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Progress in Battery Research in Selected Areas

Jun Liu

Pacific Northwest National Laboratory
Richland, WA 99352

Acknowledgement:
Jason Zhang, Jie Xiao, Yuyan Shao, Jie Xiao, Xiaolin Li

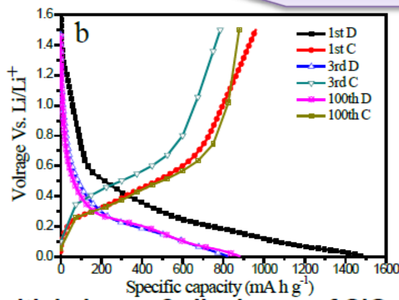
Funding: DOE Office EERE Batt,
Joint Center for Energy Storage Research (JCESR)

DOE has made significant investment in the development of battery systems

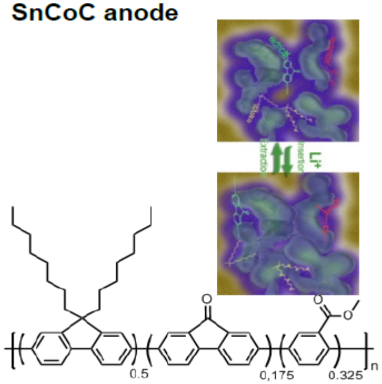
ANODES
$SiO\text{-}Sn_yCo_{1-x}Fe_xC_z$ composite coupled with conductive binder

ELECTROLYTES
High voltage electrolytes with additives to stabilize interface of cathode and anode

CATHODES
Full Gradient concentration (FCG) $LiNi_xMn_yCo_zO_2$ with high concentration of Mn at the surface of the particle

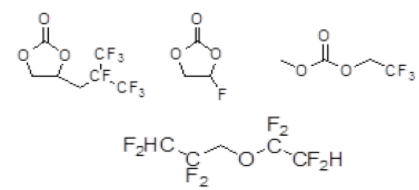


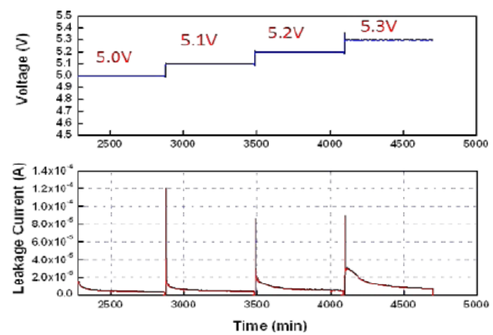
Initial charge & discharge of SiO-SnCoC anode



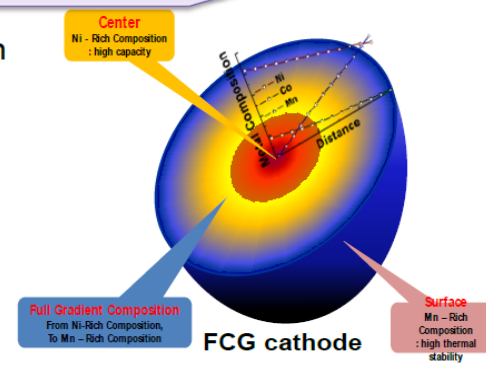
Conductive binder

Fluorine based electrolyte with additives:

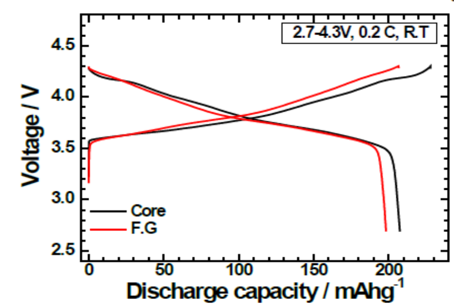




Floating test at different voltages of $LiNi_{0.5}Mn_{1.5}O_4/Li_4Ti_5O_{12}$ Cell using fluorinated electrolyte



FCG cathode

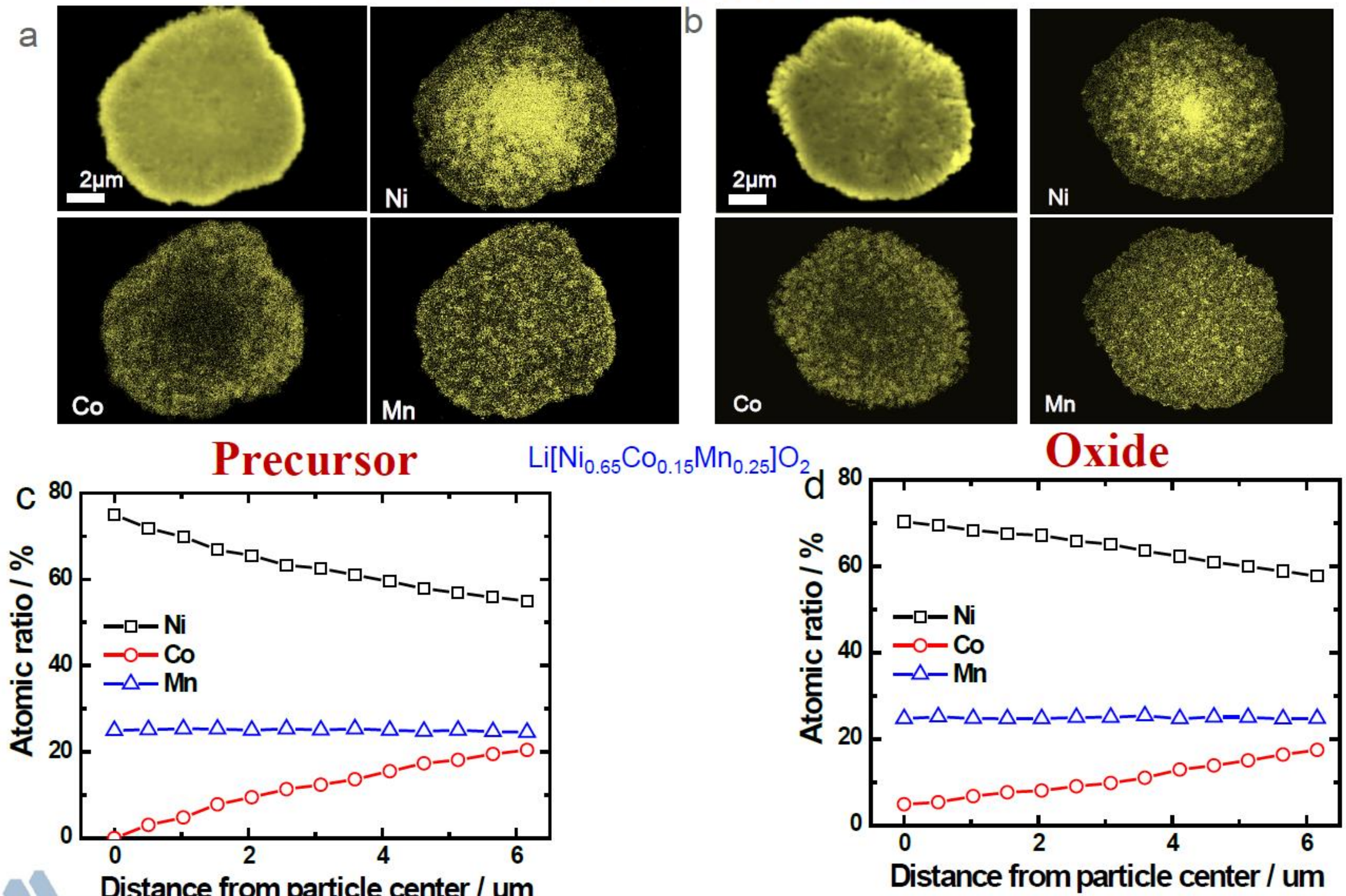


Initial charge & discharge of FCG cathode

From Khal Amine

Electrode Materials: Hierarchical Structures Control Morphology and Chemistry on Mutilscale

Cross section EPMA of precursor and (FCG) from Carbonate Process

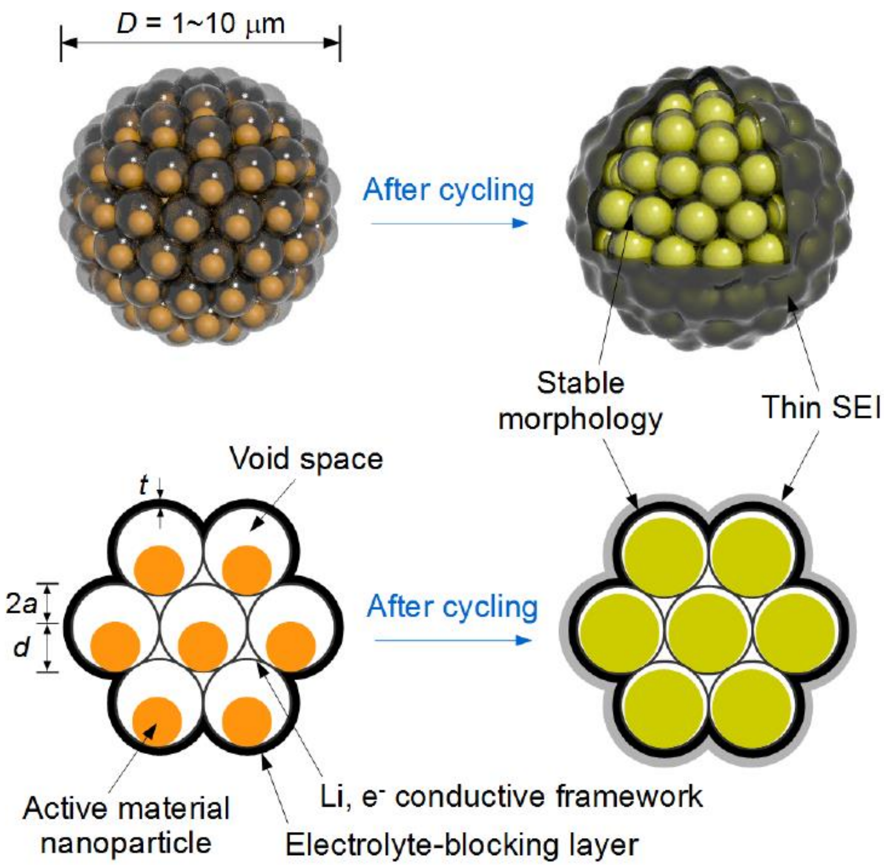


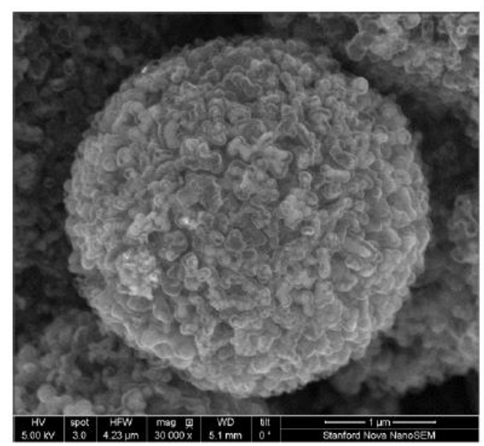
Tab density: 2.2g/cc

Hierarchical Structures in Si Anode Materials

Accomplishment

pomegranate-inspired design for Si anode





Cui group, Nature Nanotechnology, 9, 187 (2014)

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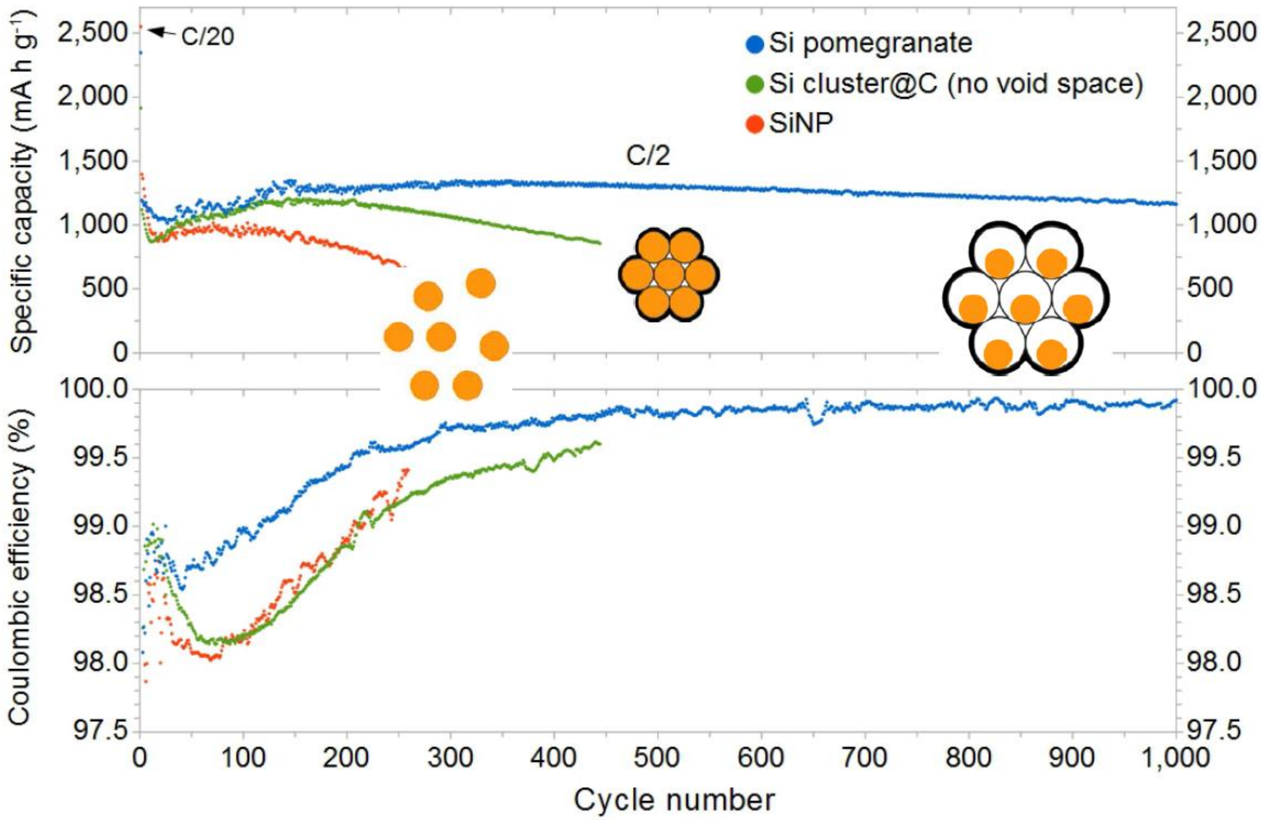
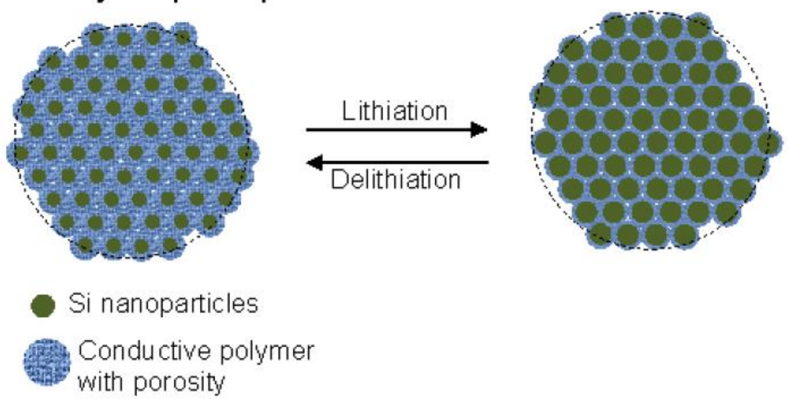
Accomplishment

-Battery performance

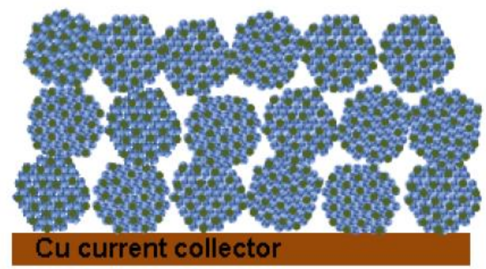


Accomplishments – Hierarchical electrode designs to improve energy density

Secondary composite particle

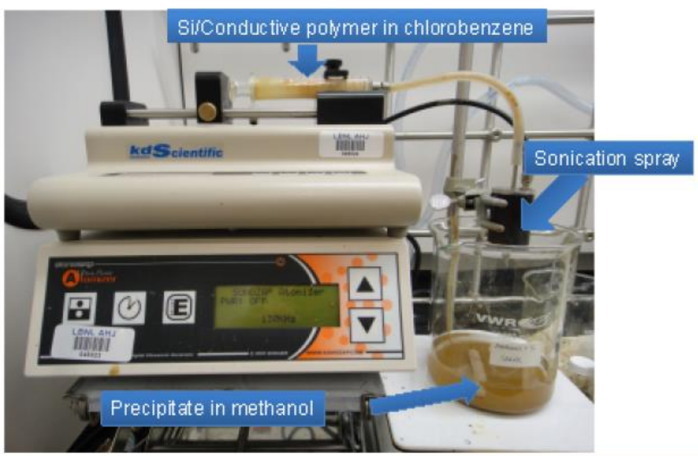


Secondary composite particles electrode

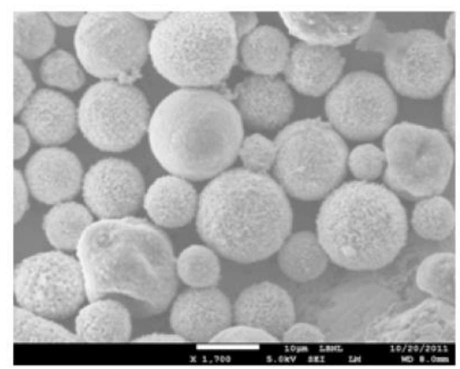


Advantages: Large micron size porosity, and stable dimension

Spray precipitation method to generate secondary particles

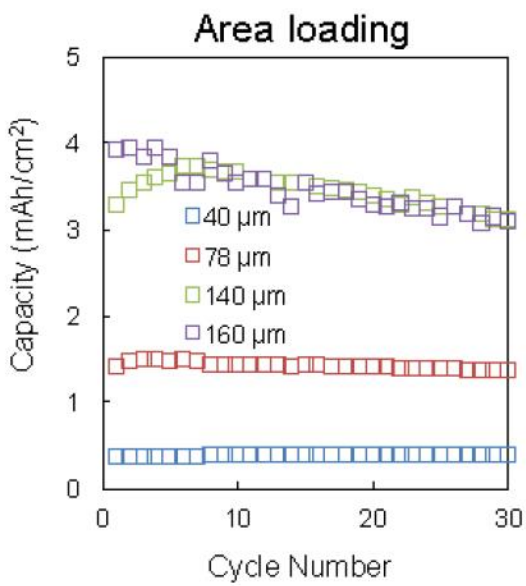


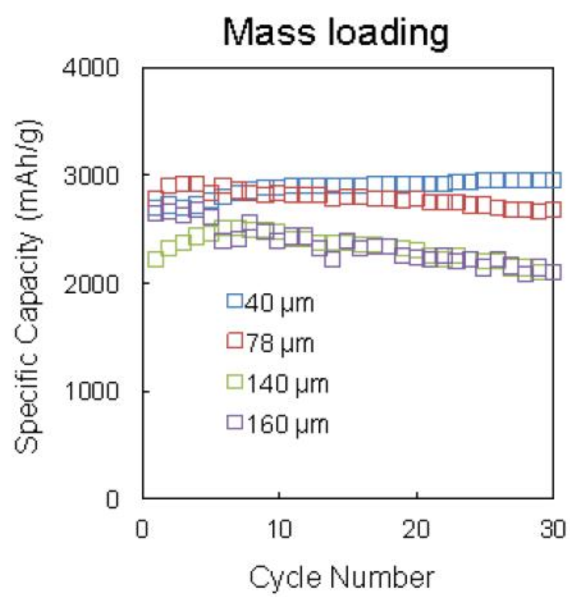
SEM image of Si/PFM Secondary particles

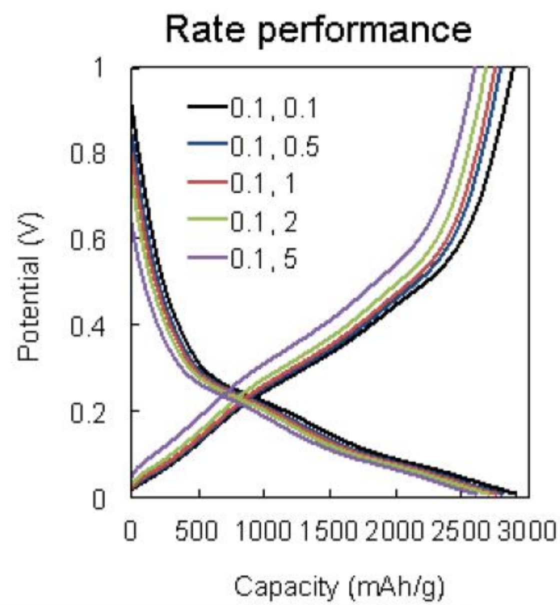


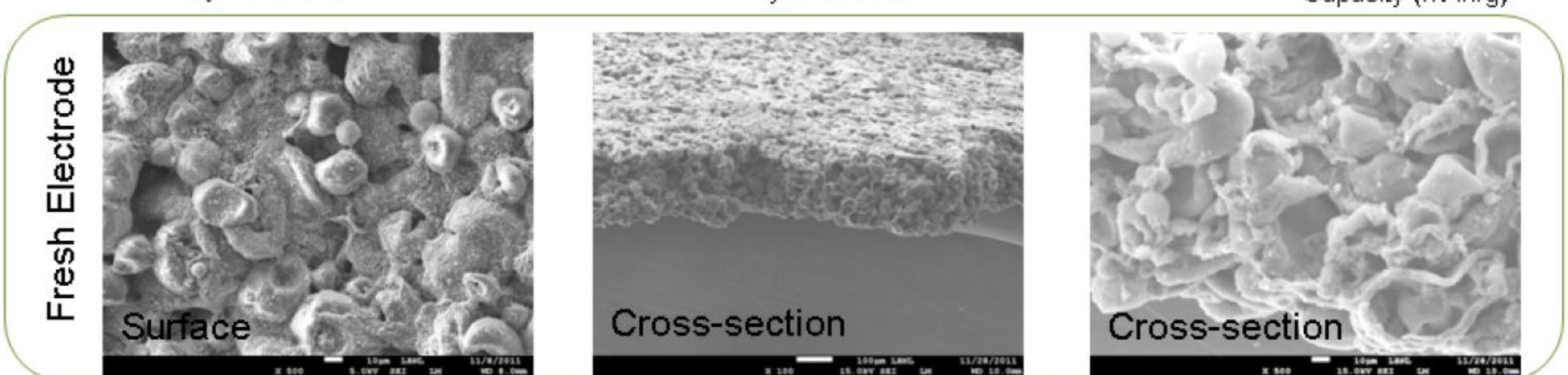
Accomplishments – Hierarchical electrode designs to improve energy density

Electrochemical performance of the Si secondary particle composite electrode









Update on Si-based High Capacity Anode

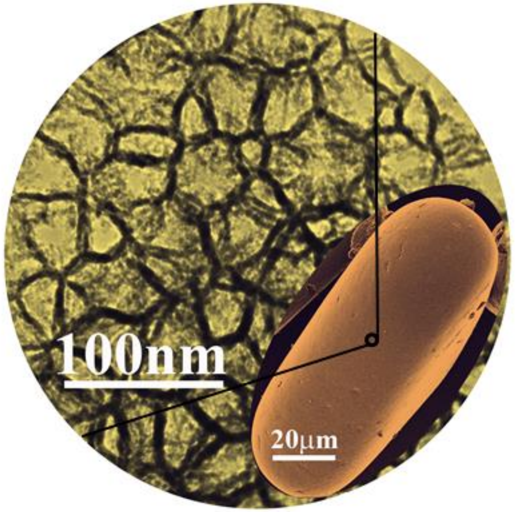
U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

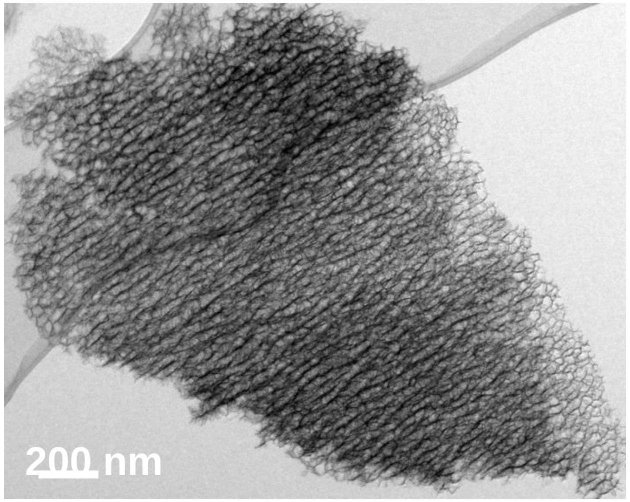
Pacific Northwest National Laboratory

Objective: Develop low cost, scalable methods for high capacity, stable, Si-based anodes.
Collaborators: Mike Sailor/UC San Diego, John Lettow/Vorbeck Inc.

Prepare and optimize mesoporous silicon sponge (MSS):

Particle size: ~ 20-40 μm
Pore size ~50 nm





Morphology of electrochemically etched Si

(In collaboration with Prof. Sailor of UCSD)

Particle volume change of Mesoporous Silicon Sponge (MSS)

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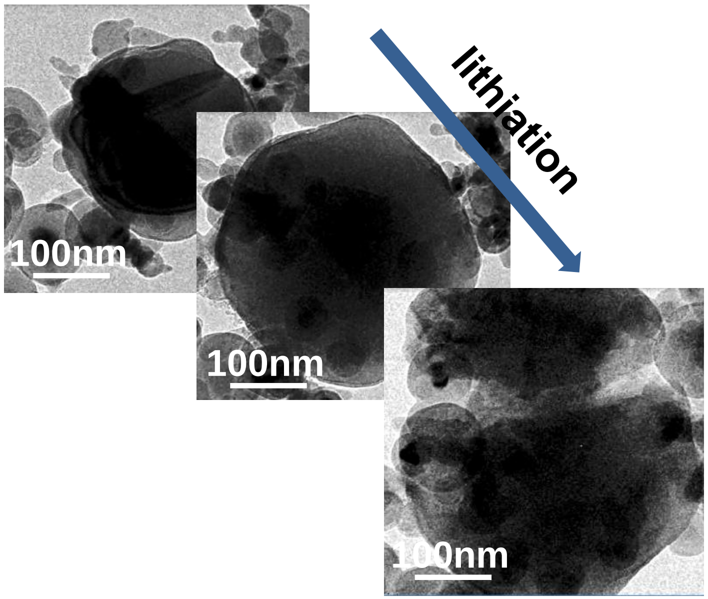

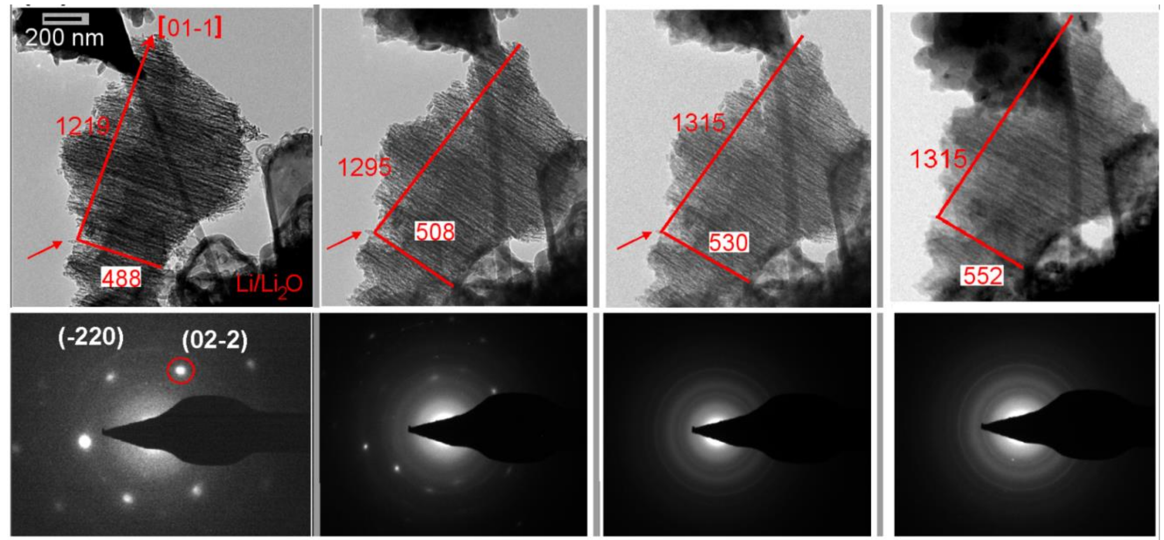

In situ TEM images before and after lithiation:

• Nanoparticles with the size > 200 nm break after deep lithiation

In situ TEM images of macroporous Si before and after lithiation:

•Expansion along the channel direction = 13.1%

• Expansion perpendicular to the channel = 7.8%

Diffraction pattern: fully amorphized after lithiation

➢ Volume expansion~30% after lithiation which is much less than ~300% volume expansion in other Si.

Li et al, accepted for publication in Nature Communications

Porous Si Electrode of ~1.5 mAh/cm²
With and without Pre-lithiation

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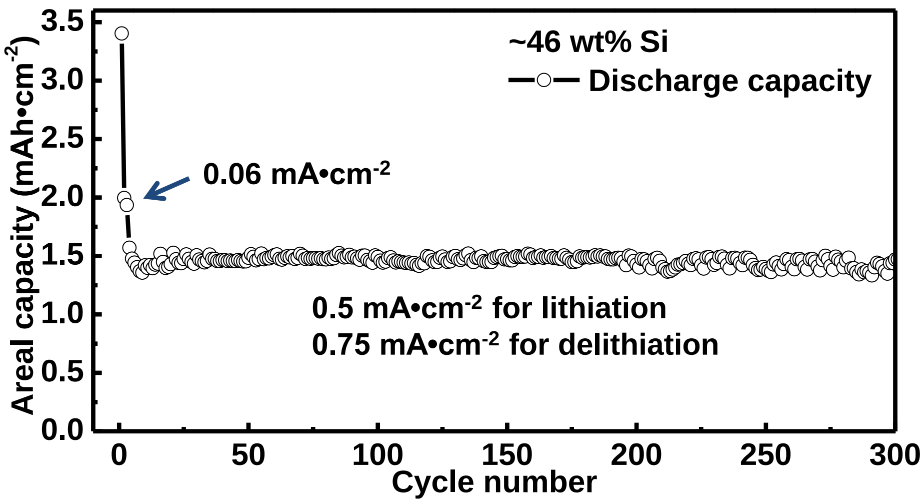

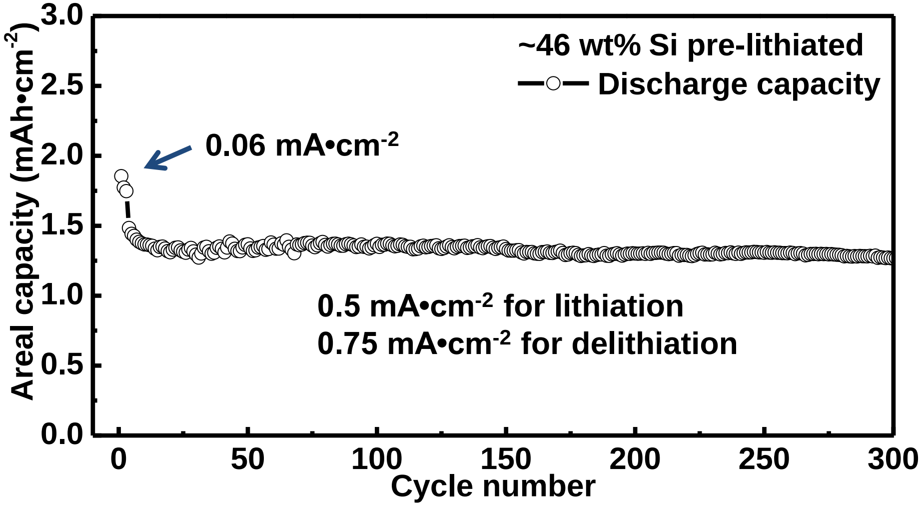

- Specific capacity: ~750 mAh/g (based on the full electrode)*
- Capacity retention: ~96% after 300 cycles
- First cycle irreversible loss is greatly reduced after prelithiation

Total electrode loading: ~2 mg/cm²
Si loading: ~1 mg/cm²
* See technical backup slides

Li et al, accepted for publication in Nature Communications

Effect of FEC
FEC Reduction and SEI formation Mechanism

XPS analysis on Li/F ratio

Elements samples	Li	C	O	F	Li/F ratio
Electrolyte (a), 2 cycles	27.7%	23.3%	24.1%	24.9%	1.11
Electrolyte (a), 35 cycles	22.7%	31.3%	37.6%	8.4%	2.70
Electrolyte (b), 2 cycles	22.9%	32.5%	32.1%	12.5%	1.83
Electrolyte (b), 100 cycles	21.0%	33.8%	31.9%	13.3%	1.58
Electrolyte (c), 2 cycles	21.1%	34.7%	32.2%	12.0%	1.76

(a) 1M $LiPF_6$ in EC/DMC (1:2 in vol), (b) 1M $LiPF_6$ in EC/DMC (1:2 in vol) with 10% FEC and (c) 1M $LiClO_4$ in pure FEC

- The ratio of Li/F in SEI layer formed in the FEC containing electrolyte is much larger than 1 and is not consistent with the value predicted by the conventional reduction mechanism.
- In the FEC-free electrolyte, composition of SEI film change significantly with increasing cycle number due to selective reduction of solvent.
- In the FEC-containing electrolyte, composition of SEI film does not change significantly with increasing cycle number, indicating the formation of stable protection layer.

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Effect of FEC: Reduction and SEI formation Mechanism

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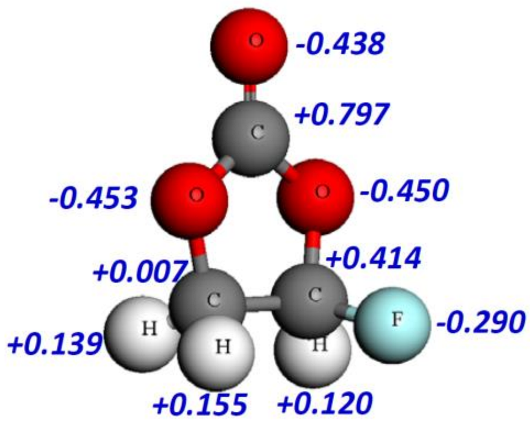
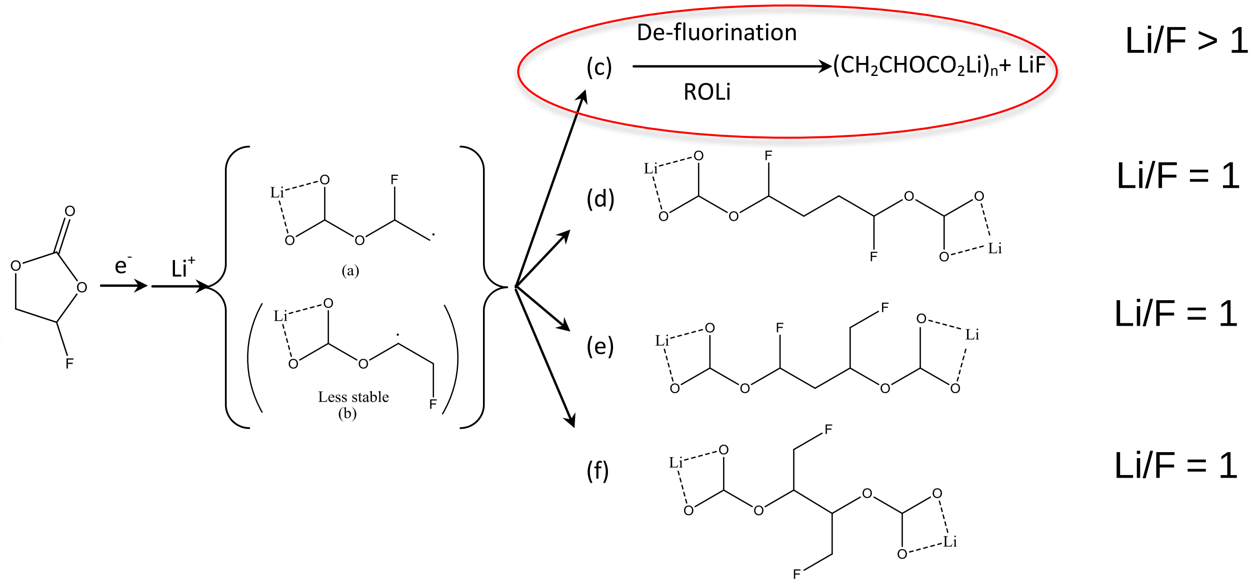
Calculated Mulliken Charges of atoms in FEC

Proposed possible reduction reaction of FEC



Fluoroethylene carbonate



- Lithium poly(vinyl carbonate) is a solid polymer with high tensile strength (good SEI).
- ROLi is the reduction products of alkyl carbonates and serves as strong bases to remove HF

Chen et al, ChemSusChem,7(2), 549–554 (2014).

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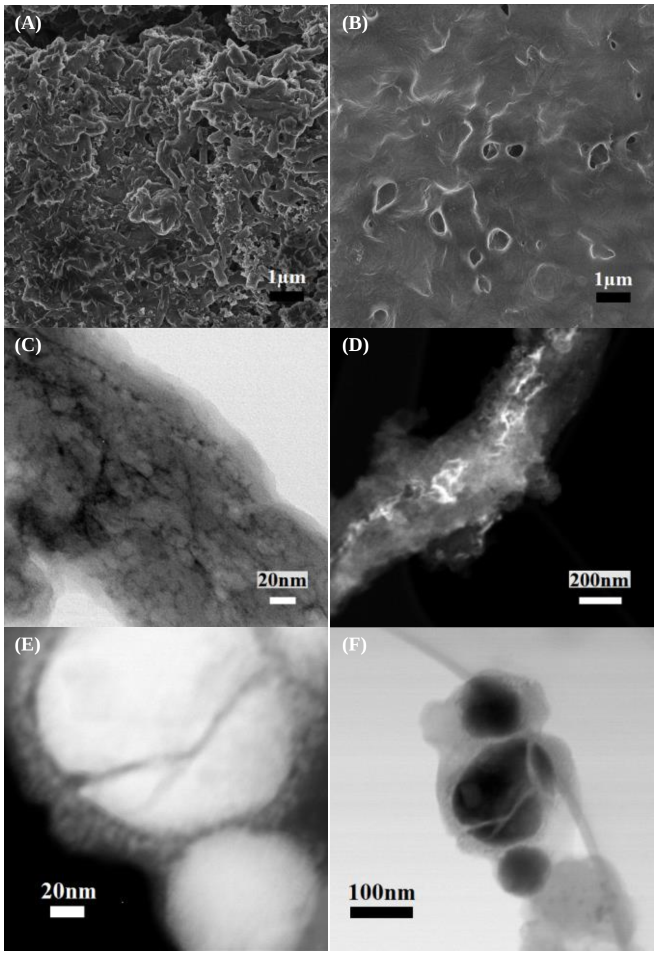
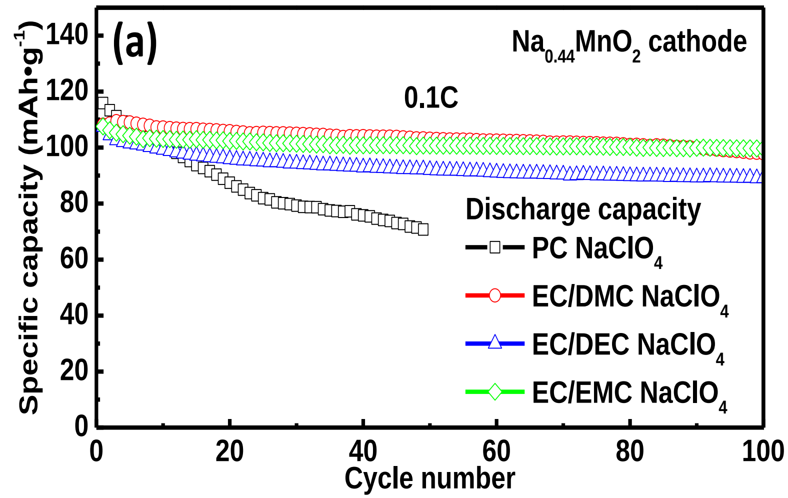
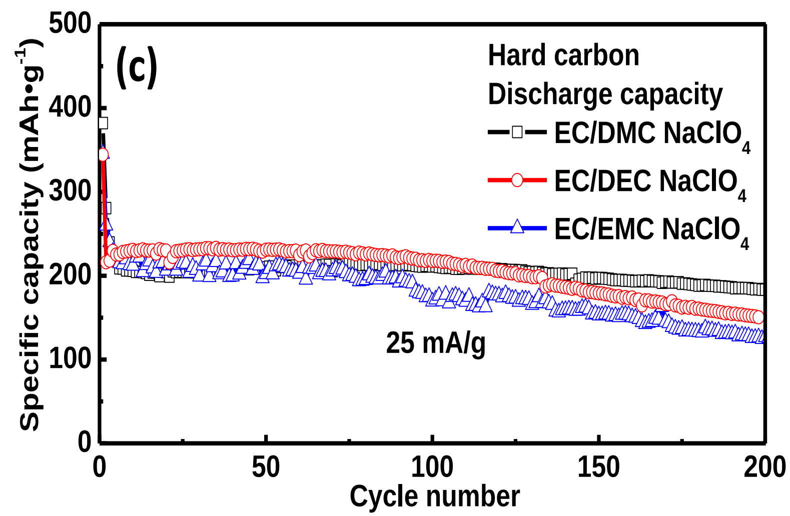
Na ion chemistry is very sensitive to electrolytes and SEI formation



SEI on Sn alloy/c anodes





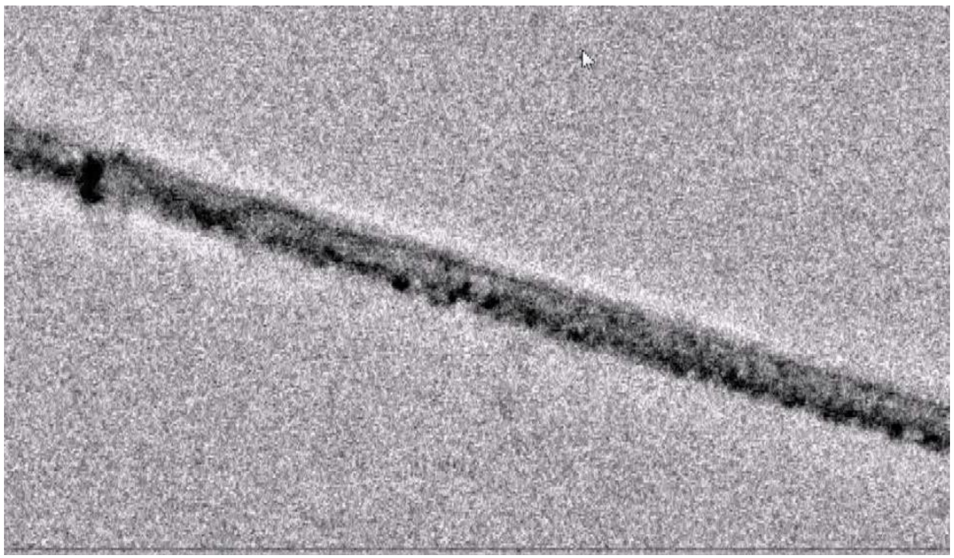
Effect of electrolytes

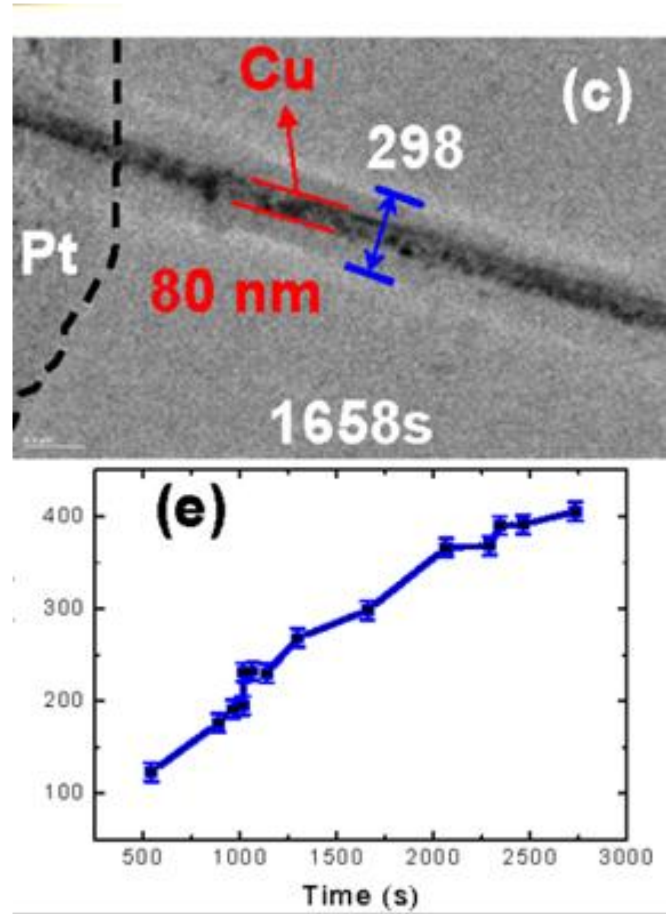
L. Jie et al, Advanced Materials, 2014

Supported by DOE BES

Liquid electrochemical cell enable in-situ TEM using real electrolyte: lithiation

- In-situ TEM study of battery using true electrolyte, paving the path for in-situ study of SEI layer



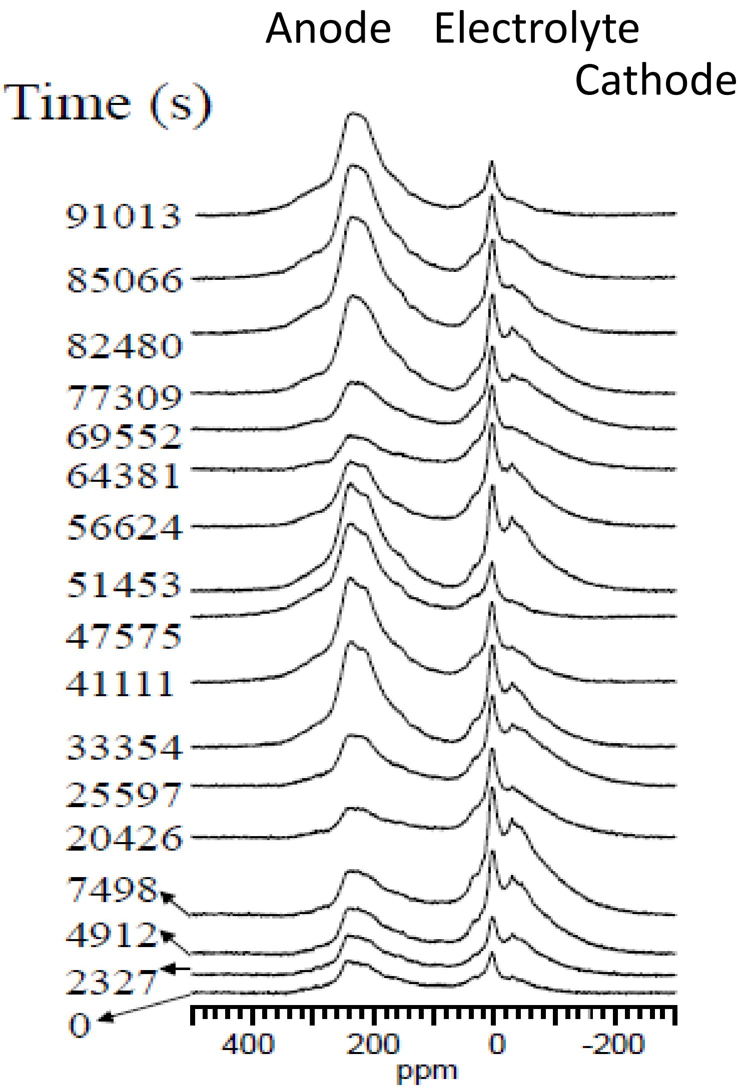


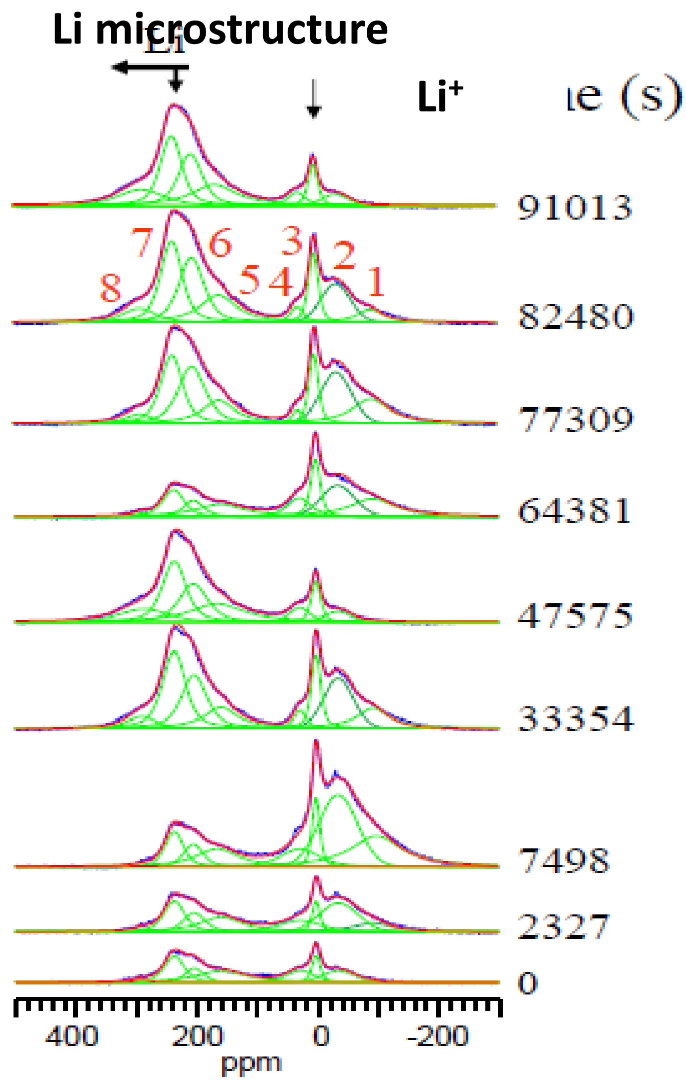
Lithiation of Si (coated with Cu on one side to increase the electron conduction) in EC-DMC based electrolyte by holding the potential at 0.03V range

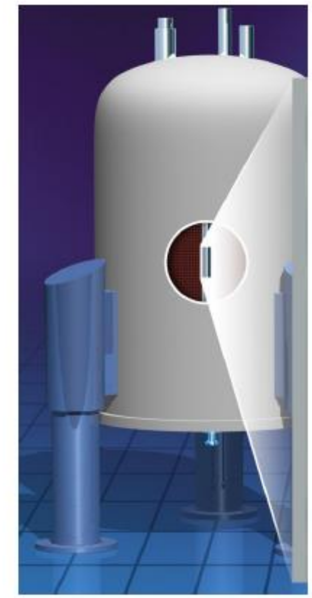
M. Gu, L. R. Parent, L. Mehdi, R. R. Unocic, M. T. M., R. L. Sacci, W. Xu, J. G. Connell, P. Xu, P. Abellan, X. Chen, Y. Zhang, D. E. Perea, L. J. Lauhon, I. Arslan, J. Zhang, J. Liu, Yi Cui, N. D. Browning, and . Wang, Nano Letters, 2013

Supported by JCESR

In-situ experiments provide information about the battery chemistry

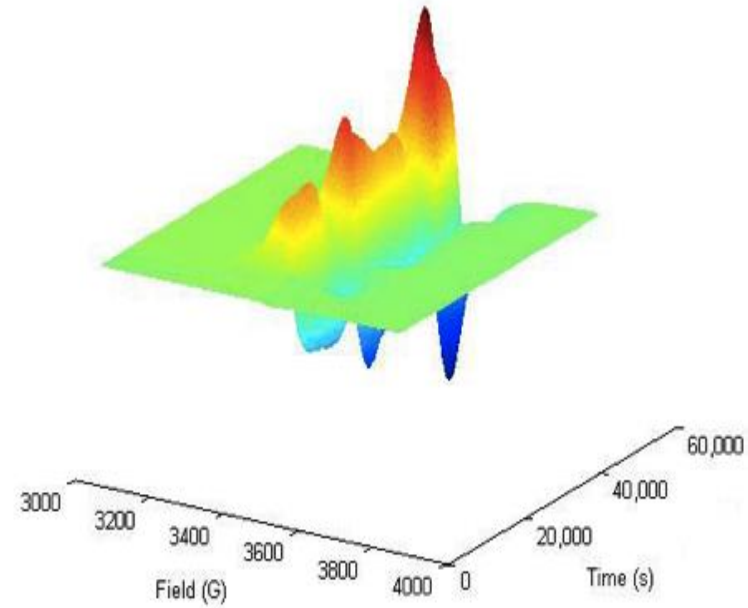






J. Hu, J. Xiao, J. Liu et al, supported by JCESR

In situ Electronic Paramagnetic Resonance (EPR) Provides Direct Evidence of $S_3^{\bullet}$ Radicals



Manuscript in preparation

- ➢ Concentration of $S_3^{\bullet}$ radicals demonstrate periodic changes during cycling. (A radical battery!)
- ➢ What are the roles of sulfur radicals in the electrochemical process?

**** Submitted***

Potential of Mg Batteries

	Li	Mg	Note
Melting point / °C	180	650	Safety
Reactivity in air	High	Low	
Volumetric capacity/ (mAh/cm^3)	2062	3832	Energy density
Electrode potential/ V (vs SHE)	3.04	2.37	
Price of metal/ ($/ton)	65K	2.7K	Cost
Earth Abundance/ ppm	20	23K	

Safe, cost-effective, high energy density (potentially).

Mg battery status and challenges

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1. Mg anode/Electrolytes: SEI-free interface

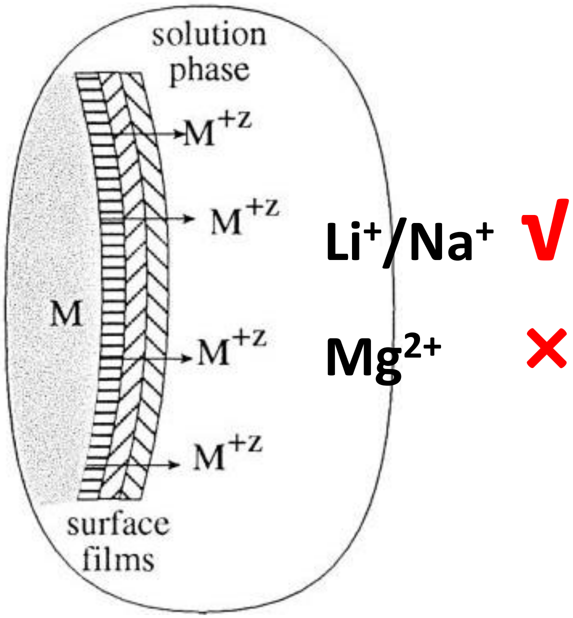
→ Conventional electrolytes (simple salt+ solvent)

→ Specially designed Mg complex electrolytes, performance depending on solution coordination

2. Cathode: Slow solid-state diffusion of divalent Mg^{2+}

→ Mo_6S_8 (128mAh/g, 1.1V)

3. More and more ……

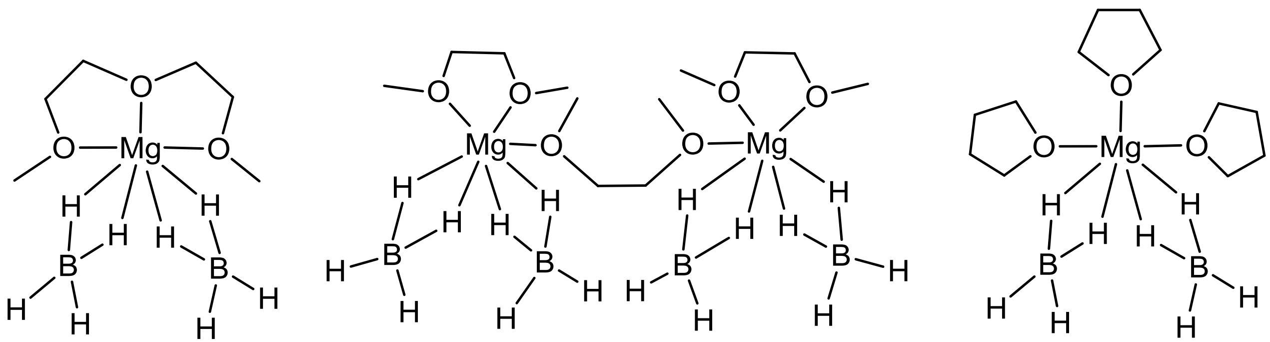


➢ **Limited fundamental understanding.**

Levi, et al. *Chem. Mater.* 2010, 22, 860–868
Aurbach, et al. *Energy Environ. Sci.*, 2013, 6, 2265–2279

How coordination affects performance: structure-property relationship

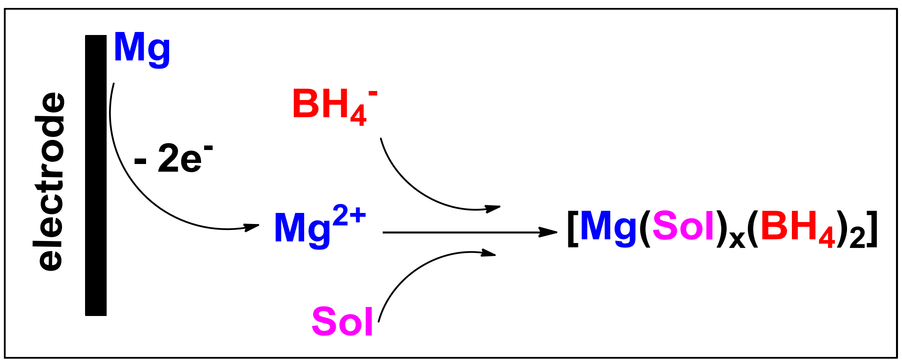
Shao, et al. *Sci. Rep.*, 2013, DOI:10.1038/srep03130



(a) $Mg(BH_4)_2DGM$ (b) $Mg_2(BH_4)_4(DME)_3$ (c) $Mg(BH_4)_2(THF)_3$

$Mg(BH_4)_2$-3THF Refs:
1. Lobkovskii, et al. J. Struct. Chem. 31, 506–508 (1990);
2. Lobkovskii, et al. J. Struct. Chem. 23, 644–646 (1982).

Enhanced Stripping Efficiency



Sol: Increased denticity and ligand strength can favor entropy effect and drive force of Mg^{2+} complexion.

→

BH_4^-: Increasing BH_4^- concentration should also favor kinetics of Mg^{2+} complexion, thus CE.

→ next slide.

Electrolyte performance: Ligand effects

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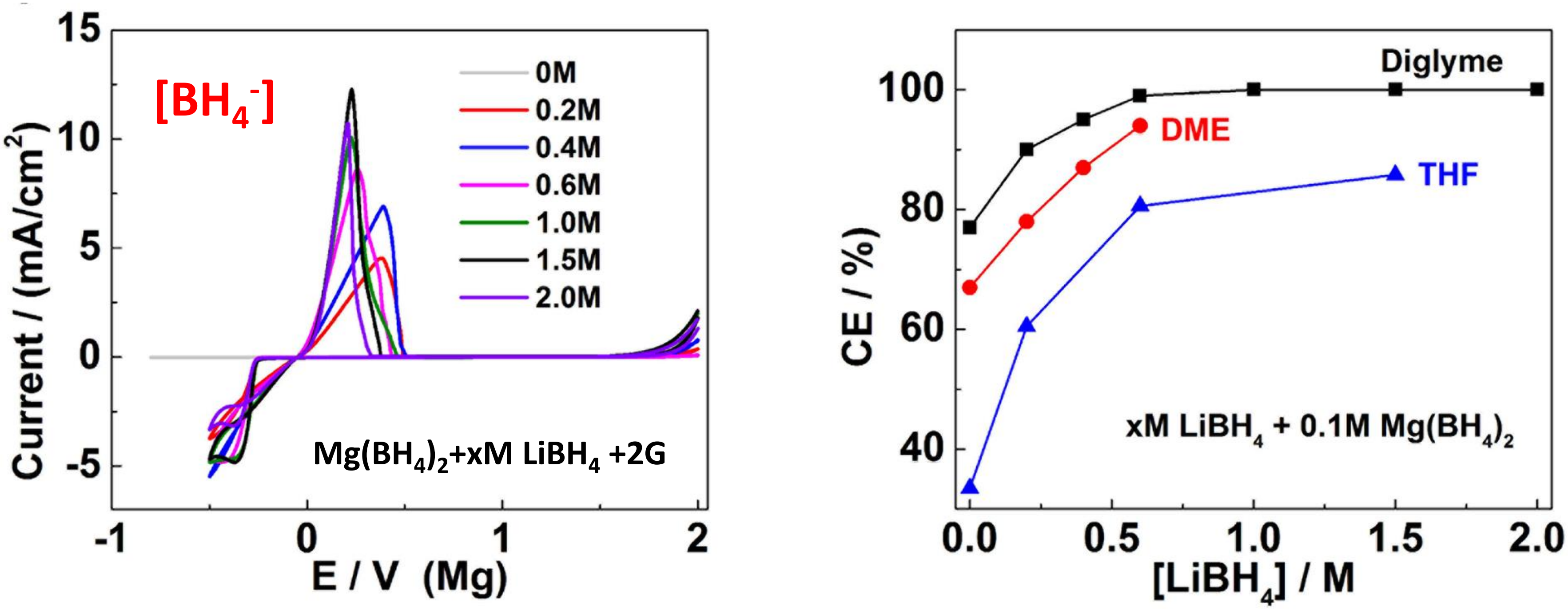
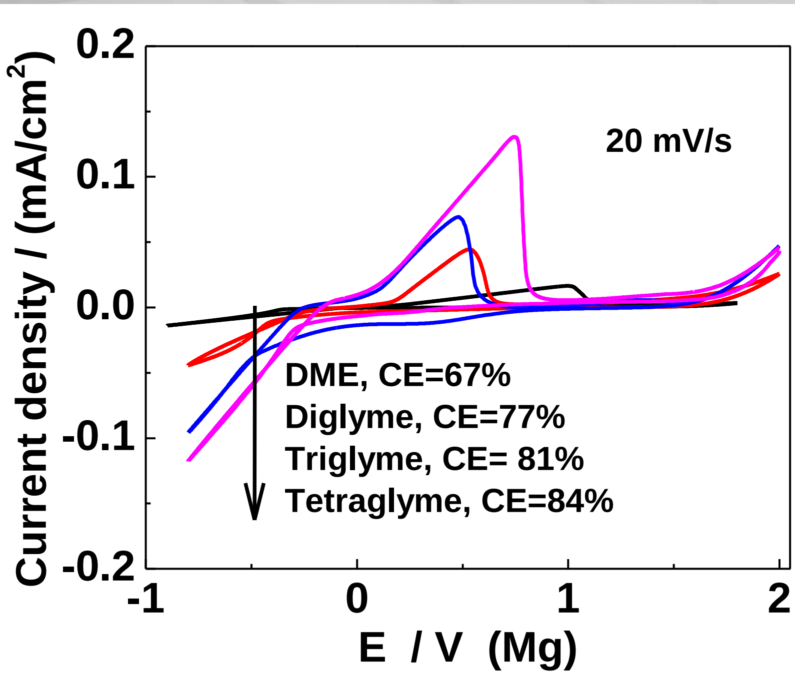
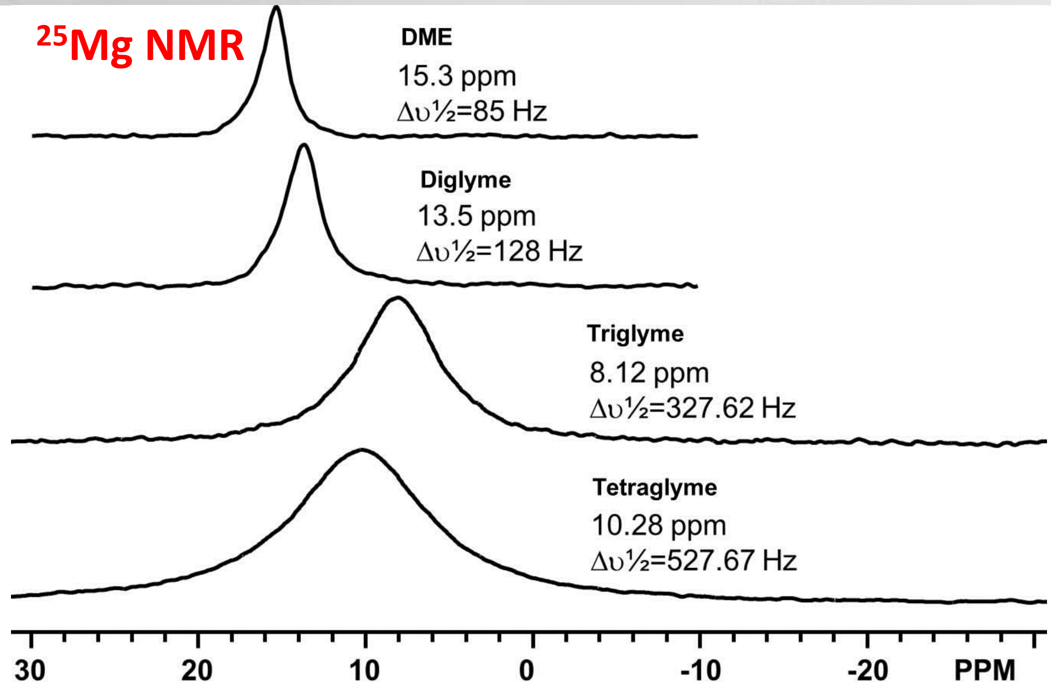


1. Solvents and $[BH_4^-]$ (ligands) affect Coulombic efficiency (CE) and current density dramatically: Diglyme>DME>THF
2. CE=100% for $Mg(BH_4)_2$/diglyme with $LiBH_4$ concentration of 1.0M and beyond.

Further exploration on solvent effect



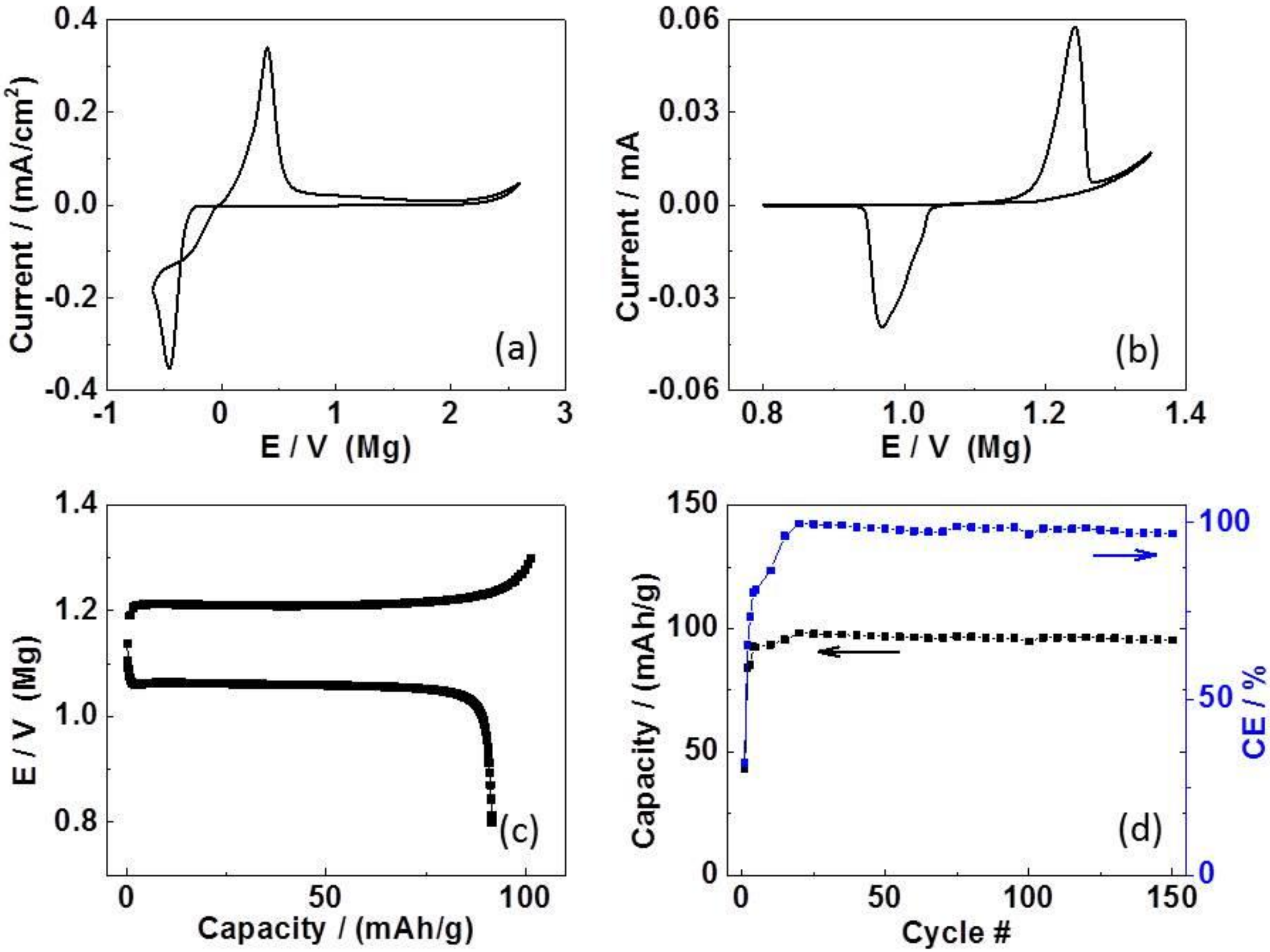


Long chain glymes → strong interaction with $Mg(BH_4)_2$ → high dissociation → high electrochemical property

→ Polymer PEO electrolyte?

Spectrum/ppm		DFT Calculation	
1G	15.3	22.26	$Mg_2(BH_4)_4$-$(DME)_3$
2G	13.5	21.23	$Mg(BH_4)_2$-DGM
3G	8.12	5.961	$Mg(BH_4)_2$-3G
4G	10.28	-12.597	$Mg(BH_4)_2$-4G
		7.329	$MgBH_4^-$-4G

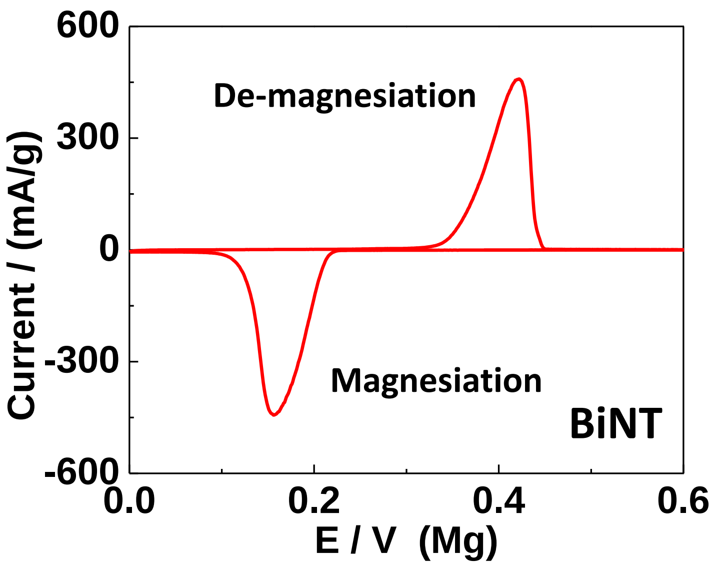
Performance of polymer Mg battery



Alternative anode enabled Mg ion battery

1. **Alternative anode with conventional electrolytes, like graphite, Si or Sn for Li ?**

2. **Slow Mg diffusion kinetics--- downsizing ?**

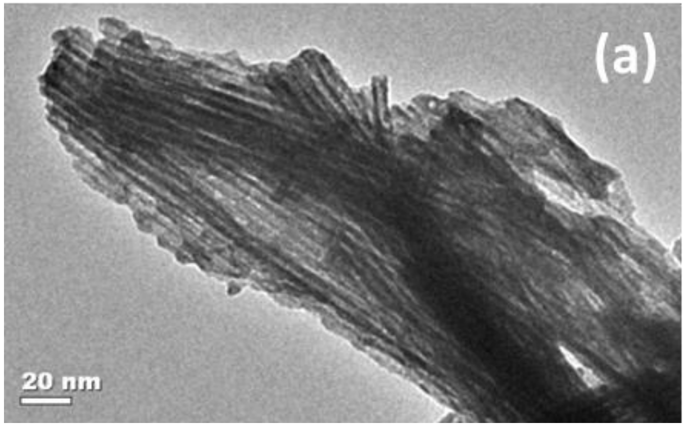


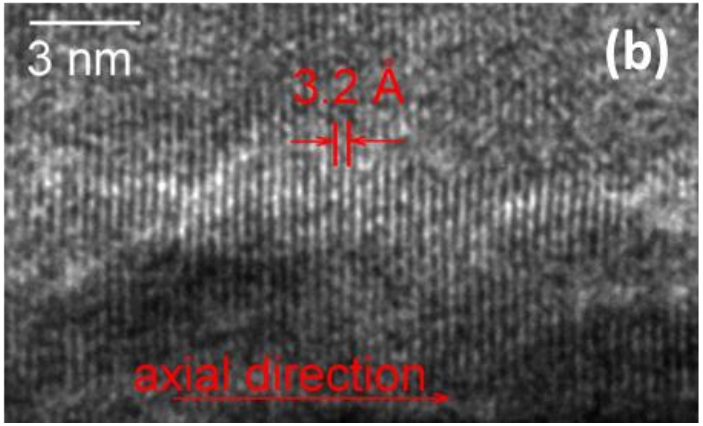
$2Bi + 3Mg^{2+} + 6e^{-} \rightarrow Mg_3Bi_2$

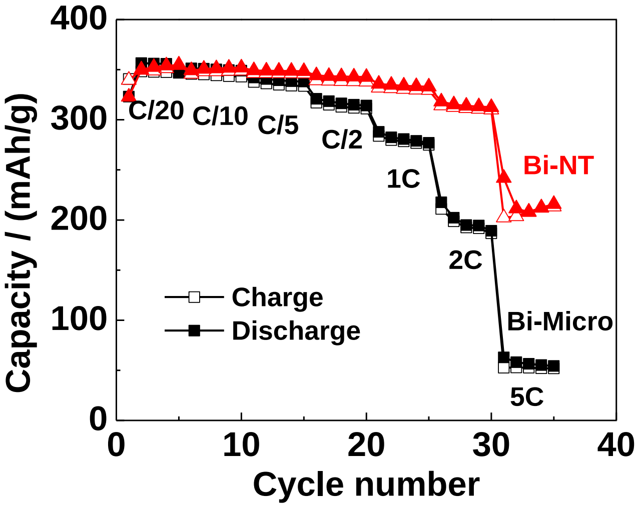
385 mAh/g, 3770 mAh/cm^3

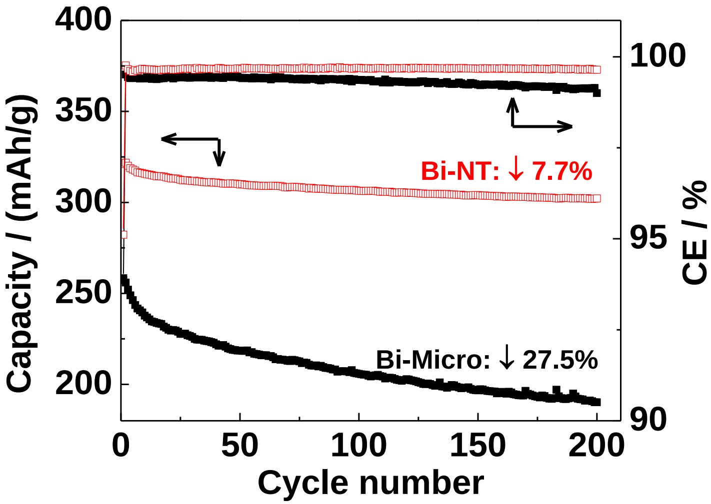
Ref. Electrochemistry Communications, 2012, 16 (1): 103–106

Bi NT anode enabled high rate, stability





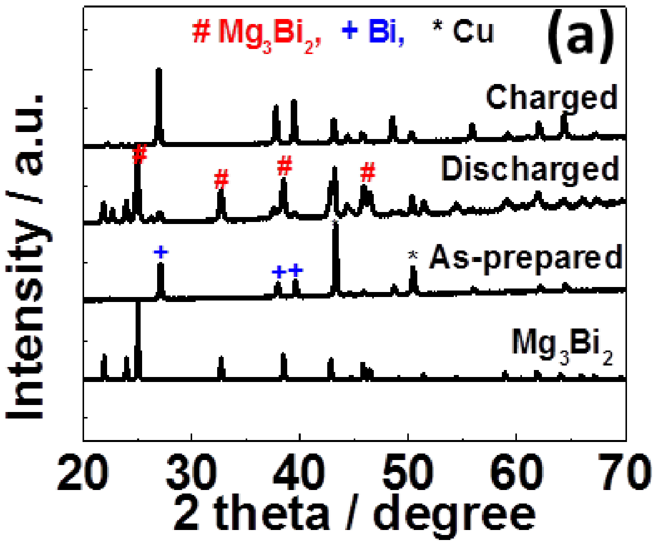




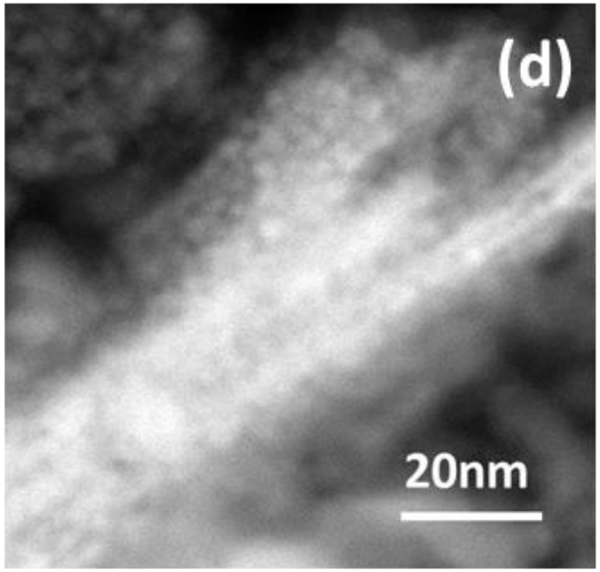
Bi-nanotube delivers ~4 times capacity of micro-Bi (5C rate) and stable cycling.

Shao et al. Nano Lett., 2014, DOI: 10.1021/nl403874y

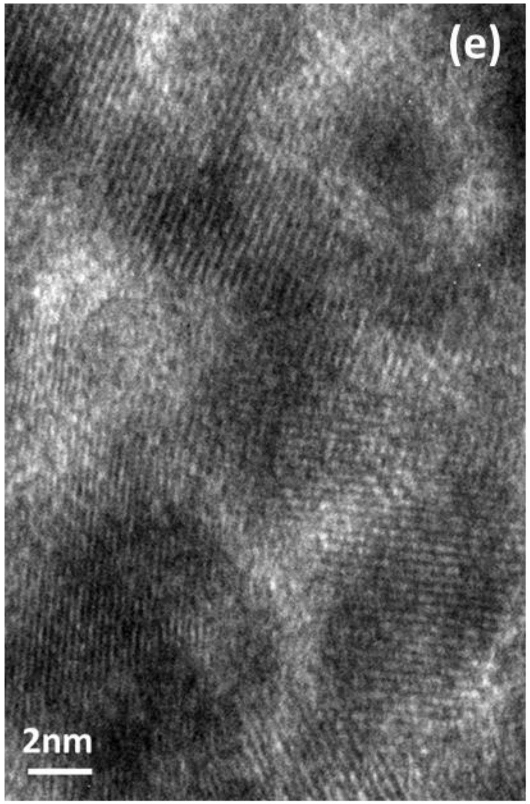
Bi NT for Mg insertion/extraction



Reversible Bi+ Mg ↔ Mg_3Bi_2



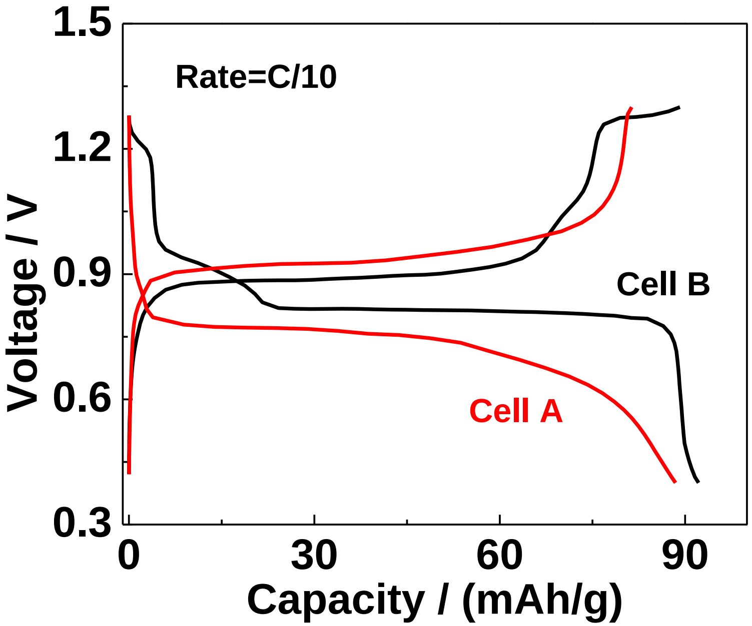
Overall NT morphology

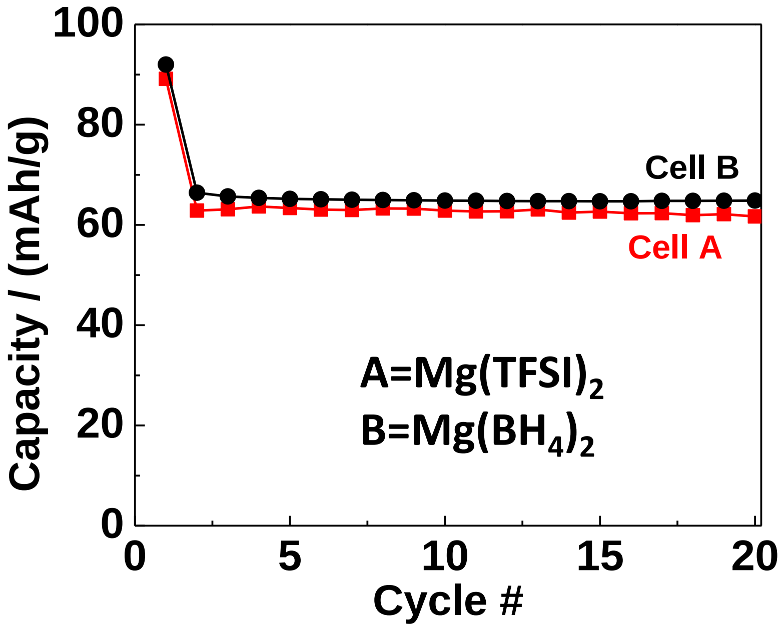


Interconnected NPs

Reversible reaction and structure integrity during discharge/charge

Bi NT anode enabled Mg ion battery





A=conventional Ely; B=Mg Ely

Compatible with conventional electrolyte.

Summary

Pacific Northwest NATIONAL LABORATORY
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- **Significant effort and progress in electrode materials.**
- **More effort on how electrolytes improve the properties of electrode materials needed.**
- **Beyond Li-ion, such as Mg ion, still in very early stage..**