Multivalent Systems: The New Frontier in Battery Research

Stan Whittingham et al @ Binghamton
An Intercalation-based Lithium Battery Cell
1970s Technology (= Structure Retention).

\[ x\text{Li} + \text{TiS}_2 \text{ gives } \text{Li}_x\text{TiS}_2 \]

Kang Xu, Chem. Rev., 2004
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Cathode Status 2019: Li-Ion Intercalation Batteries

Li$_x$TiS$_2$ $\rightarrow$ Li$_x$MoS$_2$ $\rightarrow$ Li$_x$CoO$_2$ (NMCA et al) $\rightarrow$ Li$_x$FePO$_4$

$\text{+ Li} \rightarrow$ Graphite (LTO/LNbO) $\rightarrow$ Si, Sn, or Li

**Li-Ion dominates portable and grid application**

>92% of grid battery storage is Li-ion (dwarfed by pumped hydro)

Almost 100% of EVs are Li-ion

All rechargeable portable devices are Li-ion

**NMC Cathode dominates: Li[NiMnCoAl]O$_2$**

622 is common composition (drive to decrease Co still further)

Most expensive component of battery

**LiFePO$_4$ most stable cathode**

Can we have a two electron cathode?
Why a multi-electron (multi-valent) intercalation cathode?

A multi-electron cathode:
- Cuts amount of TM needed
  - Reduces cost
  - Increases energy density by 50-70%
- Challenges
  - Will the structure tolerate a 2e change?
    - Phosphates are more stable
  - Is the voltage change tolerable?
    - For user, and for electrolyte stability
- Mobile ion options
  - I: 2 Li or 2 Na
  - II: 1 Mg, Ca or Zn
- Redox-active cathode options
  - V (5\(^+\)-3\(^+\)), Ni (4-2), Mn (4-2), [Fe (4-2)]
  - O, PO\(_4\), S, F, etc
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**Prior Results**
DOE-supported researchers made key advances in battery science and technology in 2018. For the first time, researchers at a DOE Energy Frontier Research Center reversibly inserted and extracted two lithium ions from a multi-electron lithium ion battery cathode, with full recovery upon recharging—a capability that could greatly increase battery capacity.

I: Are 2 Li-Ion Intercalation Cathodes Structurally Viable?  YES

LiₓTiS₂ → LiₓMoS₂ → LiₓCoO₂ (NMCA et al) → LiₓFePO₄ → LiₓVOPO₄

2018 Report
Feb 2019

R&D Fundamentals

Advancing the state of battery science. “DOE-supported researchers made key advances in battery science and technology in 2018. For the first time, researchers at a DOE Energy Frontier Research Center reversibly inserted and extracted two lithium ions from a multi-electron lithium ion battery cathode, with full recovery upon recharging—a capability that could greatly increase battery capacity.”

DOE Ten at Ten Award
July 2019
Why a Multi-electron $\varepsilon$-VOPO$_4$ Cathode?

**MOTIVATION**

- Stable PO$_4$ structure, eg LiFePO$_4$
- But > one Li$^+$ intercalation > ED
- Multiple redox potentials accessible

$$\varepsilon\text{-VOPO}_4 \leftrightarrow \varepsilon\text{-Li}_2\text{VOPO}_4$$

**Why a Multi-electron ε-VOPO₄ Cathode?**

**MOTIVATION**

- Stable PO₄ structure, e.g. LiFePO₄
- But > one Li⁺ intercalation > ED
- Multiple redox potentials accessible


**SYNTHESIS**

VCl₃ and P₂O₅ in 95% ethanol

Hydrothermal
180°C for 3 days

Monoclinic H₂VOPO₄

Heat Treatment
550°C for 3 hours
ε-VOPO₄ can be chemically lithiated to ε-Li₂VOPO₄

Only 8.5% volume increase; 328.14 to 356.05 Å³
Small cuboid particles

$\varepsilon$-VOPO$_4$ particles
~100-200 nm
Cuboid particles
Small cuboid particles allow two Li ions to be reversibly intercalated.

\[ \varepsilon\text{-VOPO}_4 \text{ particles} \]

\[ \sim 100-200 \text{ nm} \]

Cuboid particles

Proof of principle achieved
High Voltage Region
3.0 – 4.5V
Two-phase reaction
VOPO$_4$ + LiVOPO$_4$

Substitute, like LiFePO$_4$, to increase rate capability by changing phase diagram
Kinetics quite different for the two plateaus

High Voltage Region
3.0 – 4.5V
Two-phase reaction
VOPO$_4$ + LiVOPO$_4$

Substitute, like LiFePO$_4$, to increase rate capability by changing phase diagram

Low Voltage Region
1.6 – 3.0V
Single phase reaction
Li$_{1+x}$VOPO$_4$
Learnings from $\varepsilon$-VOPO$_4$

- Two Li ions can be reversibly intercalated into a crystalline lattice without damage to lattice
- Rate capability very different for the two voltage plateaus; need single phase reactions

VOPO$_4$ can intercalate $> 1$ Na ion

- There are more than 7 “VOPO$_4$” phases
- Na needs more open lattice than that of $\varepsilon$-VOPO$_4$
  - K can also be cycled
  - Mg is not rechargeable
Na intercalates reversibly into $K_yVOPO_4$

$\varepsilon$-VOPO$_4$

85.51Å$^3$/PO$_4$

KVPOPO$_4$

106.8Å$^3$/PO$_4$

Challenge? How to get all the K out

$KVOPO_4$: A New High Capacity Multielectron Na-Ion Battery Cathode

II: Are Multiple Charged Ions Viable for Intercalation Cathodes? Yes, but…

A multi-electron cathode:
• Cuts amount of TM needed
  • Reduces cost
  • Increases energy density by 50-70%
• Challenges
  • Will the structure tolerate a 2e change?
  • Phosphates are more stable
  • Is the voltage change tolerable?
  • Use, and electrolyte stability
• Mobile ion options
  • I: 2 Li or 2 Na
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• Redox-active cathode options
  • V (5⁺-3⁺), Ni (4-2), Mn (4-2), [Fe (4-2)]
  • O, PO₄, S, F, etc

Prior Results/Learnings
• LiTiS₂
  • Soft lattice
  • Metallic conductor
  • Two structures
    • Layered (MSW)
    • Spinel (JBG)

LiₓTiS₂ → MgₓTiS₂
The original Li-ion cathode had some unique properties?

TiS$_2$ has a layered structure

- Semi-metal
- Mixed conductor
- Li$_x$TiS$_2$, where 0 ≤ $x$ ≤ 1

10 mA/cm$^2$
No carbon black

TiS$_2$ is almost ideal cathode
- No need for CB conductor
- No phase transition
- Very fast ion conductor
- Can these properties be found in a 4 V cathode?
- Works well for Mg too
  - Mg$_{0.5}$TiS$_2$
  - Van der Ven and Nazar
  - 2016/2017

Figure 1
Theory shows 1 volt penalty for Mg vs Li intercalation: 1 Li vs 1 Mg in TiS$_2$

Theory – Anton van der Ven

- 1 volt penalty for Mg
Experiment confirms theory and shows $\text{Mg}_x\text{Ti}_2\text{S}_4$ very reversible.

**Theory – Anton van der Ven**
- 1 volt penalty for Mg

**Experiment – Linda Nazar**
- Confirms theory
- Highest Mg capacity to date (Chevrel-Aurbach)

$\text{Mg}_{60^\circ C}$
0.04 mA/cm$^2$

$60^\circ C$
Mg not competitive with Li in titanium disulfide

Theory – Anton van der Ven

➤ 1 volt penalty for Mg

Experiment – Linda Nazar

➤ Confirms theory
➤ Highest Mg capacity to date

Mg
60°C
0.04 mA/cm²

ED Li  2x Mg

Li
21°C
10 mA/cm²
SW-1976
Conclusions - Multivalent Systems: The New Frontier in Battery Research

- **Intercalation Reactions**
  - Lithium: Proof of concept achieved  
  - Sodium: OK, but low voltage  
  - **Magnesium not attractive option**  
    - No evidence yet that Mg can transfer more than 1 electron/TM (=1/2 Mg)  
    - Mg readily grows dendrites  
    - Mg moves very slowly, and high voltage penalty  
  - Calcium more attractive than magnesium  
    - Potential closer to Li; phase behavior expected to be like Na  
    - But many many challenges/opportunities

- **Conversion Reactions**
  - Lithium not looking promising: FeF$_2$, FeF$_3$, CuF$_2$, FeOF  
  - Li/Na/Mg S interest waning  
  - Li/O$_2$ no interest  
  - Metal/organic – Abruno

- **Solid State Batteries**
  - Will be very tough for Mg or Ca  
  - Need **Fundamental studies** of transport, thermodynamics, structure prediction; e.g. Mg vs Ca vs Zn