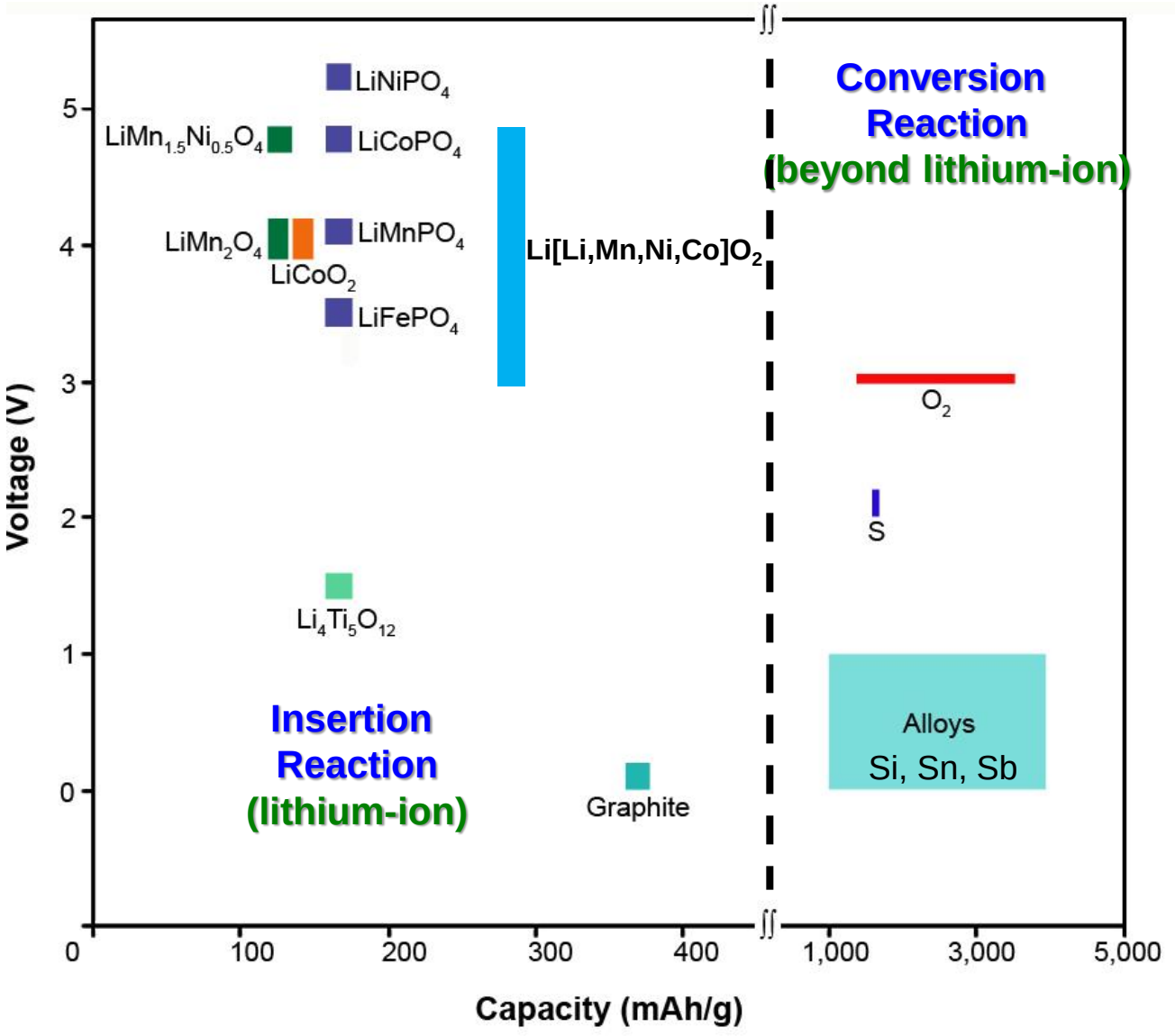
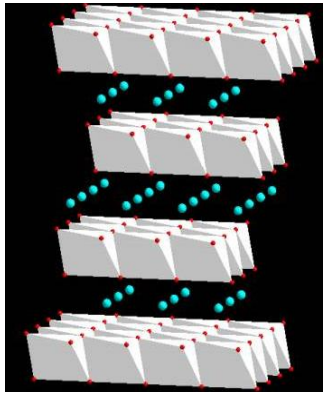
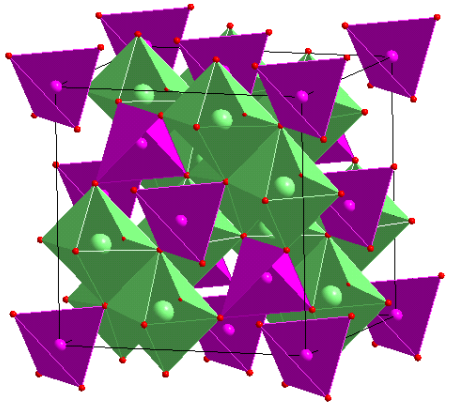
MULTI-ELECTRON CONVERSION-REACTION CATHODES

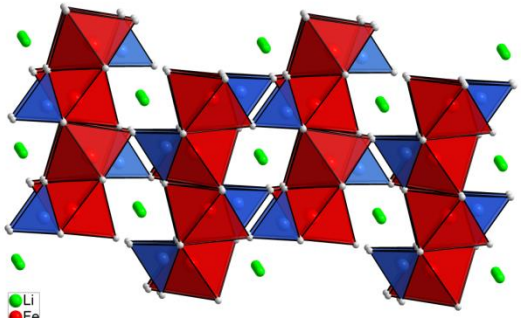
Arumugam Manthiram
Electrochemical Energy Laboratory
Materials Science and Engineering Program
Texas Materials Institute
The University of Texas at Austin
Austin, TX 78712, USA

ELECTRODE MATERIALS



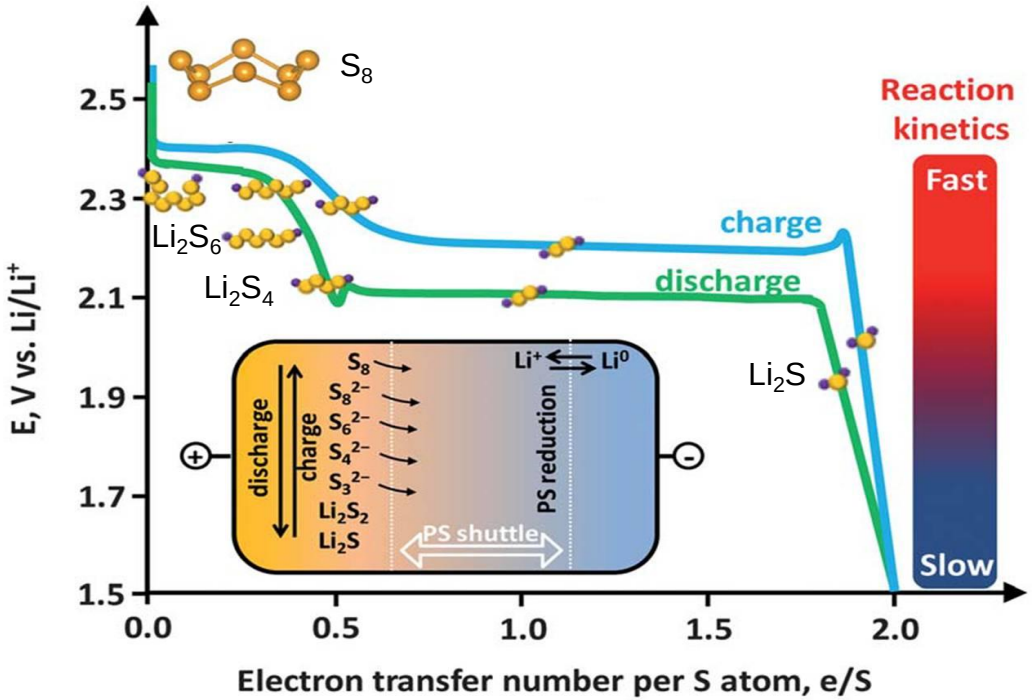


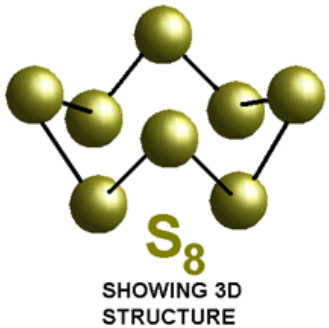




LITHIUM-SULFUR BATTERIES

LITHIUM-SULFUR BATTERIES: CHALLENGES





$$S + 2Li^+ + 2e^- \leftrightarrow Li_2S$$

2 electron reaction
1,672 Ah/kg
2,500 Wh/kg

- Poor electronic conductivity: low utilization, low sulfur content
- Polysulfide migration: poor cyclability, self discharge, low efficiency
- Large volume change: low electrochemical utilization, capacity fade
- Lithium-metal anode: degradation, short cycle life, safety concerns

A. Manthiram, S.-H. Chung, & C. Zu, *Advanced Materials* **27,** 1980-2006 (2015)
A. Manthiram, Y.-Z. Fu, S.-H. Chung, C. Zu, & Y.-S. Su, *Chemical Reviews* **114,** 11751 (2014)
A. Manthiram, Y.-Z. Fu, & Y.-S. Su, *Accounts of Chemical Research* **46,** 1125 (2013)

OUTLINE

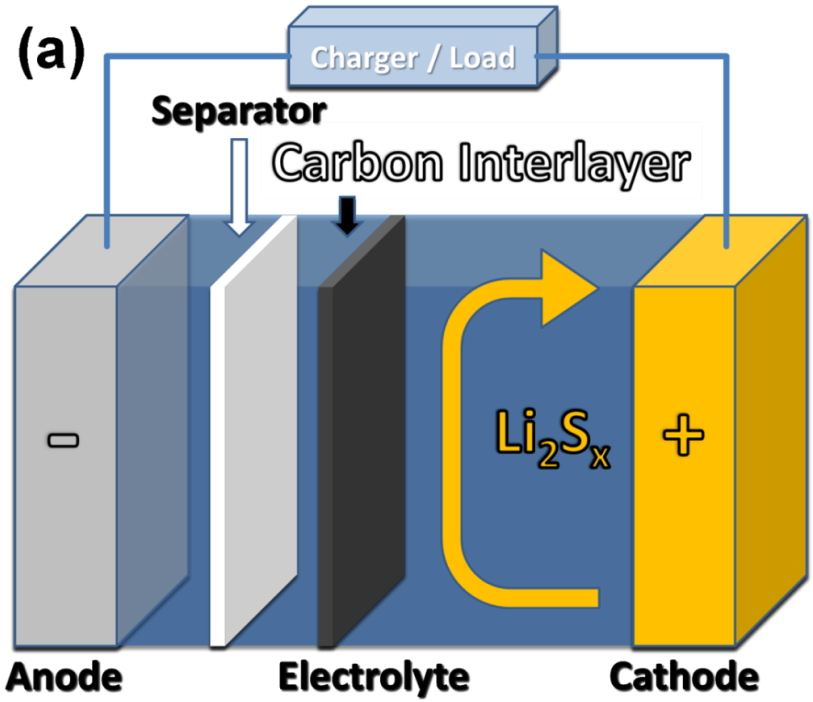
- **BIFUNCTIONAL INTERLAYERS AND COATED SEPARATORS**
- **SANDWICHED ELECTRODES**
- **Li / DISSOLVED POLYSULFIDE CELLS**
- **Li_2S UTILIZATION WITHOUT LARGE CHARGE BARRIER**
- **LITHIUM-METAL ANODE STABILIZATION**

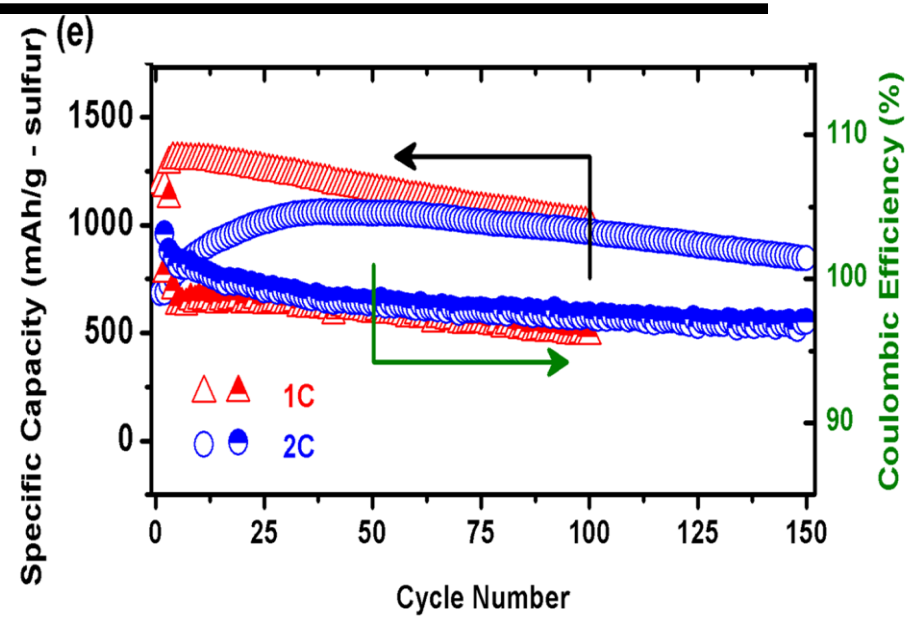
A. Manthiram, S.-H. Chung, & C. Zu, *Advanced Materials* **DOI:** 10.1002/adma.201405115 (2015)
A. Manthiram, Y.-Z. Fu, S.-H. Chung, C. Zu, & Y.-S. Su, *Chemical Reviews* **114,** 11751 (2014)
A. Manthiram, Y.-Z. Fu, & Y.-S. Su, *Accounts of Chemical Research* **46,** 1125 (2013)

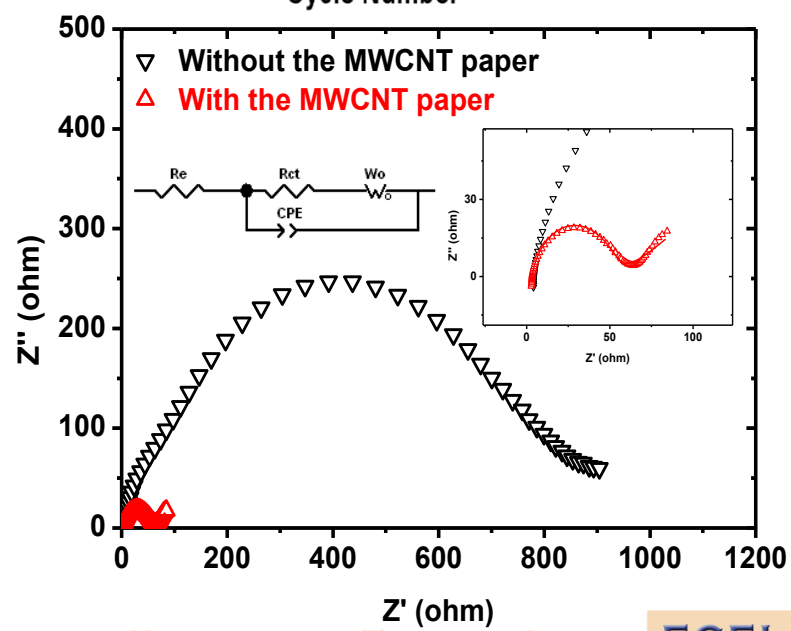
BIFUNCTIONAL INTERLAYERS

1. FREE-STANDING CARBON-PAPER INTERLAYER
2. CARBON-COATED SEPARATORS

Li-S CELL WITH A CARBON PAPER INTERLAYER



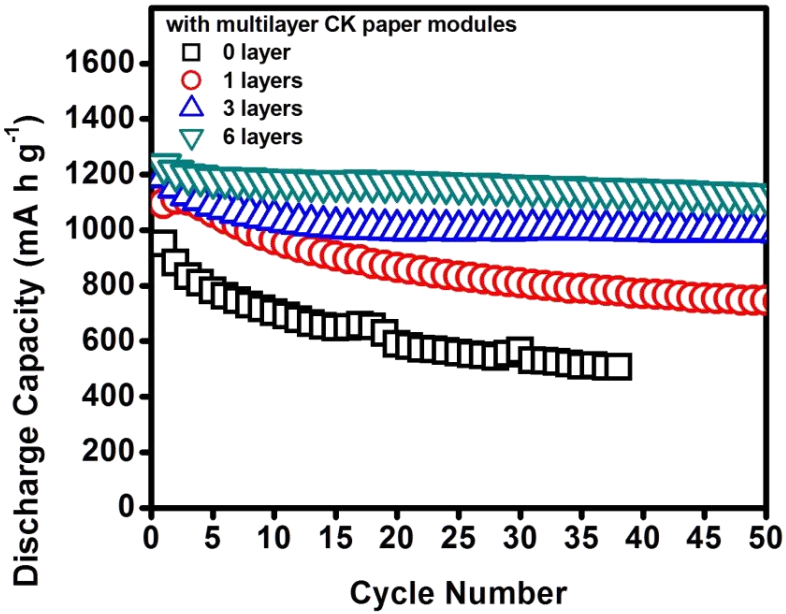


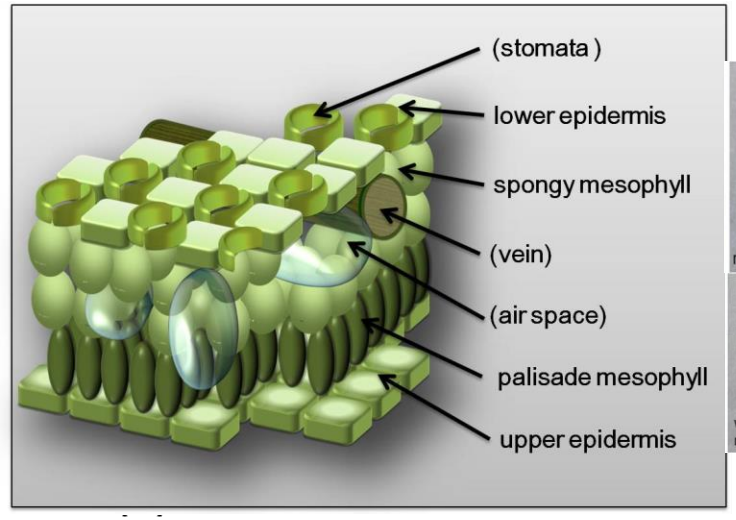


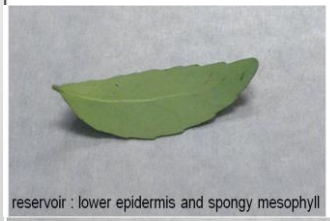
Y.-S. Su and A. Manthiram, *Nature Communications* **3**, 1166 (2012)

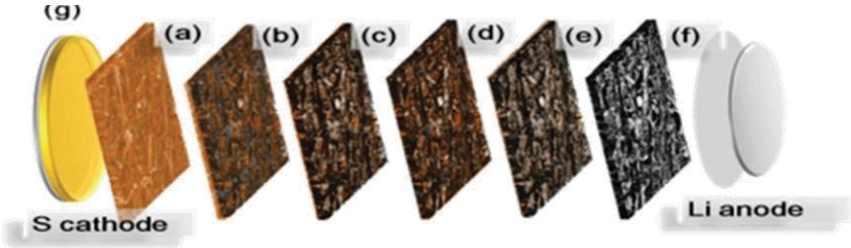
- Carbon paper interlayer traps dissolved polysulfides, serves as an upper current collector, and increases active material utilization and cycle life – allows the use of pure sulfur with high sulfur content

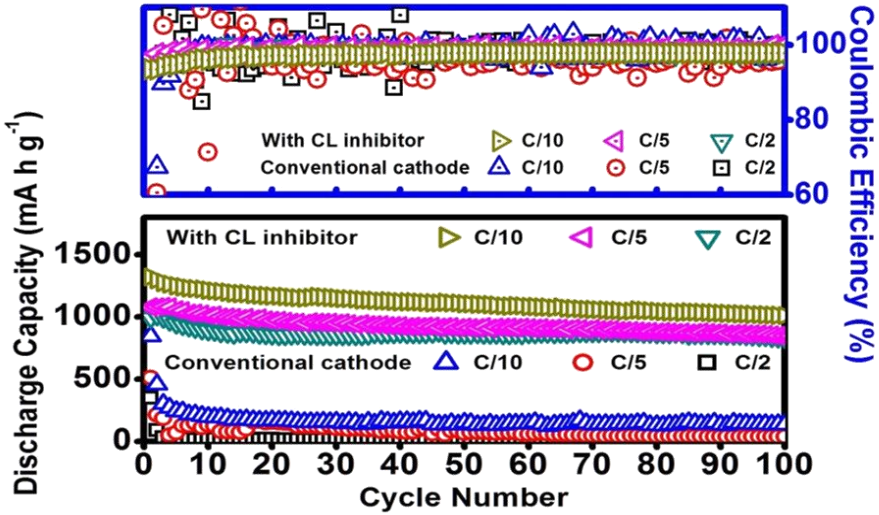
CARBONIZED KIMWIPE PAPER OR LEAF INTERLAYERS





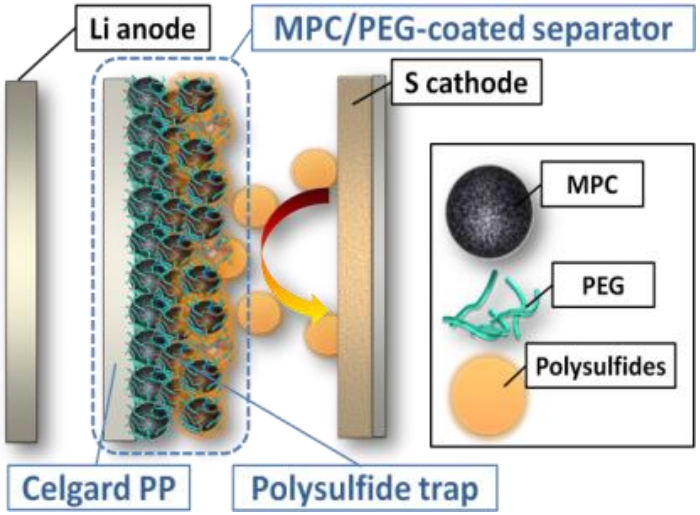


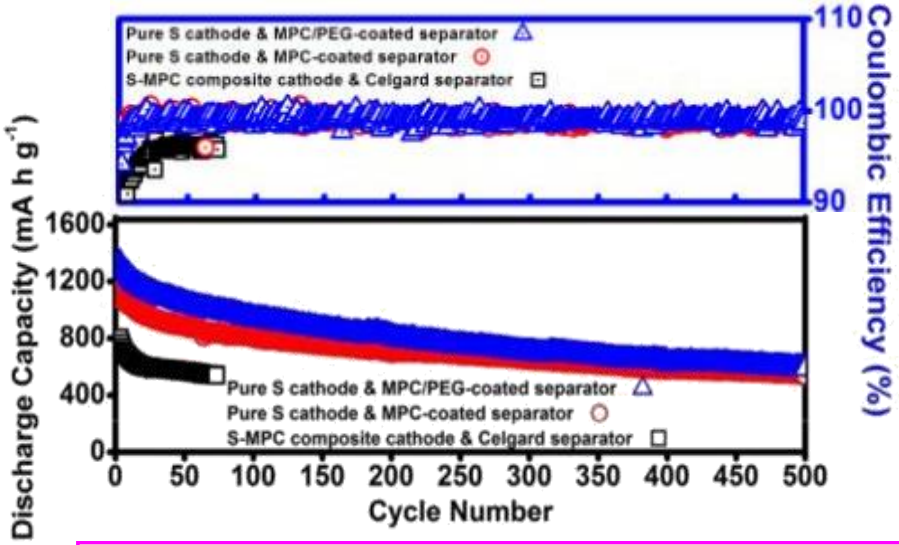




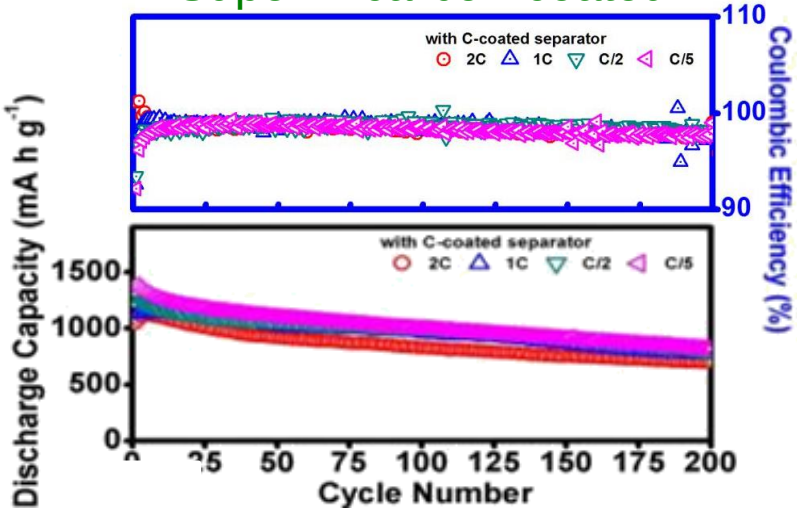
S.-H. Chung and A. Manthiram, *Chemical Communications* **50**, 4148 (2014)
S.-H. Chung and A. Manthiram, *ChemSusChem.* **7,** 1655 (2014

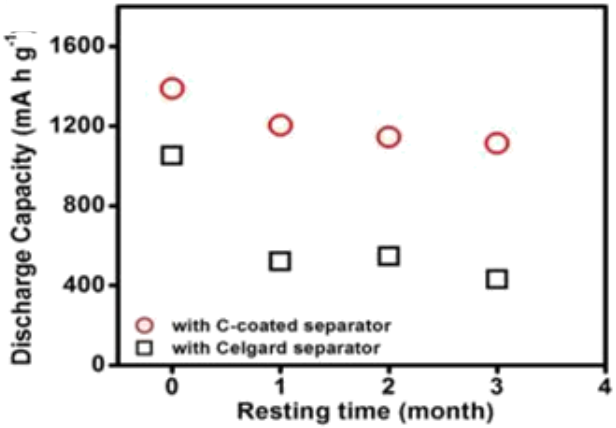
CARBON- OR CARBON/POLYMER-COATED SEPARATORS





Super P carbon-coated



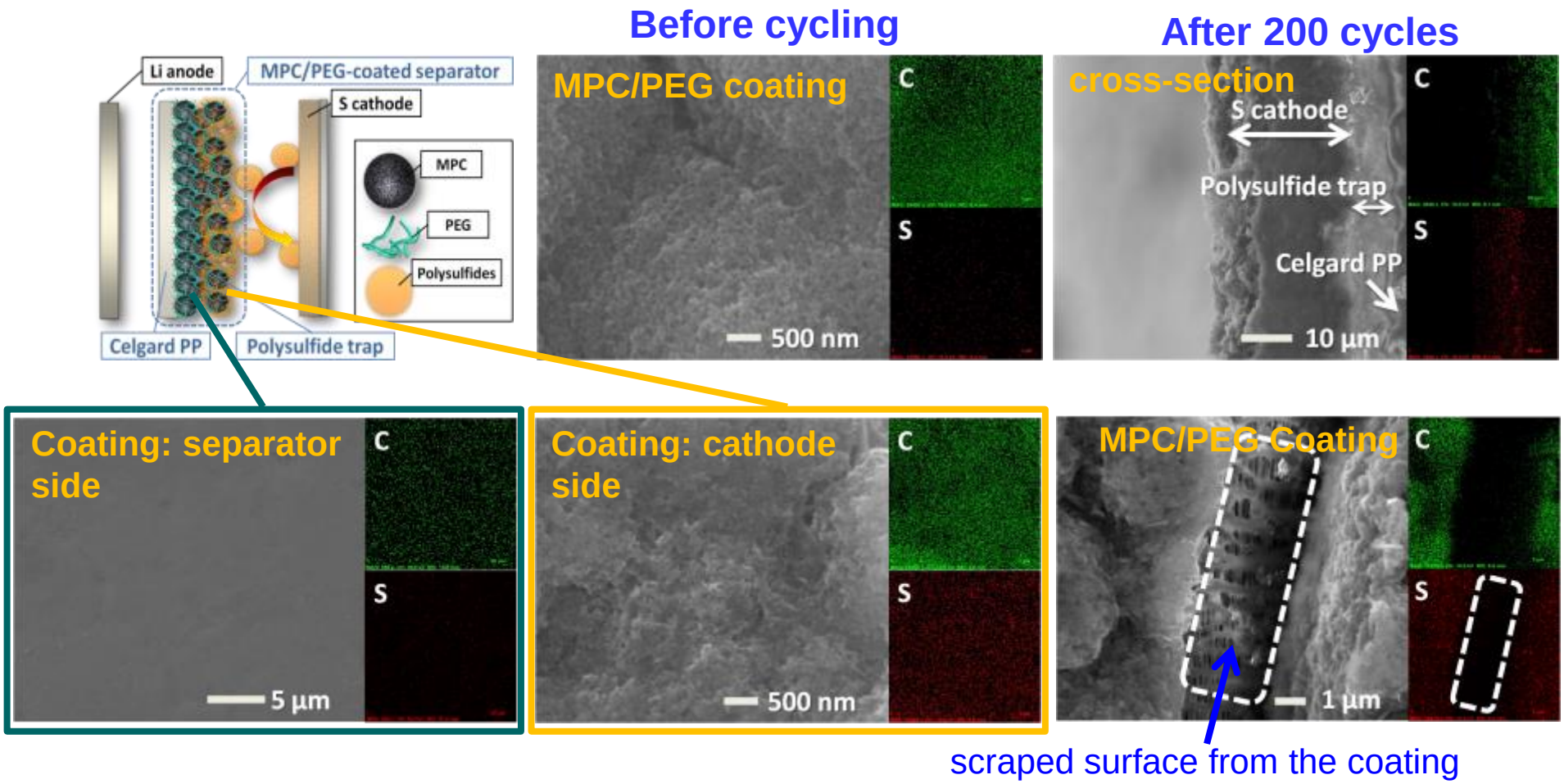


MPC/PEG: chemical/physical trap
Sulfur loading in cathodes: **70 wt. %**

S.-H. Chung and A. Manthiram, *Advanced Materials* **26**, 7352 (2014)

S.-H. Chung and A. Manthiram, *Advanced Functional Materials* **24**, 5299 (2014)

MPC/PEG COATING BEFORE/AFTER CYCLING



- The dissolved active material is absorbed by the pores and trapped by the ether groups rather than penetrating into the PP separator

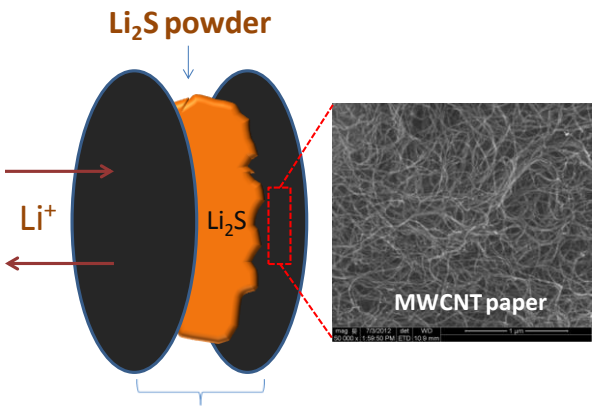
SANDWICHED ELECTRODES

1. Li_2S-MWCNT SANDWICHED ELECTRODES

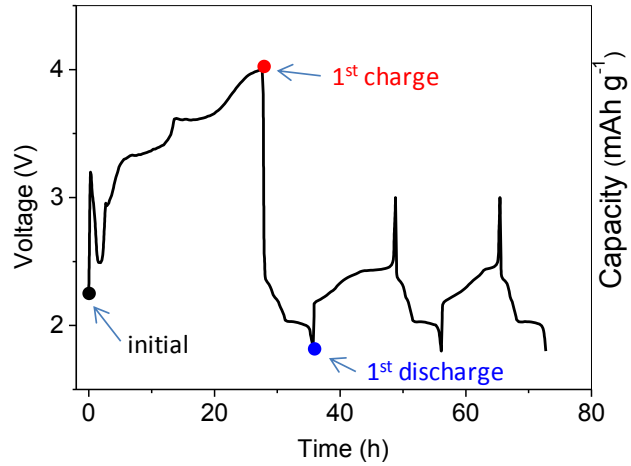
2. CARBONIZED SUCROSE-COATED EGG-SHELL MEMBRANE (CSEM)-POLYSULFIDE ELECTRODES

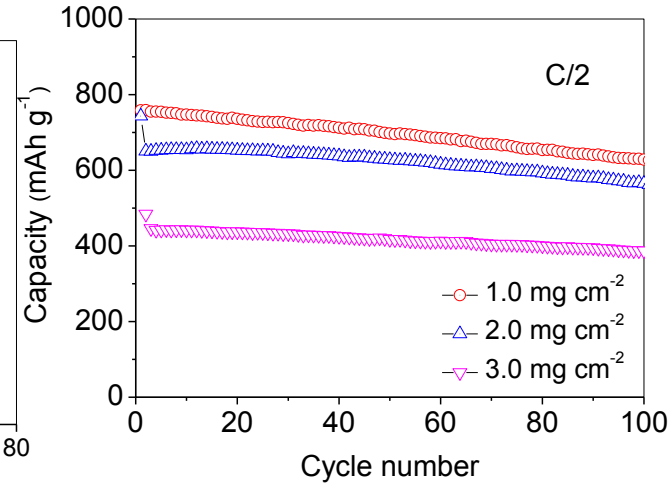
SANDWICHED ELECTRODES

MWCNT with Li_2S

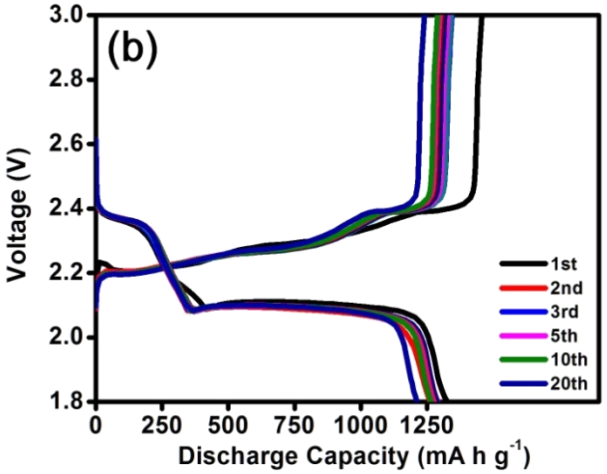


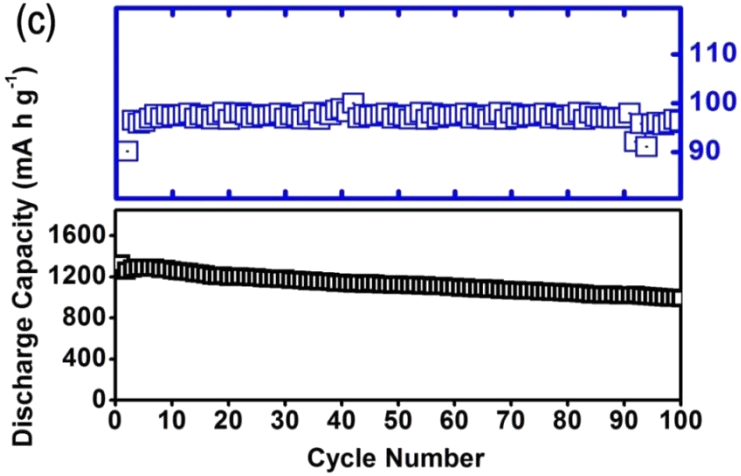
Li_2S embedded MWCNT electrode

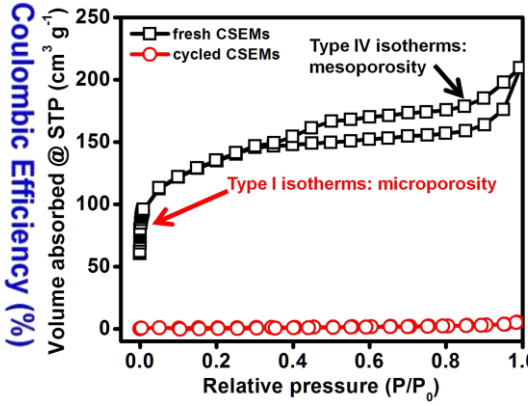




Carbonized egg-shell membrane with sulfur

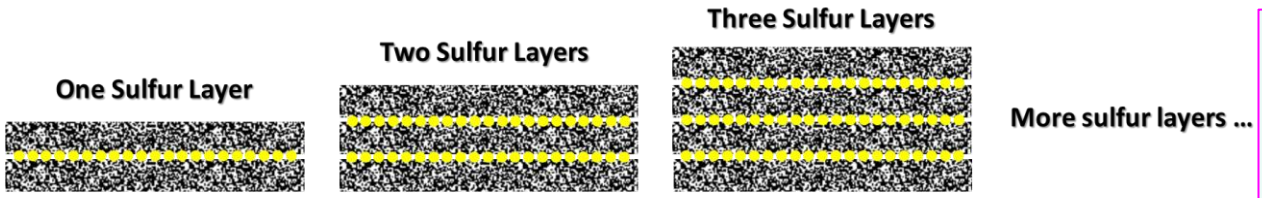




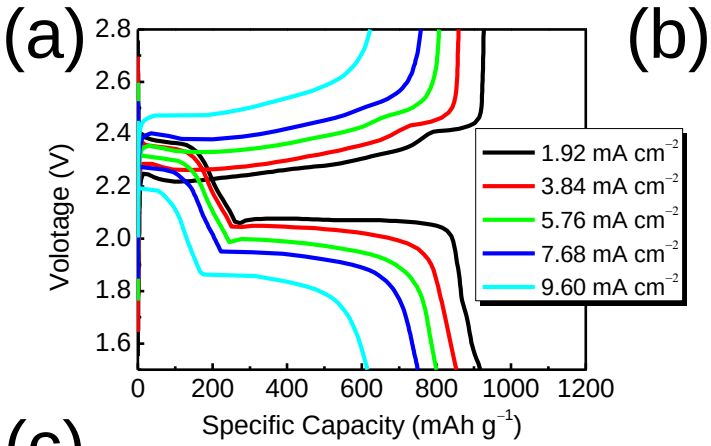


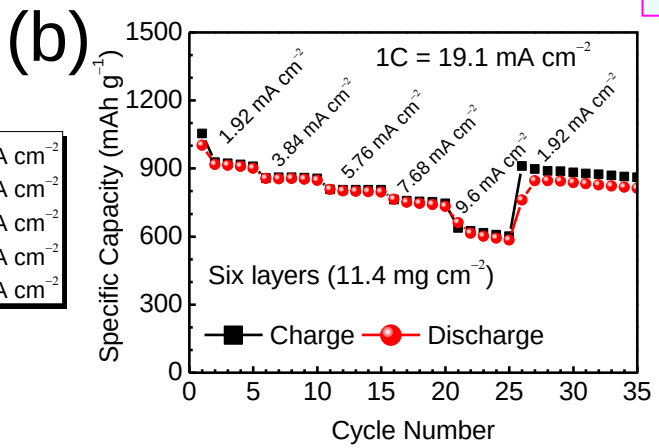
Y.-Z. Fu, Y.-S. Su, and A. Manthiram, *Advanced Energy Materials* **4**, 1300655 (2014)
S.-H. Chung and A. Manthiram, *Advanced Materials* **26**, 1360 (2014)

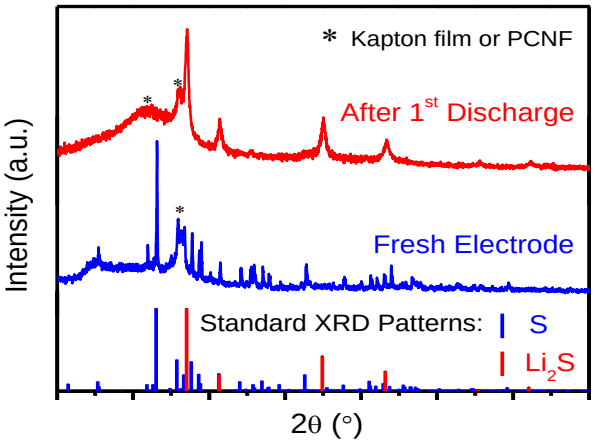
BINDER-FREE LAYER-BY-LAYER SULFUR CATHODE

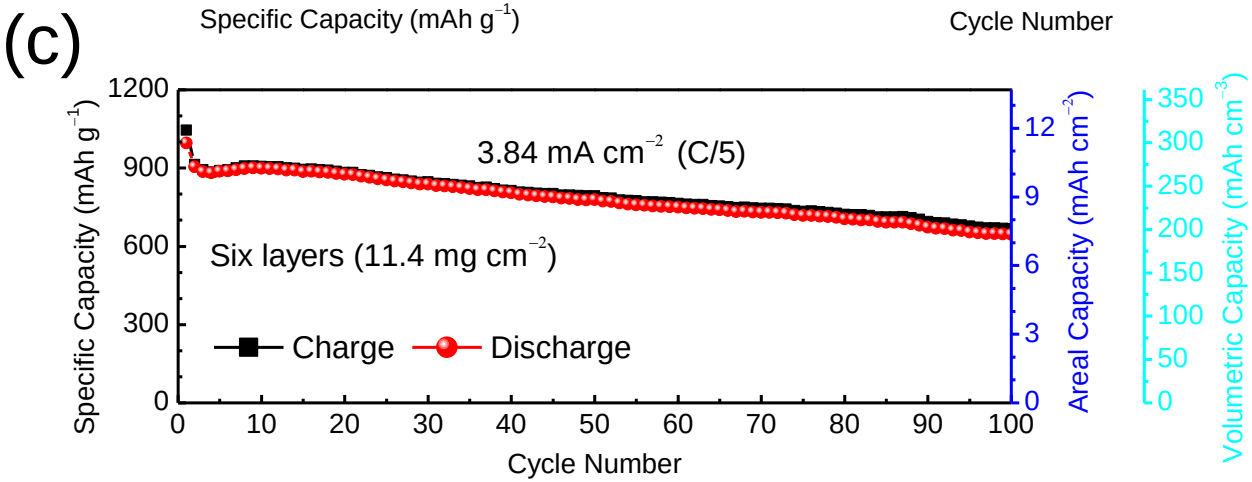


- Pure sulfur packed between porous carbon layers
- S loading increases with increasing number of layers









- 11.4 mg cm^{-2} loading with 6 layers
- ~ 9 mAh cm^{-2} at C/5 rate

L. Qie and A. Manthiram, *Advanced Materials* **27**, 1694 (2015)

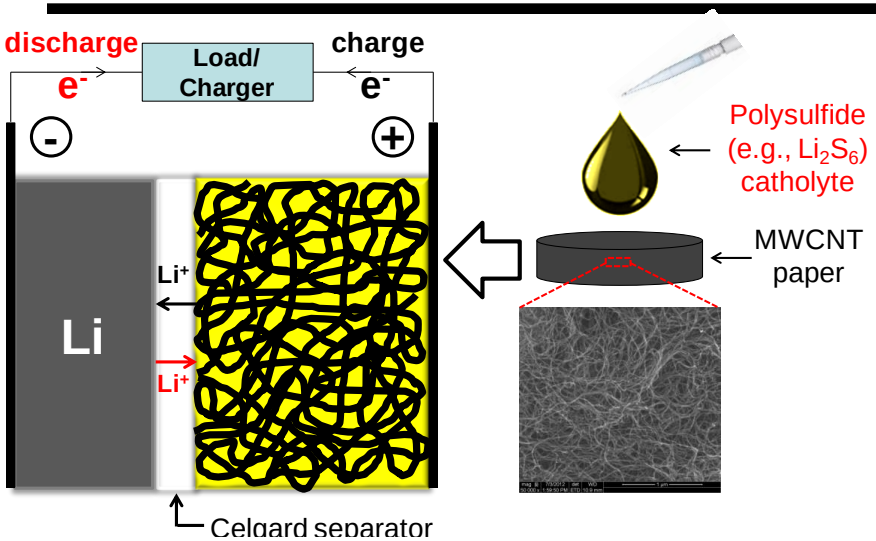
Li / DISSOLVED POLYSULFIDE CELLS

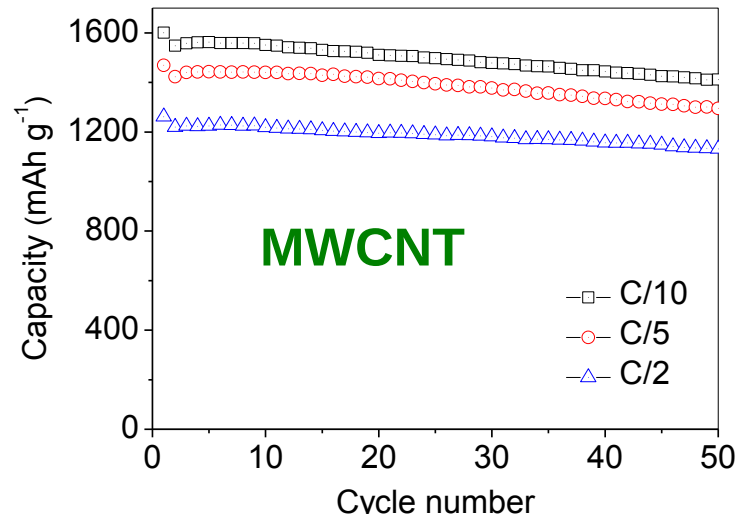
1. WITH MWCNT

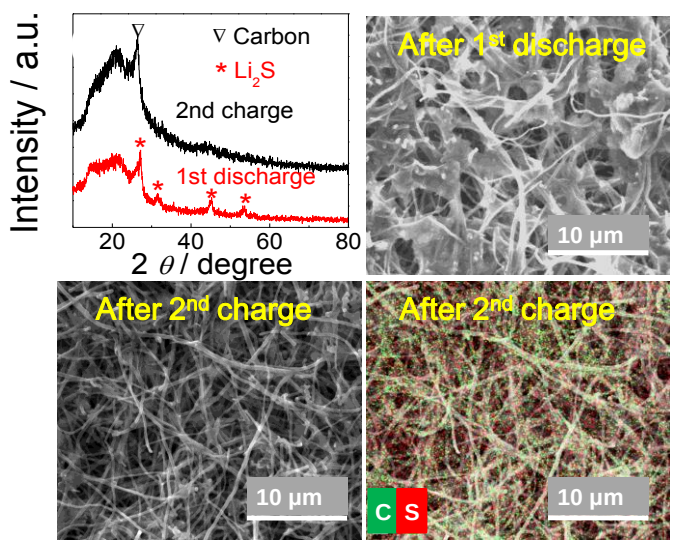
2. WITH CNF

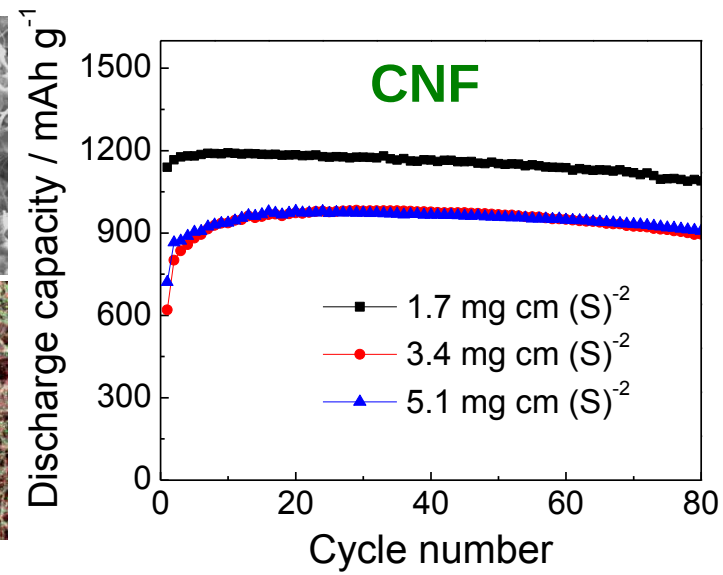
3. WITH N,S-DOPED GRAPHENE

Li/DISSOLVED POLYSULFIDE CELLS



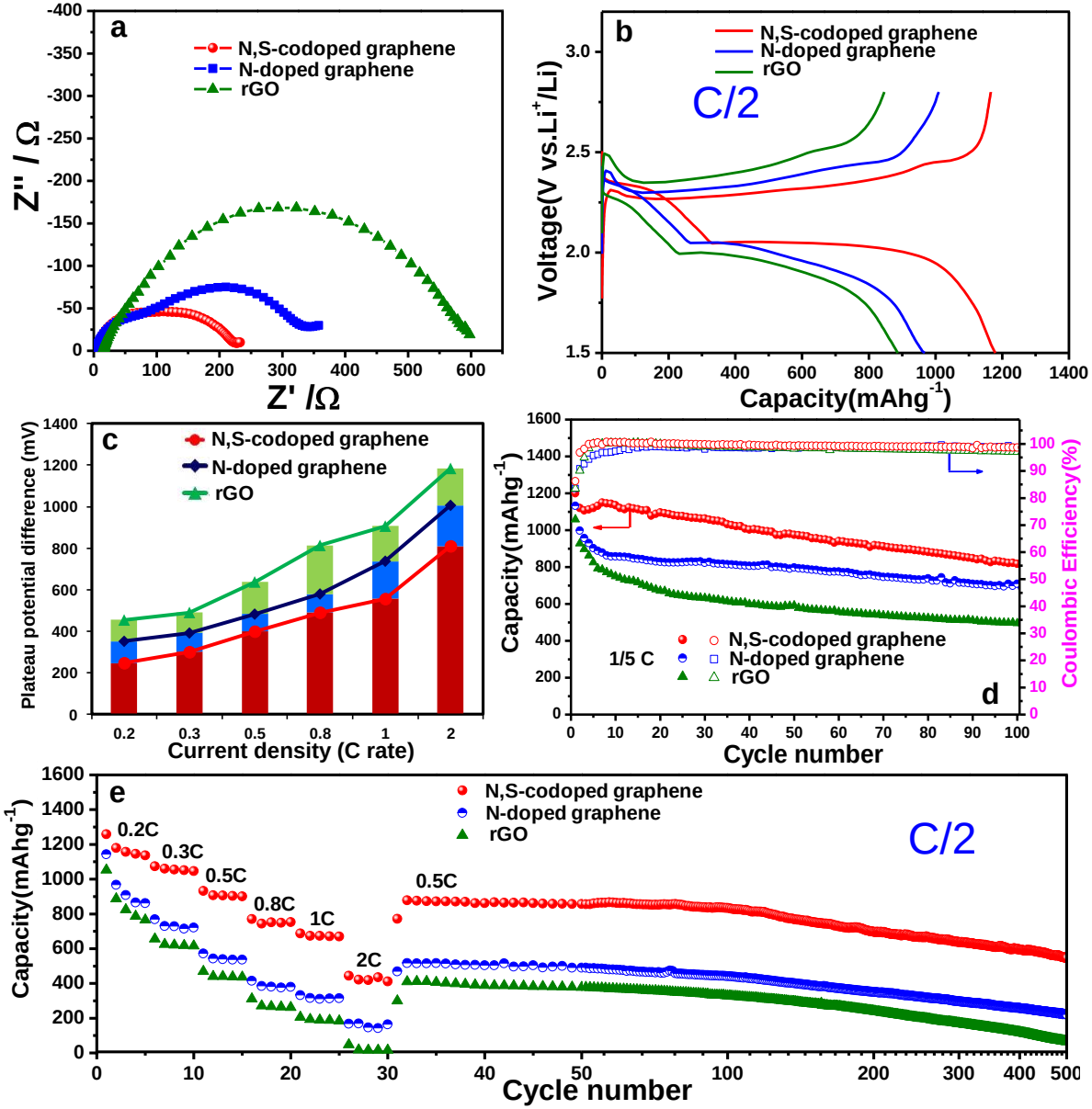






Y.-Z. Fu, Y.-S. Su, and A. Manthiram, *Angew. Chem. Int. Ed.* **52**, 6930 (2013)
C. Zu, Y. Fu and A. Manthiram, *J. Mater. Chem. A* **1**, 10362 (2013)

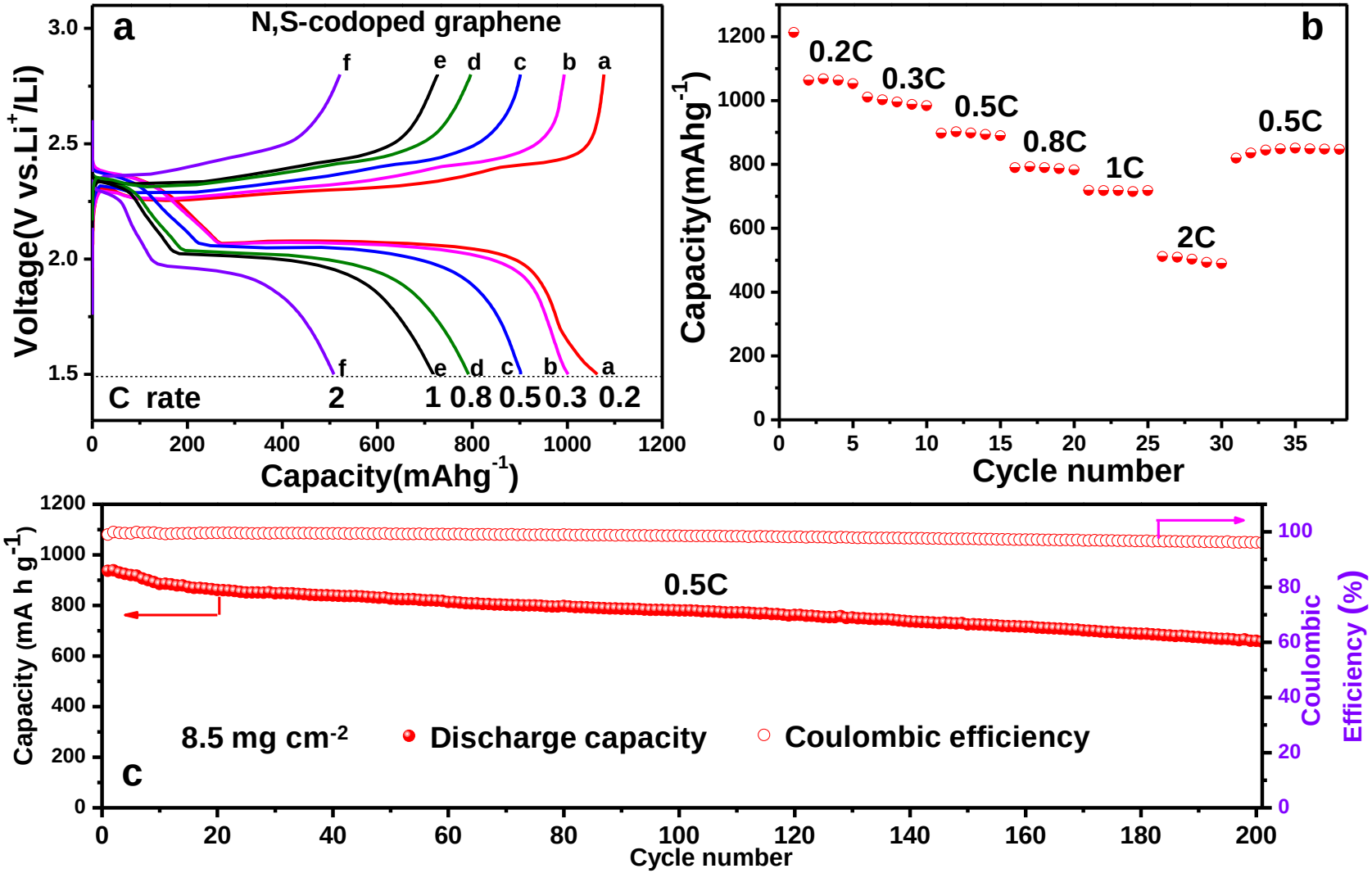
Li/POLYSULFIDE CELL WITH N,S-CODOPED GRAPHENE SPONGE



- 72 wt. % S content
- 4.6 mg cm^{-2} S loading
- Computational analysis shows chemical interaction/binding with N and S, retaining polysulfide

G. Zhou, E. Paek, G. S. Hwang, and A. Manthiram, *Nature Communications* (accepted)

Li/POLYSULFIDE CELL WITH N,S-CODOPED GRAPHENE SPONGE



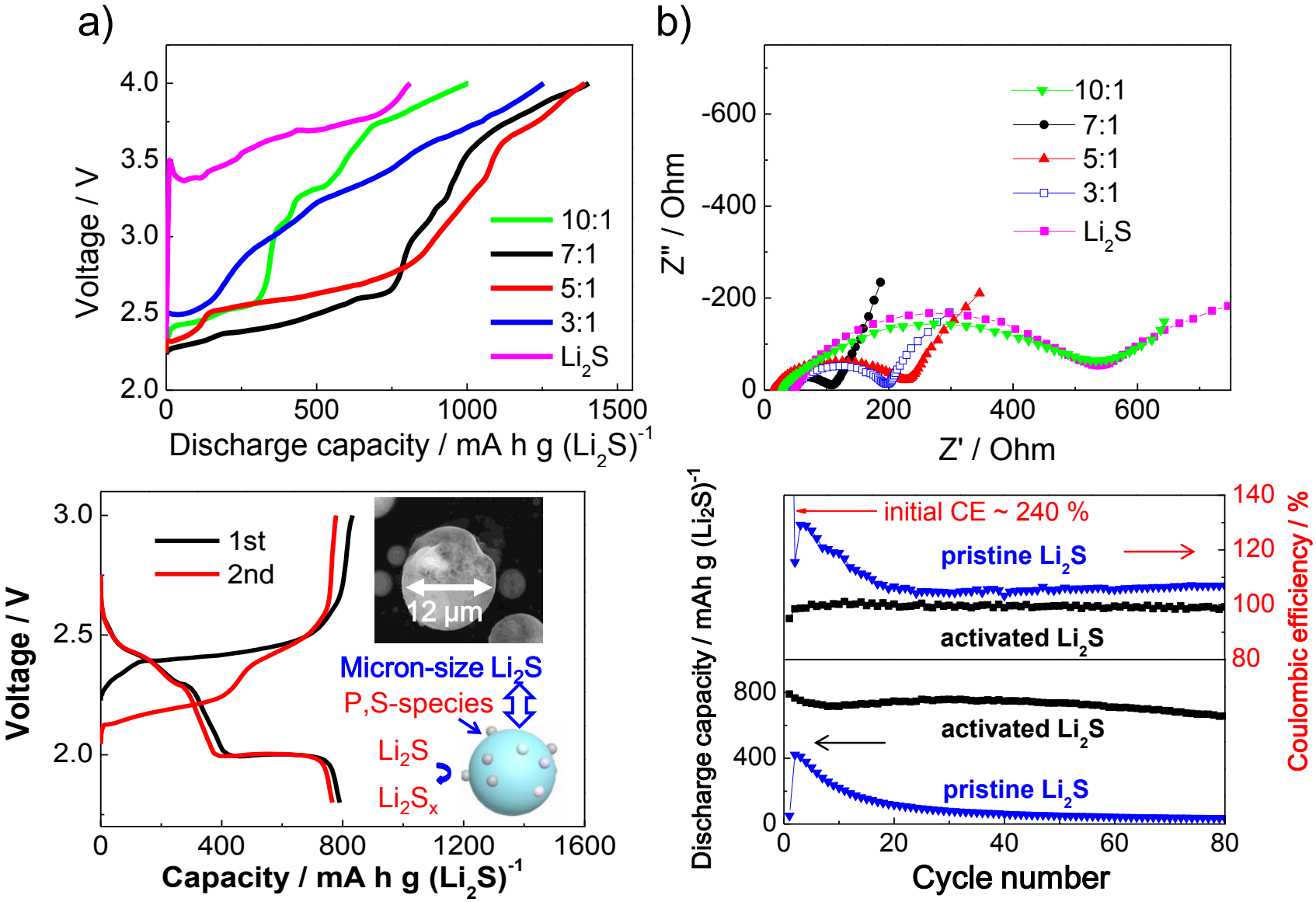
- 72 wt. % sulfur content; 8.5 mg cm^{-2} sulfur loading; graphene-coated separator

Li_2S UTILIZATION WITHOUT CHARGE BARRIER

1. ACTIVATION OF LITHIUM SULFIDE BULK PARTICLES

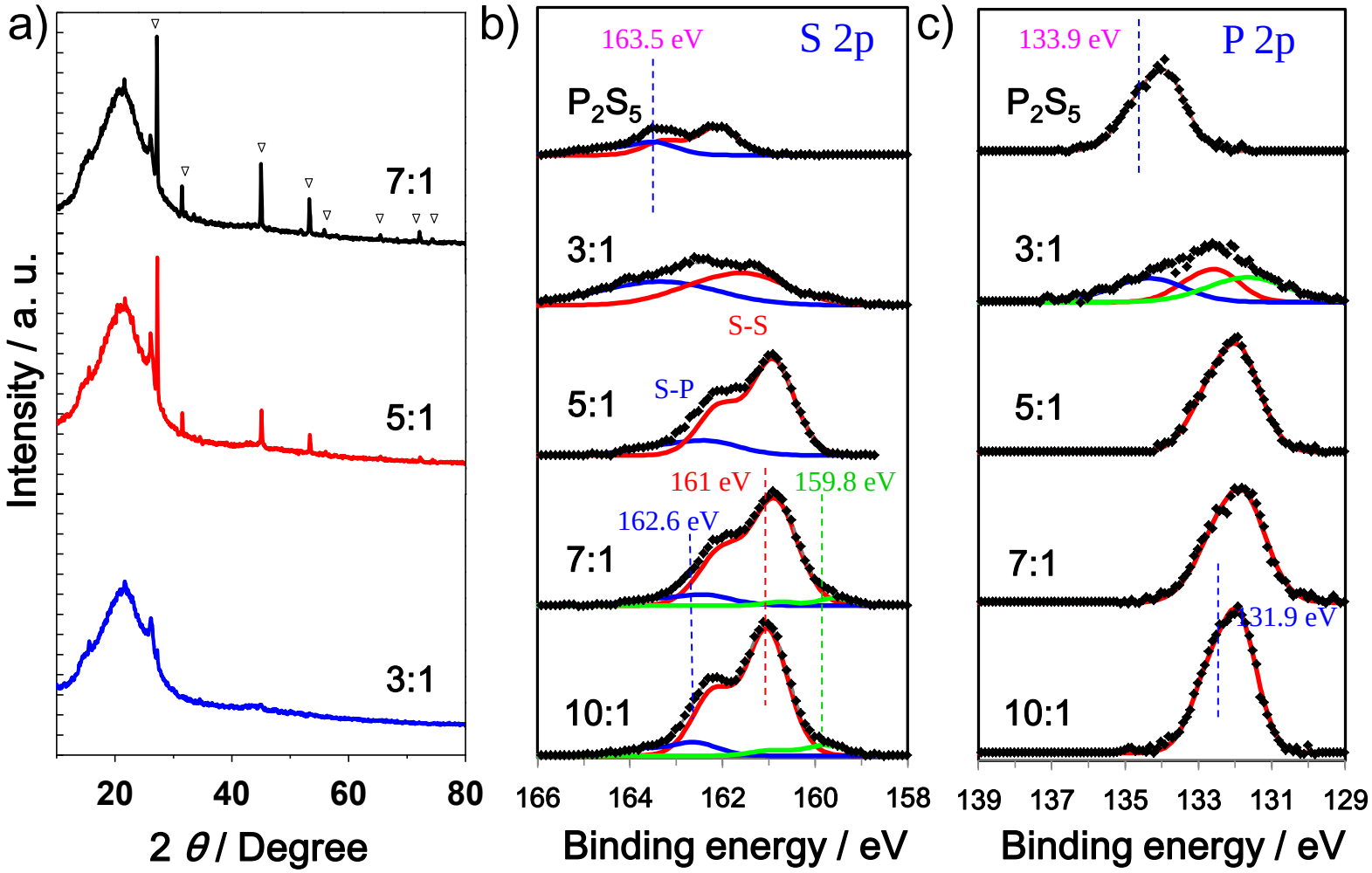
2. SYNTHESIS OF ELECTROCHEMCIALLY ACTIVE Li_2S

Li_2S ACTIVATION WITH P_2S_5



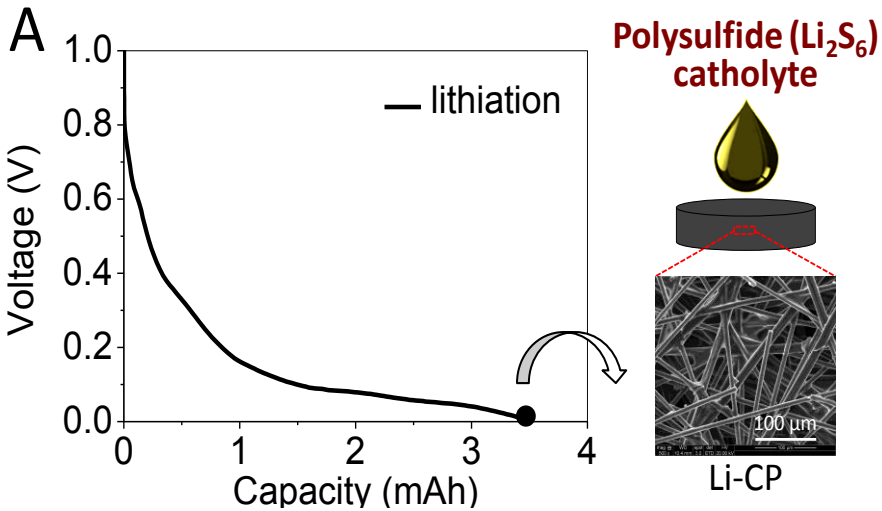
C. Zu , M. Klein, and A. Manthiram, J. Phys. Chem. Lett. **5**, 3986 (2014)

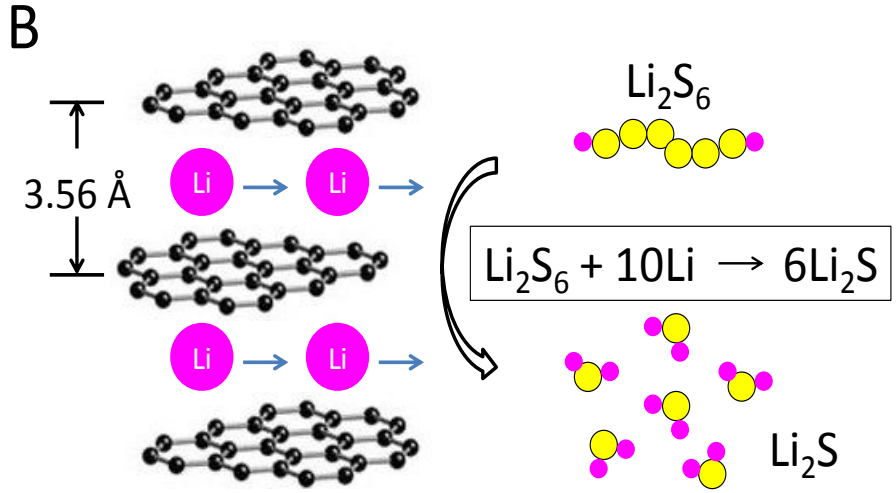
PHASE AND SURFACE CHARACTERIZATION

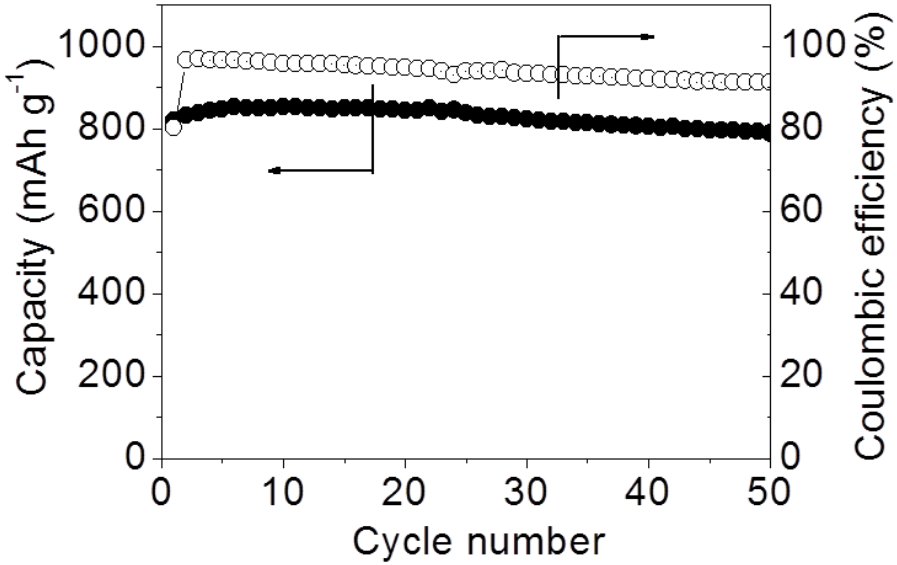


- Crystalline phase of Li_2S is retained after reaction with small amount of P_2S_5
- Surface composition changes with the evolution of new S-, and P-containing phases

SYNTHESIS OF ELECTROCHEMCIALLY ACTIVE Li_2S







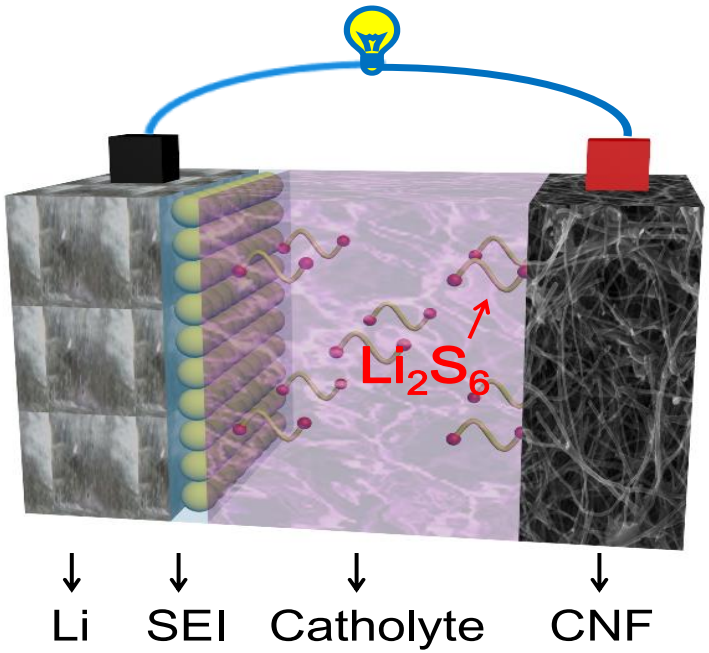
- The lithiated graphite reacts with polysulfide spontaneously, producing **amorphous** Li_2S **homogeneously distributed** on the 3-D graphite paper
- XPS analysis shows ~ 50 % of sulfur in the polysulfide was converted to Li_2S
- The formed Li_2S cycles well at 3.0 – 1.8 V without initial charging barrier

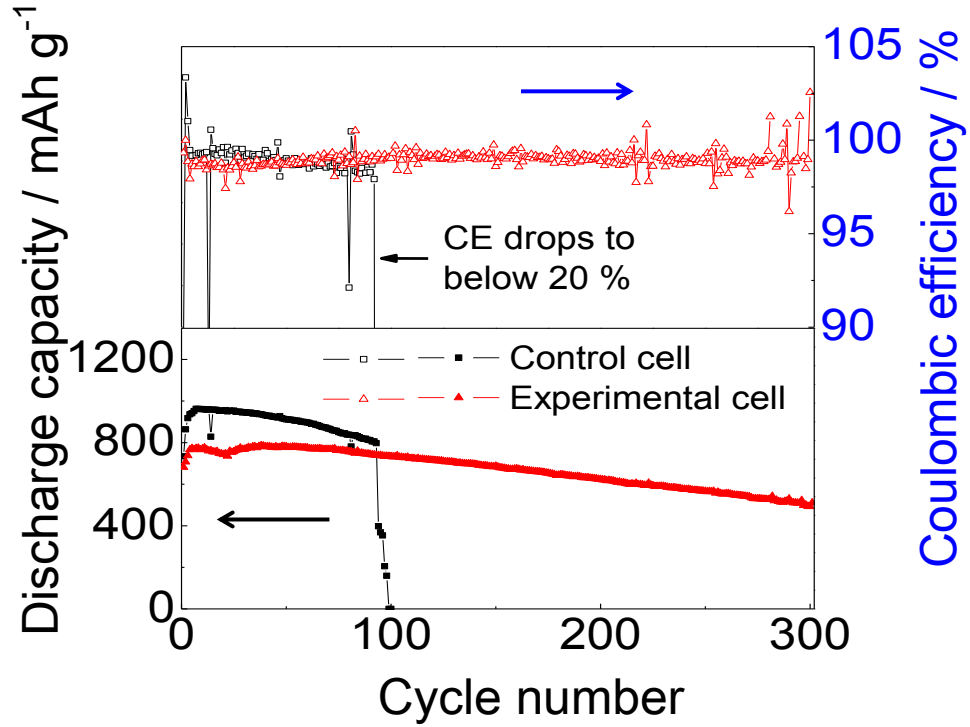
Y.-Z. Fu, C. Zu, and A. Manthiram, *J. Am. Chem. Soc.* **135**, 18044 (2013)

LITHIUM-METAL ANODE PROTECTION

BUILDING STABLE LITHIUM-SURFACE PASSIVATION

LITHIUM-METAL SURFACE STABILIZATION

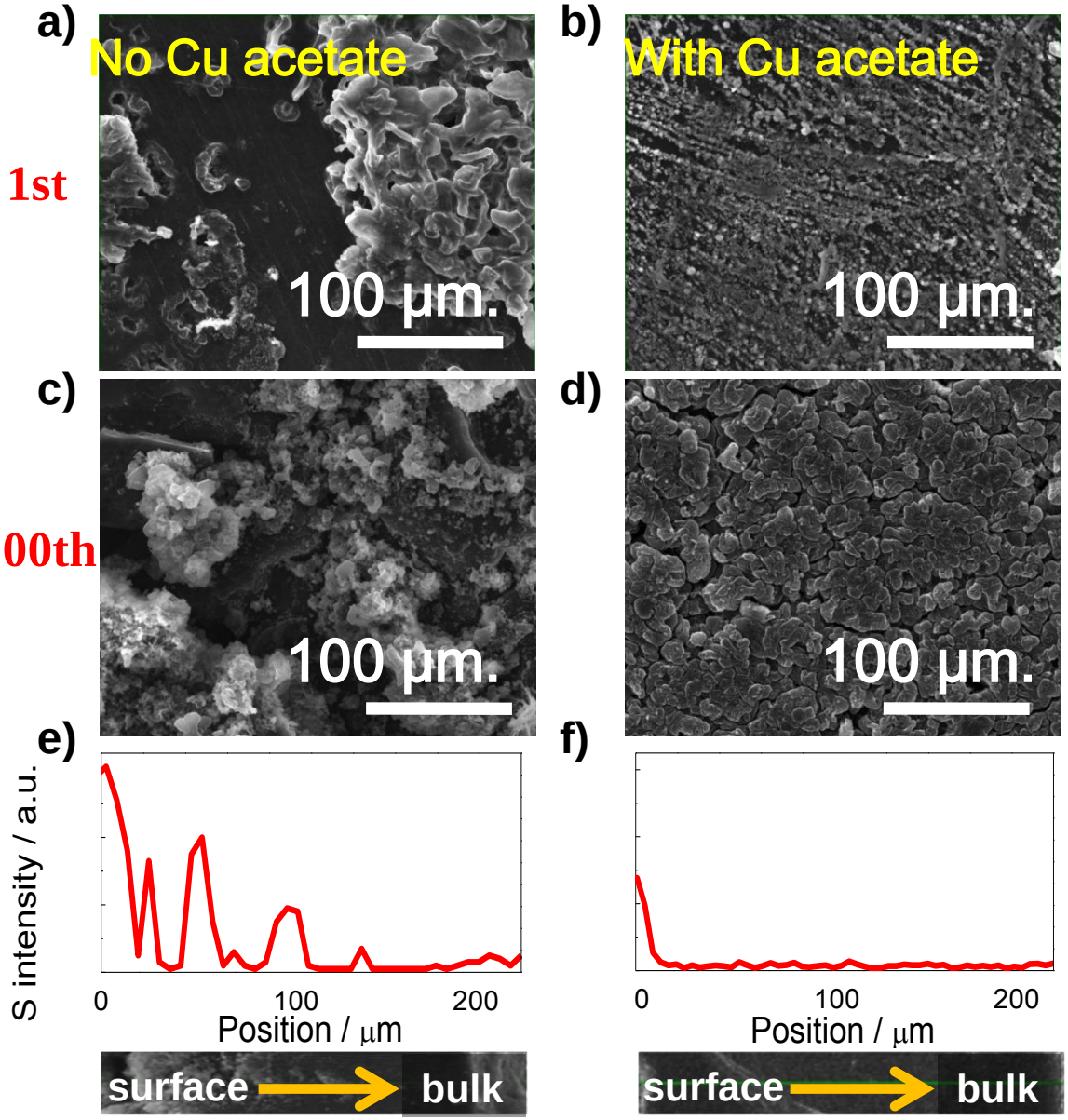




C. Zu and A. Manthiram, *Journal of Physical Chemistry Letters* **5**, 2522 (2014)

- Li/polysulfide cells with single-layer CNF current collector: polysulfides in direct contact with Li metal (sulfur: 50 wt.%, 2 mg cm^{-2})
- **Control cell (no copper acetate):** cell failure after ~ 100 cycles
- **Experimental cell (with copper acetate):** 75 % retention after 300 cycles

SEM ANALYSIS OF Li SURFACE BEFORE AND AFTER CYCLING



After 1st charge:

Control cell: Bulk Li_2S/Li_2S_2 and mossy Li

Experimental cell: S-/Cu-containing homogeneous passivation

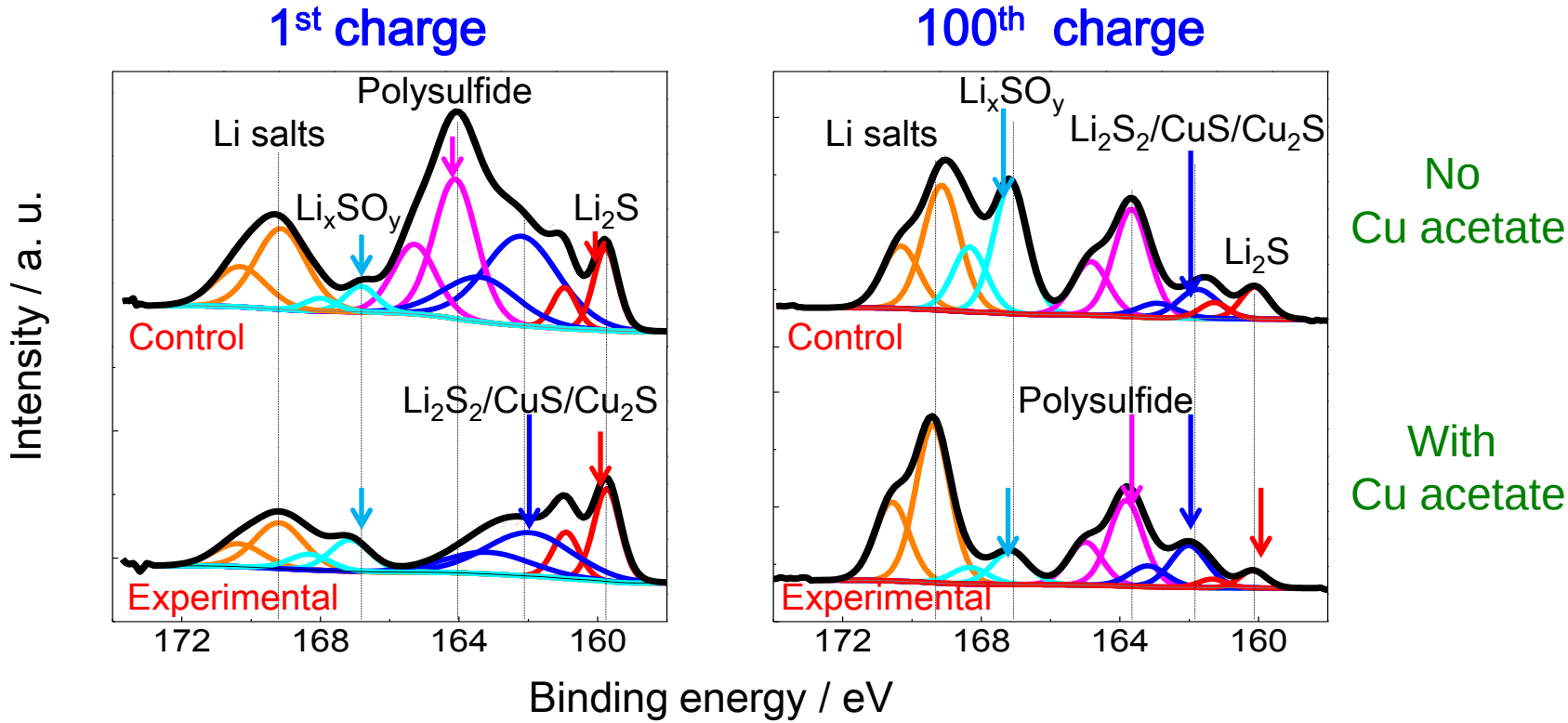
After 100th charge:

Control cell: corroded with S-containing by-products

Experimental cell: smooth with less serious corrosion

EDS after 100th charge: Sulfur species penetrates into bulk Li in control cell

XPS ANALYSIS OF Li SURFACE BEFORE AND AFTER CYCLING



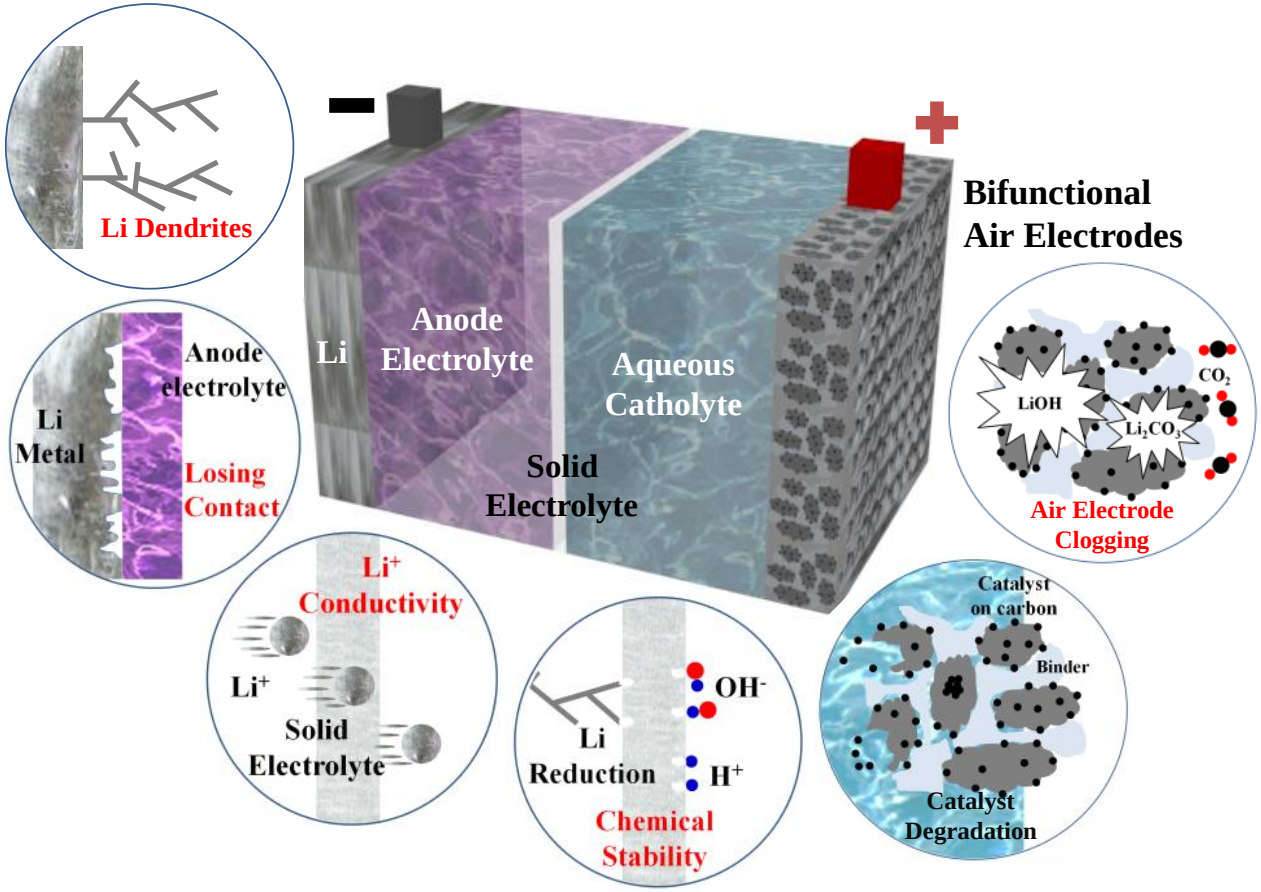
C. Zu and A. Manthiram, *Journal of Physical Chemistry Letters* **5**, 2522 (2014)

Copper acetate additive:

- Less polysulfides after 1st charge: smooth Li surface
- SEI composition: Li_2S, Li_2S_2/CuS/Cu_2S, Li salts, and Li_xSO_y
- Li_xSO_y did not increase after 100 cycles

HYBRID LITHIUM-AIR BATTERIES

CHALLENGES OF HYBRID LITHIUM-AIR BATTERIES

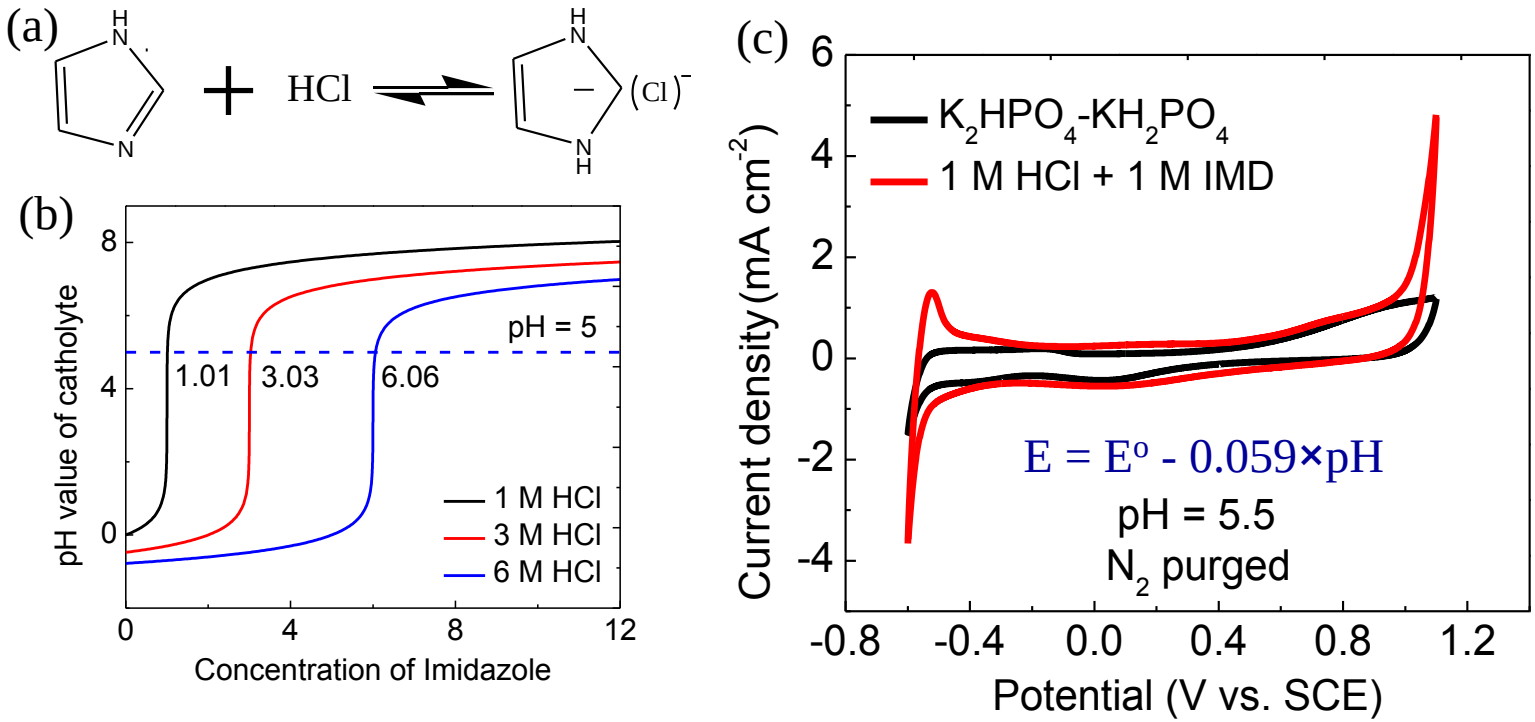


- **Solid electrolyte:** conductivity, chemical stability, working-ion selectivity
- **Li anode:** interfacial stability with solid electrolyte
- **Air electrode: cost,** catalyst activity, stability/durability, carbon corrosion

A. Manthiram and L. Li, *Advanced Energy Materials* **5** (1980)

IMIDAZOLE (IMD) BUFFER

Li | 1 M $LiPF_6$ in EC/DEC | LTAP | HCl + IMD + LiCl | Pt + IrO_2 air

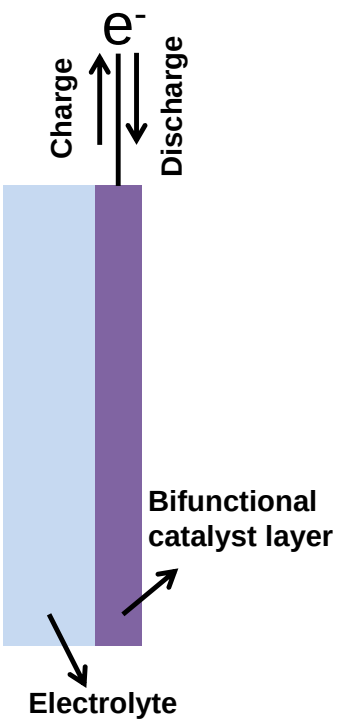


L. Li, Y. Fu, and A. Manthiram, *Electrochemistry Communications* **47**, 67 (2014)

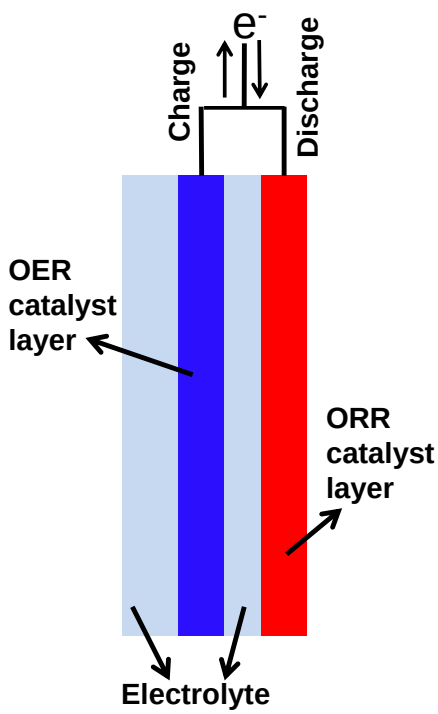
- High dissociation constant of imidazole (7.0) enables the use of many strong acids as catholytes
- With only 1 mol % excess imidazole, pH of 5 could be maintained with HCl
- Imidazole is easily oxidized at high potentials, so alternatives need to be explored

NOVEL DECOUPLED CELL CONFIGURATIION

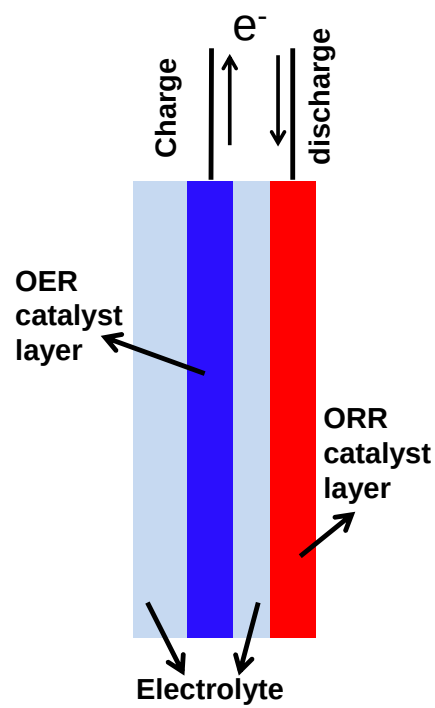
CONSTRUCTION OF BIFUNCTIONAL AIR ELECTRODES



Integrated ORR & OER electrode



Combined ORR & OER electrodes

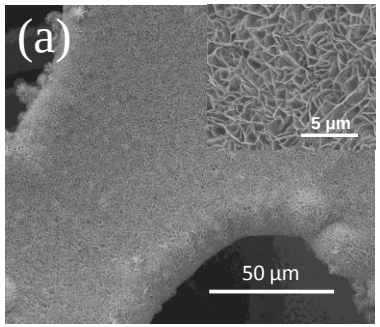


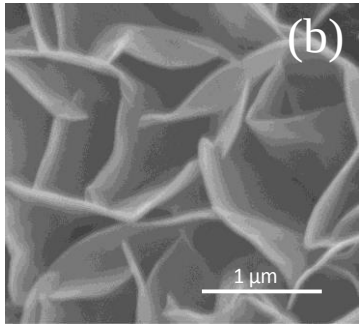
Decoupled ORR & OER electrodes

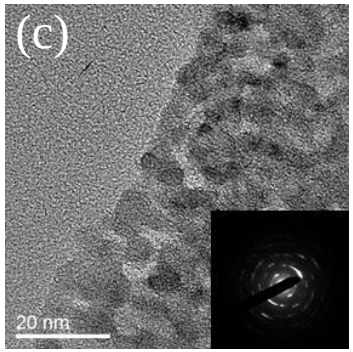
L. Li and A. Manthiram, *Nano Energy* **9**, 94 (2014)

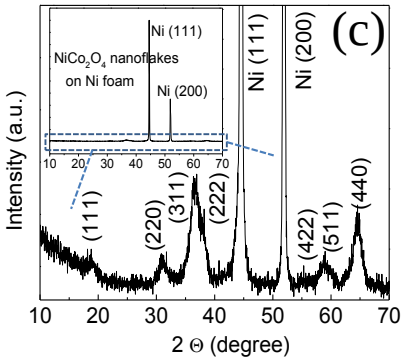
- $C + 2H_2O = CO_2 + 4H^+ + 4e^-$ $E_{298k} = 0.207$ V vs. RHE
- ORR catalysts contain carbon support or are made by carbon, which is vulnerable during the high-voltage charge (OER) process

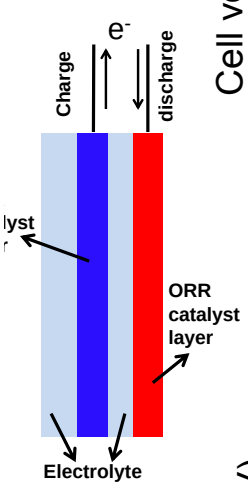
DECOUPLED FULL CELL WITH N-MC AND NCONF@Ni

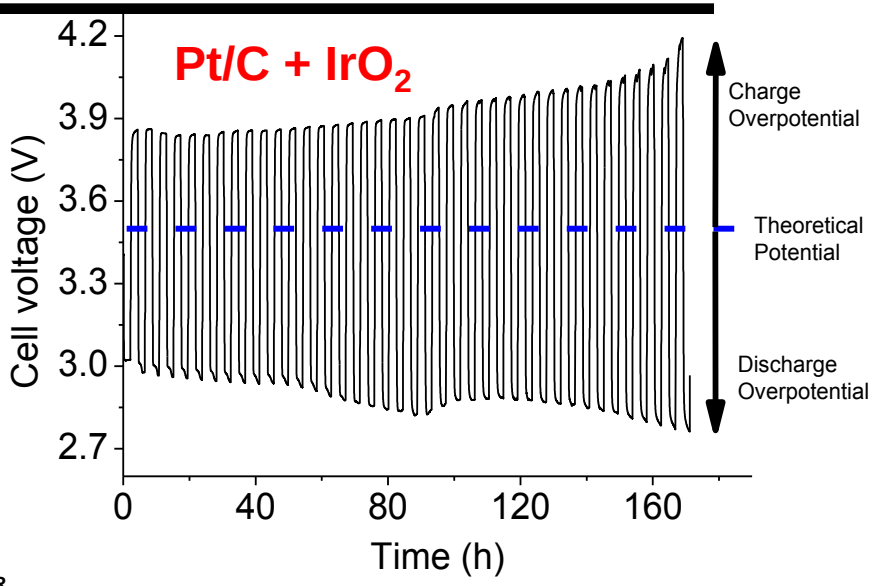


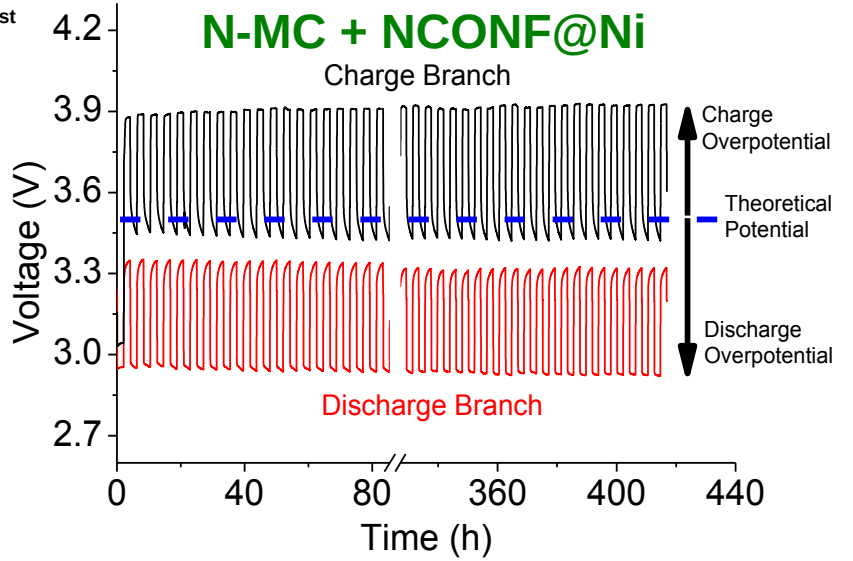




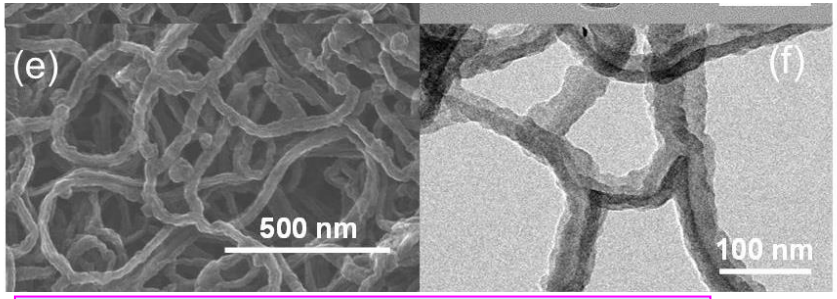








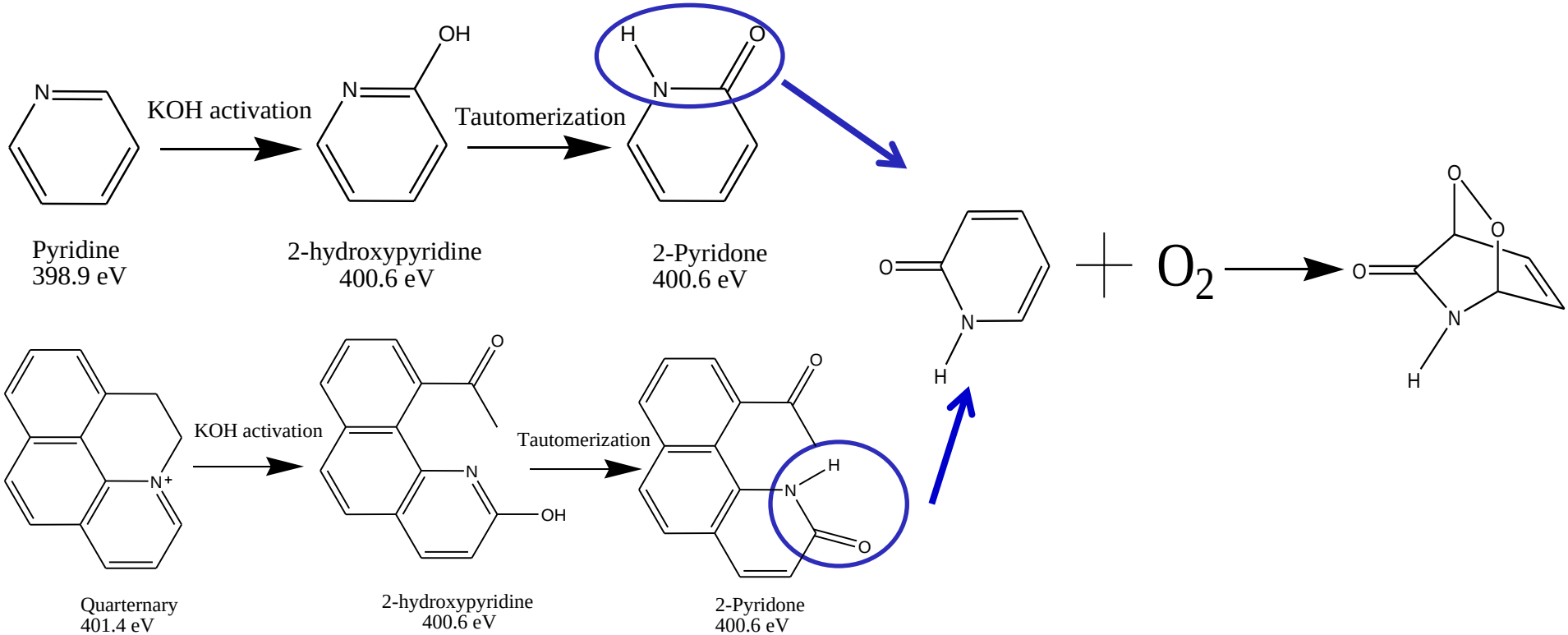
OER: $NiCo_2O_4$ grown onto Ni foam



ORR: N- and O-doped carbon

L. Li & A. Manthiram, *Energy & Environ. Sci.* **7**, 2630 (2014)

XPS ANALYSIS



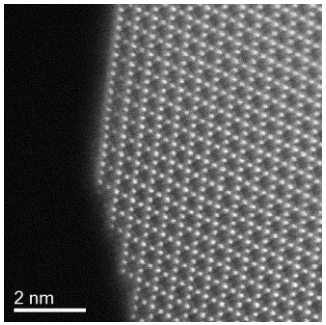
- The pyridone nitrogen is known to stabilize singlet dioxygen by forming a stable adduct similar to that in Pt

  Silva *et al.*, *J. Am. Chem. Soc.* **133**, 7823(2013)

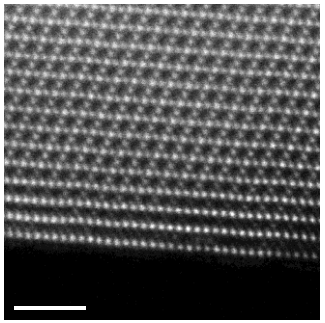
NEW ELECTROCATALYSTS

BIFUNCTIONAL CATALYSTS AND MORPHOLOGY DEPENDENCE

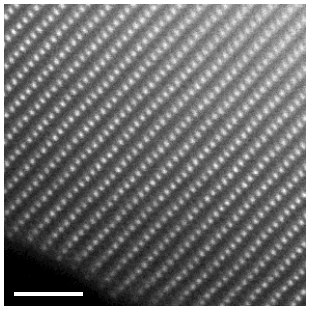
370 °C, 7 days

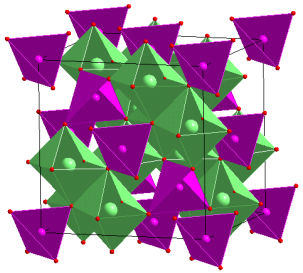


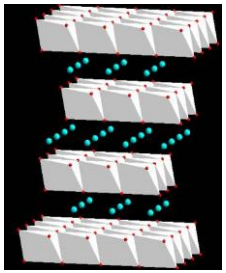
385 °C, 7 days



800 °C, 24 hours

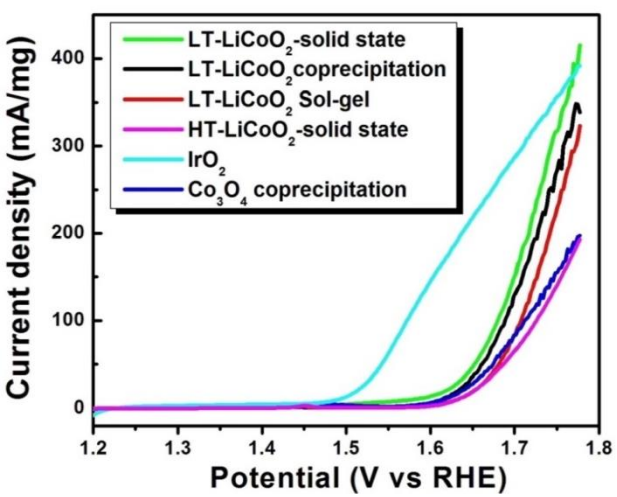


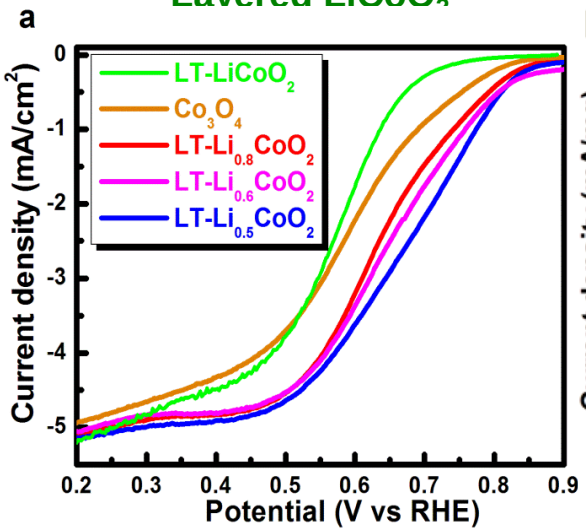


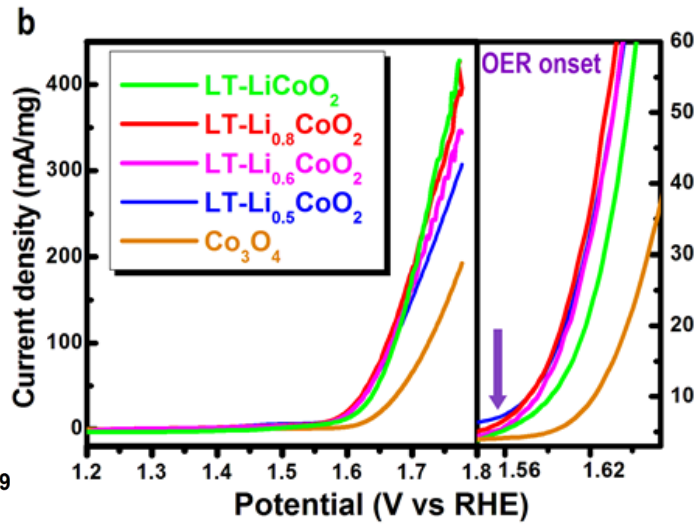


Spinel $LiCoO_2$

Layered $LiCoO_2$



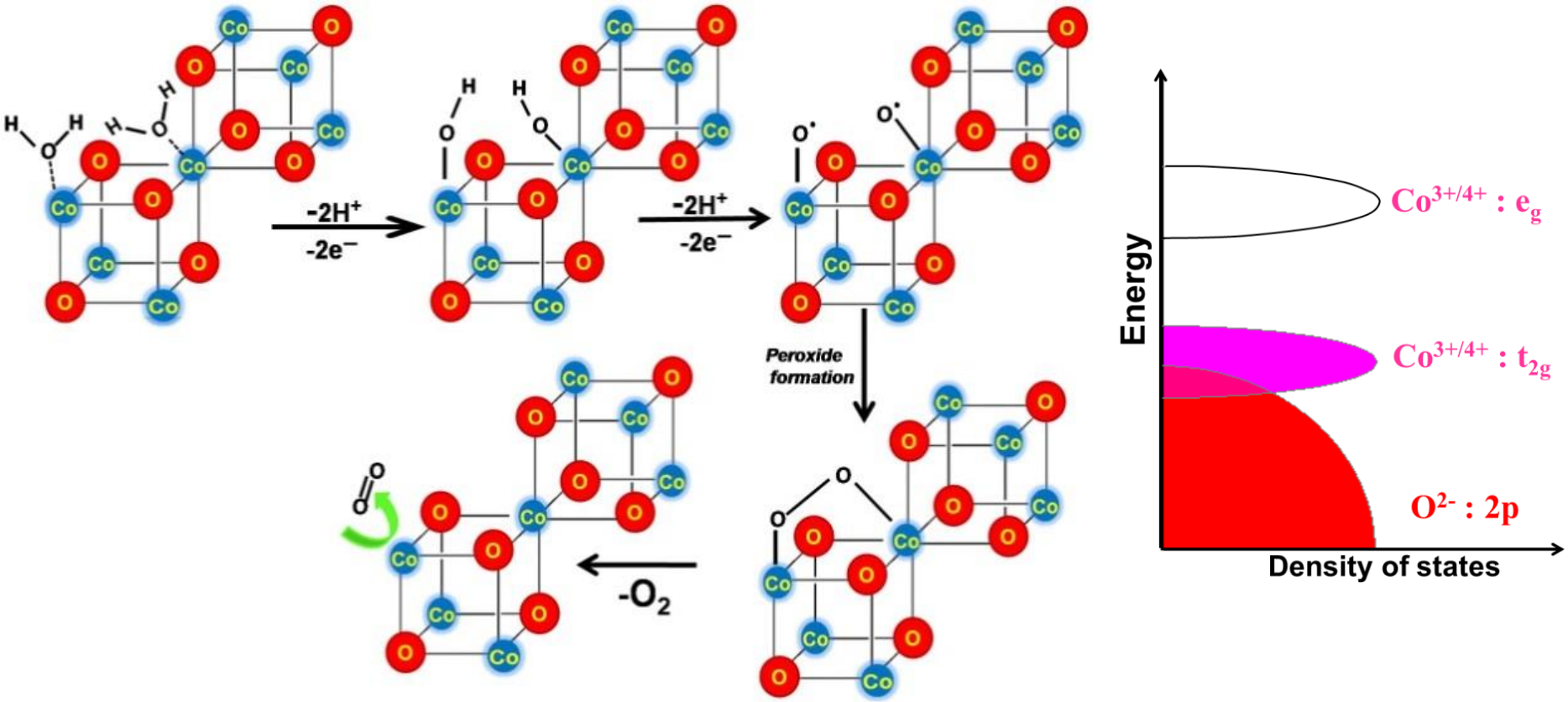




T. Maiyalagan, K. Jarvis, S. Therese, P. Ferreira, & A. Manthiram, *Nature Communications* **5**, 3949 (2014)

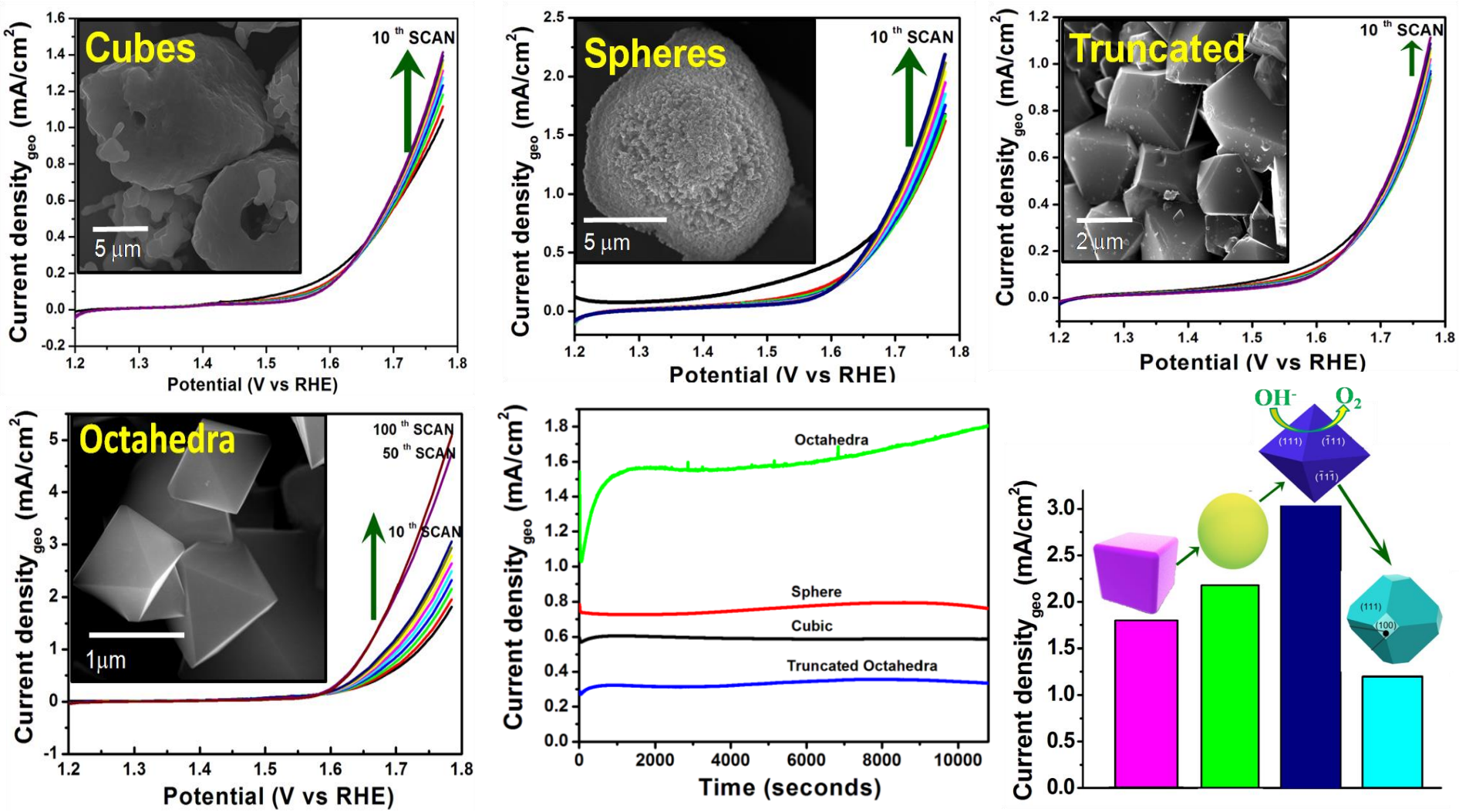
- LT-$LiCoO_2$ synthesized at < 400 °C has a lithiated spinel (ordered rock salt) structure in which the Li^+ ions occupy the 16c octahedral sites: $\{Li_2\}_{16c}[Co_2]_{16d}O_4$

OER MECHANISM ON SPINEL CATALYSTS



- Cubane-like Co_4O_4 units, analogous to that in Nature's water-oxidation catalyst $CaMn_4O_5$, may play a critical role in OER
- Pinning of $Co^{3+/4+}$:3*d* energy with the top of the O^{2-}:2*p* band along with direct t_{2g}-t_{2g} interaction (metallic) facilitates catalytic activity

OER OF $LiMn_{1.5}Ni_{0.5}O_4$: ROLE OF SURFACE PLANES



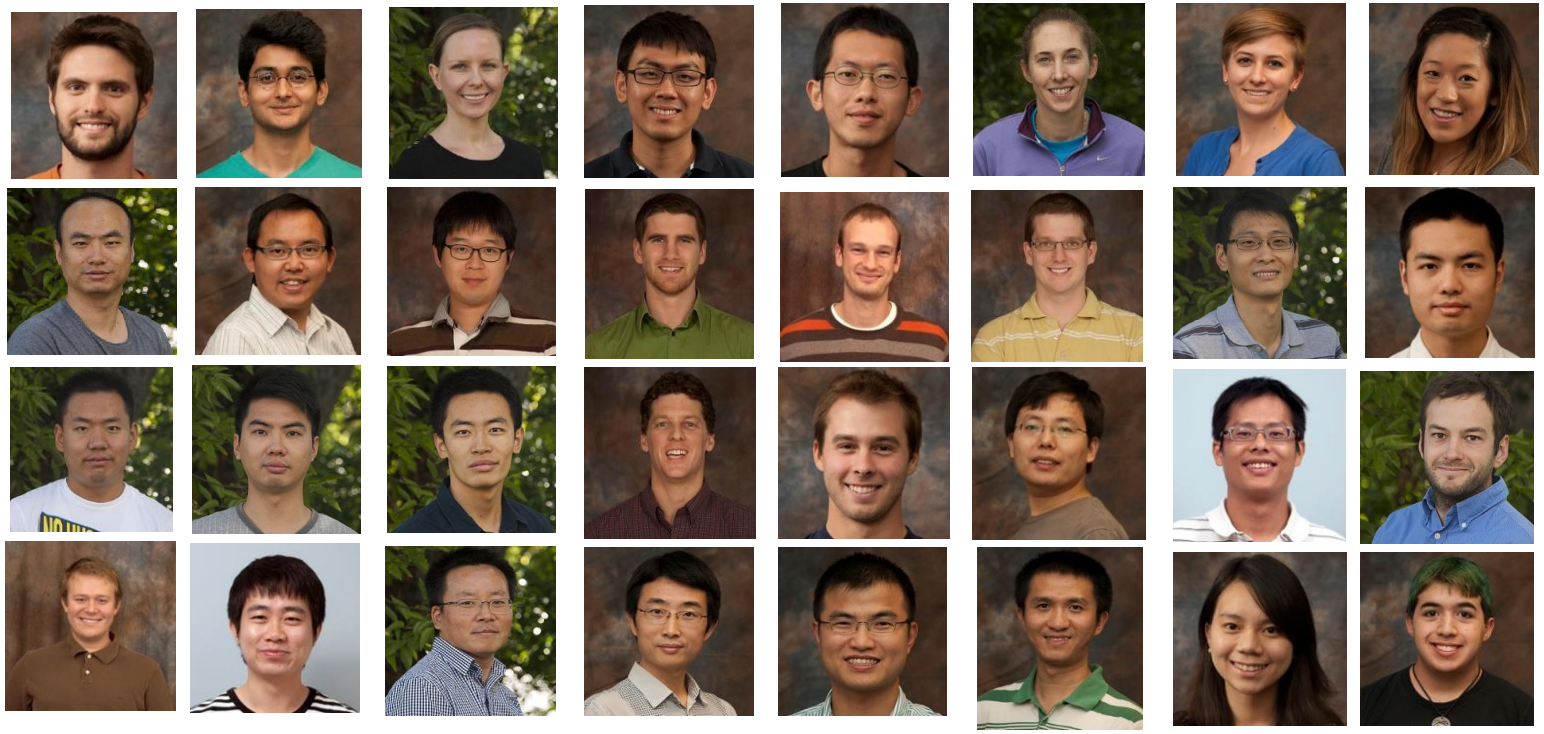
T. Maiyalagan, K. Chemelewski, and A. Manthiram, *ACS Catalysis* **4**, 421 (2014)

- Octahedral morphology with (111) facets exhibit higher OER activity in $LiMn_{1.5}Ni_{0.5}O_4$

CONCLUSIONS

- Significant progress has been made with high sulfur loading to overcome the problems of Li-S cells with a few strategies, but still challenges exist:
  - C-S composites, carbon-paper interlayers, carbon-coated separators, sandwiched electrodes, polysulfide in a carbon matrix, Li_2S particle activation, Li-metal surface protection, and solid-electrolyte use
  - Lithium-metal protection, Li_2S use, use of lithium-free anodes
- Some of the problems associated with aprotic Li-air cells could be overcome with hybrid lithium-air cells, but still challenges exist:
  - buffer catholytes, novel cell configurations, inexpensive catalysts,
  - mechanical stability of ceramic electrolyte, round-trip efficiency, solid-electrolyte and catalyst stability over a wide pH range

ACKNOWLEDGEMENTS



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