Exploring the Potential of Nb-doped $NaCrO_2$ Cathode Material

Characterisation via Raman Spectroscopy, X-Ray Diffraction and Electrochemistry

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Abstract

- $NaCrO_2$ is a promising layered oxide cathode material for sodium ion batteries but suffers from unwanted phase transitions and irreversible capacity loss upon cycling[1]. Literature[2,3] suggests that substituting the Cr^{3+} (r=0.62nm) with similarly-sized ions, such as Nb^{5+} (r=0.64 nm), could improve capacity retention by suppressing Cr^{3+} migration in $NaCrO_2$.
- $Na_{1-2x}Cr_{1-x}Nb_xO_2$ (x = 0, 0.02, 0.05) were synthesised; phases were identified using XRD. The electrochemical performance of the powders was tested on half cells against Na metal anodes. Investigation of changes in molecular structure and local chemical environments was performed using Raman spectroscopy[4].

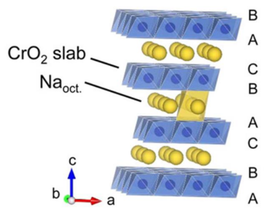


Figure 1: Schematic diagram of the crystal structure of $NaCrO_2$ [1]

Motivation

Major difficulties associated with lithium-ion batteries include the limited availability and consequent price increase of lithium. Sodium, however, has similar properties but is high in abundance and low in cost. Sodium-ion batteries are therefore a strong contender to fit this crisis[5].

Methods

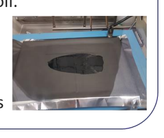
The undoped and Nb-doped powders were synthesized using solid state synthesis; they were provided by Ming He.

Composition

- Active cathode material ($Na_{1-2x}Cr_{1-x}Nb_xO_2$ (x = 0, 0.02, 0.05))
- Conductive additive (C_{65})
- Binder (PVDF)
- Mixed in ratio of 8:1:1

Drawdown

- The powders were dissolved in NMP and drawn down on a carbon coated Al foil.
- The dried slurries were further calendared under ambient conditions



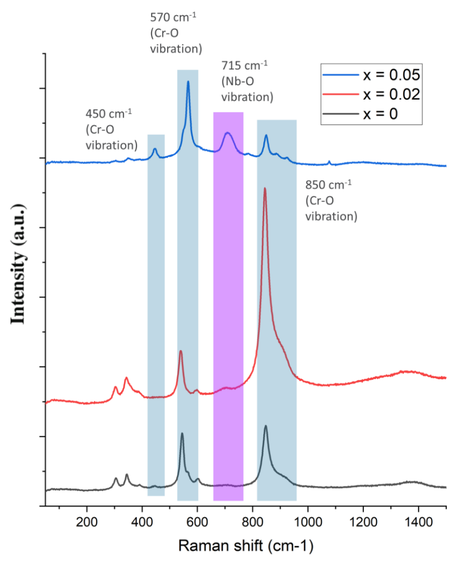
Cell Assembly

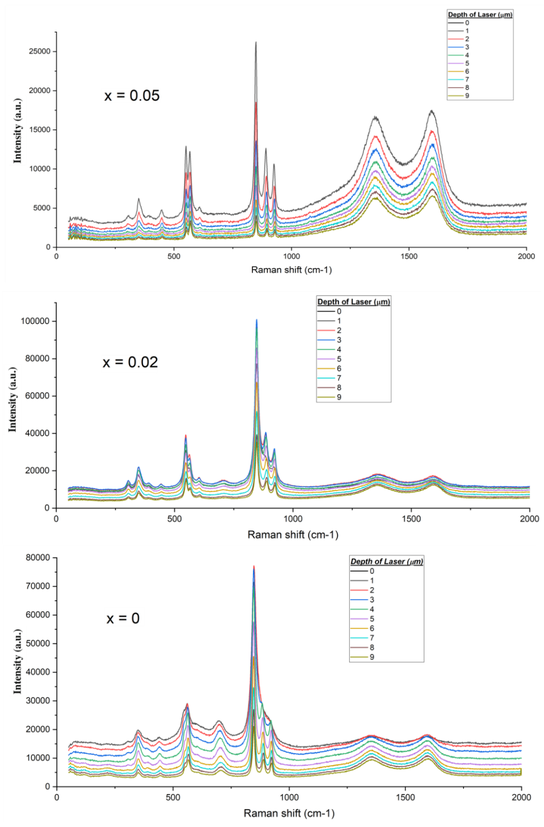
- Half coin cells were prepared with sodium metal anode and Kishida electrolyte ($NaPF_6$(EC:DEC)1:1 v)

Characterisation

- XRD
- Raman Spectroscopy
- Galvanostatic cycling

Results i) Raman Spectroscopy





(Above) Figure 2: Raman spectra of $Na_{1-2x}Cr_{1-x}Nb_xO_2$ powder (x = 0, 0.02, 0.05)

(Right) Figure 3: Depth-profiling Raman spectra of $Na_{1-2x}Cr_{1-x}Nb_xO_2$ calendared cathodes (x = 0, 0.02, 0.05)

ii) XRD

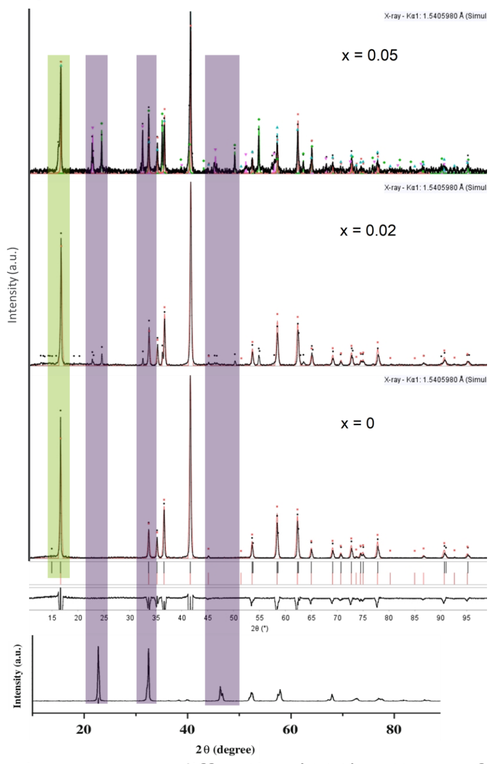


Figure 4: X-ray diffraction (XRD) patterns of $Na_{1-2x}Cr_{1-x}Nb_xO_2$ powder, and $NaNbO_3$. Provided by Ming He

iii) Electrochemical cycling

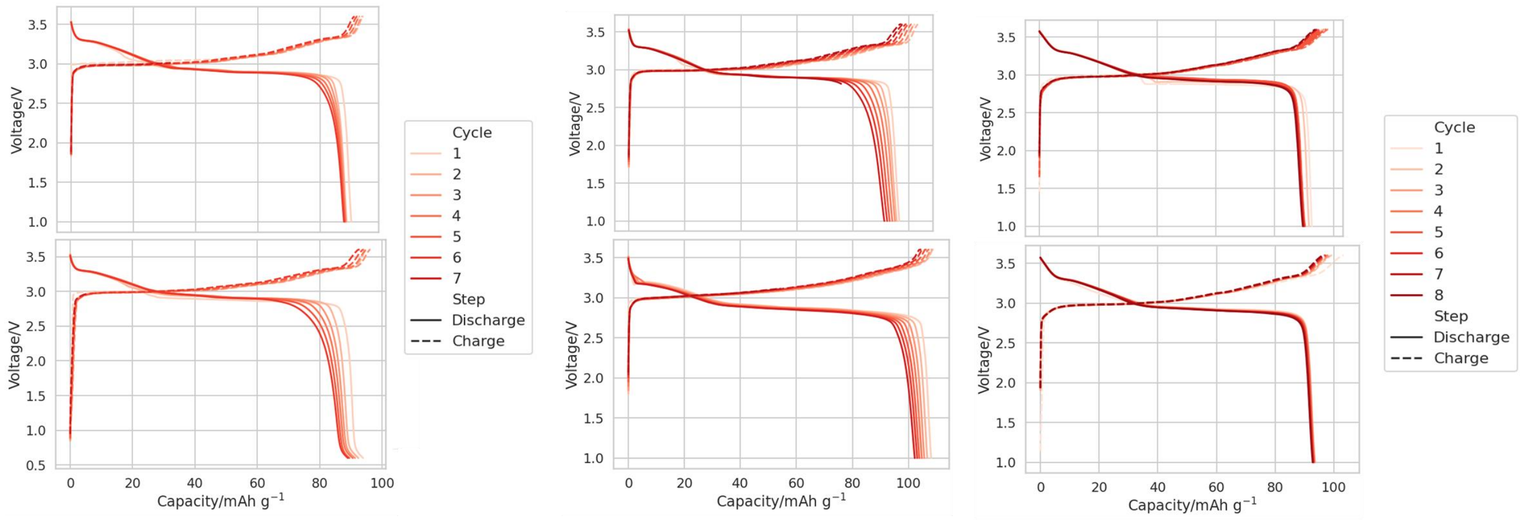


Figure 5: Galvanostatic Cycling (C-rate = 0.1) of $Na_{1-2x}Cr_{1-x}Nb_xO_2$ (x = 0, 0.02, 0.05, left to right; top is calendared electrode, bottom is uncalendared electrode).

Discussion & Conclusions

- **Raman**: As the depth of the Raman laser increases, the peak intensity decreases. There is little change in the shifts of the peaks, implying there is good mixing between constituents of the cathode. The peaks at 450 and 570 cm^{-1} correspond to the Cr–O vibrations in $NaCrO_2$[6]. The increase in the peak intensity at 715 cm^{-1} from x = 0 to x = 0.05 suggests this is a Nb-O vibration.
- **XRD:** As the doping amount of Nb increases, the peak intensity, which corresponds to a $NaNbO_3$ secondary phase, increases. $NaNbO_3$ is a stable perovskite and is electrochemically inactive. Indexing gives the layered O3 structure. As Nb^{5+} gradually replaces Cr^{3+}, the (003) peaks shift to lower angles as the Na^+ ion inter-layer separation increases[3].
- **Electrochemical cycling**: Although the voltage and capacity of $Na_{1-2x}Cr_{1-x}Nb_xO_2$ are lower than common lithium-ion cathodes, these properties are large enough to be a promising battery candidate in these regards.
- Generally, as the value of x increases, the capacity increases, implying niobium doping is effective on enhancing capacity. However, at x = 0.05, the prevalence of sodium niobate reduces the kinetics of sodium ion de/intercalation.
- Calendared electrodes also show a lower capacity than uncalendared electrodes. This may be due to over-calendaring, resulting in microscopic cracking of slurry. It could also be that the slurry was already uniform and by calendaring, the particles were dispersed unevenly. SEM could be used to test this.

Next steps

- These samples of $Na_{1-2x}Cr_{1-x}Nb_xO_2$ gave lower capacities compared to other studies of this cathode material[3]. Nano-mill the powders to reduce particle size and improve carbon coating, and study how that affects the electrochemical performance.
- Nano-mill $Na_{0.9}Cr_{0.95}Nb_{0.5}O_2$ (x=0.05) to disperse the $NaNbO_3$ phase and enhance capacity.
- Perform *in operando* Raman spectroscopy on the cell, giving a better insight than depth-profiling into the structural changes of de/intercalation. (This technique couldn't be established in time for this internship, but it's something that will be explored in the future).

References

- [1] K. Kubota et al., *J. Phys. Chem. C,* 2015, **119**, 166–175
- [2] K. Xi et al., *Nano Energy*, 2020, **67**, 104215
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- [4] R. Heintz, *Application note series on analysing cathodes, anodes and electrodes with Raman spectroscopy*, 2022, Thermo Fisher Scientific Inc., https://www.thermofisher.com/uk/en/home/global/forms/industrial/raman-spectroscopy-improving-lithium-ion-batteries-ebook.html
- [5] N. Tapia-Ruiz et al., *J. Phys. Energy*, 2021, **3**, 031503
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Intern Bio

Adam Kavanagh is studying a Master's degree in Chemistry at the University of Oxford. He's interested in the synthesis of new solid-state compounds and their applications to new technologies and will be undertaking a project with the Simon Clarke Group on the soft chemistries of layered oxide chalcogenides. He's aspiring to further his study of solid-state chemistry either academically or through industry.

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