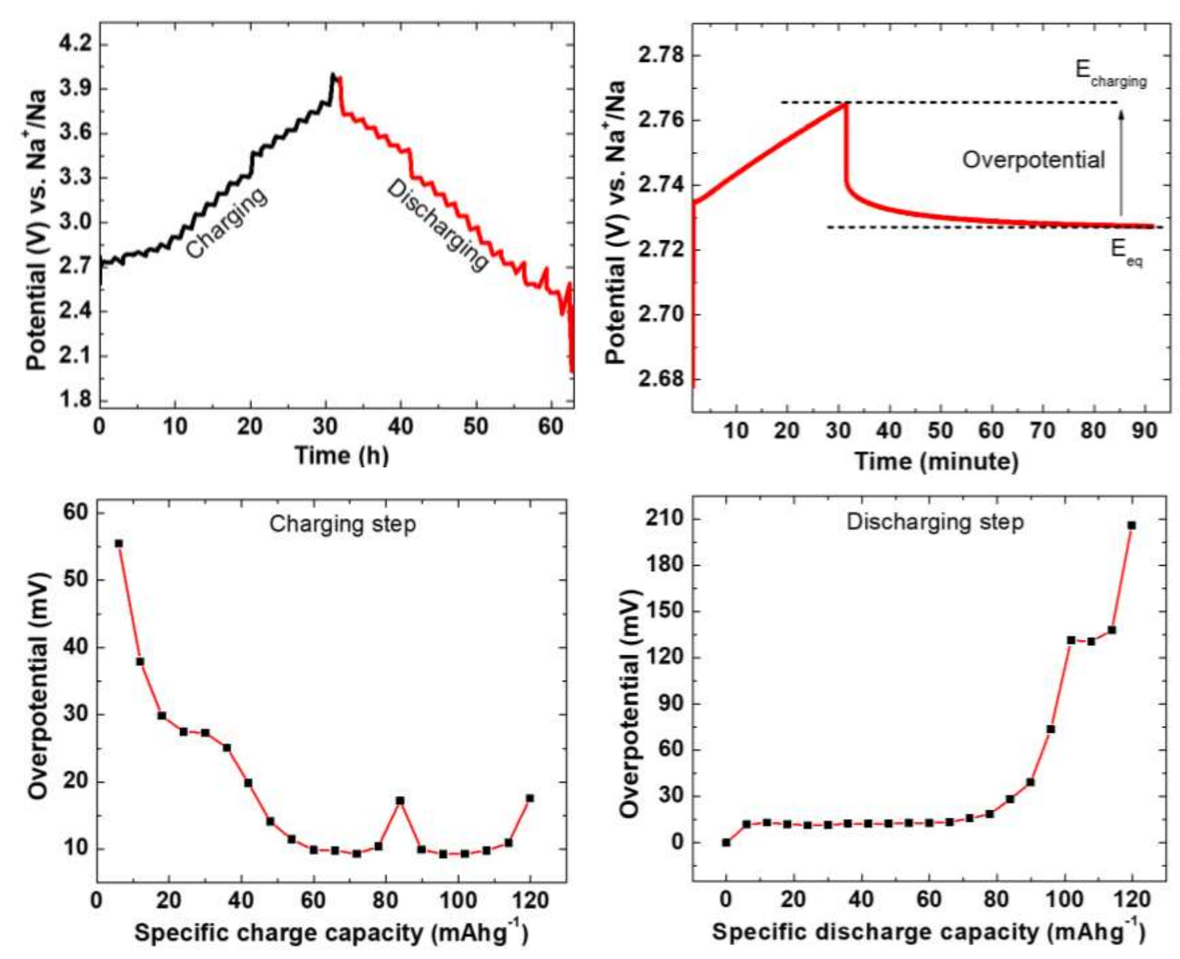
Major advantages:

- Abundance of sodium and low-cost precursors
- Stable supply chain
- Aluminum can be used as the current collector
- Propylene carbonate is a suitable solvent for SIBs
- Zero-voltage transport is possible

Key components:

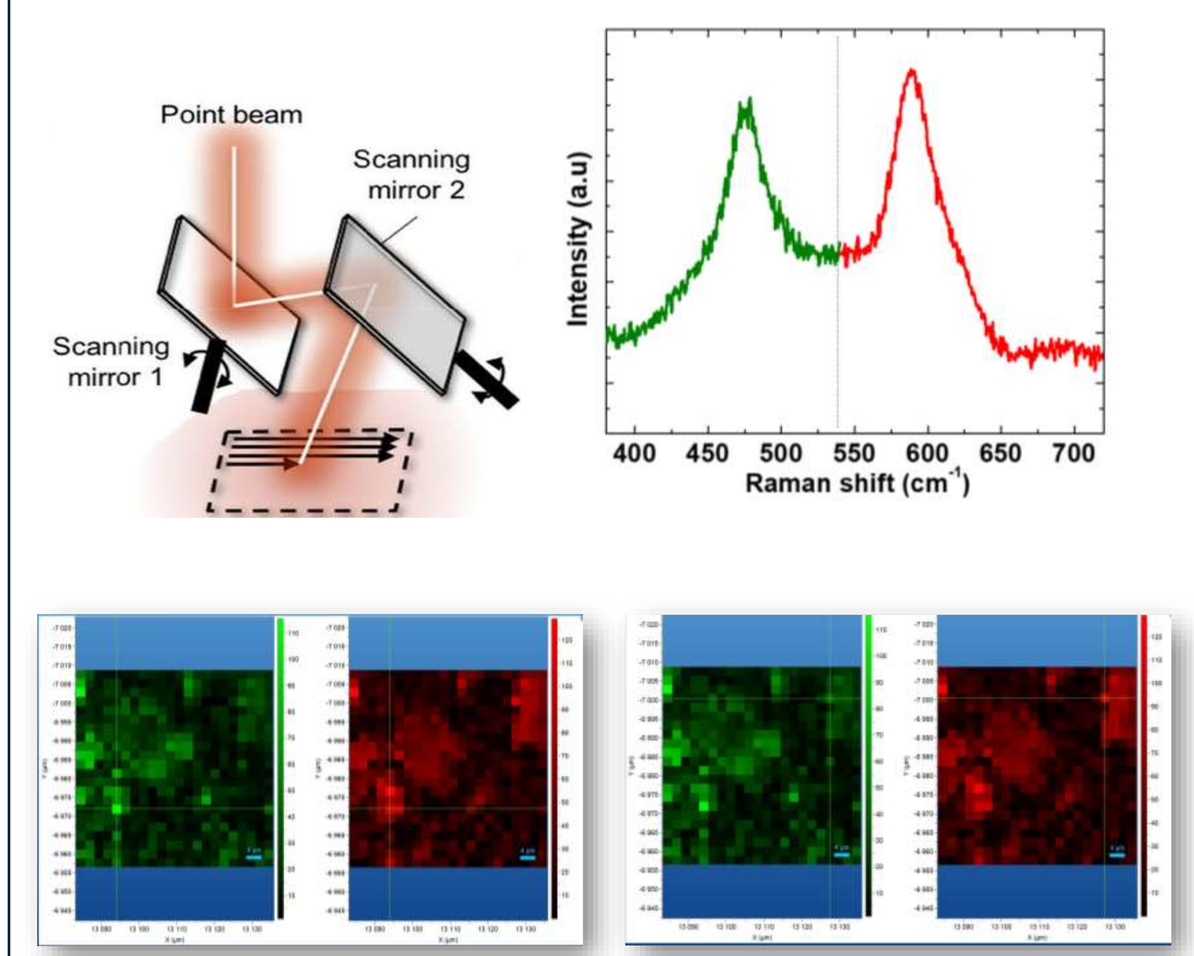
- Hard carbon is the most common anode material
- Layered transition metal oxides are ideal cathode due to their high capacity, voltage and tap density

Overpotential Analysis



Overpotential decreases significantly at higher states of charge

Raman Mapping

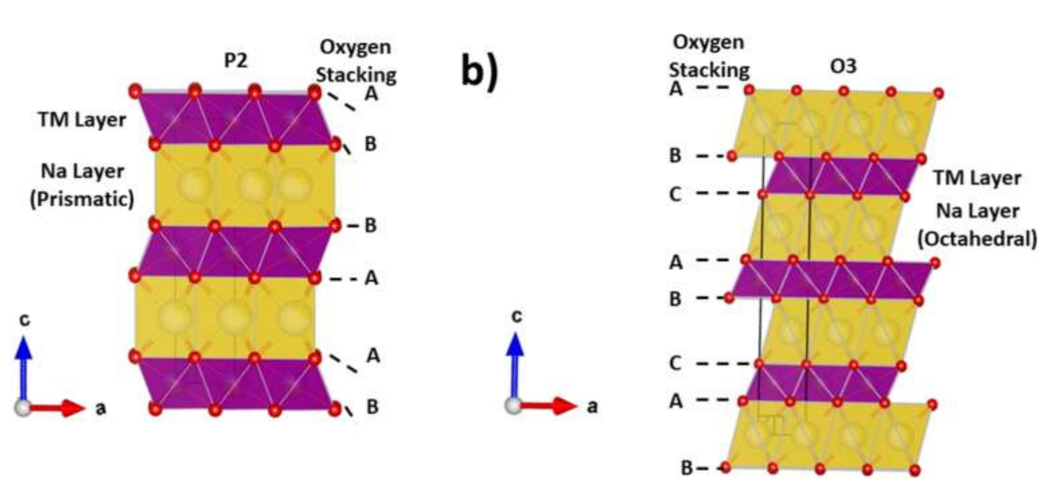


(Both peaks are strong: P2 phase)

(Only second peak is strong: O3 phase)

Raman mapping provides spatially resolved chemical and structural information

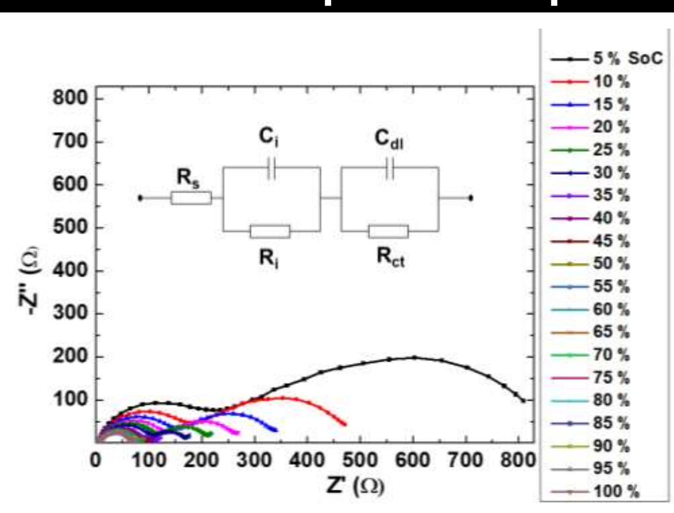
Layered Transition Metal Oxide Cathodes

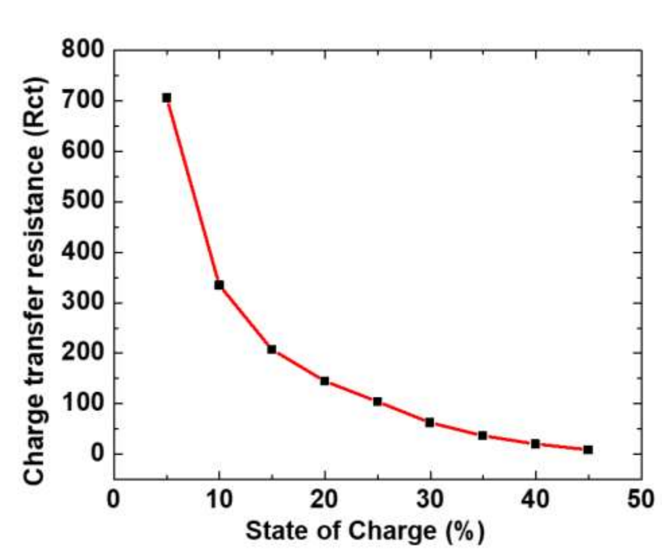


(Commun Mater 4, 2023, 1-7)

- LTMOs typically exist in P2 structure (Na occupying trigonal prismatic sites and ABBA stacking) and the O3 structure (Na occupying octahedral sites and ABCABC stacking)
- **O3 phase:** High sodium content (high capacity), low stability and poor rate performance
- **P2 phase:** Low sodium content (low capacity), high stability and rate capability

Electrochemical Impedance Spectroscopy

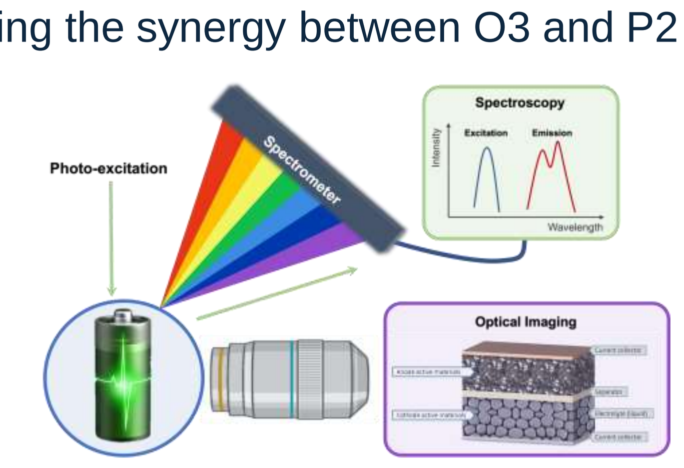




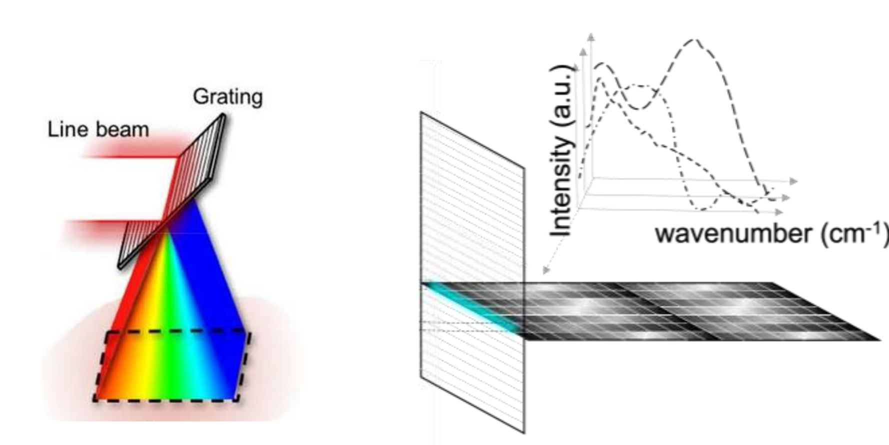
At lower states of charge, overpotential is dominated by the charge transfer kinetics

Future Work

- Operando optical imaging of particles and their cracking
- Mapping microstructural and compositional heterogeneity to understand the capacity fade mechanism
- Operando line-scan Raman spectroscopy during cycling
- Investigating the synergy between O3 and P2 phases

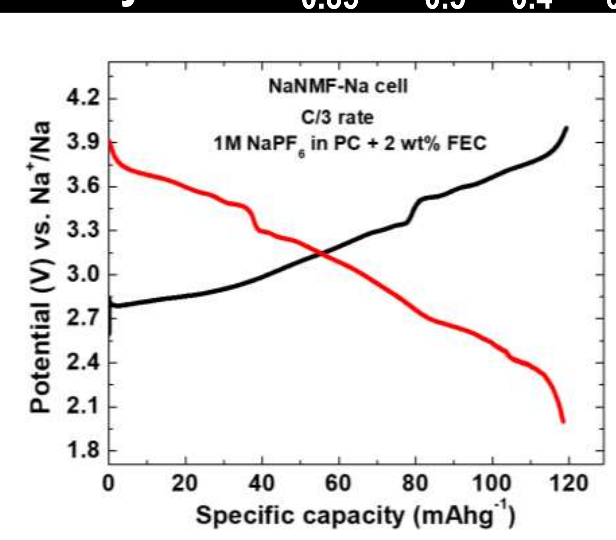


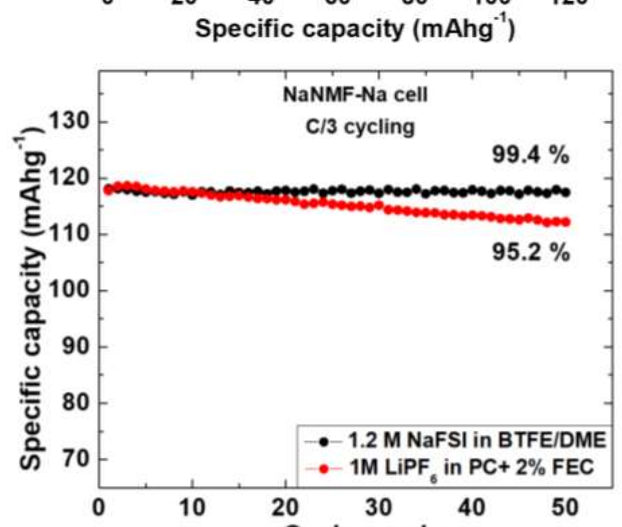
Optical imaging & spectroscopy



Operando Raman spectroscopy

P2-O3 Hybrid $Na_{0.85}Mn_{0.5}Ni_{0.4}Fe_{0.1}O_2$



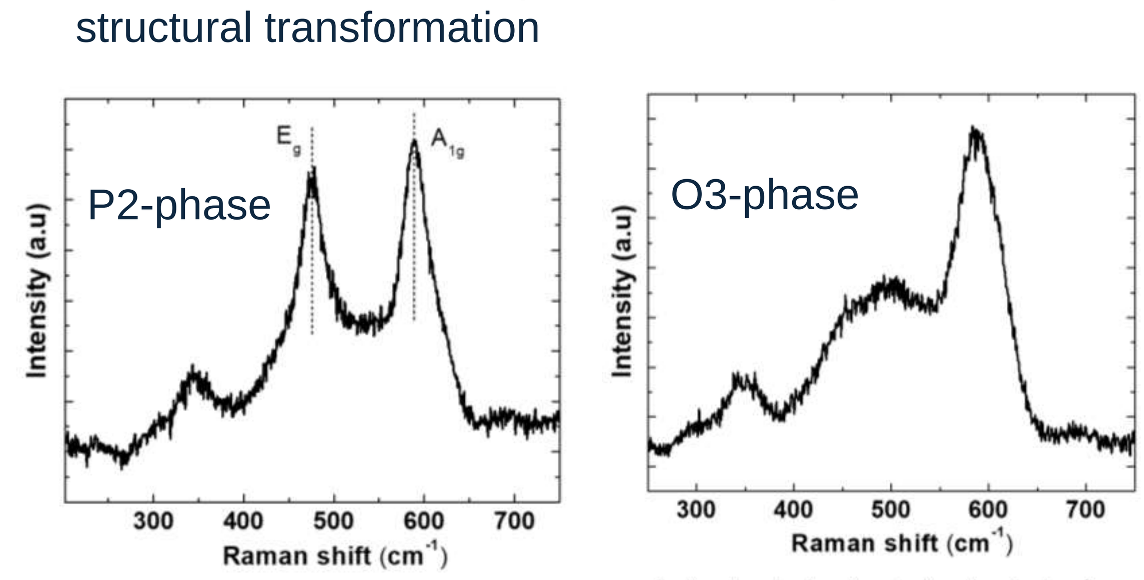


Specific capacity ~120 $mAhg^{-1}$ is obtained at C/3 rate

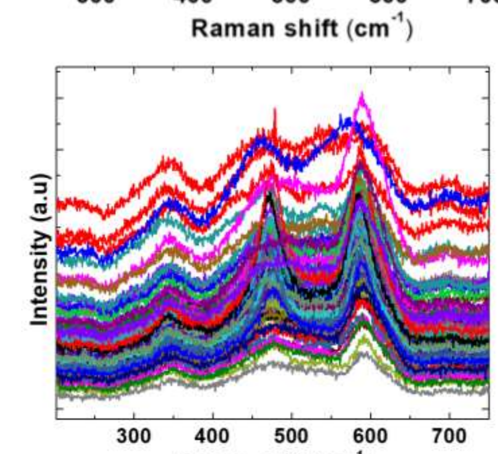
Excellent capacity retention of 99.4 % in 50 cycles

Raman Spectroscopy

- Versatile (solid, liquid or gas samples)
- Minimal sample preparation
- Non-destructive technique for evaluating chemical and structural transformation



(NaMNF Electrode)



Electrode shows a random distribution of two phases

Conclusions

- The P2-O3 hybrid $Na_{0.85}Mn_{0.5}Ni_{0.4}Fe_{0.1}O_2$ is a promising low-cost cathode material, exhibiting approximately 120 $mAhg^{-1}$ at C/3 rate in 2- 4 V
- The charge-discharge process involves phase transitions that lead to a gradual change in overpotential, which is primarily governed by R_c
- Raman mapping suggests a random distribution of O3 and P2 phases within the electrode
- Operando Raman spectroscopy, optical imaging, and XRD scanning are proposed for further investigation

Acknowledgements

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