

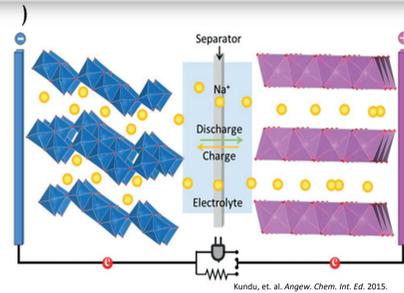
Relating Structure and Dynamics to Performance of Na-ion Battery Cathodes

ECCOMOBILITY (ORF) & HEVPD&D CREATE

Department of Chemistry and Chemical Biology, Faculty of Science, McMaster University
Chelsey Hurst, Kristopher J. Harris, and Gillian R. Goward

An Introduction to Batteries

- Growing energy demands necessitate efficient energy storage devices
- Batteries are an electrochemical energy storage technology
- Applications for batteries are diverse:
 - Portable technology
 - Grid energy storage
 - Electric vehicles

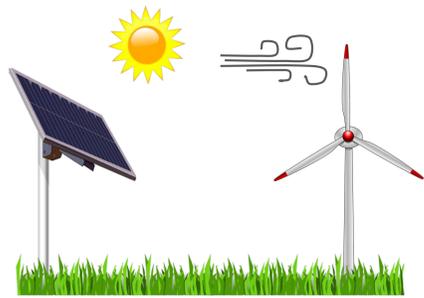


- Much of a battery's performance depends on the characteristics of the **cathode** material
- Polyanionic SIB cathodes are made with easily obtainable compounds and have structural stability
- A fundamental understanding of the mechanism of Na ion movement within SIBs will facilitate more strategic and efficient SIB research and development

- Lithium ion batteries (LIBs) are the most common battery technology in use today because of their ability to produce high energy densities (ideal for electric vehicle applications)
- Because of concerns regarding the limited Li supply, and the use of expensive metals in LIBs, researchers are investigating **sodium ion batteries (SIBs)** as a low energy density but cost effective alternative

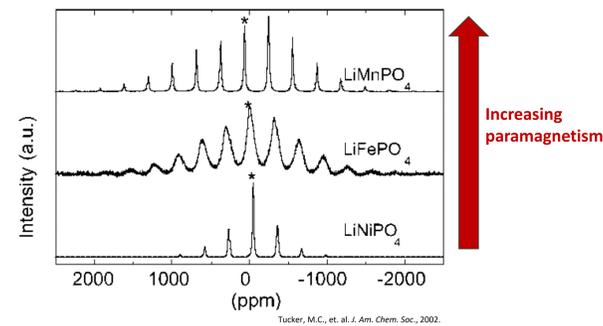
Research questions

- Are the capacity limitations in SIB cathode materials inherent to the material or due to how the material is being processed?
- What are the mechanisms of ion mobility within SIB cathodes?



Seeing Ions Through ssNMR

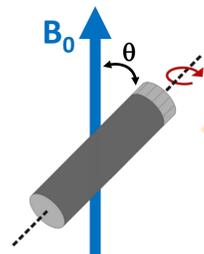
- Solid-state nuclear magnetic resonance (ssNMR) spectroscopy is an ideal technique for analyzing cathode materials because it can distinguish between unique ion sites in the structure
- Batteries operate because of ion movement, and NMR can "see" ions
- By looking at the molecular level it is possible to gain information that cannot be gleaned from examining the bulk material
- Various ssNMR techniques can probe the relationship between Na-ion dynamics and structural evolution throughout the battery cycling process



- Paramagnetic effects from transition metals in cathodes cause peak broadening and spinning sidebands (from interactions of unpaired electron spins with the external magnetic field)
- The quadrupole line-shape contributes additional peak broadening
- Various ssNMR techniques can be employed to resolve broadened peaks including fast MAS and doing experiments in higher fields

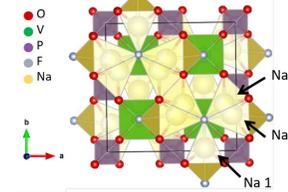
- Unlike in solution NMR, dipolar coupling (through-space interactions between molecules) cause spectral broadening
- Spinning solid samples very fast and at the "magic" angle ($\theta = 54.74^\circ$) effectively eliminates dipolar coupling
- This technique is called magic angle spinning (MAS)

$$H_{IS} = -d(3\cos^2\theta - 1)I_z S_z, \quad d = \left(\frac{\mu_0}{4\pi}\right) \frac{\hbar\gamma_I\gamma_S}{r_{IS}^3}$$

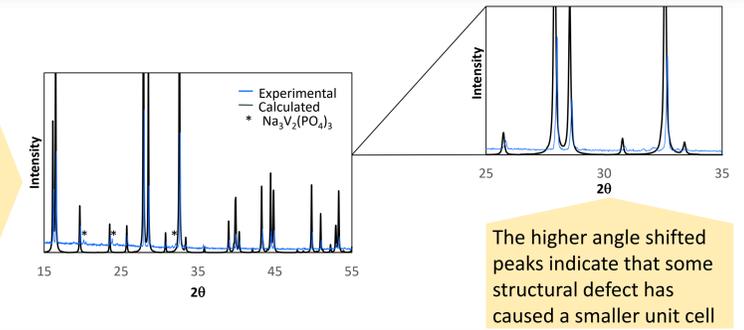


NVPF Cathode

- NVPF ($\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$) is a polyanionic SIB cathode with a power density comparable to that of LIBs (470 Wh/kg)



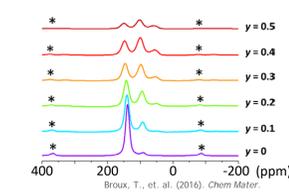
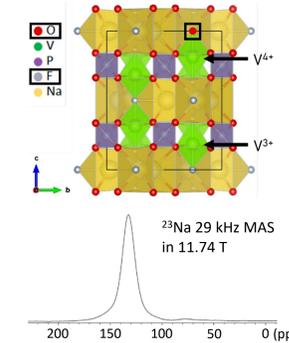
Shown is the diffraction pattern of synthesized NVPF compared to the calculated pattern. NVPF was synthesized using a high temperature solid-state method.



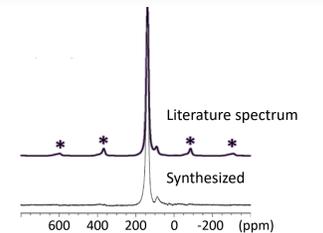
The higher angle shifted peaks indicate that some structural defect has caused a smaller unit cell

NVPF Oxygen-substitution

- F sites in NVPF can be substituted by O in the structure (Broux, et al., 2016)
- $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_{3-y}\text{O}_y$
- These oxygen defects improve the battery's electrochemical performance
- Oxygen substitution increases electronic conductivity and lowers the activation energy



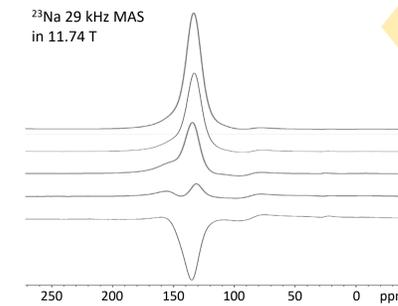
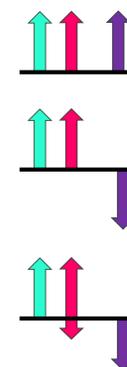
A series of ^{23}Na ssNMR spectra for compounds with varying y values in $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_{3-y}\text{O}_y$



Synthesized NVPF corresponds with the $y=0$ case \therefore there is a negligible amount of O-substitution in the structure

Selective Inversion NMR

- **Selective-inversion (SI)** is an NMR technique that can quantify Na-ion dynamics in SIB cathodes
- One peak is inverted by applying a narrow high power pulse. If ion exchange is present some of the negative magnetization is transferred to neighboring peaks as the inverted peak returns to equilibrium (mixing time)
- Because exchange increases with temperature, **rate constants for ion exchange** can be calculated by repeating the experiment with varying mixing times over a range temperatures



SI experiment of NVPF at different mixing times (2 us - 15 ms)

Challenges to SI

- Three Na sites hidden under one large peak
- The large peak in NVPF has a very short relaxation time. The mixing time must, therefore, be even shorter to be quantifiable