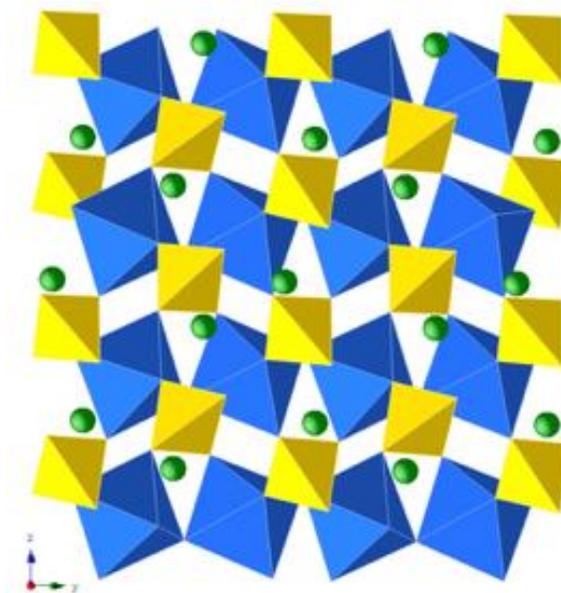
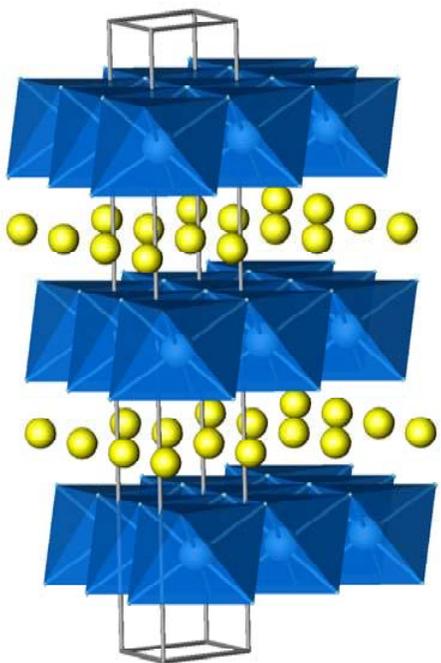




Chemical Sciences Round Table 2019

Multivalent Systems: The New Frontier in Battery Research

Stan Whittingham et al @ Binghamton



U.S. DEPARTMENT OF
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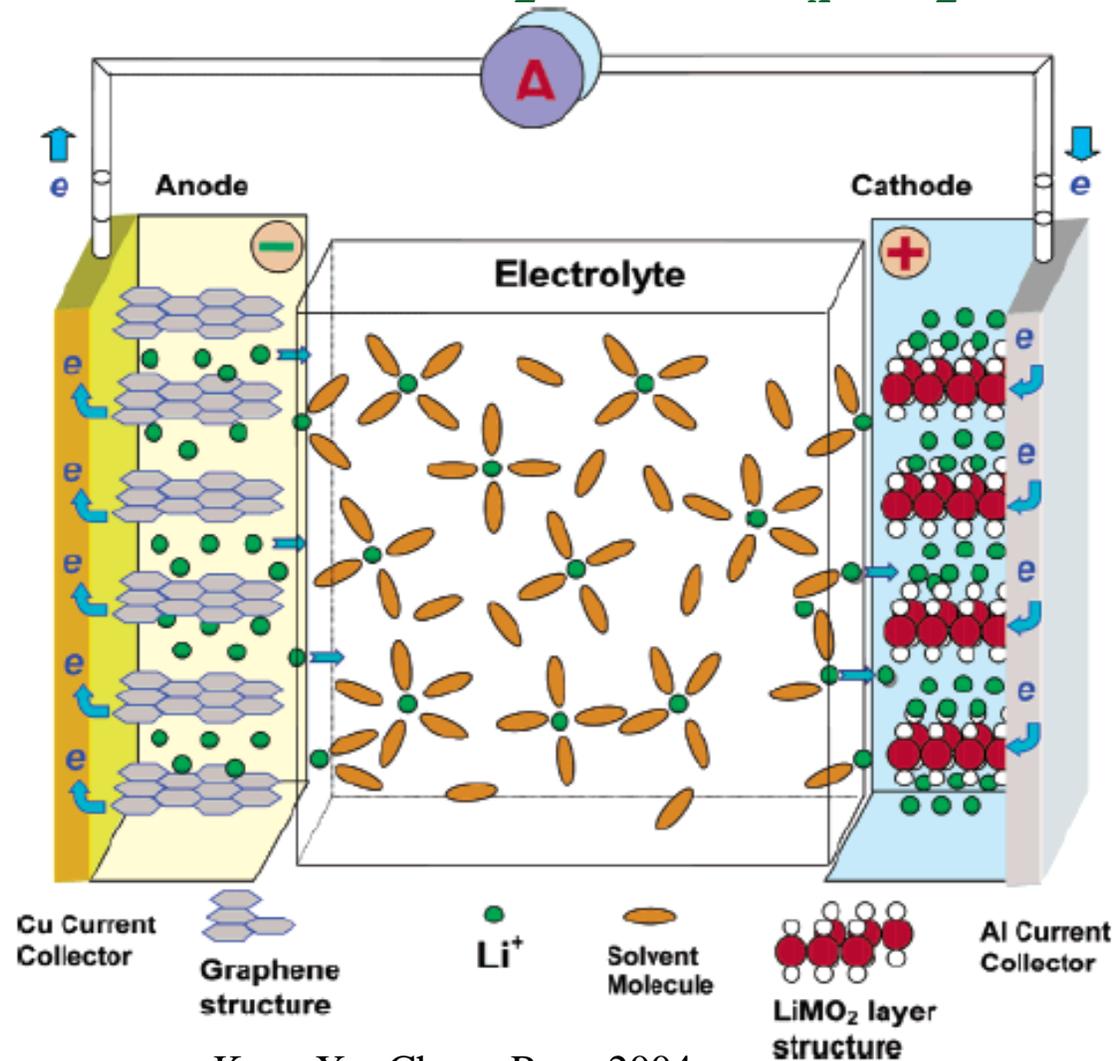
UNIVERSITY OF MICHIGAN
MIT
Massachusetts Institute of Technology

U.S. DEPARTMENT OF
ENERGY

Energy Efficiency &
Renewable Energy

BATTERY 500
CONSORTIUM

An Intercalation-based Lithium Battery Cell 1970s Technology (= Structure Retention).



An Intercalation-based Lithium Battery Cell

1970s Technology (= Structure Retention).

1972

Li



Li
in

Aluminum



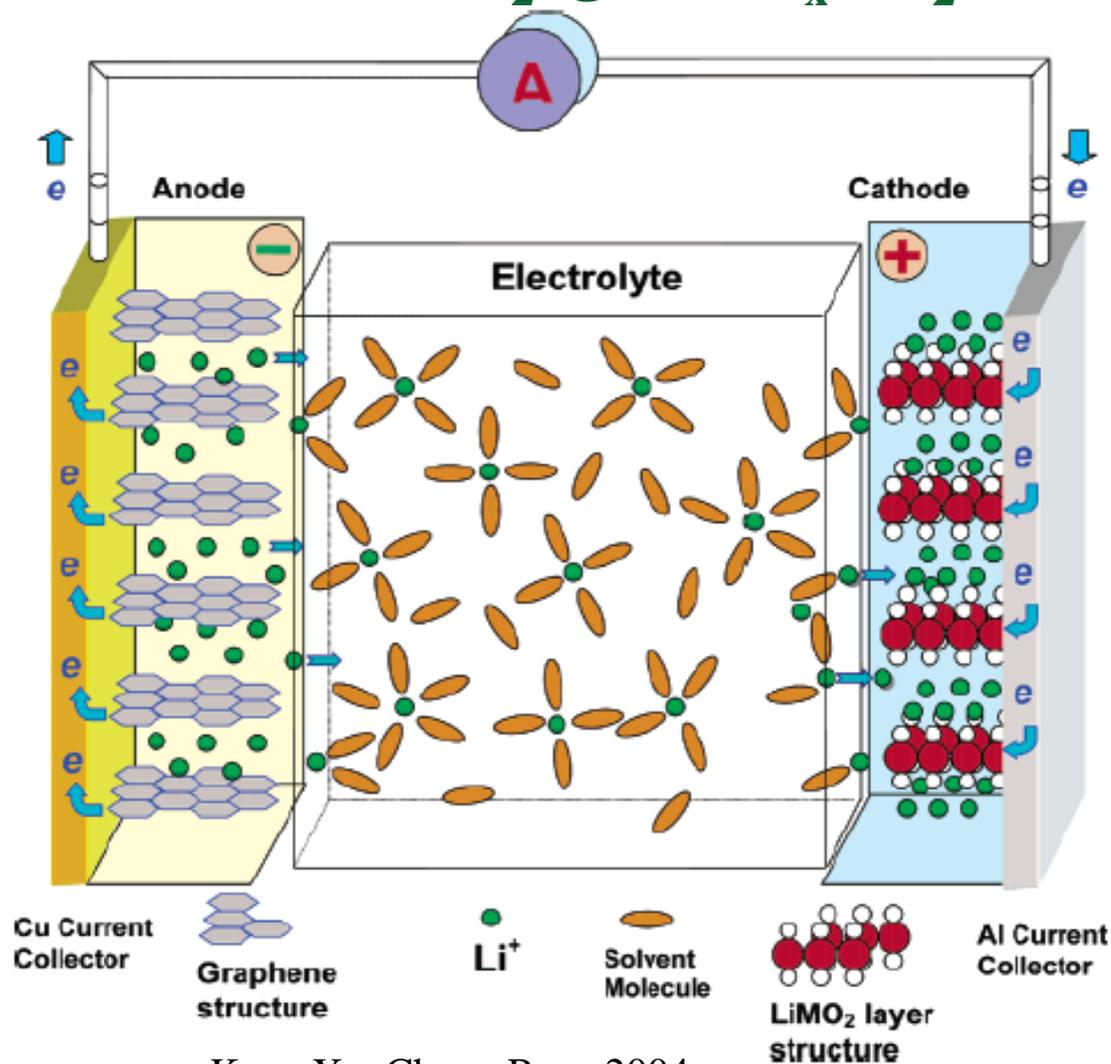
Carbon



Sn or Si



Li



Li_xTiS_2



← Li, Mg

LiCoO_2



NMC

NCA



LiFePO_4

LiFeMnP

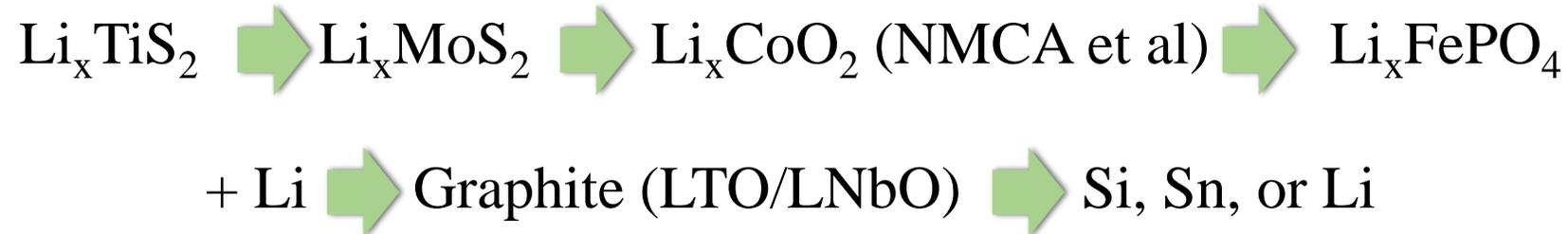


← 2 Li, Na

LiVOPO_4

2019

Cathode Status 2019: Li-Ion Intercalation Batteries



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

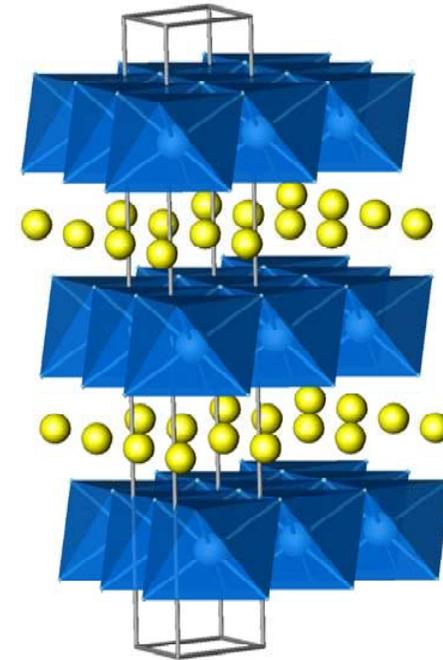
NMC Cathode dominates: $\text{Li}[\text{NiMnCoAl}]\text{O}_2$

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:

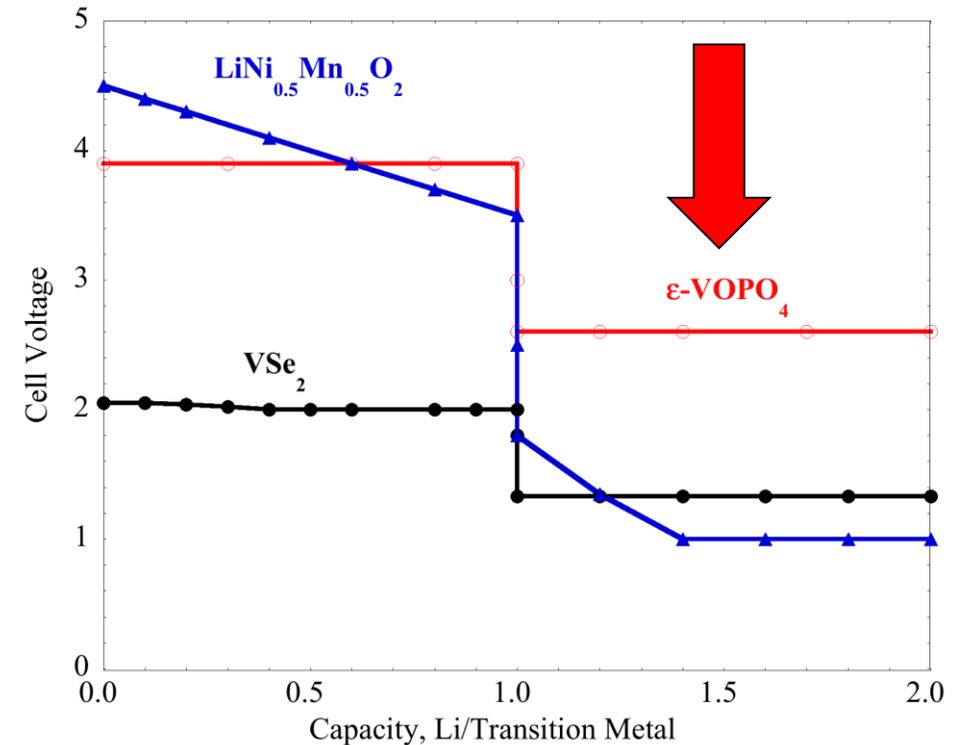
- Cuts amount of TM needed
 - Reduces cost
 - Increases energy density by 50-70%
- Challenges
 - Will the structure tolerate a 2e change?
 - Phosphates are more stable
 - Is the voltage change tolerable?
 - For user, and for electrolyte stability
- Mobile ion options
 - I: 2 Li or 2 Na
 - II: 1 Mg, Ca or Zn
- Redox-active cathode options
 - V (5⁺-3⁺), Ni (4-2), Mn (4-2), [Fe (4-2)]
 - O, PO₄, S, F, etc

Why a multi-electron (multi-valent) intercalation cathode?

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 - V (5⁺-3⁺), Ni (4-2), Mn (4-2), [Fe (4-2)]
 - O, PO₄, S, F, etc

Prior Results



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



2018 Report
Feb 2019



DOE Ten at Ten Award
July 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.”

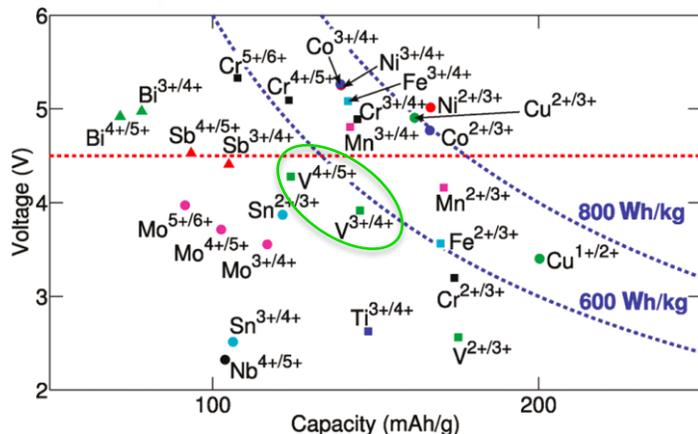
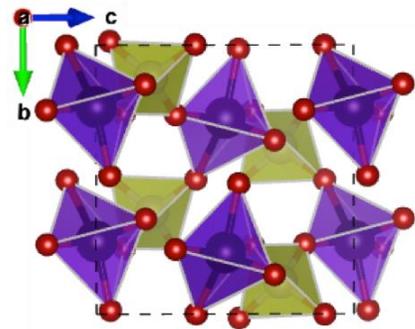


Science &
Technology
Highlights

Why a Multi-electron ϵ -VOPO₄ Cathode?

MOTIVATION

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



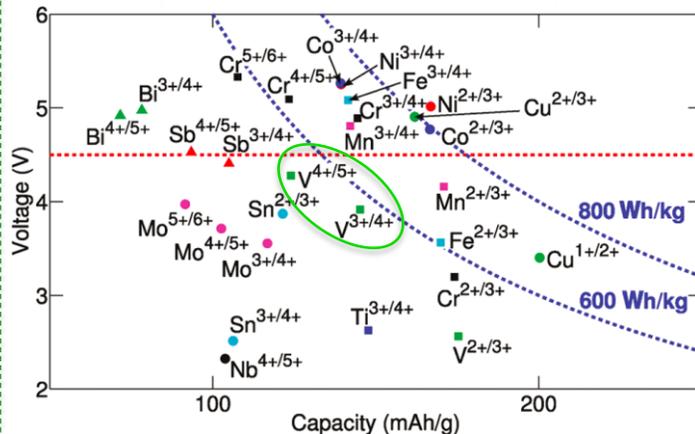
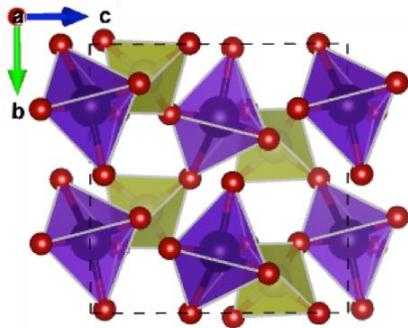
G. Hautier, Chem. Mater. 23, 3495, (2011)

Why a Multi-electron ϵ -VOPO₄ Cathode?

MOTIVATION

SYNTHESIS

- Stable PO₄ structure, eg LiFePO₄
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G. Hautier, Chem. Mater. 23, 3495, (2011)

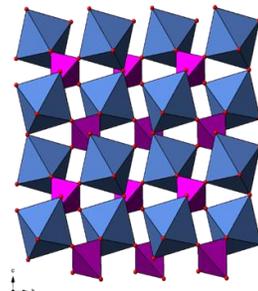
VCl₃ and P₂O₅ in 95% ethanol



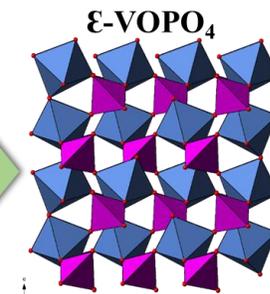
Hydrothermal
180°C for 3 days



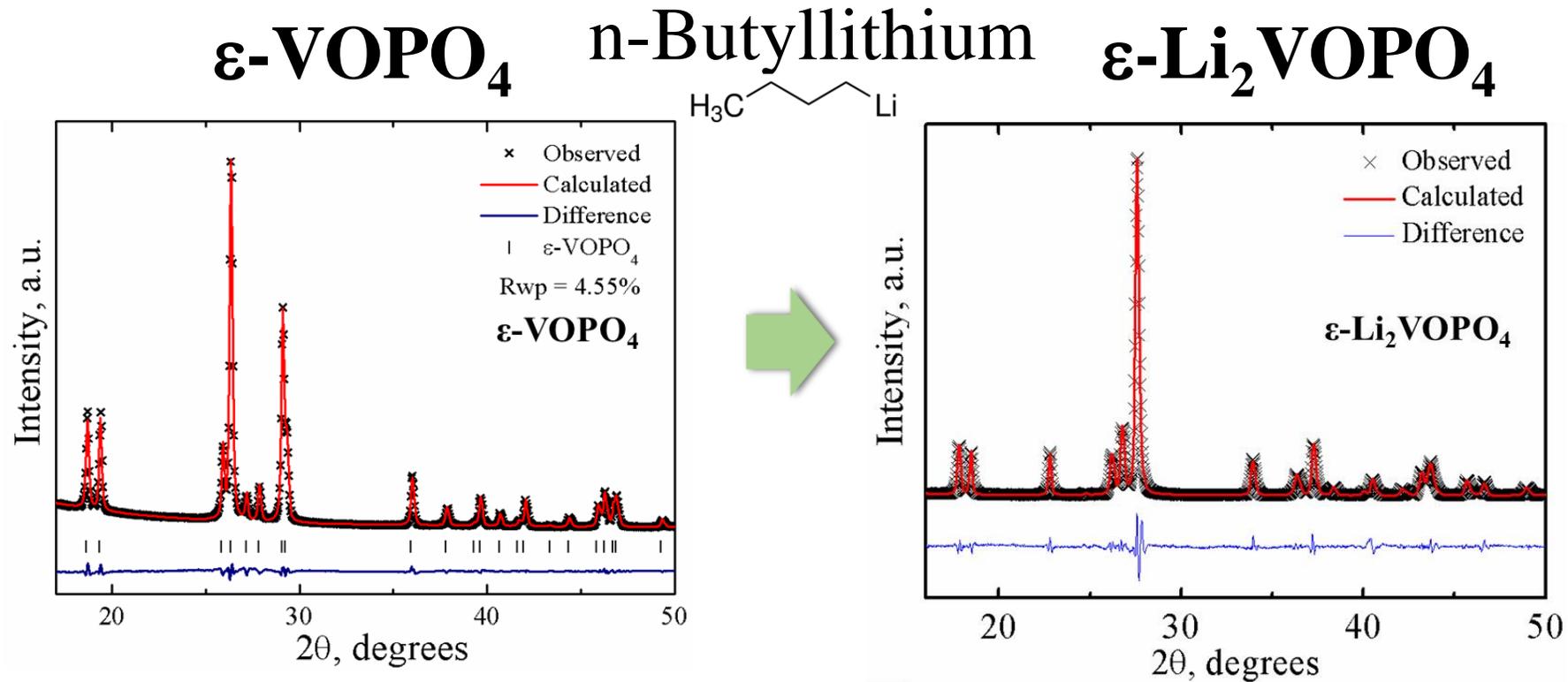
Monoclinic H₂VOPO₄



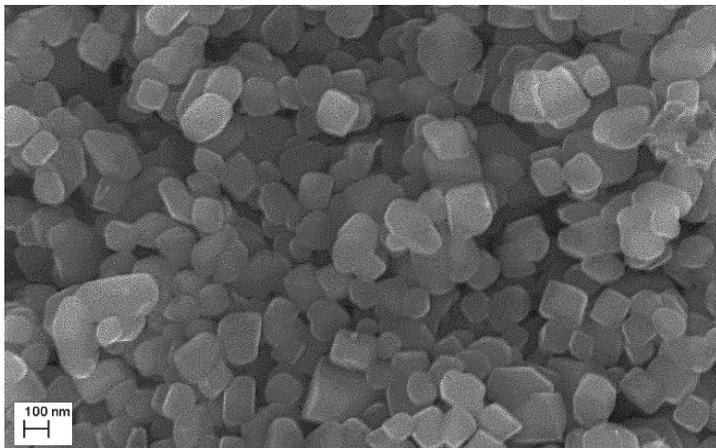
Heat Treatment
550°C for 3 hours



ϵ -VOPO₄ can be chemically lithiated to ϵ -Li₂VOPO₄

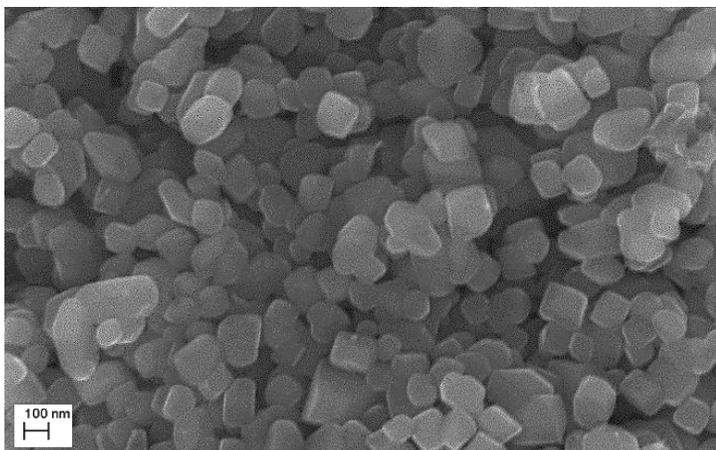


Small cuboid particles

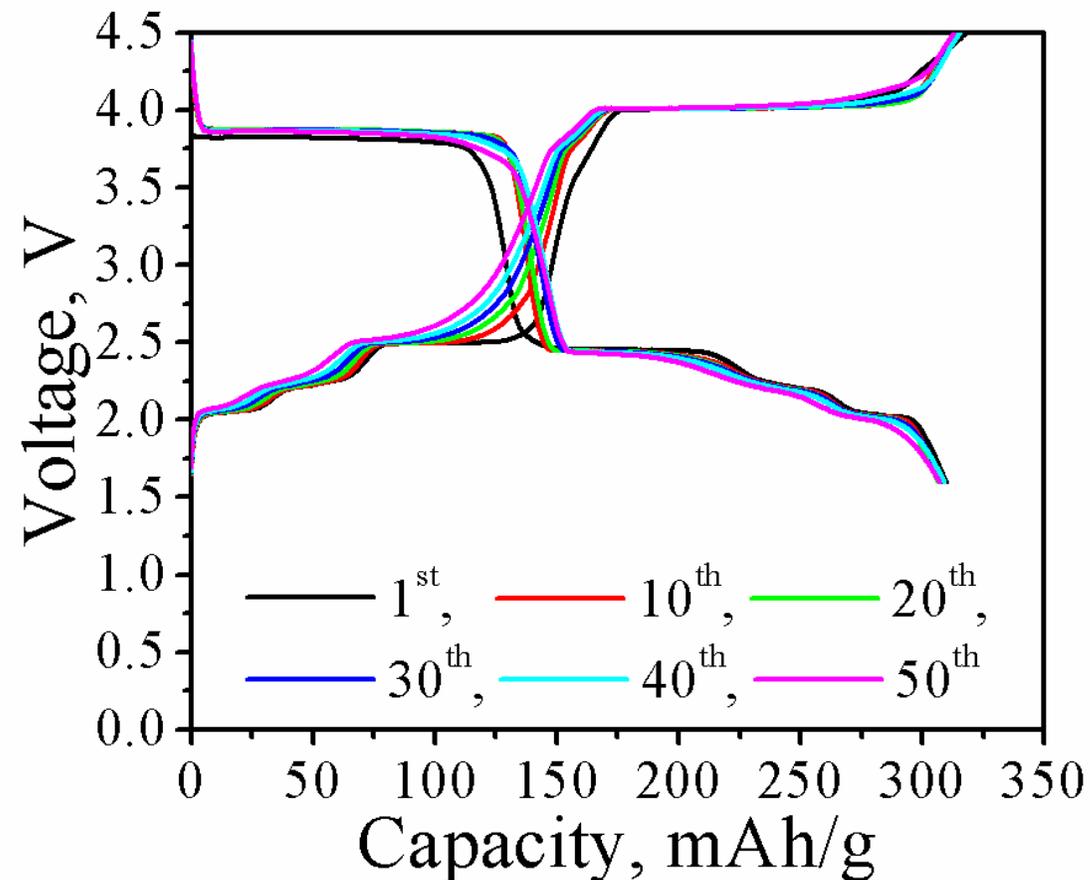


ϵ -VOPO₄ particles
~100-200 nm
Cuboid particles

Small cuboid particles allow two Li ions to be reversibly intercalated



ϵ -VOPO₄ particles
~100-200 nm
Cuboid particles



Proof of principle achieved

ChemComm

COMMUNICATION

 Check for updates

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Received 26th March 2018,
Accepted 17th June 2018

DOI: 10.1039/c8cc02386g

rsc.li/chemcomm

Enabling multi-electron reaction of ϵ -VOPO₄ to reach theoretical capacity for lithium-ion batteries†

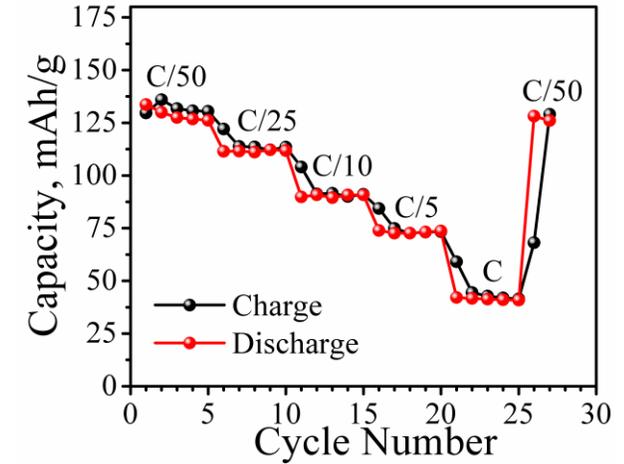
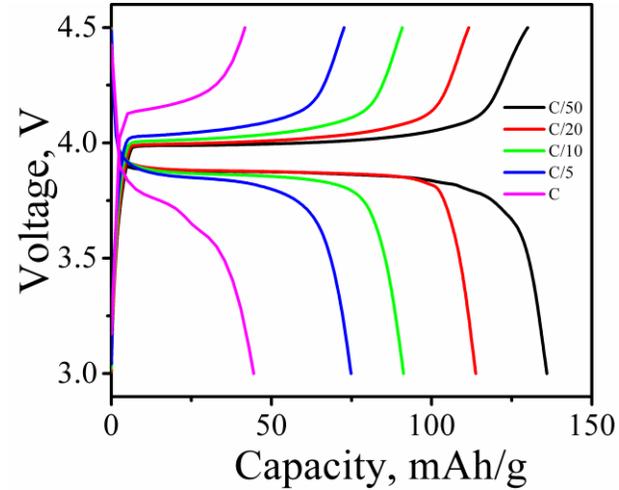
Carrie Siu,^a Ieuan D. Seymour,^b Sylvia Britto,^b Hanlei Zhang,^a Jatinkumar Rana,^a Jun Feng,^a Fredrick O. Omenya,^a Hui Zhou,^a Natasha A. Chernova,^a Guangwen Zhou,^b Clare P. Grey,^b Louis F. J. Piper^a and M. Stanley Whittingham^{b*}



Kinetics quite different for the two plateaus

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

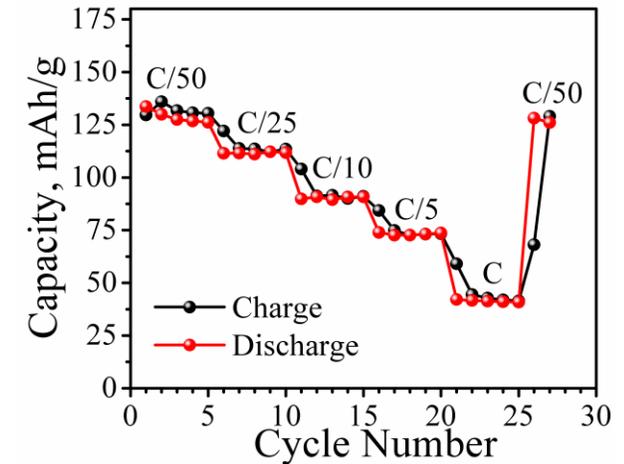
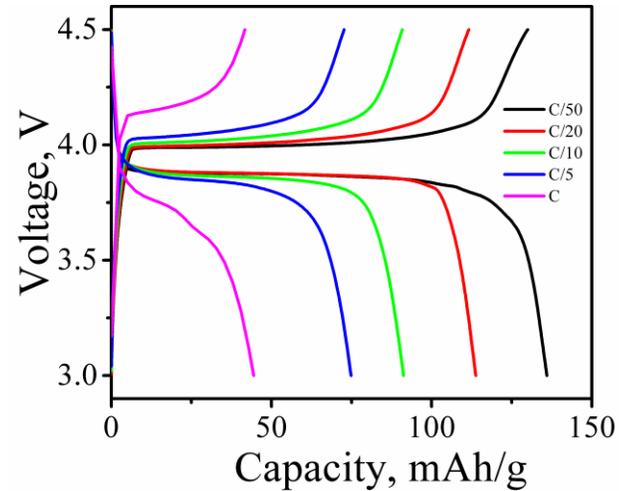
Substitute, like LiFePO_4 , to increase rate capability by changing phase diagram



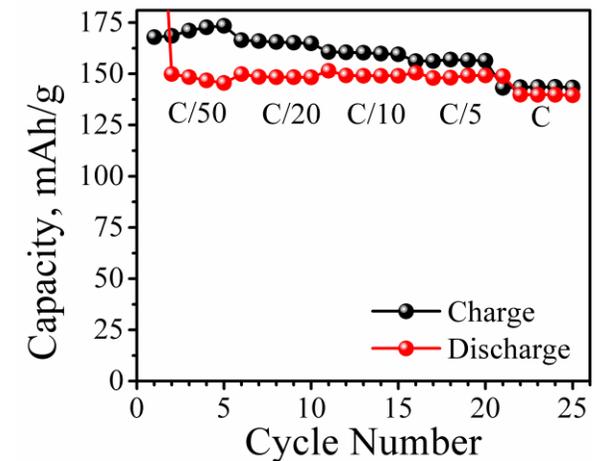
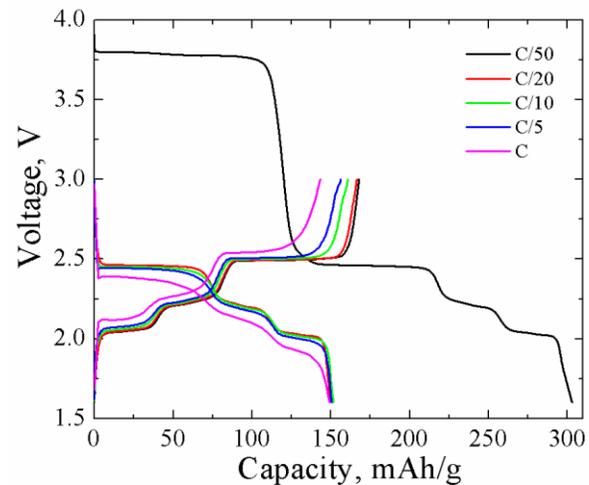
Kinetics quite different for the two plateaus

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

Substitute, like LiFePO_4 , to increase rate capability by changing phase diagram



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



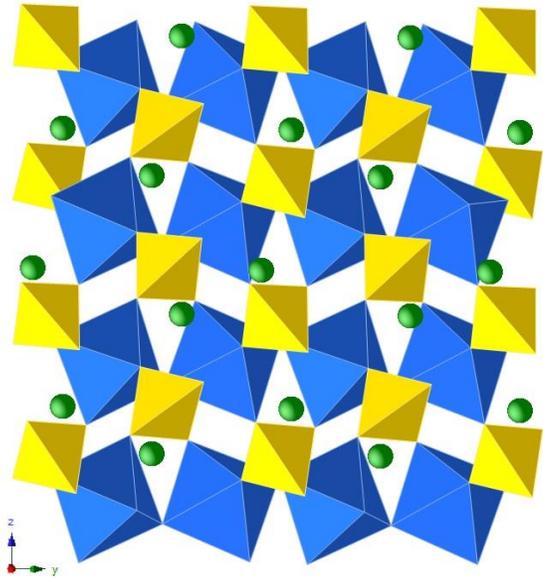
Learnings from ϵ -VOPO₄

- 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**

VOPO₄ can intercalate > 1 Na ion

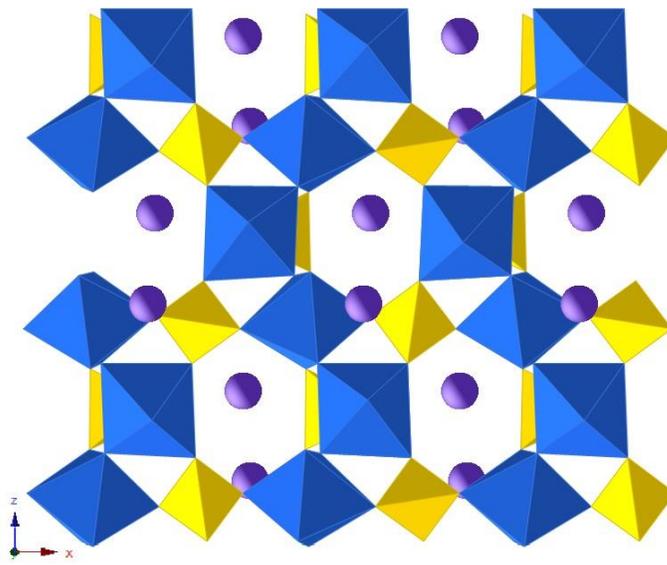
- There are more than 7 “VOPO₄” phases
- Na needs more open lattice than that of ϵ -VOPO₄
 - K can also be cycled
 - Mg is not rechargeable

Na intercalates reversibly into K_yVOPO_4



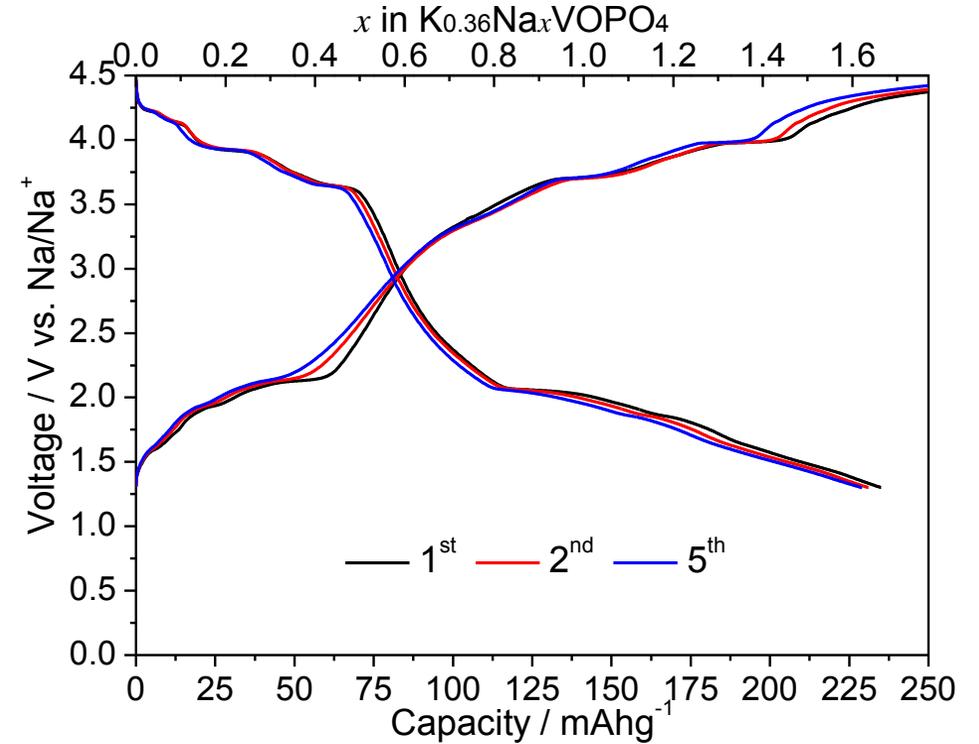
ϵ -VOPO₄

85.51 Å³ / PO₄



KVOPO₄

106.8 Å³ / PO₄



FULL PAPER

Sodium-Ion Batteries

ADVANCED
ENERGY
MATERIALS

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KVOPO₄: A New High Capacity Multielectron Na-Ion Battery Cathode

Jia Ding, Yuh-Chieh Lin, Jue Liu, Jatinkumar Rana, Hanlei Zhang, Hui Zhou, Iek-Heng Chu, Kamila M. Wiaderek, Fredrick Omenya, Natasha A. Chernova, Karena W. Chapman, Louis F. J. Piper, Shyue Ping Ong, and M. Stanley Whittingham*

Challenge?
How to get all the K out

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
 - **II: Mg, Ca or Zn**
- 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)**

The original Li-ion cathode had some unique properties?

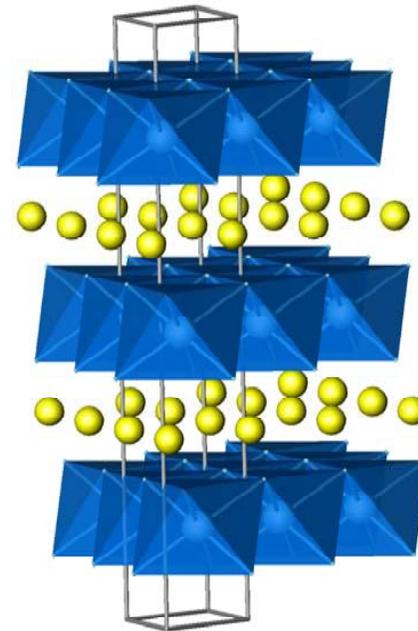
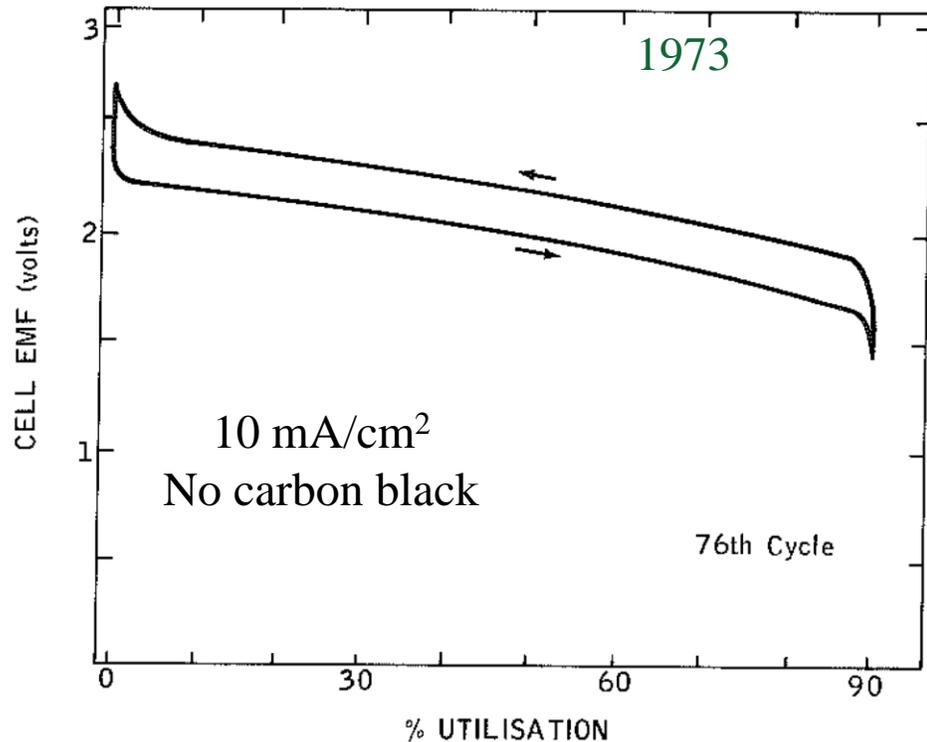


TiS_2 has a layered structure

Semi-metal

Mixed conductor

Li_xTiS_2 , where $0 \leq x \leq 1$



TiS_2 is almost ideal cathode

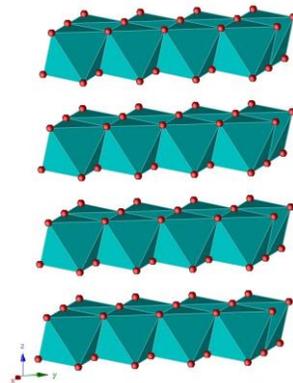
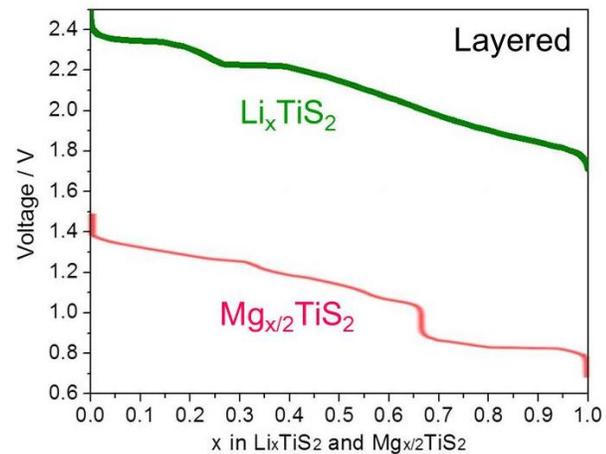
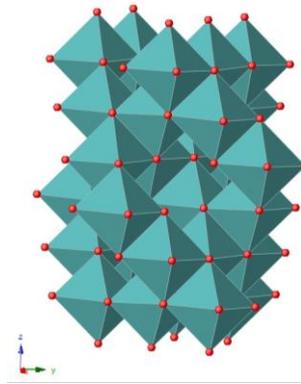
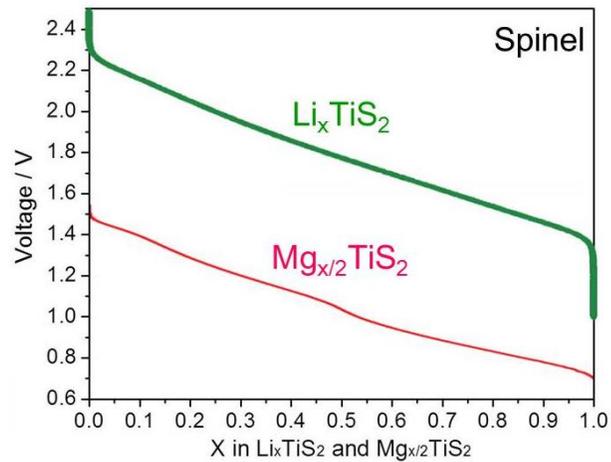
- No need for CB conductor
- No phase transition
- Very fast ion conductor
- Can these properties be found in a 4 V cathode?
- Works well for Mg too
 - $\text{Mg}_{0.5}\text{TiS}_2$
 - Van der Ven and Nazar
 - 2016/2017

Theory shows 1 volt penalty for Mg vs Li intercalation: 1 Li vs 1 Mg in TiS_2

Theory – Anton van der Ven

Li_xTiS_2 vs Mg_xTiS_2

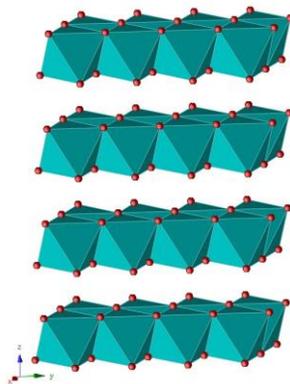
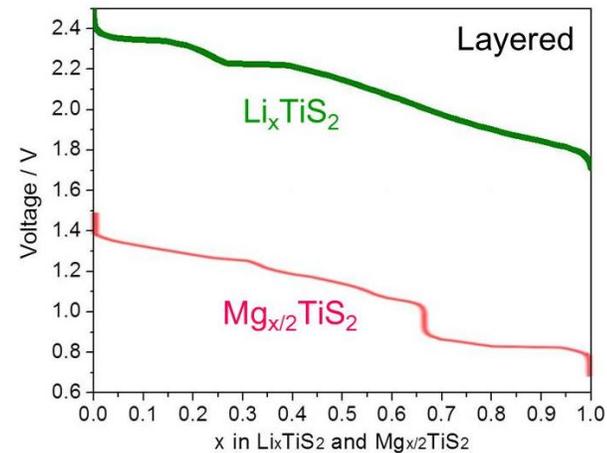
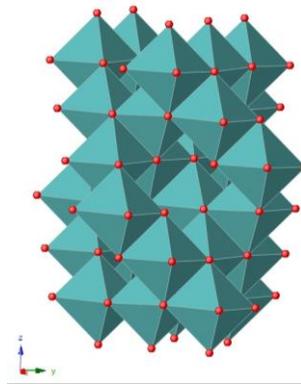
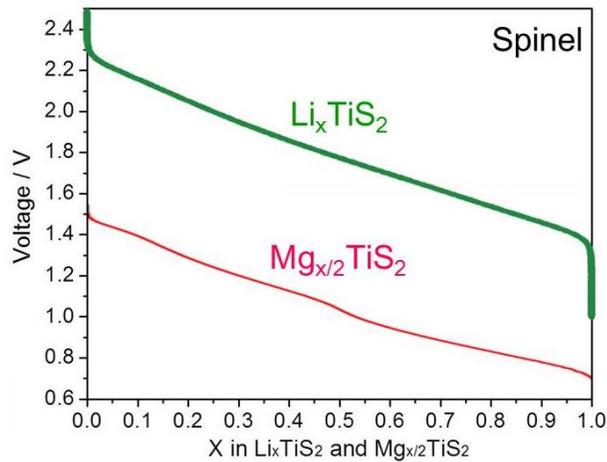
➤ 1 volt penalty for Mg



Experiment confirms theory and shows $\text{Mg}_x\text{Ti}_2\text{S}_4$ very reversible

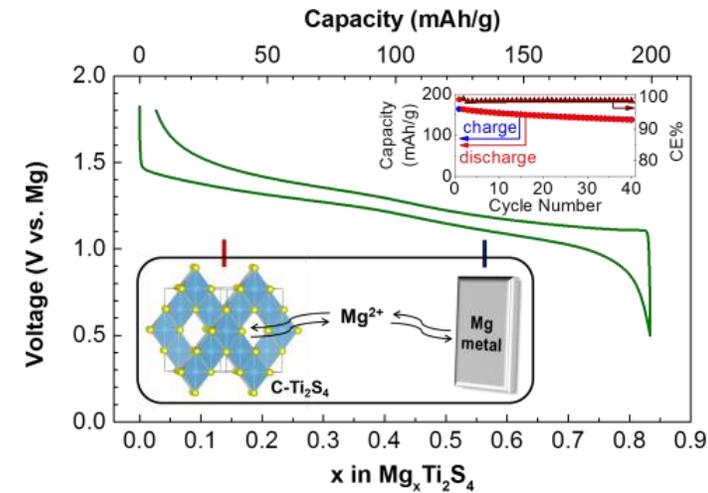
Theory – Anton van der Ven

- 1 volt penalty for Mg



Experiment – Linda Nazar

- Confirms theory
- Highest Mg capacity to date (Chevrel-Aurbach)

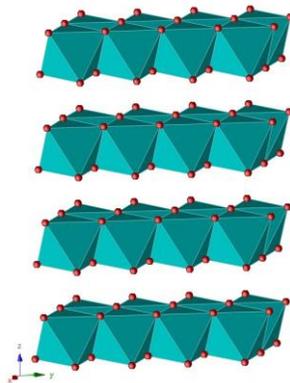
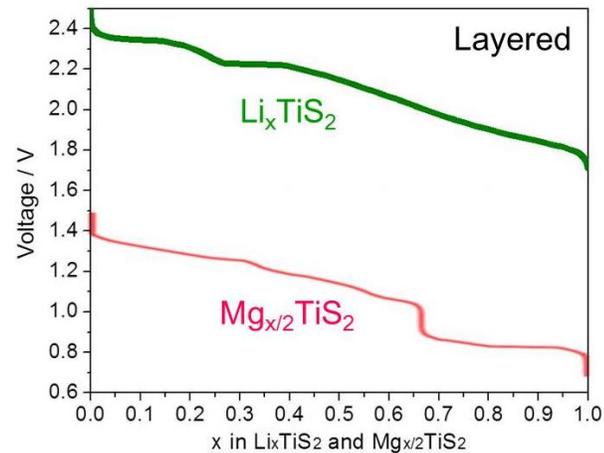
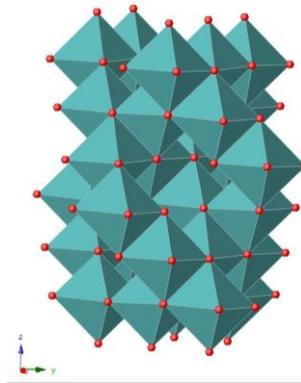
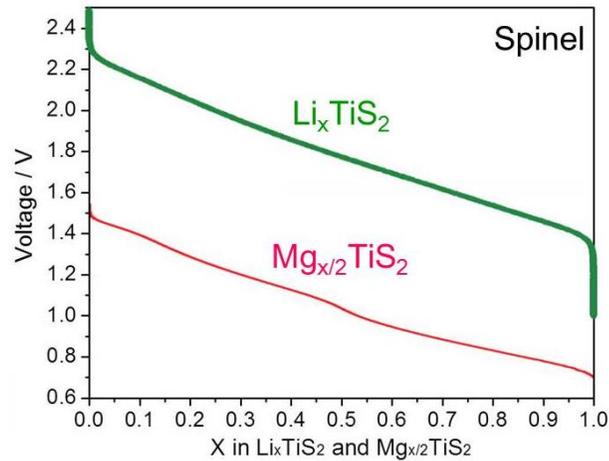


Mg
60°C
0.04 mA/cm²

Mg not competitive with Li in titanium disulfide

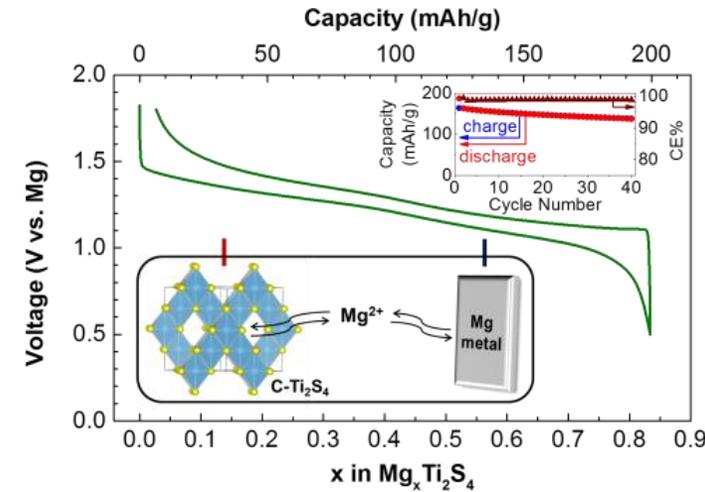
Theory – Anton van der Ven

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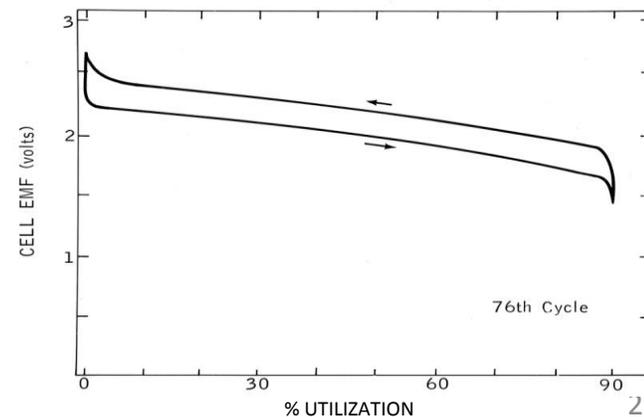
Experiment – Linda Nazar

- 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



Sarbajit Banerjee, Texas
A&M
ACS Energy Letters, 2019

✓ 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 ²¹