# Summary of Chinese Battery Research in CERC

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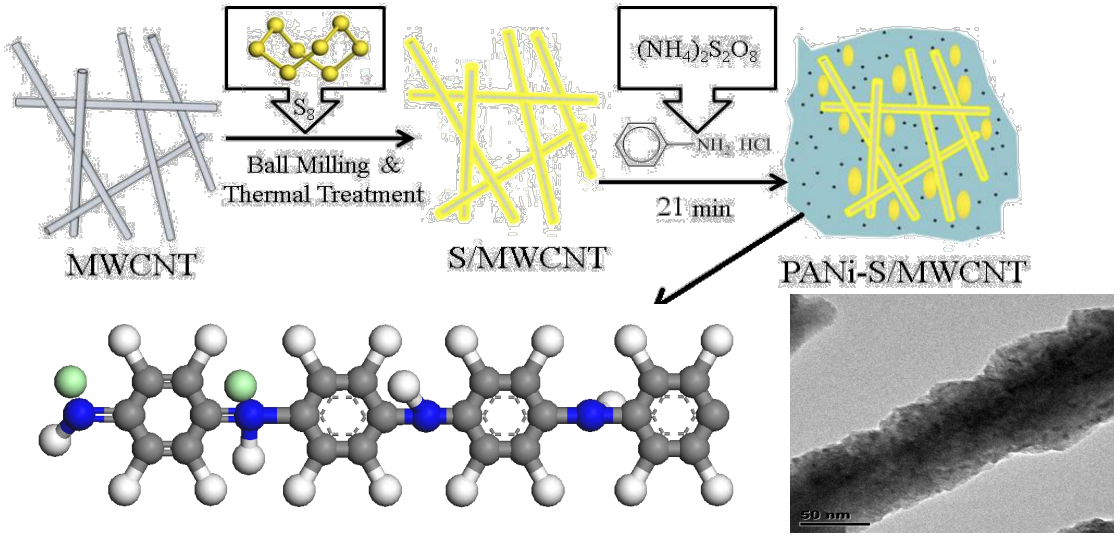
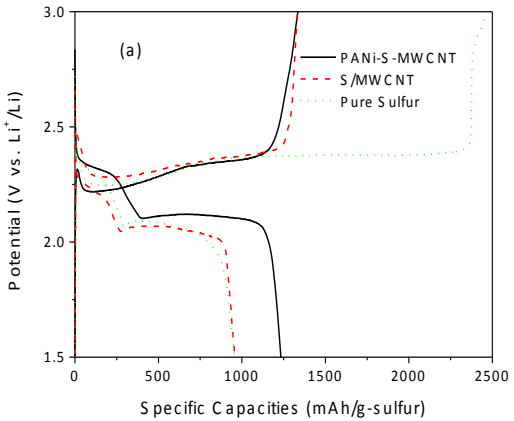
# Common interests on the cooperation in battery researches

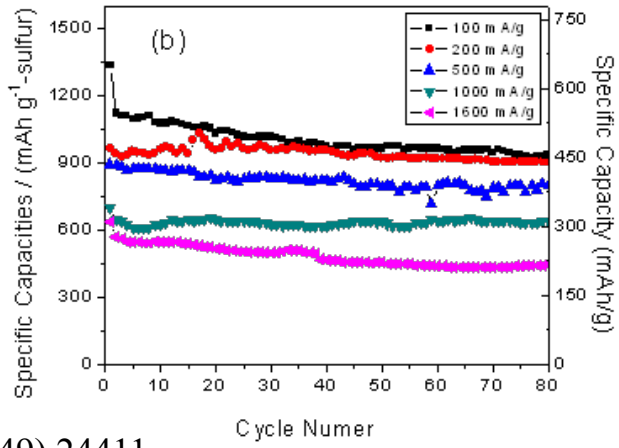
1. **Characterize Degradation Mechanisms in Li-Ion Batteries**
   - Multi-scale Characterization of bulk degradation mechanisms
   - Characterization of Solid Electrolyte Interfaces
   - Computational study of degradation mechanisms resulting from phase transformations
2. **Advance High Energy Density Battery Chemistries**
   - Advanced Li-ion chemistries
   - Li-sulfur batteries and their key materials
   - Metal-air batteries
3. **Reduce Obstacles to Battery Implementation**
   - Safety
   - Reuse & recycling
   - Testing protocols & standardization
4. **Develop Accurate Models of/Controls for Battery Systems**
   - Multi-scale modeling
   - Control strategies and health management

# Composite S/C material for Li-S batteries

*Feng Wu, (BIT)*



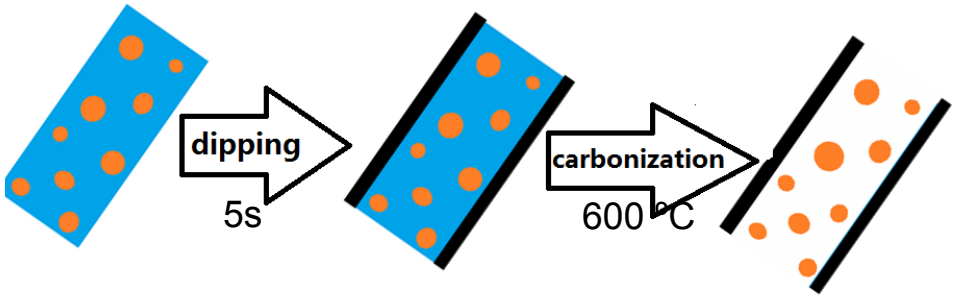




*J. Phys. Chem. C*, 2011, *115* (49),24411

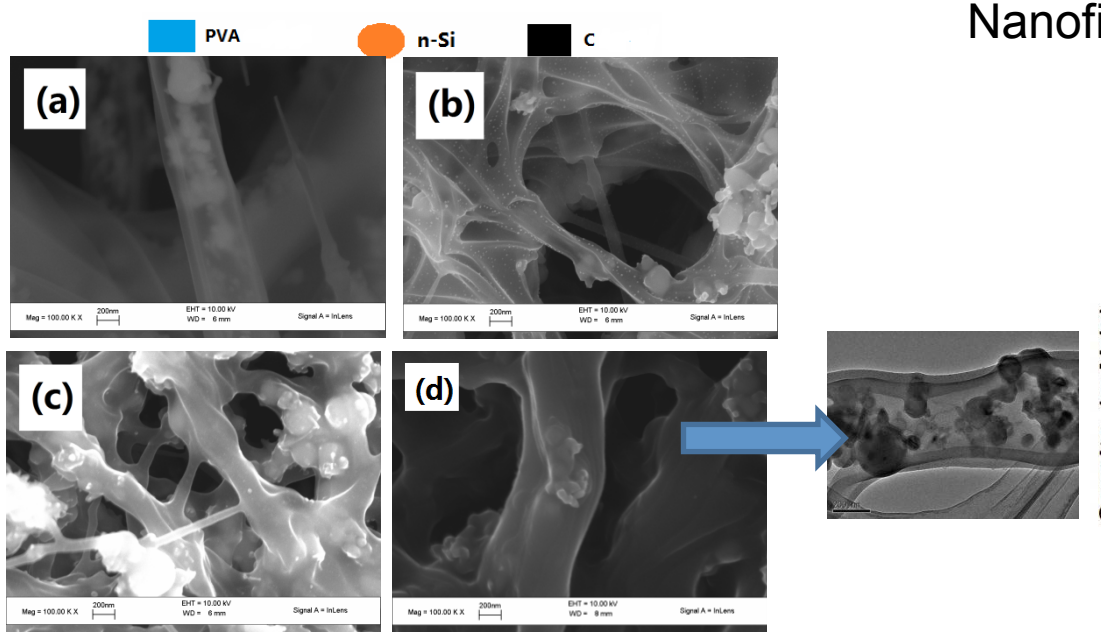
- **PANi was not only uniformly coated onto the surface of the S/MWCNT composite.**
- **The polymerization created a shell to prevent shuttle mechanism, which led to the elevation of the columbic efficiency doubled up to 90%.**
- **The discharge capacity kept at 1334.4 mAh $g^{-1}$. Rapid polymerization prompted up the rate performance to 634.1 mAh/g at 1C.**

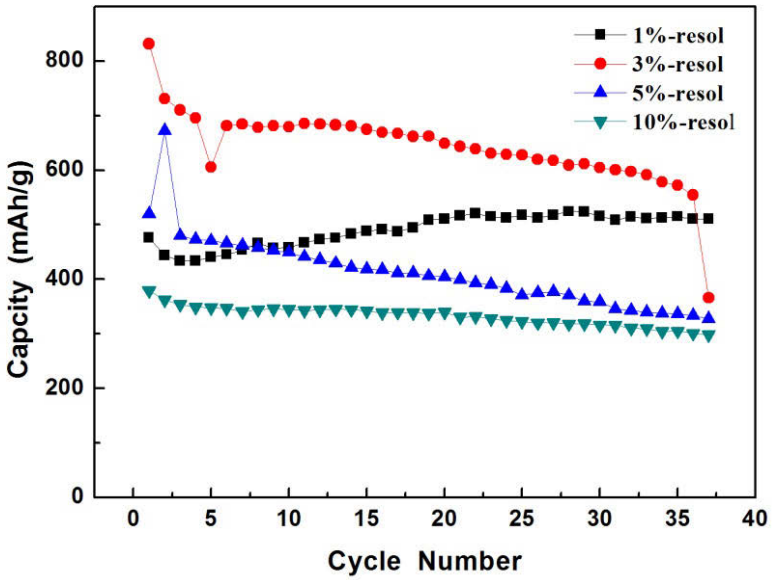
# Si-Composites by coating Si/PVA fiber with Resol Resin

*Feiyu Kang (THU)*




A method for preparation the kind of Si/C composite Anode Materials for LIB have been developed by Dipping Resol Resin on the Surface of Si/PVA Electrospinning Nanofibers

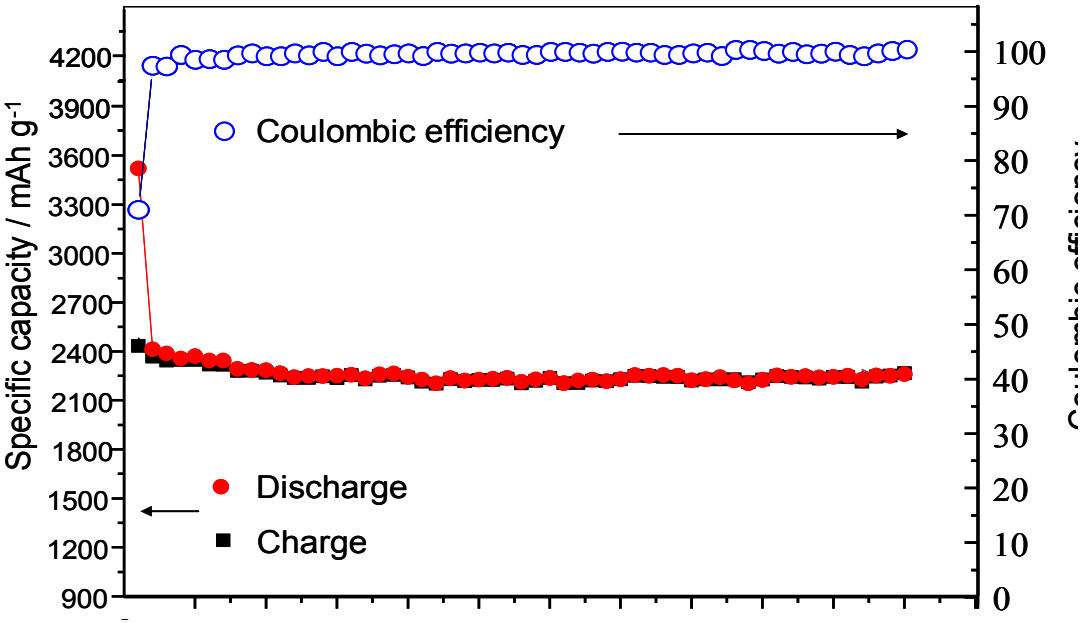


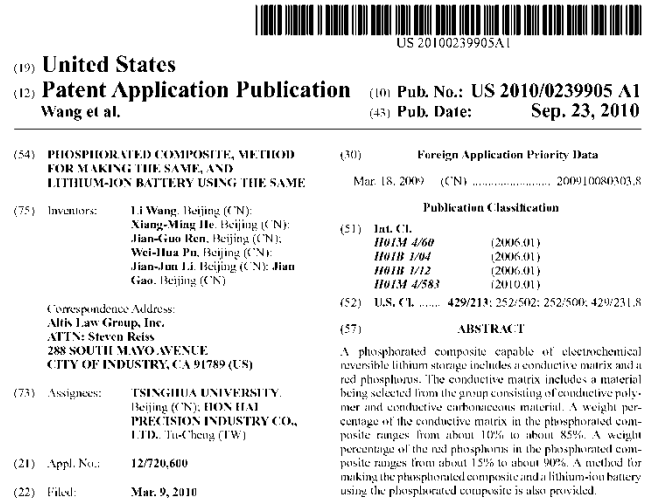




**Effect of concentration of Resol solution (a)10%-resol; (b)5%-resol; (c) 3%-resol; (d) 1%-resol**

# Nano-Structured Phosohorus Composite Anode Materias

*Xiangming He*, Ect., *(THU)*



US 20100239905A1

(19) United States

(12) Patent Application Publication

Wang et al.

(10) Pub. No.: US 2010/0239905 A1

(43) Pub. Date: Sep. 23, 2010

(54) PHOSPHORATED COMPOSITE, METHOD FOR MAKING THE SAME, AND LITHIUM-ION BATTERY USING THE SAME

(75) Inventors: Li Wang, Beijing (CN); Xiang-Ming He, Beijing (CN); Jian-Guo Ren, Beijing (CN); Wei-Hua Pu, Beijing (CN); Jian-Jun Li, Beijing (CN); Jian Gao, Beijing (CN)

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(21) Appl. No.: 12/720,600

(22) Filed: Mar. 9, 2010

(30) Foreign Application Priority Data

Mar. 18, 2009 (CN) ..... 200910080303.8

Publication Classification

(51) Int. Cl.

H01M 4/60 (2006.01)
H01B 1/04 (2006.01)
H01B 1/12 (2006.01)
H01M 4/583 (2010.01)

(52) U.S. Cl. ..... 429/213; 252/502; 252/500; 429/231.8

(57) ABSTRACT

A phosphorated composite capable of electrochemical reversible lithium storage includes a conductive matrix and a red phosphorus. The conductive matrix includes a material being selected from the group consisting of conductive polymer and conductive carbonaceous material. A weight percentage of the conductive matrix in the phosphorated composite ranges from about 10% to about 85%. A weight percentage of the red phosphorus in the phosphorated composite ranges from about 15% to about 90%. A method for making the phosphorated composite and a lithium-ion battery using the phosphorated composite is also provided.

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**Lithium Batteries**

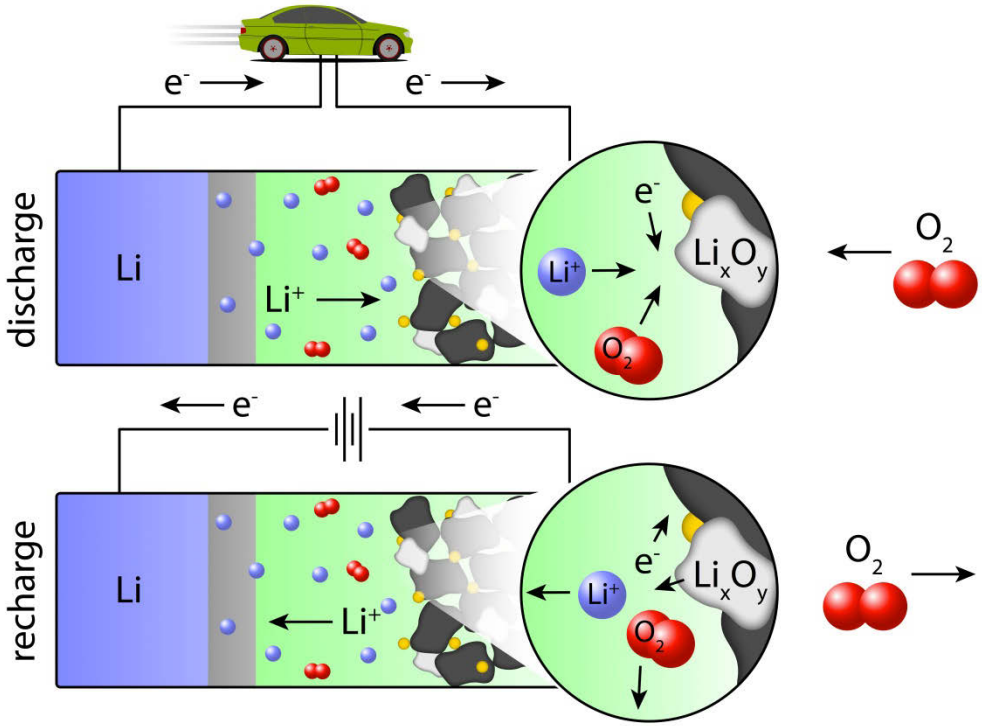
DOI: 10.1002/anie.200((will be

Angewandte Communications

## Nano-Structured Phosphorus Composite as High Capacity Anode Materials for Lithium Batteries**

*Li Wang, Xiangming He*, Jianjun Li, Wenting Sun, Jian Gao, Jianwei Guo and Changyin Jiang*

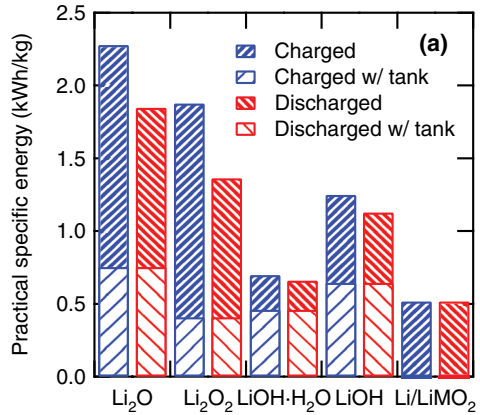
# Li-air Batteries



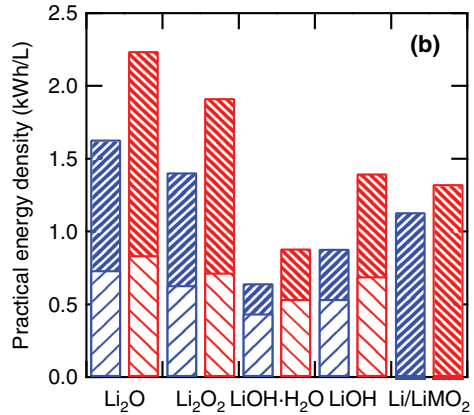

$2Li^+ + O_{2(g)} + 2e^- \rightarrow Li_2O_{2(s)}$ $U^o = 2.96$ V

$2Li^+ + ½\ O_{2(g)} + 2e^- \rightarrow Li_2O_{(s)}$ $U^o = 2.92$ V

**Estimated practical specific/volumetric energy density**




300-400% vs. Li-ion




30-60% vs. Li-ion

Li-air projected cost: $100/kWh[1], $238/kWh[2]

[1]Johnson Controls, 2011 Battery Congress

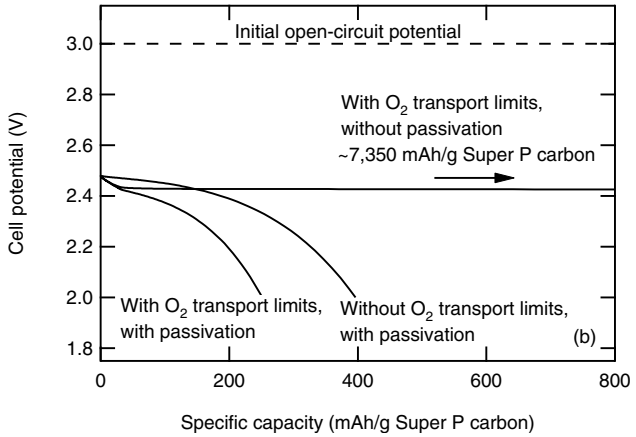
[2]J. Power Sources 199 (2012) 247– 255

JES **159**, 2193, R1 (2012).

# Fundamental Understanding of Cathode Phenomena

**A primary objective is to reveal which factors most strongly limit performan**

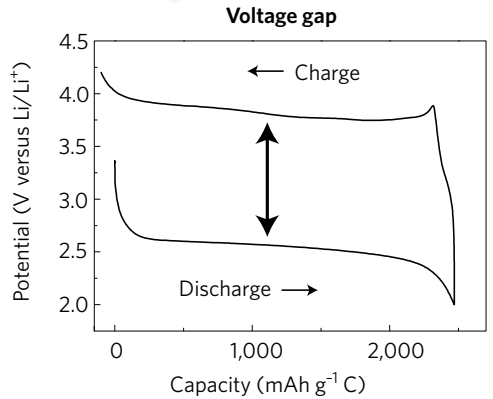
Continuum-scale models and flat-electrode experiments suggest that electrical passivation can limit capacity

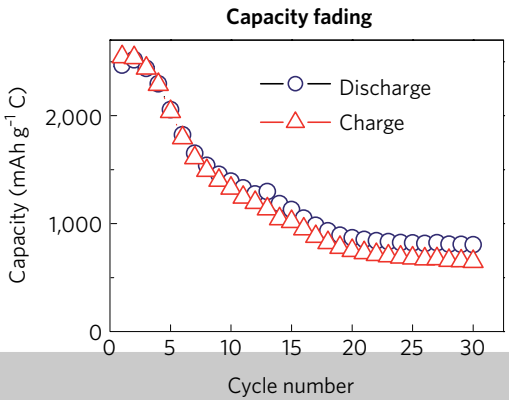



Simulated discharge curves illustrating the effects of $O_2$ transport or electrical passivation.

J. Electrochem. Soc. 158, A343 (2011)

High efficiency and long cycle-life are also challenges

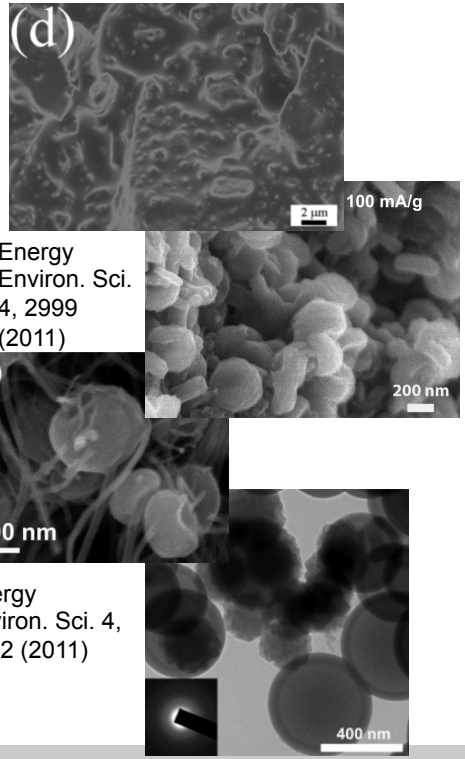



Nature Mat. 11, 19 (2012)

Morphology of discharge phase can vary dramatically

Energy Environ. Sci. 5, 8927 (2012)




Energy Environ. Sci. 4, 2999 (2011)

Energy Environ. Sci. 4, 2952 (2011)

Nano Lett. 12, 4333 (2012)

# A Comparison of US and Chinese Battery Testing Protocols

I Bloom(ANL), D. Robertson(ANL) J. Christophersen(INL)
Wang Fang(CATARC)and Fan Bin (CATARC)

- Eight 7.5-Ah LiFePO4 cells were received in January 2012
- Test plan:
  - USABC EV DST cycling at 25°C
  - China QC/T 743 and 846 protocols at 25°C
- Testing started in 03/2012: four cells are being tested per protocol
- **Similarities in the two sets of protocols**
  - Usable DOD (energy) window, temperature, capacity measurements at RPT and EOT at 80% performance degradation
- **Differences in the two sets of testing protocols**
  - Constant-current cycling vs. dynamic, power-based cycling profile
  - Power density measurement at 50% DOD (10-s pulse) vs. peak power estimation at 80% DOD (30-s pulse)
  - RPT frequency: 24 cycles (6 days, Chinese) vs. 50 cycles (10.5 days, USABC)
  - RPT duration: 18 h vs. 35 h

Early results indicate that the USABC test protocol stresses the cells more than the Chinese test protocol

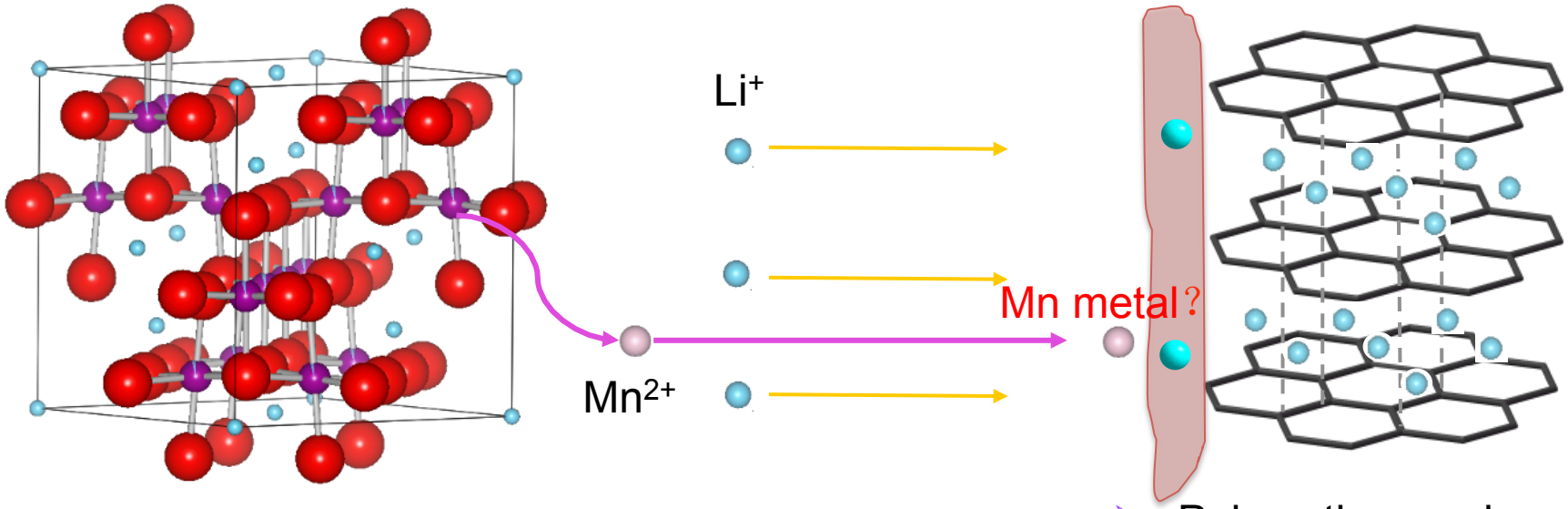
# Capacity fading mechanism of LMO/C system

- Dissolution-deposition of Mn from cathode to anode

**Disproportionation:**

$LiMn_2O_4 \rightarrow Li[Li_xMn_{2-x}]O_4 + Mn^{2+}$

SEI layer




- Loss of active $LiMn_2O_4$
- Impedance rising due to inactive products

- Poison the anode

But HOW?

Vetter, J. *et.al* . *Journal of Power Sources* **2005**, *147*, 269.
Whittingham, M. S. *Chem. Rev.* **2004,** 104, 4271-4301

# Challenges for the Mn DMD process

- **The oxidation and bonding state of Mn** deposited on anode is not clear yet;

- **The reaction mechanism of the Mn deposition** is yet to be discovered;

# Half cells-$LiMn_2O_4$ *vs.* Li anode

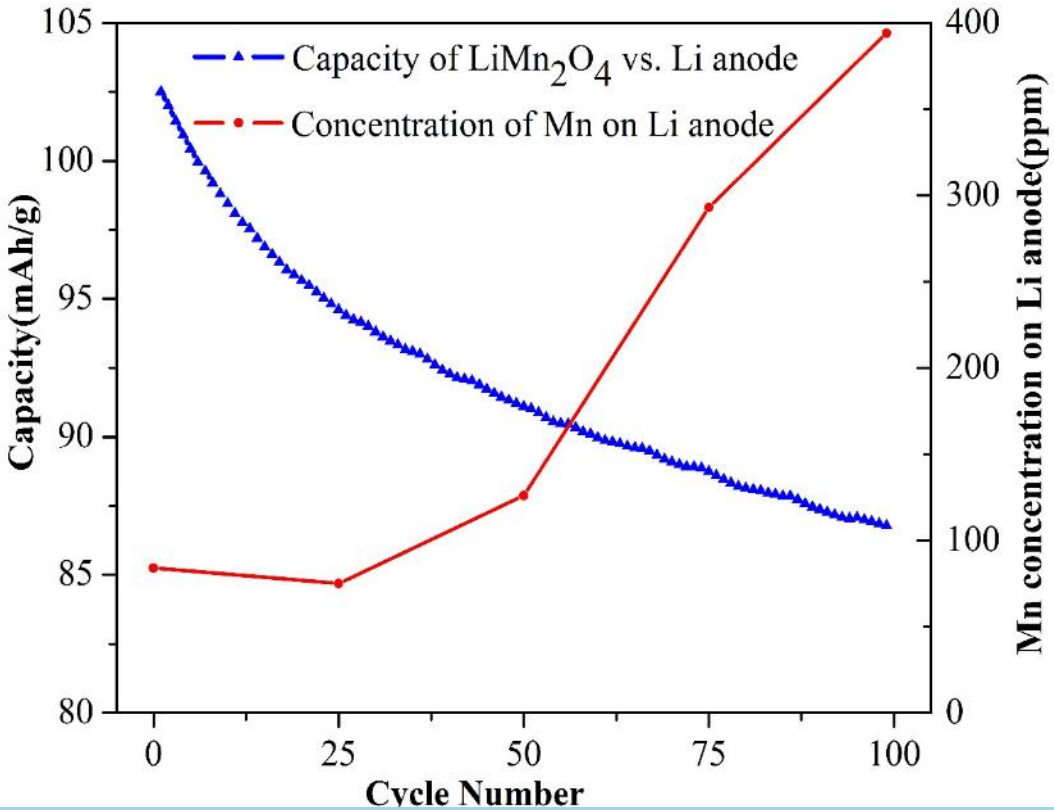



Figure 1. Cycle performance of $LiMn_2O_4$/Li metal cell (blue curve) and concentration of Mn deposited on Li anodes after different charge -discharge cycles (red curve).

Li anodes were separated and tested by ICP for concentration of Mn deposited on anodes

- A significant amount of Mn (~85 ppm) was already deposited on the anode after the formation cycles, and gradually increased with the cycling.
- The concentration of Mn reached up to about 400 ppm after 100 cycles of charge and discharge.
- Correlation between manganese deposition on the anode and capacity fading in LMO -based cells?

# Full cells-$LiMn_2O_4$ *vs.* Different anodes

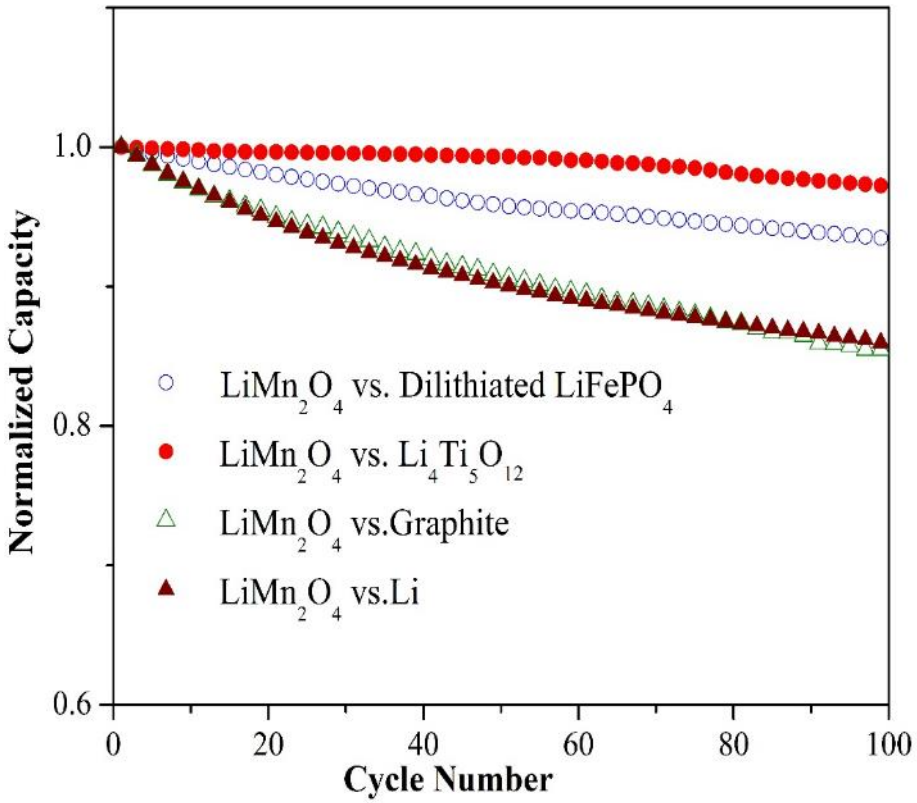



Figure 2. Cycle performance of coin cells with LiMn2O4 cathodes vs. anodes with different Li -intercalation potentials.

- MCMB-LMO shows the same capacity fade as Li-LMO
- LTO-LMO shows less capacity fade
- Mn deposition related?