

CALCIUM-PILLARED COBALT-FREE P3 SODIUM-ION CATHODE MATERIALS

A Structural and Electrochemical Investigation



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ABSTRACT

A series of **P3-NaMO₂** cathode materials (where M = Mn and Ni) were **doped with calcium** with the objective of improving cycle life by suppressing phase transitions during charging and discharging. This poster focuses on **electrochemical data** analysis from **coin cells** and **structural information** obtained from **powder X-ray diffraction (PXRD)**. Analysis of these data confirms that calcium pillaring was successful and enhances cycle life.

MOTIVATION

- Sodium-ion batteries** are an attractive alternative to lithium-ion batteries due to the **lower cost** and **greater abundance of sodium**, **reduced environmental** and **social issues** linked to the supply chain of battery materials and **safety advantages**.^[1] Developing a cathode material with high cyclability is a necessary step in making sodium-ion technology commercially viable.
- Advantages of a **P3 phase cathode** include ^[2] (Fig. 1) :
 - Higher discharge capacities** than P2 due to higher sodium content.
 - Better rate performance** than O3 due to large interlayer spacing.
- Sodium ions are removed from the cathode during charging, increasing the repulsion between the oxide layers, causing **phase transitions**. The resulting expansion and contraction of *c*-axis perpendicular to the layers can lead to stacking faults, increasing capacity fade and reducing cycle life. Locking the layers in place by **pillaring** is anticipated to suppress these phase transitions.
- Matsui et al. showed that P3-Na_xNi_{1/3}Mn_{1/3}Co_{1/3}O₂ doped with calcium had improved cycling performance due to a **suppressed phase transition** (O3' -O1).^[3] However, cobalt mining is associated with poor working conditions and contamination making it **desirable to develop a cobalt-free P3 cathode**.^[4]
- The materials studied here are calcium-doped **P3-Na(NiMn)O₂**.

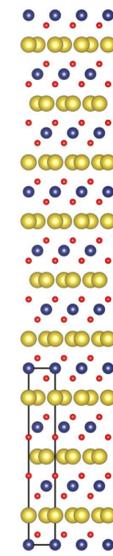


Fig. 1: P3 structure: Na = yellow, M = blue, O = red

METHODS

- Coin cell preparation:** cathode material synthesis (series labelled P3-Ca0 to P3-Ca6 with increasing calcium content), electrode synthesis (adding carbon black and binder) and cell assembly (using a hard carbon anode and NaPF₆ electrolyte).
- Full-cell cycling:** constant current between 1–4.2 V at a rate of C/5.
- PXRD and Rietveld analysis:** PXRD data collected for the cathode materials over a range of 10 – 70° using a Cu Kα₁ source. Rietveld analysis was carried out using TOPAS.

PXRD RESULTS

- Rietveld analysis** (Fig. 2) used to identify phases present within the cathode samples, calculate their weight and mole percentages and determine lattice parameters associated with the P3 phase.
- CaMnO₃ and CaNiMnO₄ present at higher Ca stoichiometries only (Fig. 3) – **Ca²⁺ intercalates into sodium layer** in P3 phase until reaching maximum, with further Ca²⁺ forming additional phases.

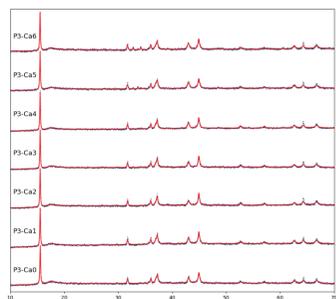


Fig. 2: PXRD data: black = observed data, red = calculated data

- Ca²⁺ entering the Na⁺ layer leads to greater attraction to oxide layers: *c* lattice parameter decreases (Fig. 4). After limit of Ca²⁺ substitution reached (P3-Ca4), Na⁺ removed from cathode but not replaced with Ca²⁺, which leads to increased repulsion between oxide layers: *c* lattice parameter increases.

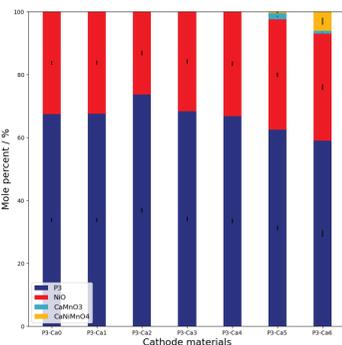


Fig. 3: Mole percentages of cathode materials calculated from results of Rietveld analysis. Error of 1 std deviation shown as black bar.

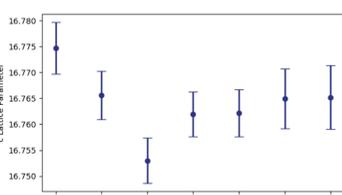


Fig. 4: *c* lattice parameter from Rietveld analysis. X is proportional to fraction of Ca. Error of 1 std deviation.

ELECTROCHEMICAL RESULTS

- All cathode materials with Ca successful pillared and had a **longer cycle life** than the P3 cathode without pillaring (Fig. 5). Increasing calcium content up to Ca2 linked to increased cycle life.
- P3-Ca2 best performing** (Fig. 5) – aligns with the lowest *c*-lattice parameter. Initial specific discharge capacity: **120 mAh/g** (Fig. 7).
- Peaks in a dQ/dV against voltage plot (Fig. 6) indicate a phase change. The peak between 4–4.2 V disappears for P3-Ca0 after 15 cycles, suggesting a change in mechanism which is detrimental to cycle life. Ca pillaring **maintains structural stability**. The 4–4.2 V peak is still present suggesting no mechanism change, leading to **stable cycling**.

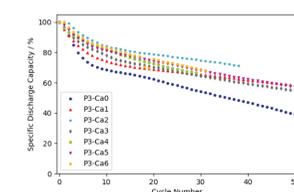


Fig. 5: Percentage of initial specific discharge capacity remaining against cycle number. At time of writing, some cathodes had not yet reached 50 cycles due to starting cycling at different times. Specific capacity was calculated considering the weight percentages from the Rietveld analysis.

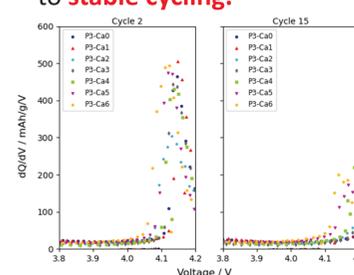


Fig. 6: dQ/dV against voltage for all the cathodes in the range 3.8–4.2 V after 2 and 15 cycles

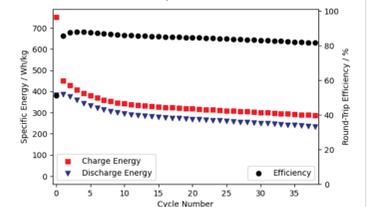
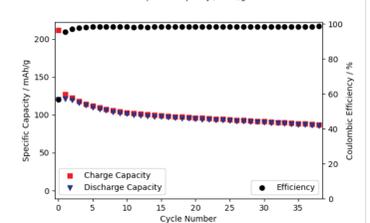
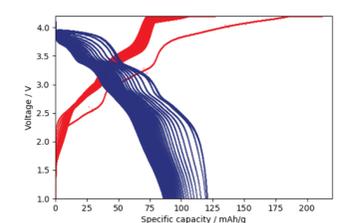


Fig. 7: Plots relating to the best performing cathode (P3-Ca2). Top: charge-discharge voltage profile. Middle: specific capacity against cycle number. Bottom: specific energy against cycle number. Specific capacities and energies were calculated considering the weight percentages from the Rietveld analysis.

CONCLUSIONS

- Electrochemical data indicates that pillaring **improves cycle life** in the P3 material investigated.
- Increasing calcium up to Ca2 improves cycling (with **P3-Ca2 performing the best**).
- P3-Ca4 is the **limit of calcium** entering the sodium layer before other phases form.

IMPACT/ NEXT STEPS

- Improve understanding of pillaring for this material:
 - Collect **synchrotron PXRD** data to **improve refinement** of lattice parameters and phases present.
 - Why is P3-Ca2 is the best?** Repeat cathode synthesis, consider sodium ordering.
 - Collect **in operando PXRD** to determine which **phase transition(s)** may be being impacted by pillaring in the P3 materials.
- Optimise cathode synthesis** method to **reduce the percentage of inactive phases**.
- Pillaring is a **universal technique** that could be employed on the best-in-class P3 cathode materials to **improve cycle life**.

REFERENCES

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INTERN BIO

Rebecca is entering the third year of her MChem Chemistry degree at the University of Oxford. She has recently been nominated for a Shimadzu prize for one of the 'best performances' in 2nd year Practical Chemistry. Rebecca is also interested in computational work within chemistry, particularly within inorganic and physical chemistry. She is aspiring to complete a PhD, enabling a career in research to contribute to finding practical solutions to environmental problems.



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