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

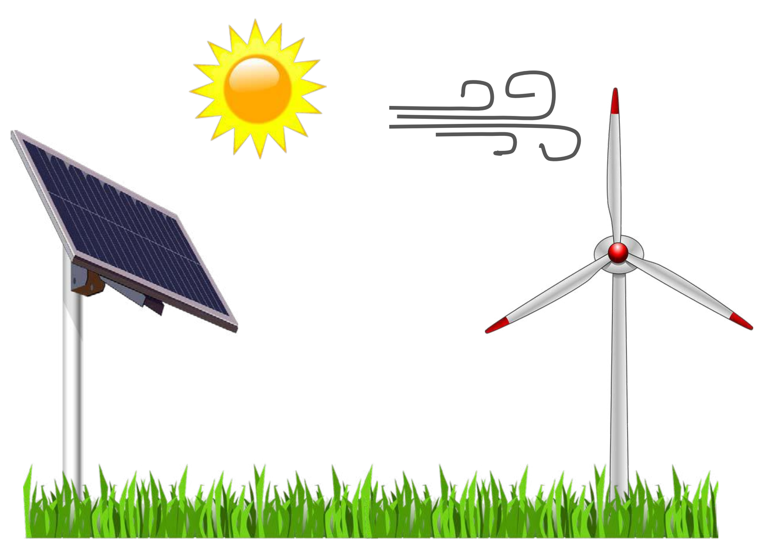
EECOMOBILITY (ORF) & HEVPD&D CREATE

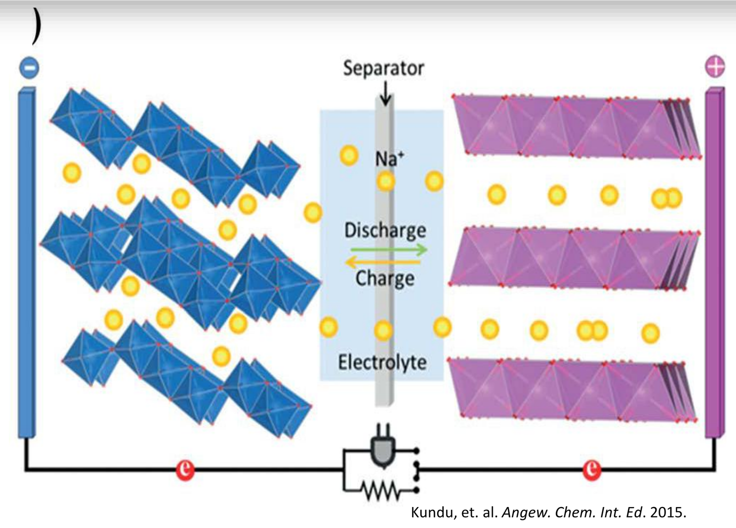
Department of Chemistry and Chemical Biology, Faculty of Science, McMaster University

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





Kundu, et. al. Angew. Chem. Int. Ed. 2015.

- 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

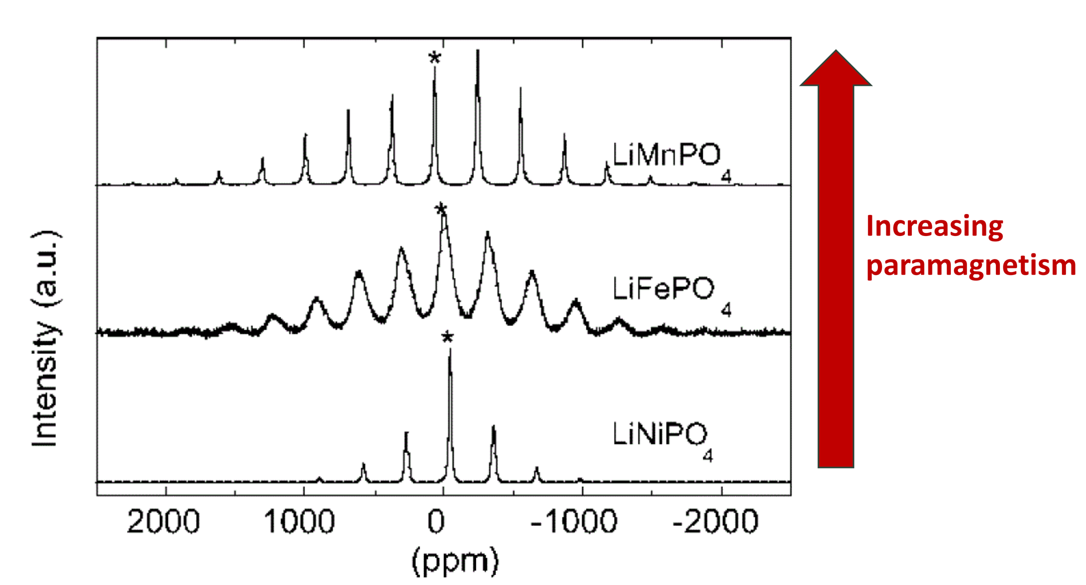
- Much of a battery's performance depends on the characteristics of the **cathode** material
- Polyanionic SIB cathodes are made with easily obtainable compounds and have structural stability
- A fundamental understanding of the mechanism of Na ion movement within SIBs will facilitate more strategic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

Research questions

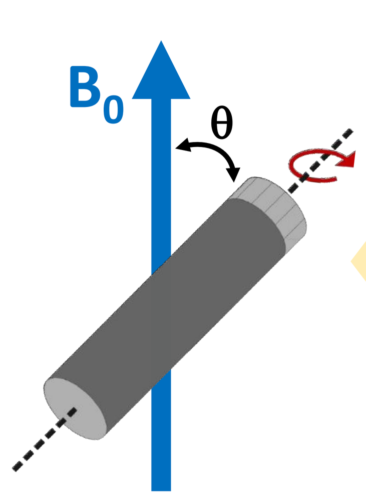
- Are the capacity limitations in SIB cathode materials inherent to the material or due to how the material is being processed?
- What are the mechanisms of ion mobilityt within SIB cathodes?

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



Tucker, M.C., et. al. J. Am. Chem. Soc., 2002.



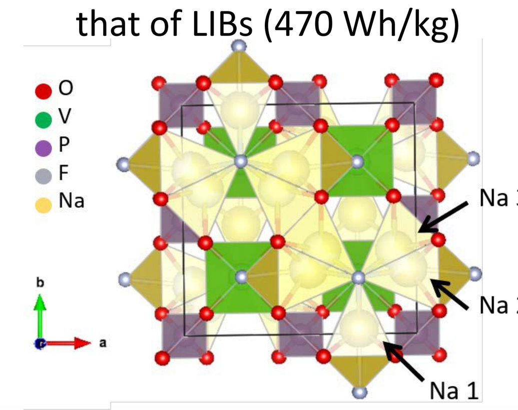
- Unlike in solution NMR, dipolar coupling (through-space interactions between molecules) cause spectral broadening
- Spinning solid samples very fast and at the "magic" angle (θ = 54.74°) effectively eliminates dipolar coupling
- This technique is called magic angle spinning (MAS)

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

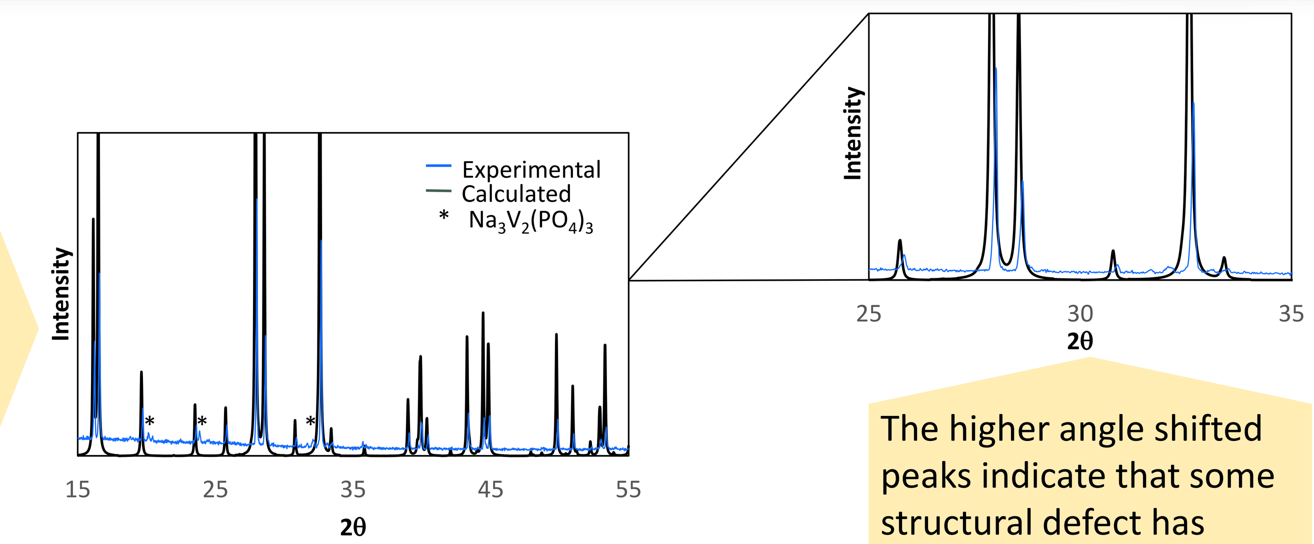
- Paramagnetic effects from transition metals in cathodes cause peak broadening and spinning sidebands (from interactions of unpaired electron spins with the external magnetic field)
- The quadrupole line-shape contributes additional peak broadening
- Various ssNMR techniques can be employed to resolve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

NVPF Cathode

- NVPF ($Na_3V_2(PO_4)_2F_3$) is a polyanionic SIB cathode with a power density comparable to that of LIBs (470 Wh/kg)



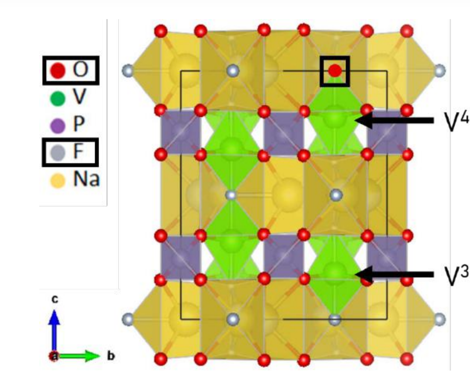
Shown is the diffraction pattern of synthesized NVPF compared to the calculated pattern. NVPF was synthesized using a high temperature solid-state method.

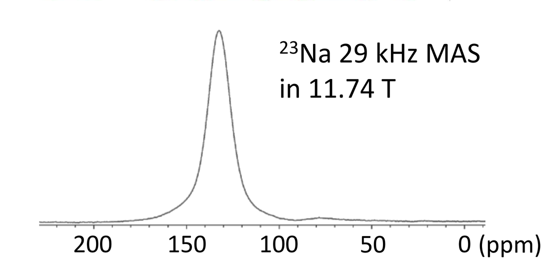


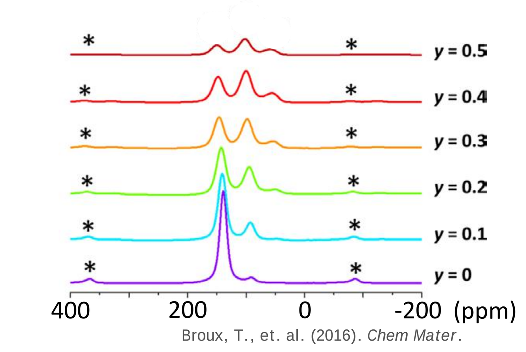
The higher angle shifted peaks indicate that some structural defect has caused a smaller unit cell

NVPF Oxygen-substitution

- F sites in NVPF can be substituted by O in the structure (Broux, et. al., 2016)
- $Na_3V_2(PO_4)_2F_{3-y}O_y$
- These oxygen defects improve the battery's electrochemical performance
- Oxygen substitution increases electronic conductivity and lowers the activation energy

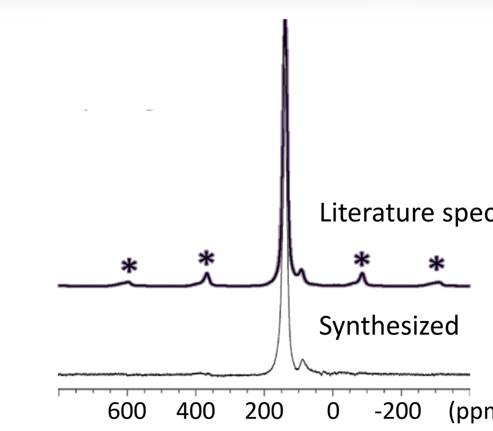






Broux, T., et. al. (2016). Chem Mater.

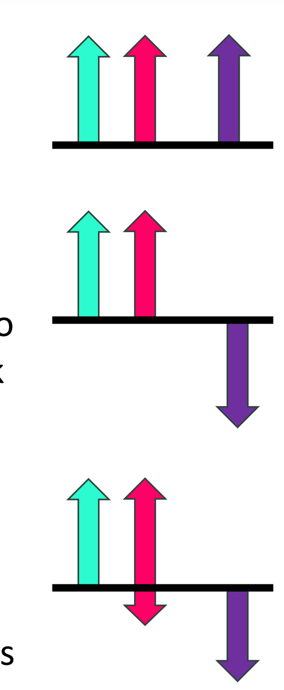
A series of ^{23}Na ssNMR spectra for compounds with varying y values in $Na_3V_2(PO_4)_2F_{3-y}O_y$

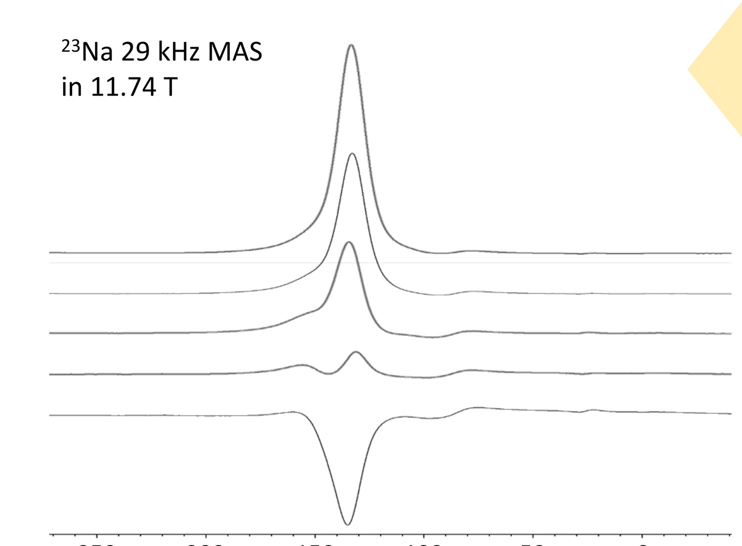


Synthesized NVPF corresponds with the y=0 case ∴ there is a negligible amount of O-substitution in the structure

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

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