Advanced experimental and theoretical techniques for the investigation of lithium- and sodium-ion batteries

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Outline

• Electrical energy storage in the U.S.

• Overview of rechargeable batteries.

• Solid–state nuclear magnetic resonance (ssNMR) applied to battery research.

• Case studies:
  ▪ Increasing the structural stability of sodium transition metal oxide (Na$_x$MO$_2$) cathodes through transition metal substitution.
  ▪ Investigating short–range order and redox processes in high energy density cation–disordered Li$_{1+x}$M$_{1-x}$O$_2$ cathodes.
Electrical energy storage in the U.S. (as of June 2018)

- The U.S. has the infrastructure to generate up to 1,082 GW of electricity, but it can only store up to 25.2 GW.

- Only 2.5% of delivered electric power in the U.S. is cycled through a storage facility.
  - For comparison: Europe → 10% and Japan → 15%.

- California leads the U.S. in terms of energy storage, with 220 grid-connected energy storage projects (4.2 GW).

Daily Energy Storage and Load Leveling

What is the best type of rechargeable battery?

• No rechargeable battery combines: small size, light weight, high energy density, long cycle life, safety (low toxicity and low flammability) and low cost.

Different battery types serve different applications.

Electric Vehicles
- Light weight
- High gravimetric energy density (Wh/kg)
- Fast charge
- Safe
- Li-ion, NiMH

Portable electronics
- Small size
- High volumetric energy density (Wh/L)
- Safe
- Li-ion, Li-ion polymer, NiMH

Grid storage
- Low cost per energy unit ($/Wh)
- Long cycle life
- Ni-Cd, Li-ion, Pb-acid, redox flow, molten salt (Na–S)
- In development: Na–, Mg–, K–ion.

Defense
- Very high gravimetric energy density
- High power
- Preferably domestic production
- Li-ion, Ag–Zn
Working principles of an intercalation-type rechargeable battery

- Intercalation Li–ion batteries are based on reversible Li$^+$ extraction/insertion at the anode and cathode, with essential retention of the crystal structure of the electrode material.

- Energy density depends on the amount of charge that can be stored in the electrodes (capacity) and the potential difference between the anode and the cathode.

Diagram adapted from Goodenough, Park, JACS 135(4) (2013)
Why is ssNMR a powerful tool for battery research?

- Shift = chemical environment of species under observation (e.g. $^7$Li).
- NMR is quantitative and site-specific.
- Broadening can give insights into the kinetics of ion motion and structural disorder.
- Study electrode samples at different stages of charge/discharge to monitor structural changes and redox processes.

Coin cell for battery testing

Electrode sample composed of nuclear spins = tiny bar magnets.

NMR experiment consists in manipulating these spins in an external magnetic field ($B_0$).

ssNMR of paramagnetic (battery) materials

Electrode materials often contain paramagnetic transition metal species (e.g. Ni, Co, Mn), e.g., the NaMnO$_2$ cathode.

Strong paramagnetic interactions lead to broad signals & large chemical shifts.

Charge : NaMn$^{3+}$O$_2$ → Na$_{1-x}$Mn$^{3+}_{1-x}$Mn$^{4+}_x$O$_2$ + xNa$^+$.

- Magic angle spinning (MAS) of sample during signal acquisition.

- Go to low magnetic fields:

  $^{23}$Na spin echo
  60 kHz MAS
  $B_0 = 23.5$ T

  $^{23}$Na spin echo
  60 kHz MAS
  $B_0 = 4.7$ T
First principles calculations of NMR parameters assist the interpretation of paramagnetic NMR spectra

Paramagnetic shift: \[ \delta = \frac{10^6 \mu_0 \mu_B \mu_N g_e g_N}{3 \hbar \omega_0} \Phi |\psi^{\alpha-\beta}(r)|^2 \]

Unpaired spin density at nuclear position can be computed.

- Unpaired spin density is transferred from paramagnetic metal (Mn) to the NMR nucleus (Na) via Mn–O–Na spin transfer pathways (P_i).
- Chemical shift contributions from individual Mn–O–Na transfer pathways (P_i) are additive.

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  ▪ Investigating short-range order and redox processes in high energy density cation-disordered Li$_{1+x}$M$_{1-x}$O$_2$ cathodes.
Why Na-ion batteries?

- Sodium is far more abundant in Earth’s crust and more widely distributed than lithium.

<table>
<thead>
<tr>
<th></th>
<th>Na</th>
<th>Li</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ratio of reserves</td>
<td>1000</td>
<td>1</td>
</tr>
<tr>
<td>Price (for carbonates) / USD.ton⁻¹</td>
<td>150</td>
<td>5000</td>
</tr>
</tbody>
</table>

- Na–ion batteries offer economic and environmental advantages in comparison with Li–ion batteries.

Sodium transition metal oxide (Na$_x$MO$_2$) cathodes

- Na$_x$MO$_2$ cathodes are competitive with current Li-ion commercial cathodes in terms of volumetric energy density.

\[ \text{Energy density} = \text{Potential} \times \text{Capacity} \]

Structural transformations in P2-type $\text{Na}_x\text{MO}_2$ cathodes

The P2 layered structure

Poorly reversible structural transformations occur at low Na contents (high voltage) and lead to lower Na$^+$ ion conductivity.

- High performance $\text{Na}_x\text{MO}_2$ cathodes require strategies to mitigate phase transitions during electrochemical cycling.
TM substitution enhances the stability of the P2 structure

- Mn substitution leads to an extension of the range of Na contents over which the P2 structure is stable.

Effects of Li substitution on the stability of the P2-Na$_{2/3}$Ni$_{1/3}$Mn$_{2/3}$O$_2$ cathode

Hypotheses:
- Li substitution on Ni sites in the transition metal lattice.
- Li immobile during cycling: structural role, electrochemically inactive.
Impact of Li substitution on the electrochemistry


**Electrochemical profile:** Voltage vs. Capacity plot.

**Capacity** proportional to amount of Na\(^+\) that can be extracted and reinserted.

Na extraction = charge
Na reinsertion = discharge

P2–Na\(_{2/3}\)Ni\(_{1/3}\)Mn\(_{2/3}\)O\(_2\)

P2 to O2 (XRD)
Impact of Li substitution on the electrochemistry

No phase transformation up to 4.4 V (XRD)

Electrochemical profile: Voltage vs. Capacity plot.

Capacity proportional to amount of Na\(^+\) that can be extracted and reinserted.

Na extraction = charge
Na reinsertion = discharge

\[
\text{P2–Na}_{2/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2
\]
\[
\text{P2–Na}_{0.8}\text{Li}_{0.12}\text{Ni}_{0.22}\text{Mn}_{0.66}\text{O}_2
\]
Impact of Li substitution on the electrochemistry

No phase transformation up to 4.4 V (XRD)

Li doping leads to:
• fewer electronic and structural processes on (dis)charge,
• No P2 to O2 phase transition up to 4.4 V,
• 0.35 remaining Na at the end of charge.

Impact of Li substitution on the electrochemistry

No phase transformation up to 4.4 V (XRD)

\[ V_{\text{Na}} \]

\[ Na_{\text{extraction}} \]

\[ Na_{\text{reinsertion}} \]

First cycle

\[ \text{Capacity (mAh.g}^{-1}\text{)} \]

\[ V_{\text{Na}} \]

\[ \text{P}2-\text{Na}_{2/3}\text{Ni}_{1/3}\text{Mn}_{2/3}\text{O}_2 \]

\[ \text{P}2-\text{Na}_{0.8}\text{Li}_{0.12}\text{Ni}_{0.22}\text{Mn}_{0.66}\text{O}_2 \]

Li doping leads to:
- fewer electronic and structural processes on (dis)charge,
- No P2 to O2 phase transition up to 4.4 V,
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Where does Li go?

As-synthesized Li-substituted phase

\[ ^7\text{Li} \text{ pj-MATPASS} \]
\[ 60 \text{ kHz MAS} \]
\[ B_0 = 4.7 \text{ T} \]

Li in MO\(_2\) layers

\[ \text{Li environments not native to P2/O2 structures} \]

Li in interlayer space (O-type stacking faults)

Computed shift within the 358–549 ppm range.

<table>
<thead>
<tr>
<th>Coordination</th>
<th>Computed (\delta) / ppm</th>
<th>Expt. (\delta) / ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 Mn, 0 Ni</td>
<td>1572-1812</td>
<td>1704</td>
</tr>
<tr>
<td>5 Mn, 1 Ni</td>
<td>1273-1486</td>
<td>1465</td>
</tr>
<tr>
<td>4 Mn, 2 Ni</td>
<td>974-1160</td>
<td>1150</td>
</tr>
</tbody>
</table>

\[ \bullet \text{Li NMR reveals that Li is not only found in the TM layers, but also in the interlayer space.} \]

Tracking Li during charge and discharge

Na reinsertion

Na extraction

<table>
<thead>
<tr>
<th>Li proportion (%)</th>
<th>Pristine</th>
<th>4.1 V ch</th>
<th>4.4 V ch</th>
<th>2 V disch</th>
<th>after 5 cycles</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMO₂ layer</td>
<td>85</td>
<td>68</td>
<td>5</td>
<td>67</td>
<td>63</td>
</tr>
<tr>
<td>Interlayer</td>
<td>15</td>
<td>4</td>
<td>38</td>
<td>5</td>
<td>8</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
<td>72</td>
<td>43</td>
<td>72</td>
<td>71</td>
</tr>
</tbody>
</table>

\( x_{Na} = 0.78 \)
\( x_{Na} = 0.35 \)
\( x_{Na} = 0.45 \)
\( x_{Na} = 0.80 \)

\(^{\uparrow}\) Li environments not native to P₂/O₂ structures

Preventing high voltage transitions in P2-Na$_{2/3}$MnO$_2$ via Mg doping

\[ \text{Na}_x\text{MnO}_2 \]

\[ \text{Na}_x\text{Mn}_{1-y}\text{M}_y\text{O}_2 \]

Study II

P2 phase stability range increased

Effect of Mg substitution on the electrochemistry

Electrochemical profiles for P2-Na$_{2/3}$MnO$_2$, 5% Mg-doped, 10% Mg-doped

- Mg doping leads to fewer electronic and structural processes on (dis)charge.

Rate performance of 5% Mg-doped compound

- 5% Mg doped compound exhibits an exceptional rate performance.

Rate performance is linked to intricate structural transformations occurring at low and at high potentials

- Follow structural transformations during discharge with X-ray diffraction and $^{23}$Na NMR @ 4.7 T.

Two phases, $x=1$ phase rate-limiting

Rate performance is linked to intricate structural transformations occurring at low and at high potentials

- Follow structural transformations during discharge with X-ray diffraction and $^{23}$Na NMR @ 4.7 T.

Rate performance is linked to intricate structural transformations occurring at low and at high potentials

- Follow structural transformations during discharge with X-ray diffraction and $^{23}\text{Na}$ NMR @ 4.7 T.

Rate performance is linked to intricate structural transformations occurring at low and at high potentials

- Follow structural transformations during discharge with X-ray diffraction and $^{23}\text{Na}$ NMR @ 4.7 T.

- The proportion of high voltage OP4 phase is reduced upon Mg doping.

- Highly distorted P2' ($Cmcm$) phase formed at end of discharge ($x=1$) leads to a poorer rate performance for the $x = 0.1$ compound.
Improving the stability of the P2 structure by doping on the TM site: Summary

- TM substitution with lower valent Li$^+$ and Mg$^{2+}$ ions leads to a greater Na content at high voltage and to a more stable P2 phase: transitions to OP4 or O2 phases are delayed to higher potentials.

- In turn, a more stable P2 phase results in tremendous enhancements in the electrochemical performance, both in terms of rate performance and long-term capacity retention.

- Delicate balance between the amount of dopant species and phase stability at low potentials (end of discharge) and high potentials (end of charge).

- Li$^+$ is not as stable as Mg$^{2+}$ in the TM layers and can migrate to the interlayer space or it can be extracted from the cathode material during charge.
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Moving away from conventional layered oxide cathodes: disorder and fluorination

- Layered LiMO$_2$
  - Large volume changes on Li extraction/insertion.
  - No F substitution possible.

- Cation-disordered Li$_{1+x}$M$_{1-x}$O$_2$
  - Negligible volume changes.
  - F substitutes O in the bulk.
High energy density at a lower cost!

Energy density (Wh/kg)

Can reach ~1000 Wh/kg of energy density!

Enable the use of cheap and abundant metals.

Cation-disordered $\text{Li}_{1+x}\text{M}_{1-x}\text{O}_2$

The Li$_{1.15}$Ni$_{0.45}$Ti$_{0.3}$Mo$_{0.1}$O$_{1.85}$F$_{0.15}$ (LNF15) cathode

15% Li excess for Li percolation

$\text{d}^0$ metals stabilizing the disordered structure

redox active (Ni$^{2+/4+}$)

The study of these materials is challenging:

- Cation disorder results in a range of Ni environments with different redox potentials.
  - Classical characterization tools (XAS) are not suited for the study of local electrochemical properties.

- O and F cannot be distinguished with X-ray diffraction, nor with neutron diffraction.
  - Try $^{19}$F solid-state NMR... but this is also tricky.

M = Ni, Ti, Mo
$^{19}$F NMR reveals that F has integrated the bulk cathode material, but a detailed assignment requires simulations.

$^{19}$F spin echo
60 kHz MAS
$B_0 = 11.75$ T

* spinning sidebands

$^{19}$F pj–MATPASS isotropic spectrum

Predicted NMR parameters for F environments in LNF15

Spin density transfer pathways from Ni to F, for Ni in first three coordination shells around F, are denoted $P_1$, $P_2$ and $P_3$.

Shift contributions for Ni$^{2+/3+}$ in $P_1$, $P_2$ and $P_3$:

<table>
<thead>
<tr>
<th>Interaction type</th>
<th>$\delta$(Ni$^{2+}$)/ppm*</th>
<th>$\delta$(Ni$^{3+}$)/ppm*</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_1$ (~2.1 Å)</td>
<td>5521</td>
<td>5767</td>
</tr>
<tr>
<td>$P_2$ (~3.6 Å)</td>
<td>-27</td>
<td>-4</td>
</tr>
<tr>
<td>$P_3$ (~4.6 Å)</td>
<td>13</td>
<td>49</td>
</tr>
</tbody>
</table>

Paramagnetic linebroadening:

| # nn Ni | $|\Delta \delta|$(Ni$^{2+}$)/ppm* | $|\Delta \delta|$(Ni$^{3+}$)/ppm* |
|---------|-------------------------------|--------------------------|
| 0 Ni in $P_1$ | 291                           | 261                      |
| 1 Ni in $P_1$ | 5057                          | 5842                     |
| 2 Ni in $P_1$ | --                            | 5503                     |


* Average values obtained from hybrid DFT/HF calculations in CRYSTAL14 code using B3LYP functional with 20% and 35% HF exchange.
Monte Carlo simulations can help us determine the most favorable distribution of F sites in the material.

- Two simulations* at 973 K (~synthesis temperature) and at $10^8$ K (~statistical limit):

*Structure selection was performed using a cluster expansion Hamiltonian and DFT-computed interaction energies.

What type of F environments can NMR probe in the cathode?

Paramagnetic NMR calculations indicate that only F nuclei with no Ni nearest-neighbor can be observed with NMR.

Monte Carlo simulations & DFT calculations indicate that F substitution induces some short-range order, whereby most F are surrounded by 6 Li (~50%) and 5 Li (45%), and only 20% F are directly bonded to Ni.

Work in progress:

- Implementation of 2D $^7$Li–$^{19}$F correlation experiments to obtain further information on short-range order in these disordered rocksalts (e.g. Li–F distances).

Short-range order and redox processes in cation-disordered Li$_{1+x}$M$_{1-x}$O$_2$ cathodes: Summary

- The combination of solid-state NMR, Monte Carlo simulations and DFT calculations is a powerful approach for the study of structural and electrochemical processes in disordered compounds.

- F substitution for O in LiMO$_2$ cathodes facilitates the exploration of anionic sites in LiMO$_2$ electrodes using NMR spectroscopy ($^{19}$F vs. $^{17}$O NMR).

- F substitution induces short-range order in the material, by incorporating in Li-rich environments. F becomes undercoordinated on Li extraction.

- F substitution improves the capacity and reversibility of the redox processes by increasing the amount of Ni$^{2+}$ in the as-synthesized material.
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