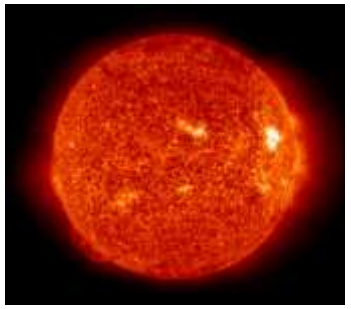
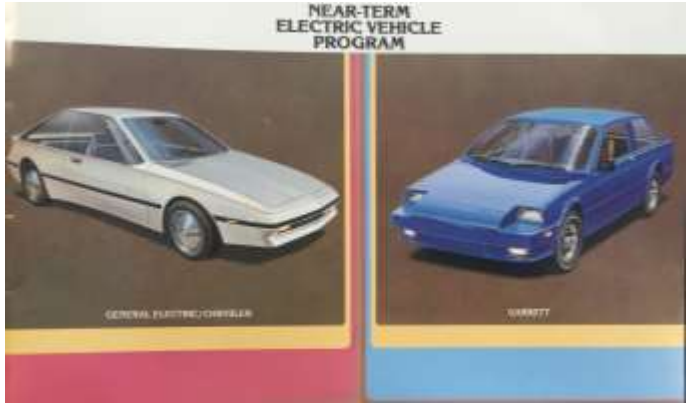
Report of Chief Science Officer

Trends for the Future of High Energy Density Battery Technology



M. Stanley Whittingham

Binghamton University (SUNY)



U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

BATTERY 500 CONSORTIUM

BINGHAMTON UNIVERSITY
STATE UNIVERSITY OF NEW YORK

From 1973: The Progress in Li-Ion Intercalation Batteries

Li_xTiS_2 ➡ Li_xMoS_2 ➡ Li_xCoO_2 (NMCA et al) ➡ Li_xFePO_4

+ Li ➡ Graphite (LTO/LNbO) ➡ Si, Sn, or Li

Cathode challenges and Needs:

- High **Ni NMC** will dominate for EVs, but for grid etc
  - Greater safety
  - Lower lifetime cost
  - Flexibility

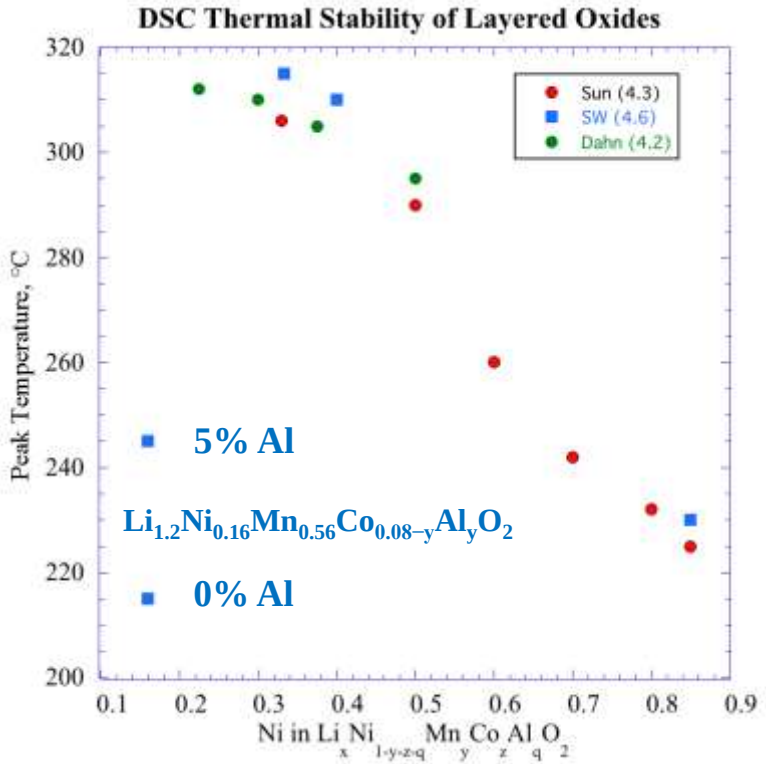
$LiFePO_4$ most stable cathode

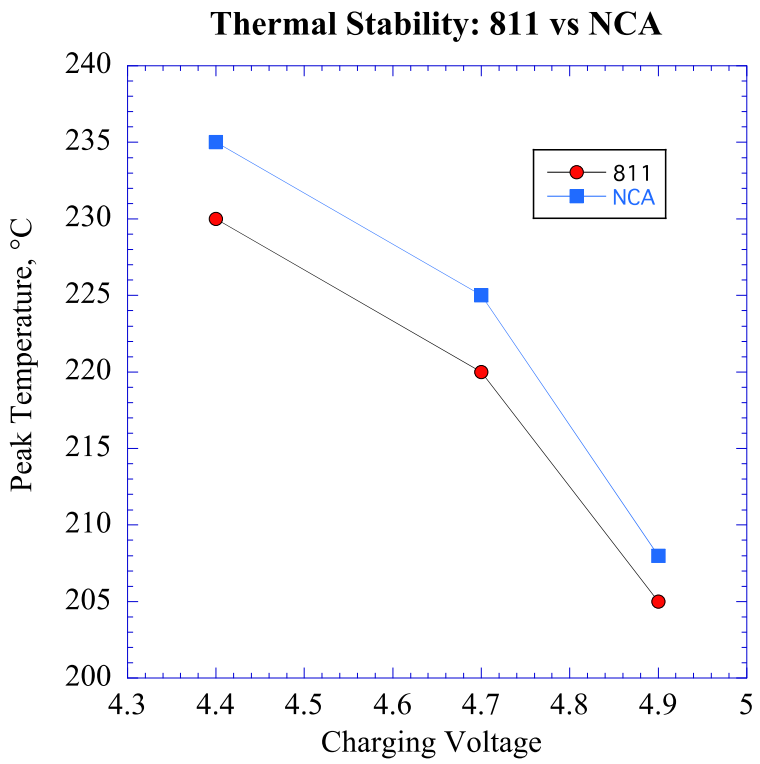
- But low ED
- Is **$LiMnPO_4$** an answer? Gives 4 volt discharge.
- Or can we have a two electron cathode?
  - Anode: 2 Li, 2 Na, 1Mg, 1 Ca
  - Cathode: V^{5+} to V^{3+}; Ni^{4+} to Ni^{2+}

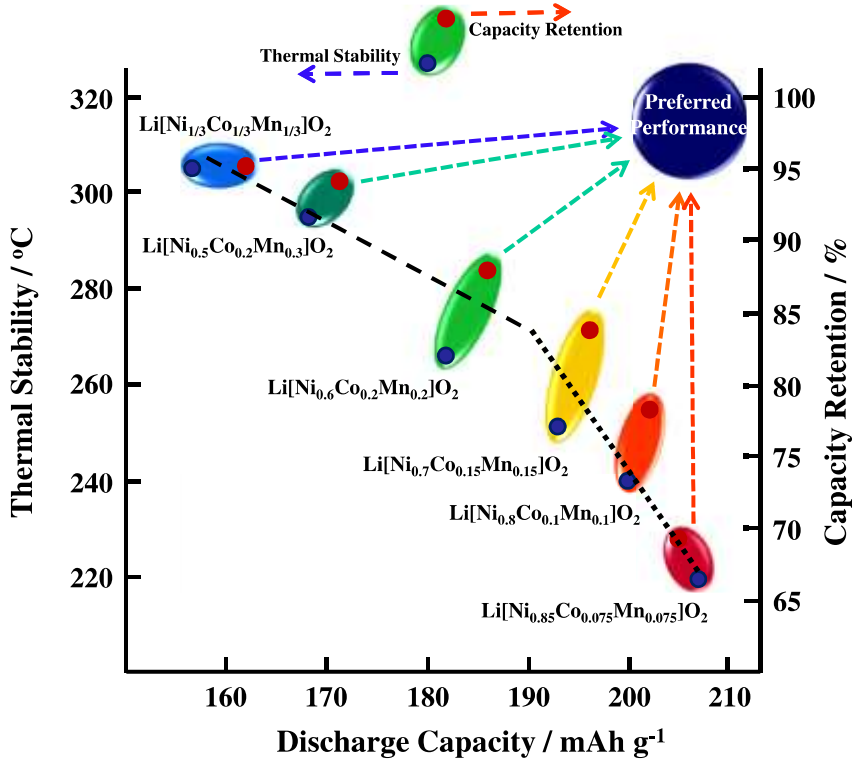
The Stability of High Ni NMCA Intercalation Batteries

- **Increasing the nickel content increases the capacity**
- **Increasing the nickel content reduces the thermal stability**
  - **[**Ni] more important than charging voltage
  - Al has minimal effect on thermal stability for NMCA
  - 811 gases more than NCA

$Li[NiMnCoAl]O_2$

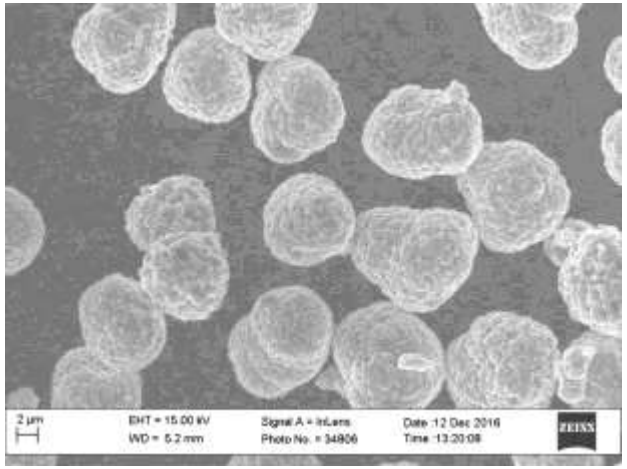


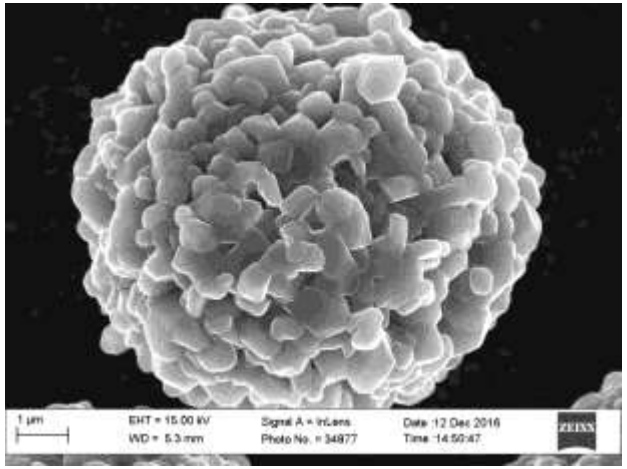


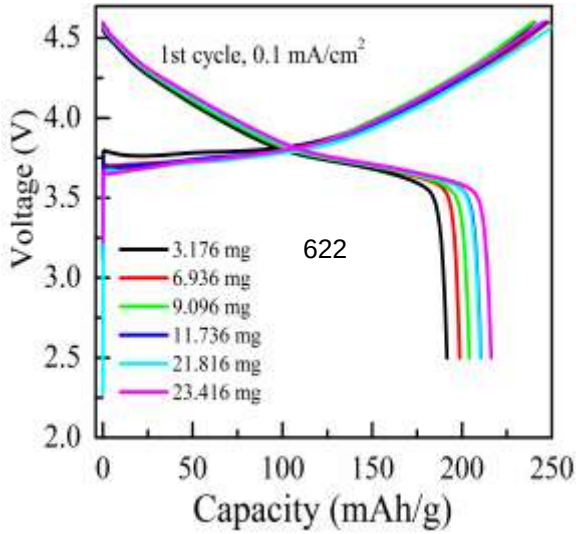


Noh et al. J. Power Sources, 233, 121 (2013)

NMC 622 Replacing 333 as Today's Choice (40% less $)







EcoPro Material

Layered oxides today:

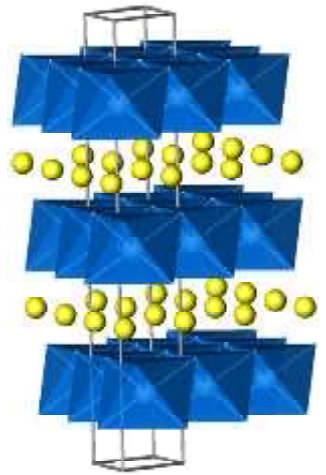
- Capacities of 160-180 Ah/kg achieved in commercial cells when charging limited to 4.2-4.3 V
- 4.5 V charging leads to capacities exceeding 220 Ah/kg
  - Capacity fading increases with increase of charging voltage

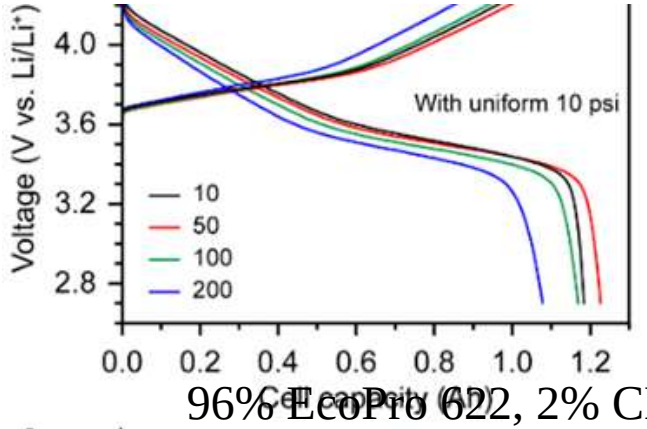
For next 5-10 years

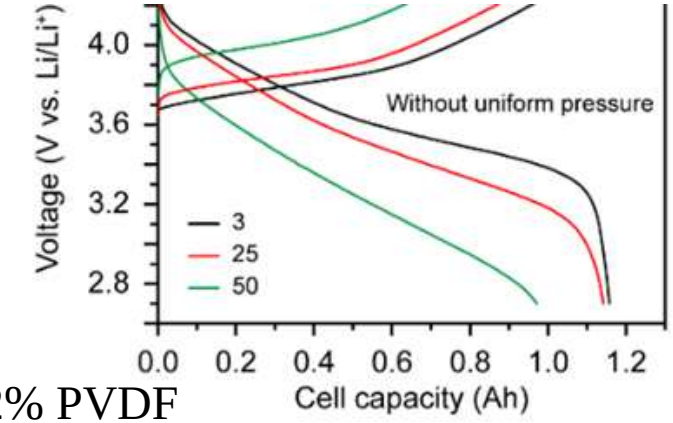
- Layered oxides will be the cathode of choice
  - Capacity in commercial cells will keep increasing
  - Charging voltage likely to be limited to 4.3 V, unless new electrolyte
    - This will lead to need for higher Ni content, e.g. 811 > 622

Battery500 Achieved >300 Wh/kg with NMC 622

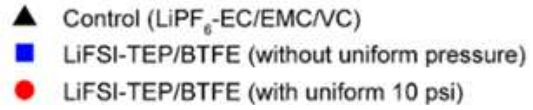
- **$LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ was baseline for the consortium**
  - X-ray characterization normal
    - less than 3% Ni/Li mixing (ideal amount)
  - Morphology good
  - Electrochemistry good
  - **Achieved 300 Wh/kg goal**

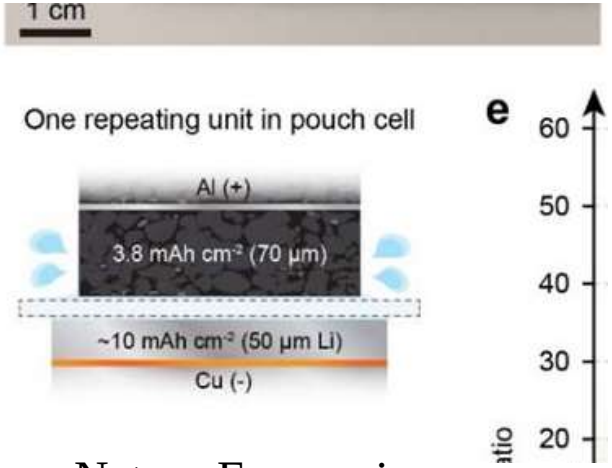






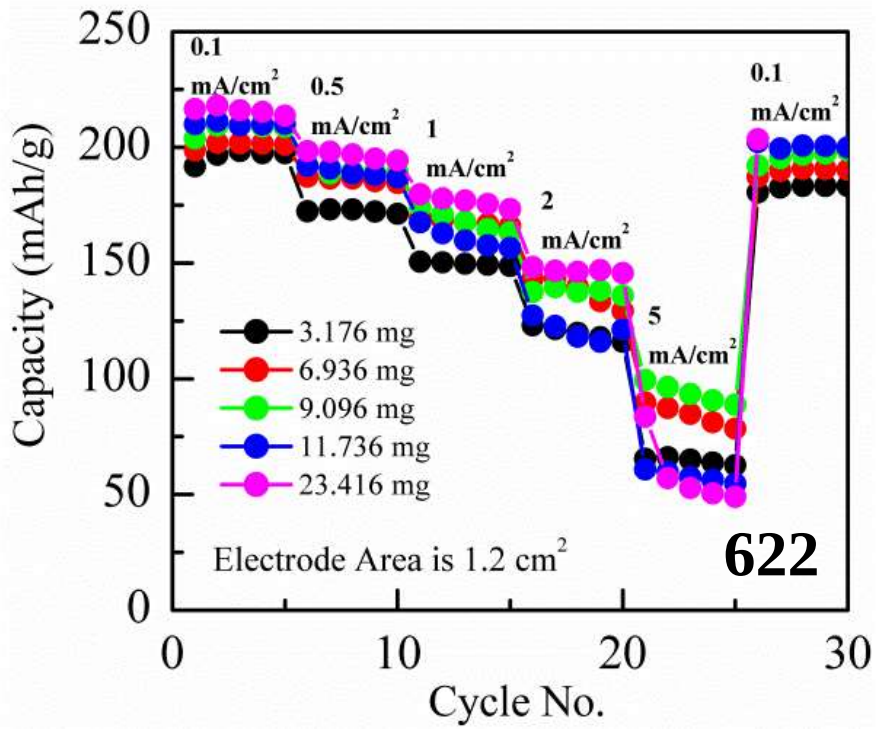
96% EcoPro 622, 2% CB, 2% PVDF

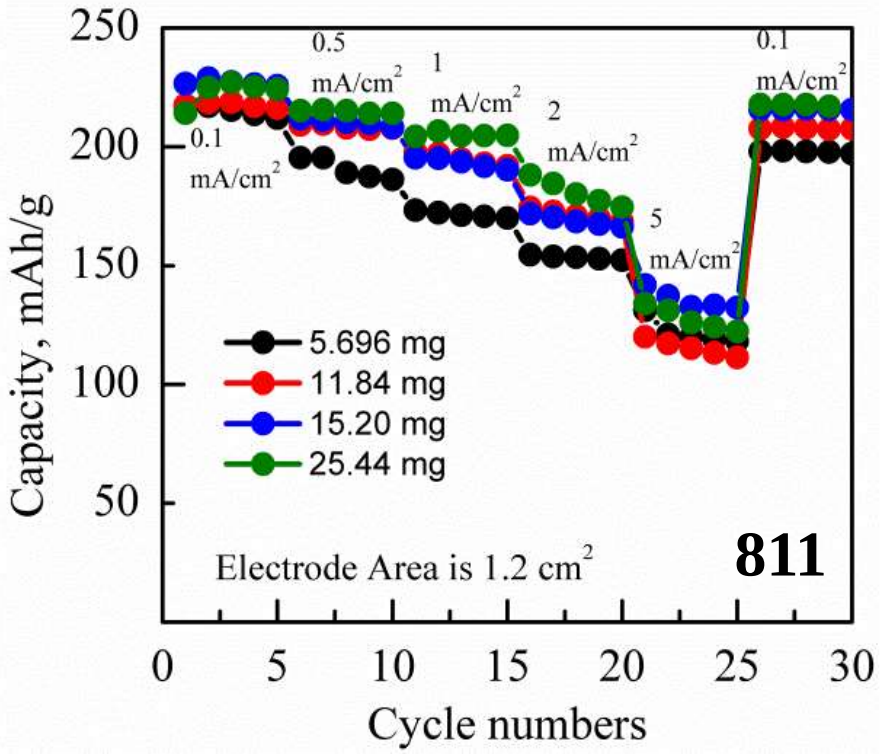




Nature Energy, in press

NMC 811 Superior to 622 NMC; Achieved 350 Wh/kg, but ….





- The cells cycled at different current densities, mA/cm², from 2.5 to 4.6 V
- 622 show dependency of loading on electrochemical performance at high rates
- 811 has better rate capability compared to 622, less thermally stable and more air sensitive

Progress in Li-Ion Intercalation Batteries: From $LiFePO_4$ to M_xVOPO_4

Li_xTiS_2 → Li_xMoS_2 → Li_xCoO_2 (NMCA et al) → Li_xFePO_4 → **Li_xVOPO_4**

$LiFePO_4$ most stable cathode

But low ED

One Approach is multi-electron using Vanadium Redox

Cuts amount of TM needed

Vanadium is 4th most abundant TM

Phosphates are more stable than oxides

$VOPO_4$

Many structural variants

Anode: 2 Li, 2 Na, 1Mg, 1 Ca

Cathode: V^{5+} to V^{3+}

Are 2 Li-Ion Intercalation Cathodes Structurally Viable? YES

Li_xTiS_2 → Li_xMoS_2 → Li_xCoO_2 (NMCA et al) → Li_xFePO_4 → **Li_xVOPO_4**

Science & Technology Highlights

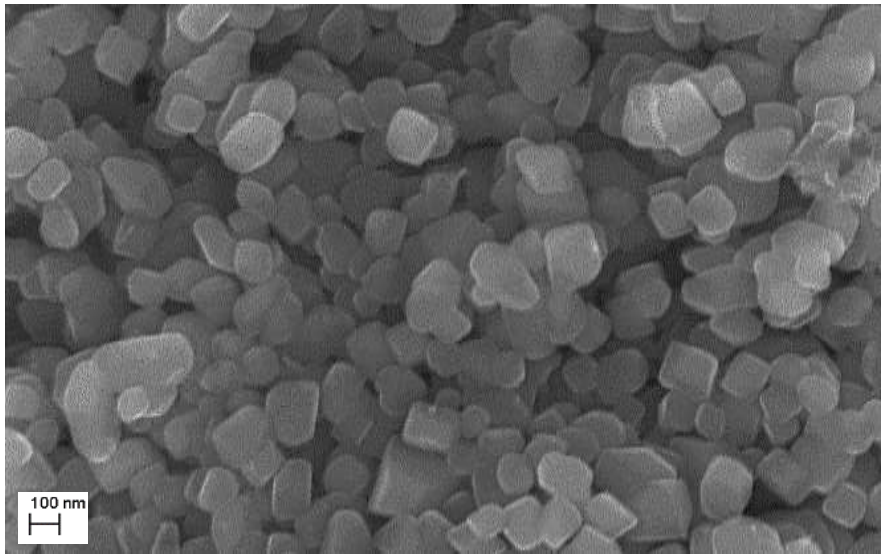
2018 Report
Feb 2019

R&D Fundamentals

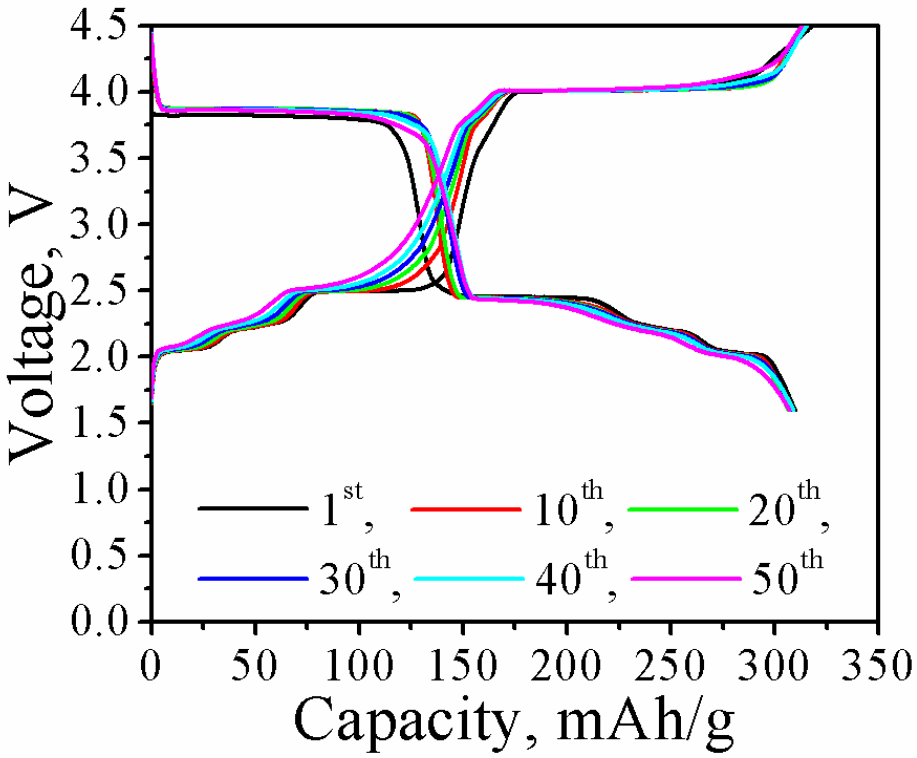
Advancing the state of battery science.

"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."

Small cuboid particles allow two Li ions to be reversibly intercalated



Synthesis is criticall
ε-$VOPO_4$ particles
~100-200 nm
Cuboid particles



ChemComm

COMMUNICATION

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Cite this: *Chem. Commun.*, 2018, 54, 7802

Received 26th March 2018,
Accepted 17th June 2018

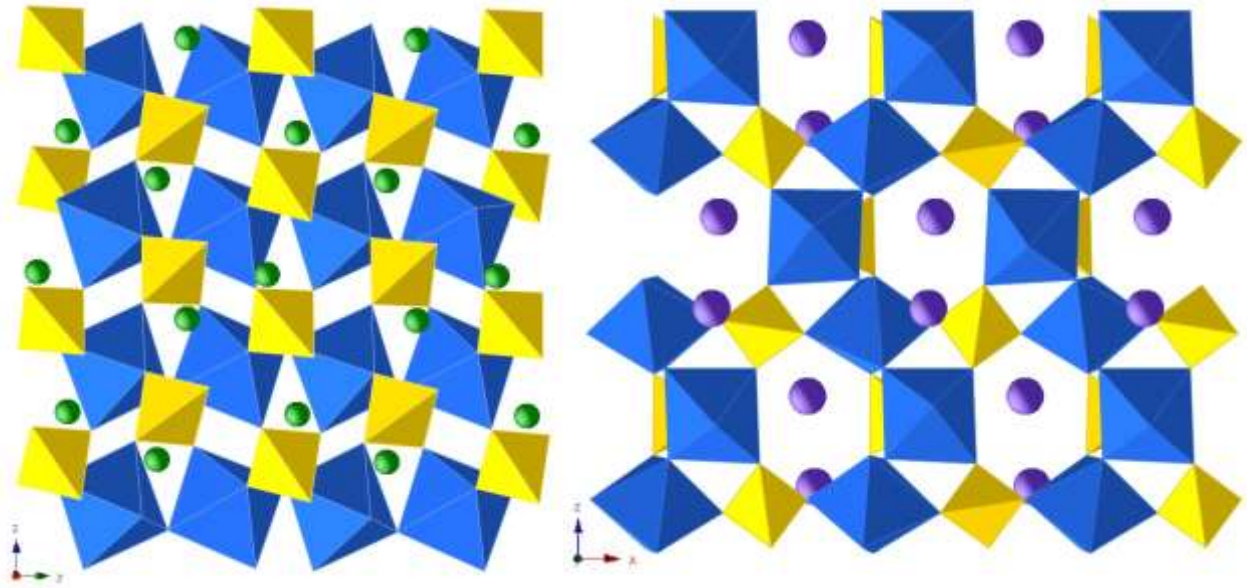
DOI: 10.1039/c8cc02386g

rsc.li/chemcomm

Enabling multi-electron reaction of ε-$VOPO_4$ 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,[a] Clare P. Grey,[b] Louis F. J. Piper[a] and M. Stanley Whittingham*[a]

Structural design allows other ions to be intercalated

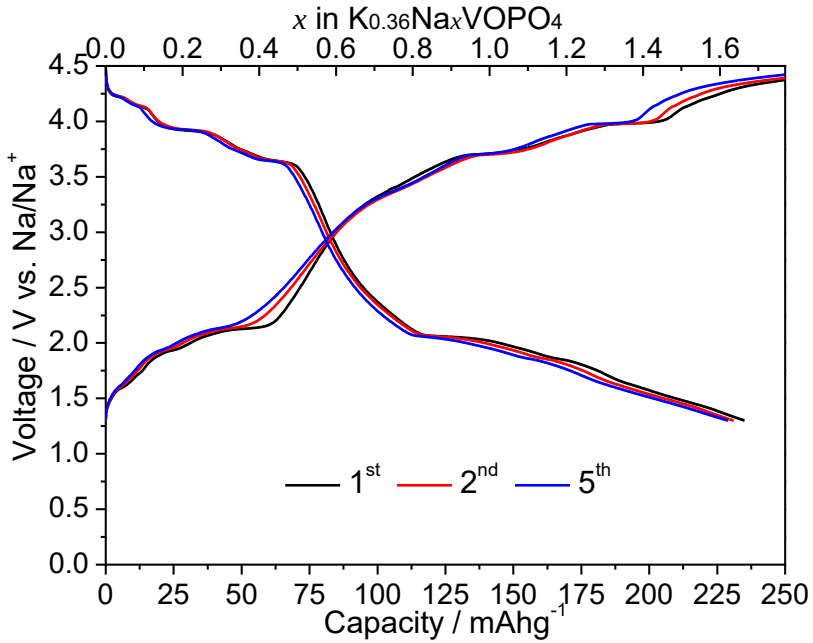


ε-$VOPO_4$

85.51Å^3 /PO_4

$KVOPO_4$

106.8Å^3 /PO_4



- There are more than 7 "$VOPO_4$" phases
- Na needs more open lattice than that of ε-$VOPO_4$
  - K can also be cycled
  - Mg is not rechargeable

FULL PAPER

Sodium-Ion Batteries

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$KVOPO_4$: 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**

What are the battery systems of the future?

- ✓ **Lithium intercalation systems will dominate for next 5-10 years**
  - ✓ NMCA likely to be dominant
  - ✓ $LiFePO_4$/$LiMnPO_4$ /LiVOPO4 systems still have key markets
  - ✓ **Need safe and stable electrolytes**
- ✓ **Na cells (1-2 Na) may also be viable for fixed storage, but safety issues (mp 100°C)**
- X **Magnesium not a technical option**
  - X No evidence that Mg can transfer more than 1 electron/TM (=1/2 Mg); lower voltage than Li
  - X Mg readily grows dendrites
  - ✓ "Anything Mg can do, Li can do better"
- ✓ **Calcium more attractive than magnesium**
- ✓ **Lithium sulfur has the highest ED but is a real bear**
- X **Lithium air not viable technically and no ED incentive**
- ✓ **Zinc systems have renewed interest for low ED applications**