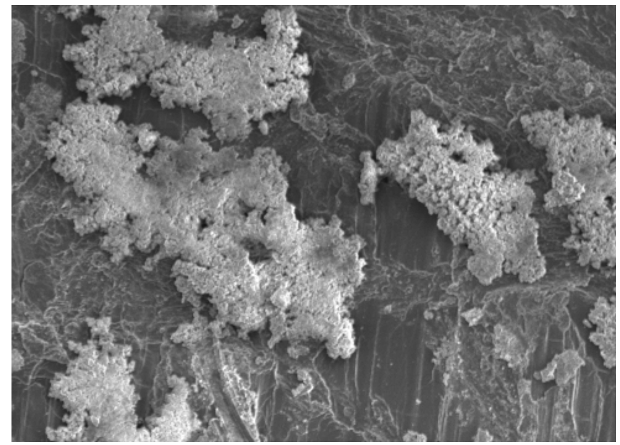
19th International Conference on Atomic Layer Deposition

ALD and MLD on Lithium Metal – A Practical Approach Toward Enabling Long Lasting, High Energy Density Batteries



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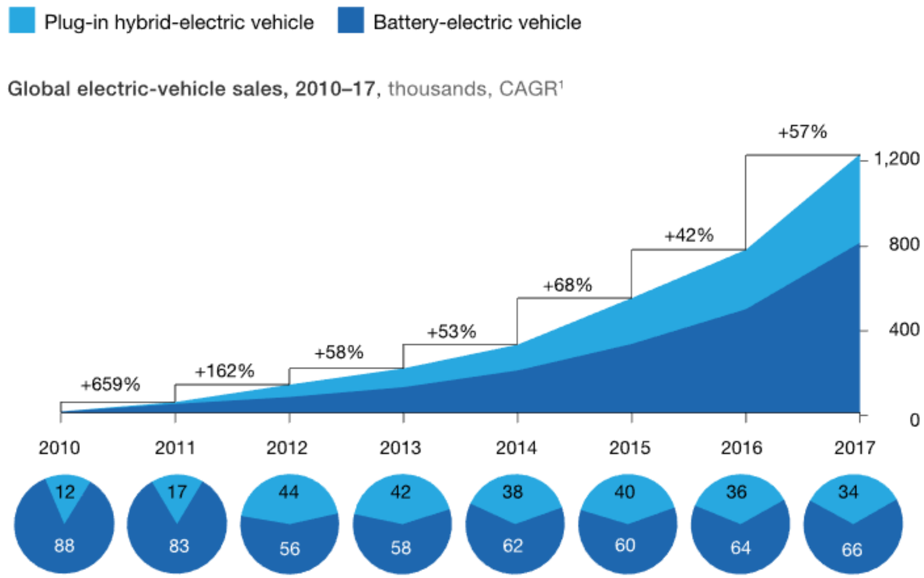
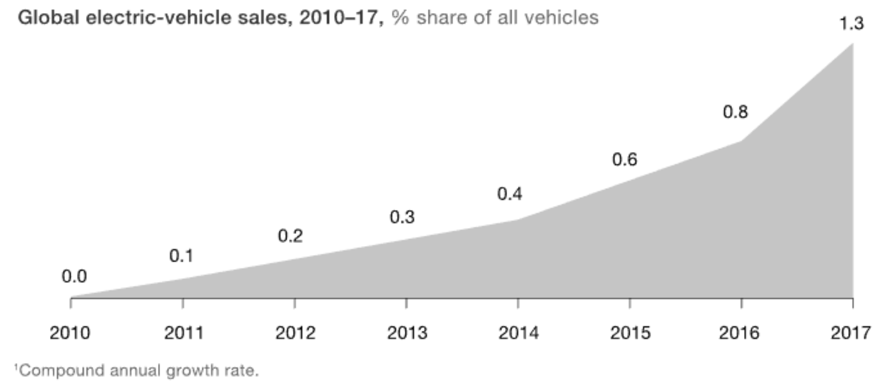
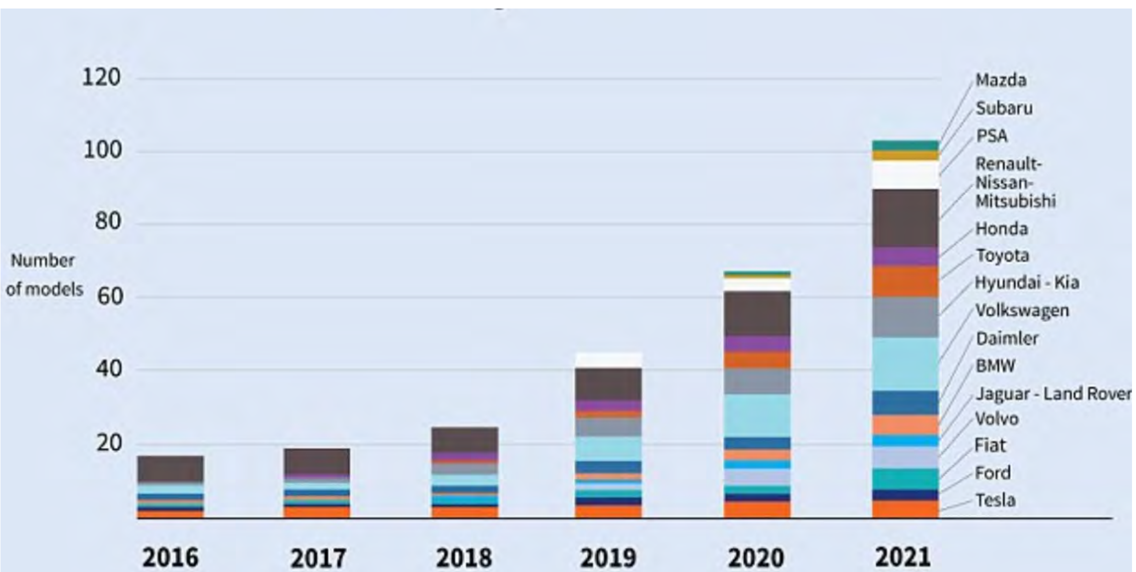
Tuesday July 23rd 2019

Session: AA2-TuM

Growing Electrical Vehicle Market







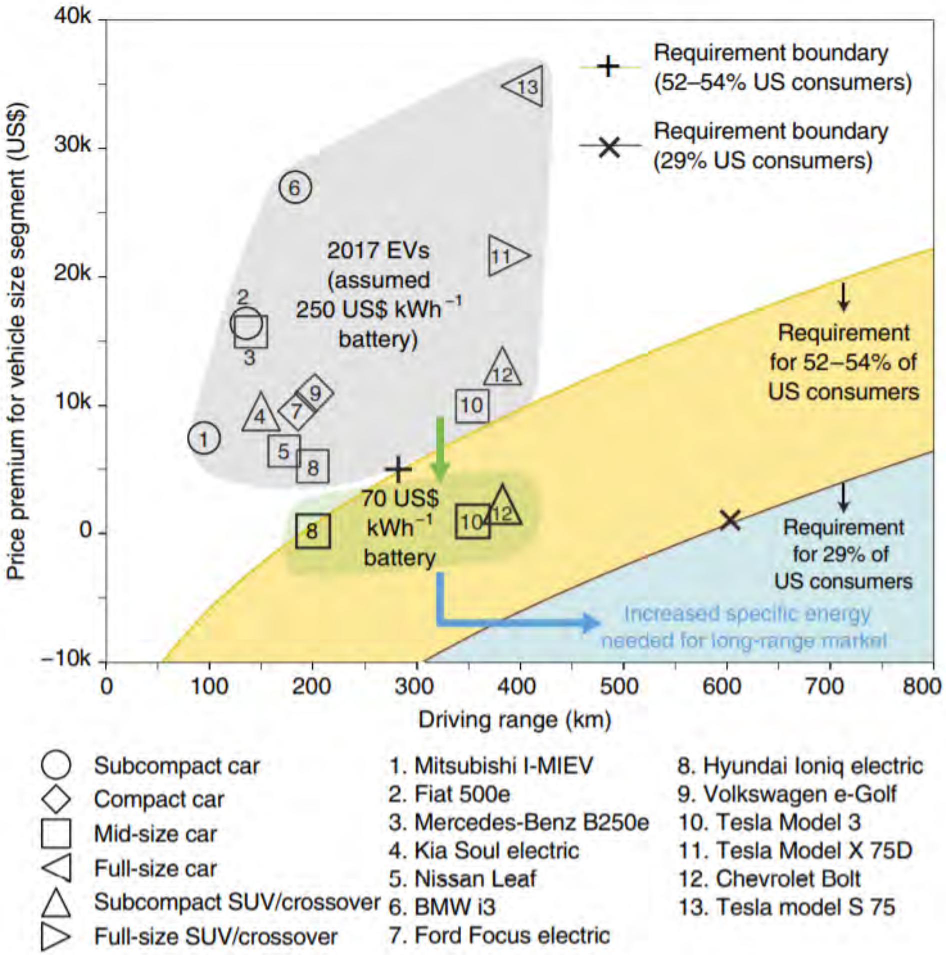
Electric vehicle market has significantly grown in the past decade

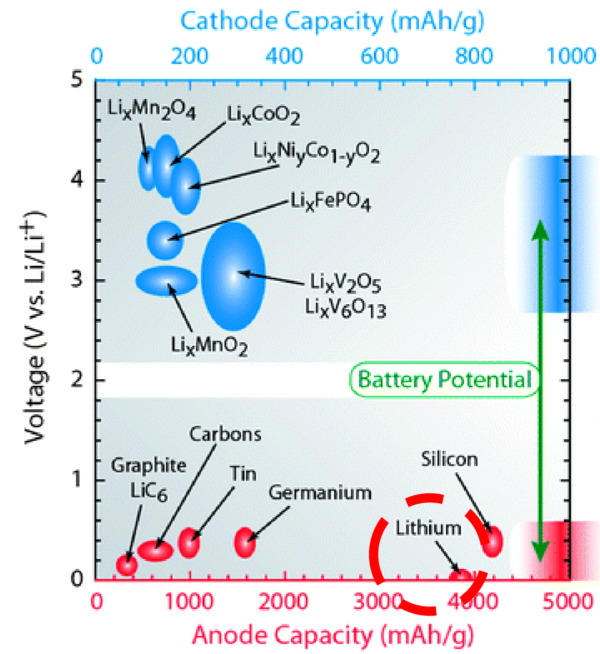
An increasing number of manufactures are entering the electric vehicle market

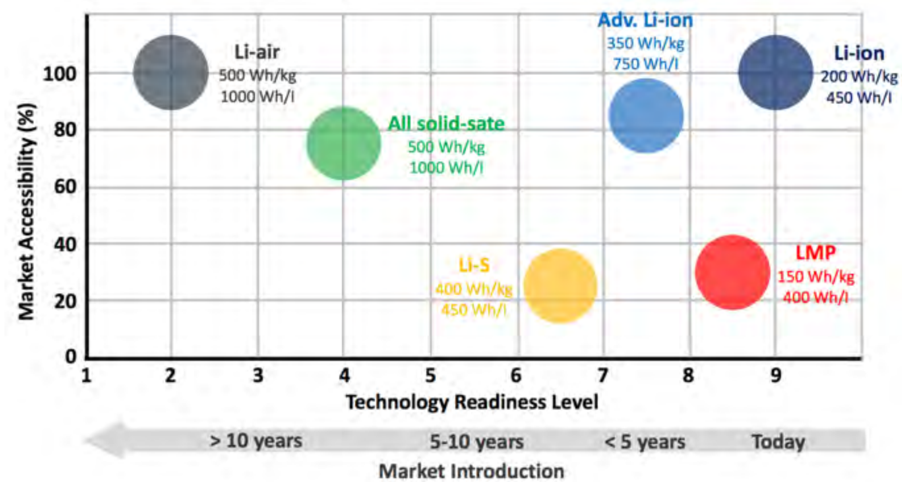
Hertzke, P., Muller, N., Schenk, S. & Wu, T. The global electric-vehicle market is amped up and on the rise. *McKinsey & Company*(2018).

New Materials Required for the Future

To meet future demand and extend EV range, adoption of new materials is required.







Cano, Zachary P., et al. "Batteries and fuel cells for emerging electric vehicle markets." *Nature Energy* 3.4 (2018): 279.
Osiak, Michal, et al. "Structuring materials for lithium-ion batteries:" *Journal of Materials Chemistry A* 2.25 (2014): 9433-9460.

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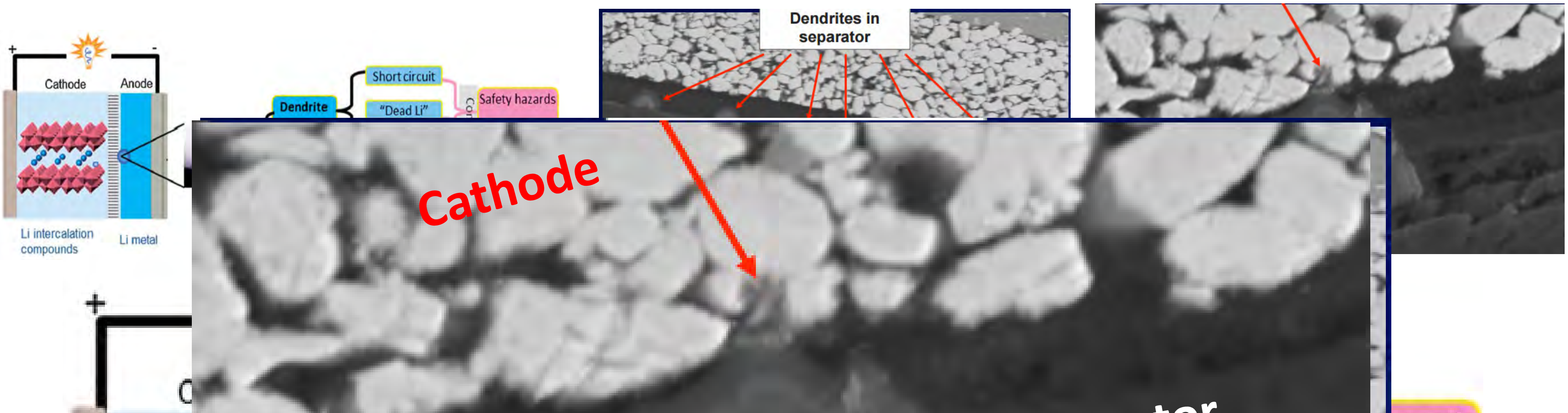
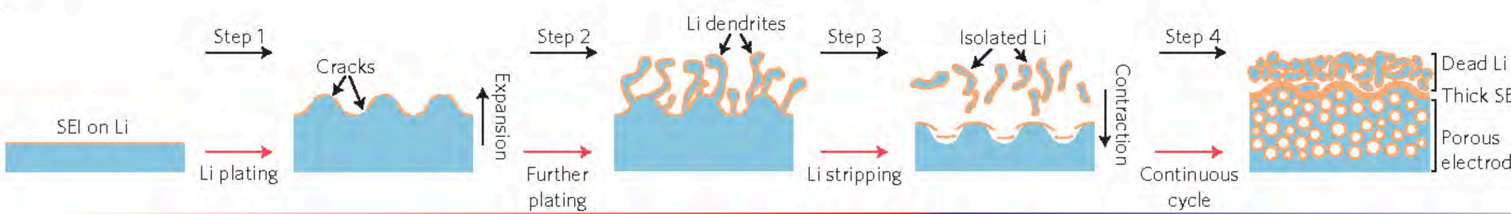
Problem With Li Metal Anodes



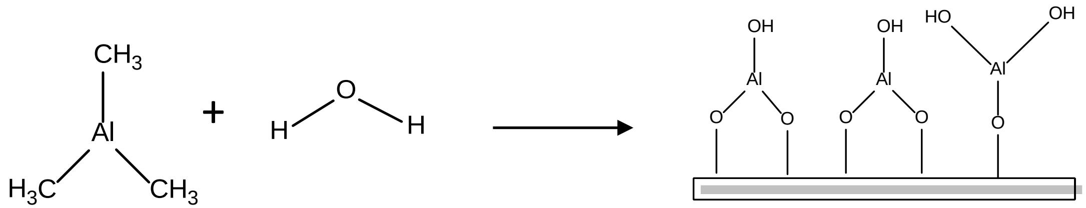
1. High Reactivity of Lithium
2. Uncontrolled Formation of Solid Electrolyte Interface (SEI)
3. Infinite Volume Change



Kim, J. G.; Son, B.; Mukherjee, S.; A Review of Lithium and Non-Lithium Based Solid State Batteries. *J. Power Sources* **2015**, *282*, 299–322.
Lin, Dingchang, Yayuan Liu, and Yi Cui. "Reviving the lithium metal anode for high-energy batteries." *Nature nanotechnology* 12.3 (2017): 194.

Use ALD and MLD to Passivate Surface

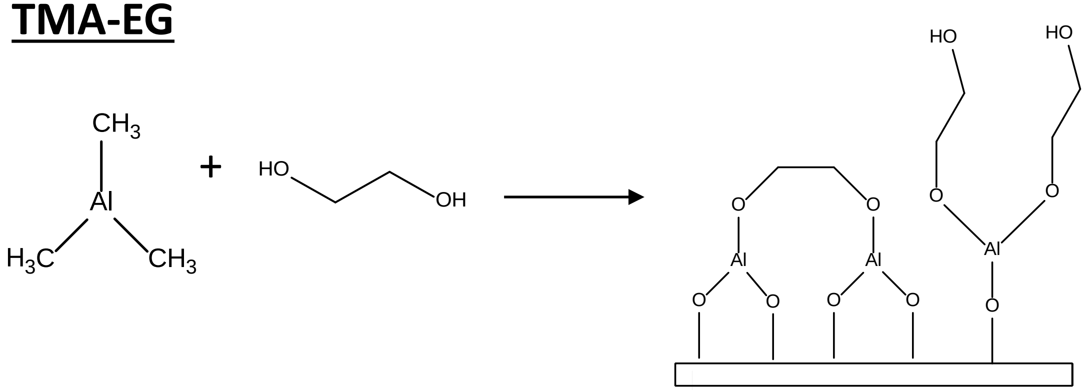
TMA-H_2O



- Previous research indicates positive results
- Can be done at low temperatures (RT)

- Water can react with Li
- Dense film may not allow for good Li^+ conduction

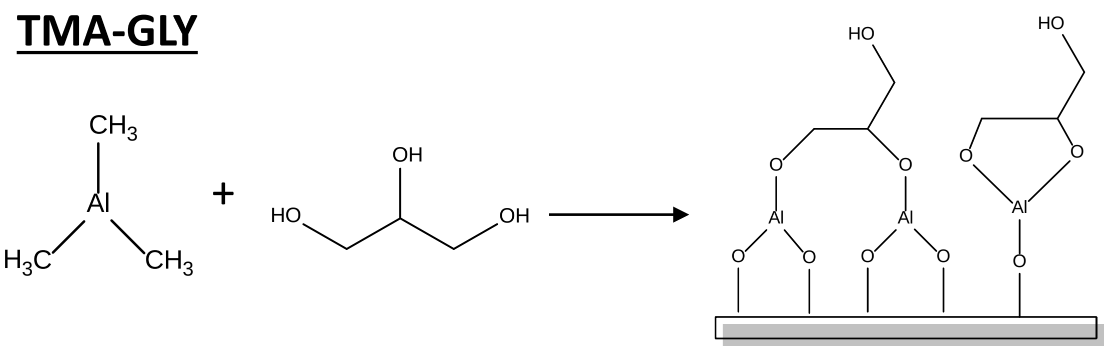
TMA-EG



- Increase film flexibility by MLD linkage
- Relatively low deposition temperature (90°C)
- Does not include water

- Increase chance of double side reactions
- Long purge times

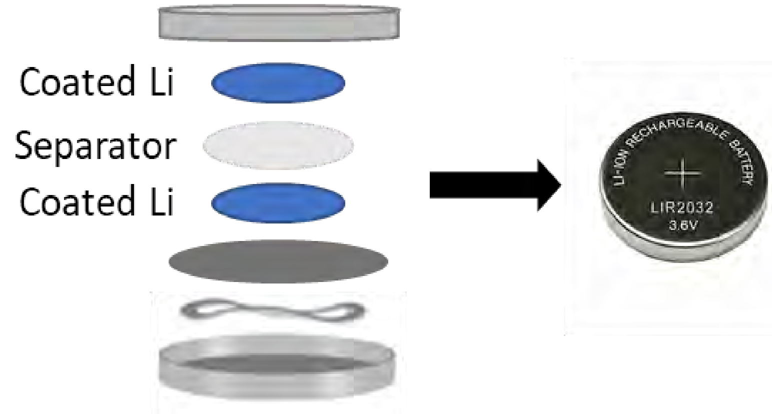
TMA-GLY

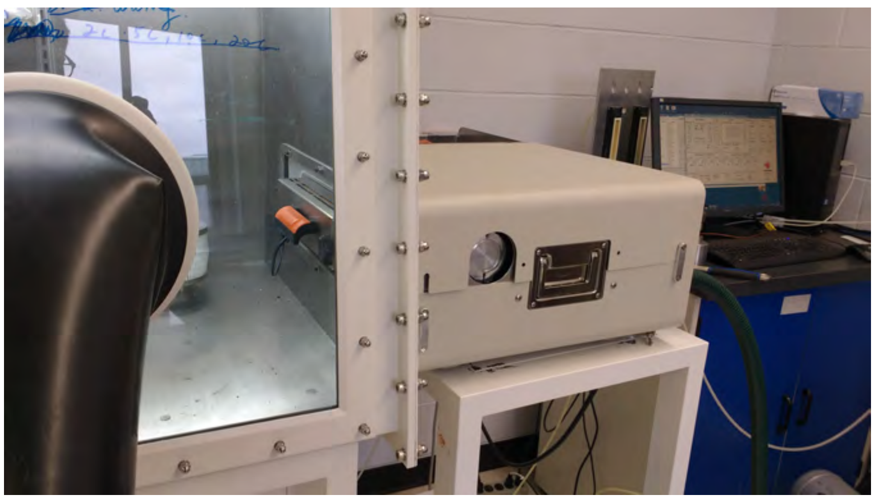


- Highly Robust
- Continued reaction (dbl side reaction do not limit surface sites)
- Increased cross linking

- Requires high deposition temperatures (150°C)
- Long purge times

Symmetrical Cell Testing





Current Density (mA cm^{-2}): How quickly Li is transferred from electrode → electrode
Capacity (mAh cm^{-2}): How much Li is transferred per charge/discharge cycle

Symmetrical Cell Testing

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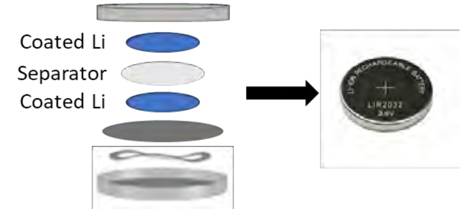
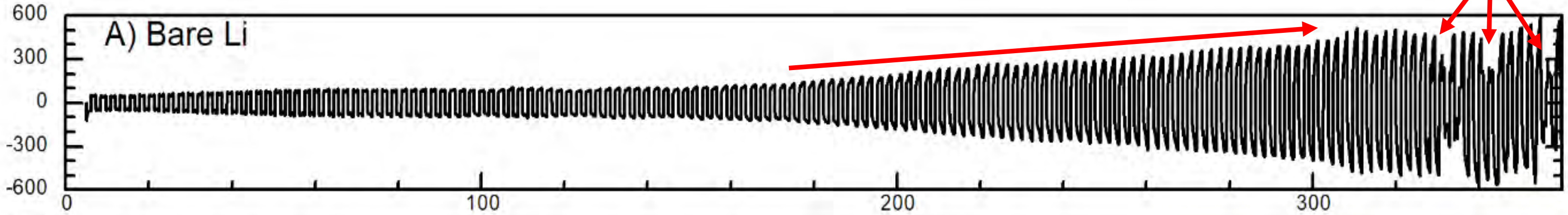


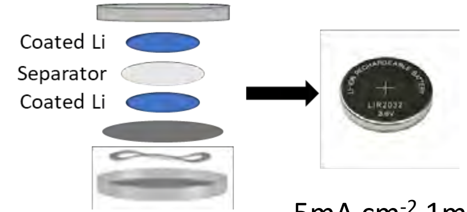
EC:DEC:DMC
1M LPF_6
(carbonate)

Soft short circuit

1mA cm^{-2} 1mAh cm^{-2}



Symmetrical Cell Testing



EC:DEC:DMC
1M LPF_6
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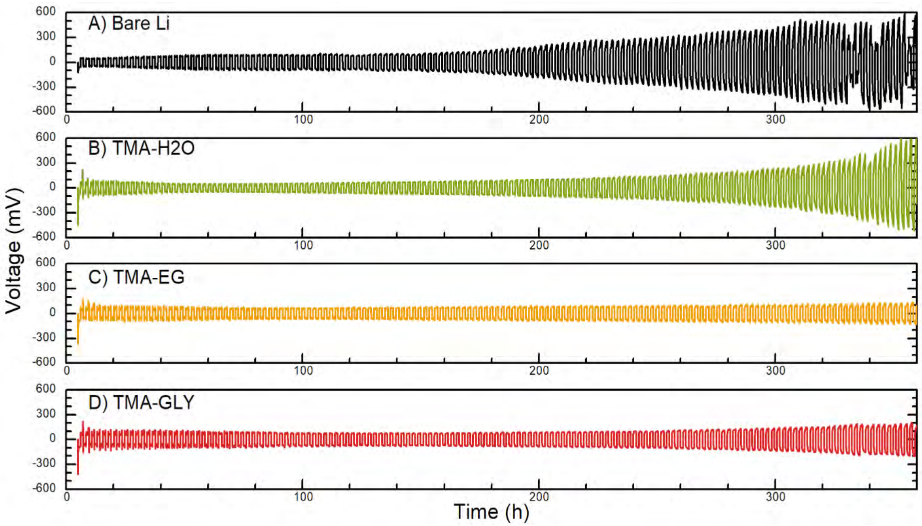
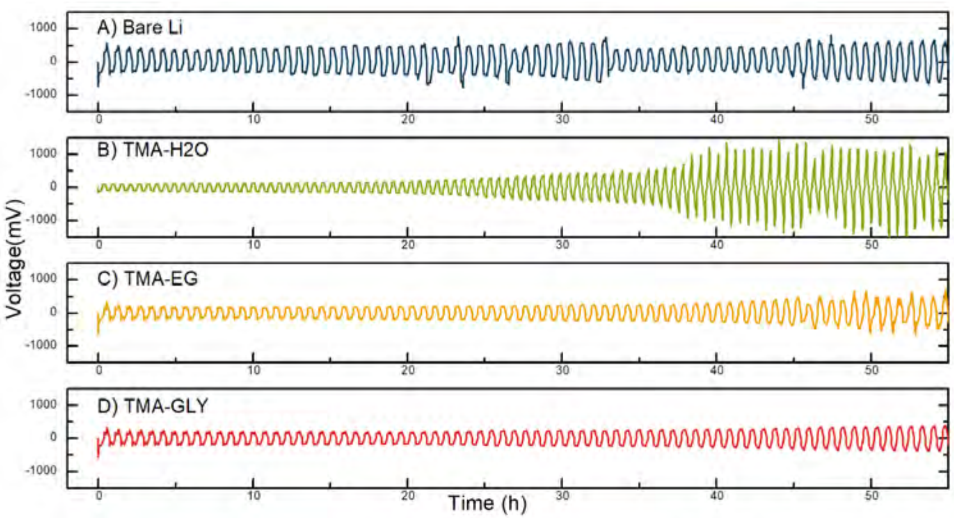
Current Density ($mA\ cm^{-2}$): How quickly Li is transferred from electrode → electrode
Capacity ($mAh\ cm^{-2}$): How much Li is transferred per charge/discharge cycle

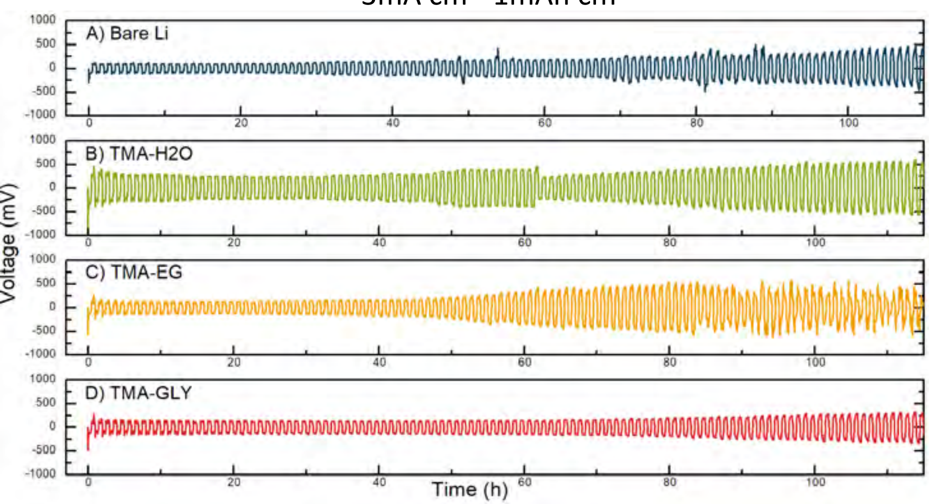
1mA cm^{-2} 1mAh cm^{-2}



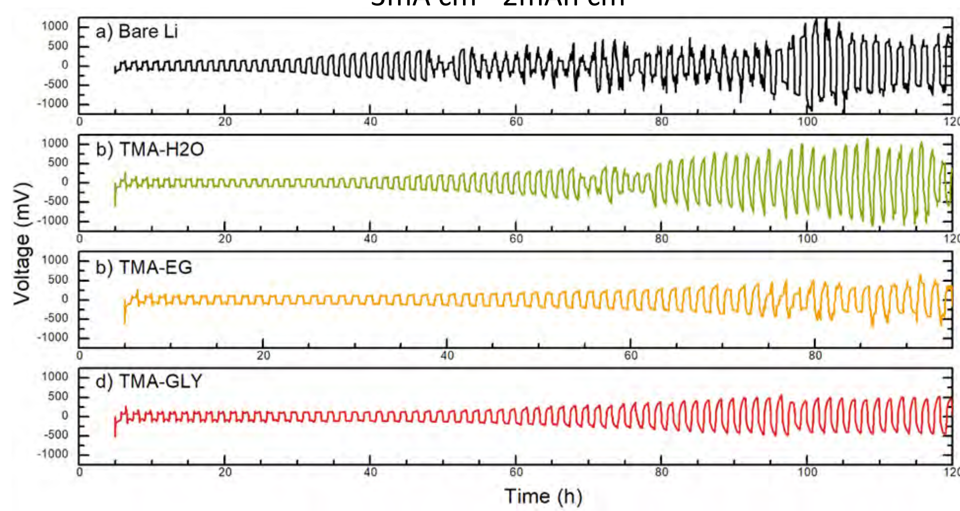
5mA cm^{-2} 1mAh cm^{-2}



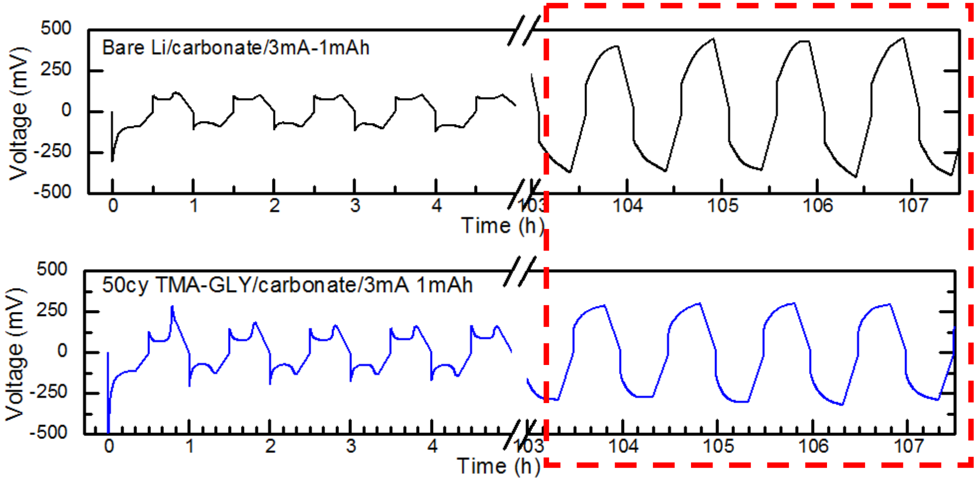
3mA cm^{-2} 1mAh cm^{-2}

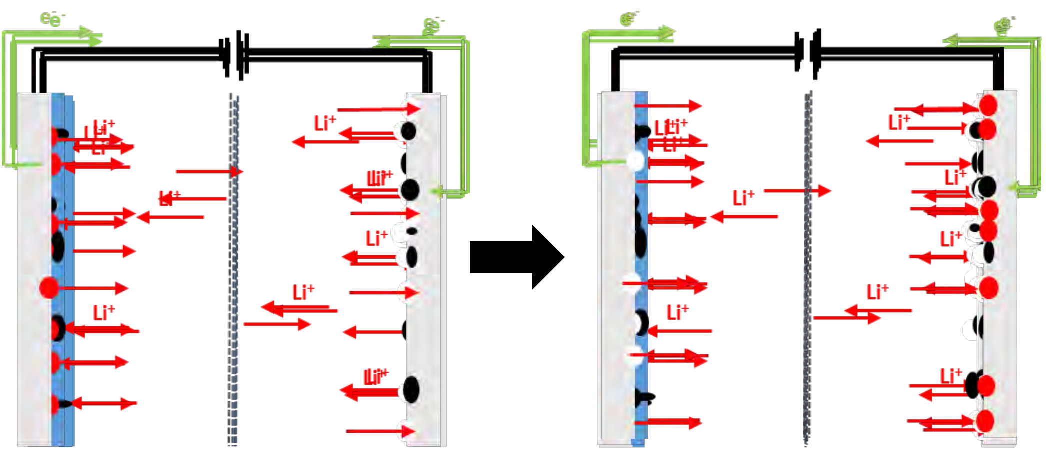


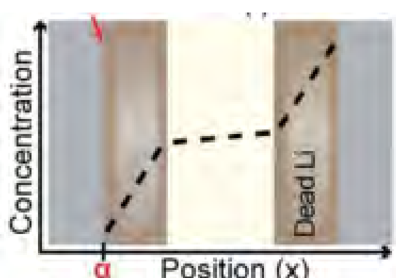
3mA cm^{-2} 2mAh cm^{-2}



Understanding the Li Mechanism





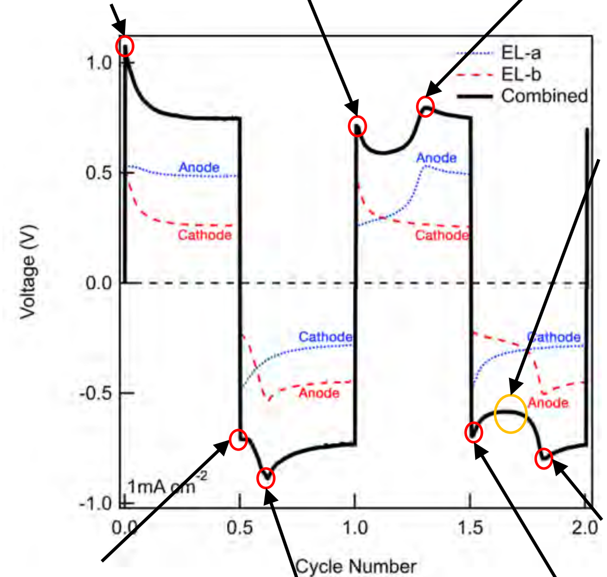


No longer reaction limited
now
mass transfer limited

Plating in pits of cathode + stripping from anode dendrites.

Transition to stripping from dendritic lithium at anode to bulk lithium, creation of addition pits.

Plating on cathode. Stripping from anode, creation of pits



Delay and decrease in overpotential due to excess lithium. Do not need to transition from dendrite to bulk as quickly.

Transition to stripping from dendritic lithium to bulk lithium off cathode (formation of dead Li)

Stripping from dendrites formed on cathode. Plating in pits on anode

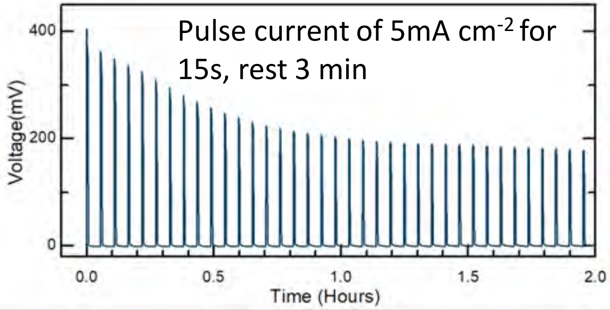
Transition to stripping from dendritic lithium to bulk lithium off cathode (formation of dead Li)

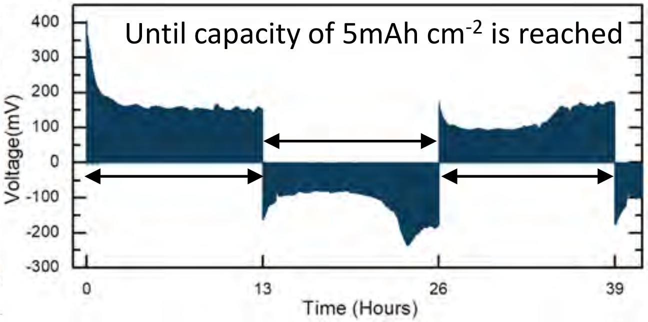
Stripping from dendrites formed on cathode. Plating on previous dendrites as well as in pits, pushing dead lithium up.

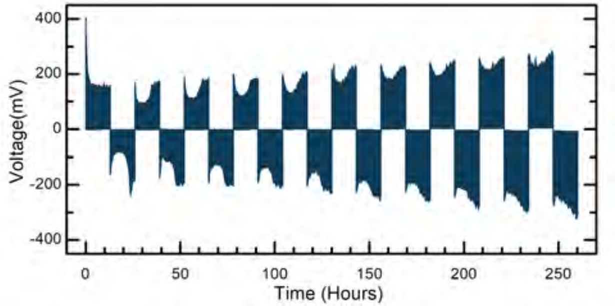
Wood, Kevin N., et al. "Dendrites and pits: Untangling the complex behavior of lithium metal anodes through operando video microscopy." *ACS central science* 2.11 (2016): 790-801.

Galvanostatic Intermission Titration Technique

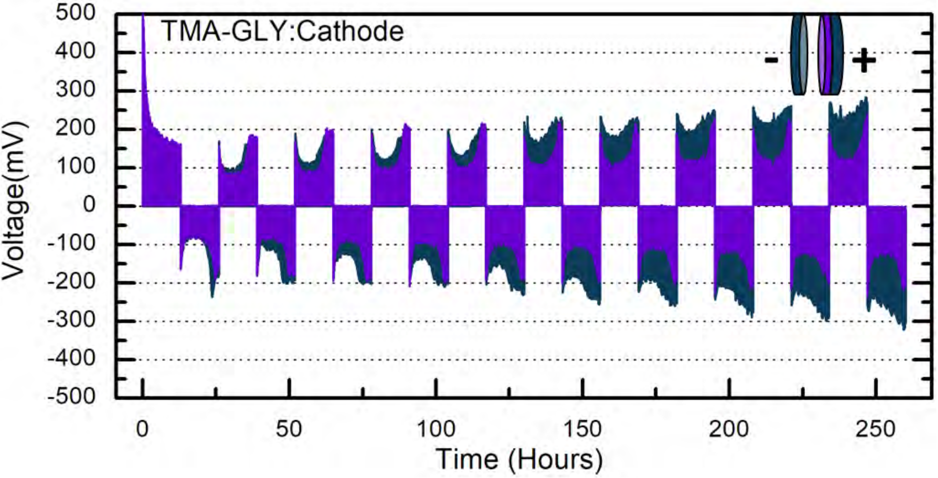
GITT can limit the effects of evolving concentration gradients on cell polarization by depositing small amounts of Li at near static-equilibrium conditions.



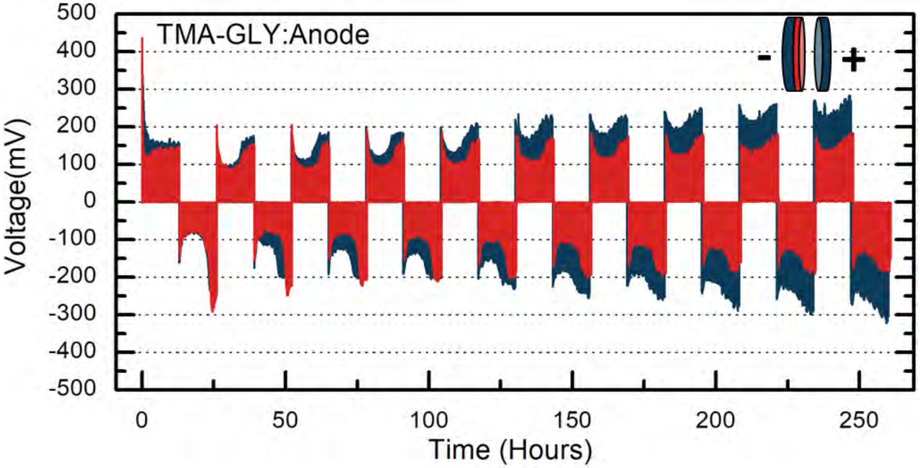




By using half-cell configuration, where one Li electrode is bare and the other is coated, we can deconvolute the effects of stripping and plating of coated Li

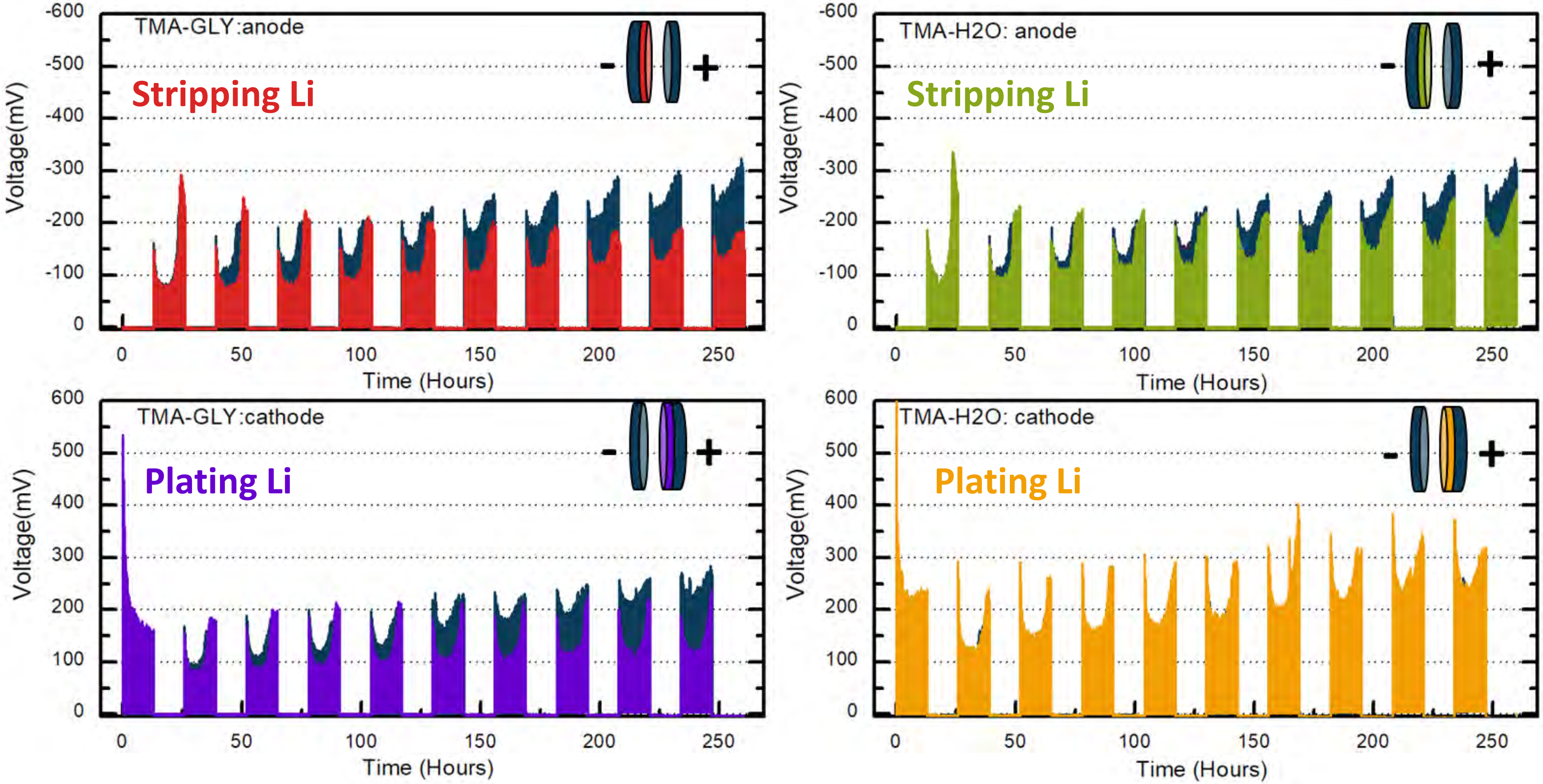


Plating Characteristics

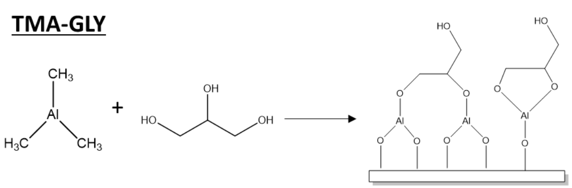


Stripping Characteristics

Using GITT to Understand Role of ALD:MLD



TMA-GLY



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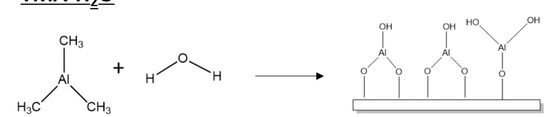
TMA-H_2O



- Previous research indicates positive results
- Quick short reaction
- Can be down at low temperatures (RT)

- Water can react with Li
- Dense film may not allow for good Li^+ conduction

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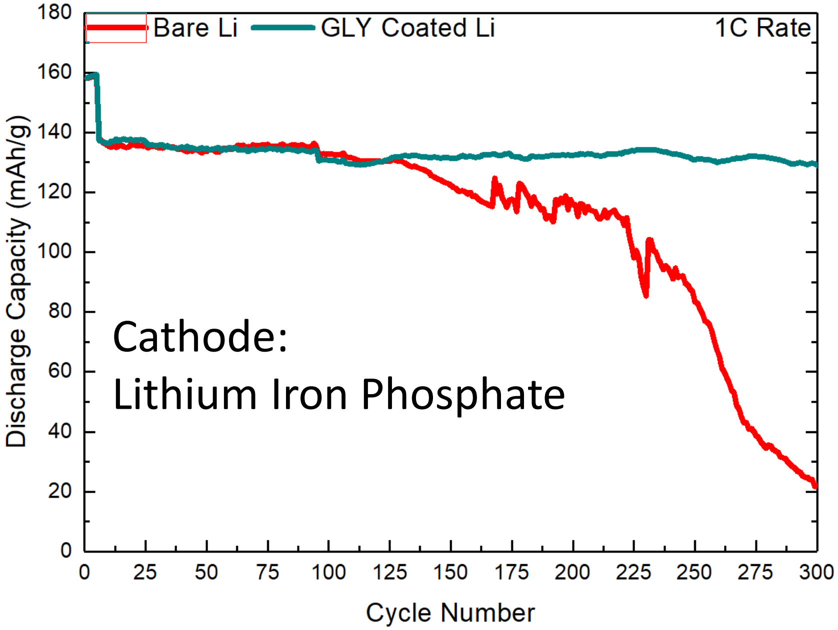
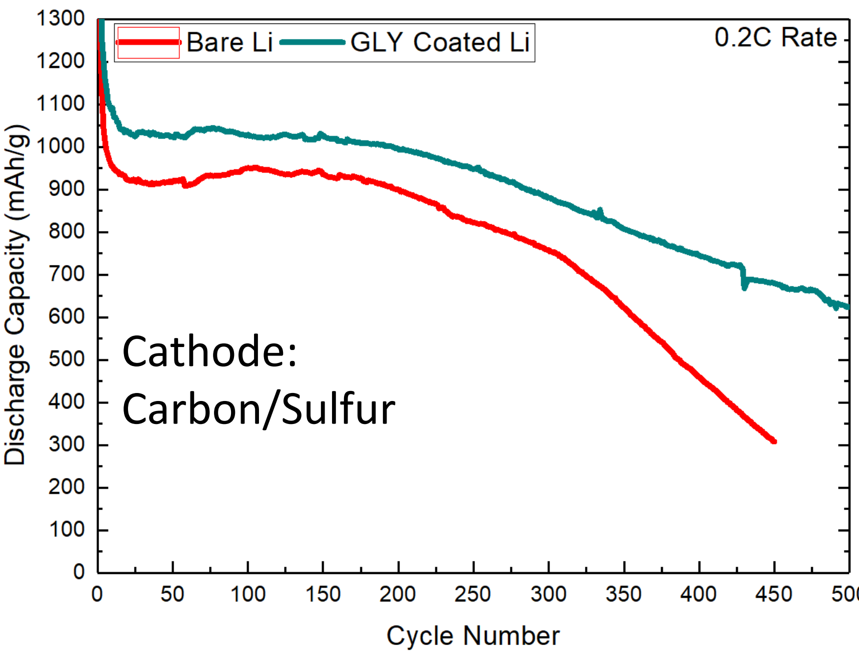
Full Cell Battery Data

- Conducted full cell battery testing using 50cy TMA-GLY coated Li anodes with two different cathode materials:
  - Lithium Iron Phosphate (LFP) – Future Li-Ion Battery
  - Carbon/Sulfur – Li/S Battery

- LFP – Lithium Ion Battery
  - Considered a more environmentally friendly material compared to $LiCoO_2$
  - Coin cells tested using loading of ~ 10mg
  - Carbonate based electrolyte (1M $LiPF_6$ in EC, DEC, EMC w FEC)
  - Constant current in a voltage range of 2.5-4.2V

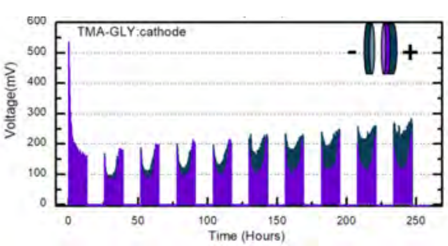
- Carbon/Sulfur – Lithium-Sulfur Battery
  - Much higher energy density compared to Lithium ion
  - Coin cells tested using loading of ~1mg
  - Ether Based electrolyte (1M LiTFSI in DOL, DME w $LiNO_3$)
  - Constant current in a voltage range of 1.8-2.8V

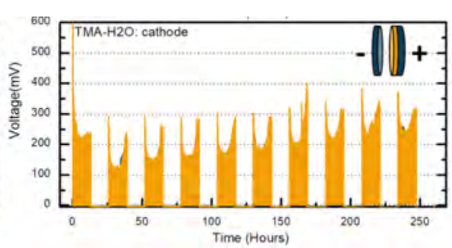


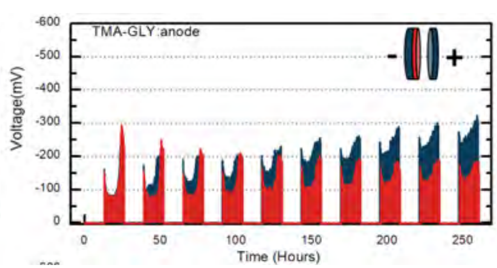


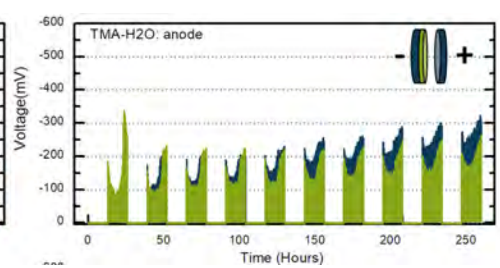
Final Remarks

- First comparison of Li coated with TMA-H_2O, TMA-EG and TMA- GLY
- Galvanostatic cycling of Li-Li symmetric cells identified that TMA-GLY can improve the lifetime of Li compared to TMA- H_2O and TMA-EG
- GITT is a powerful technique that can be used to eliminate the effects of concentration gradients that build up within the cell
- Stripping and plating is an easier process on Li coated with TMA-GLY compared to TMA-H_2O
- Full Cell Data shows the coated Li works well for both LFP and Li-S cathode systems









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Dr. Sun's Nanomaterials and Energy Group

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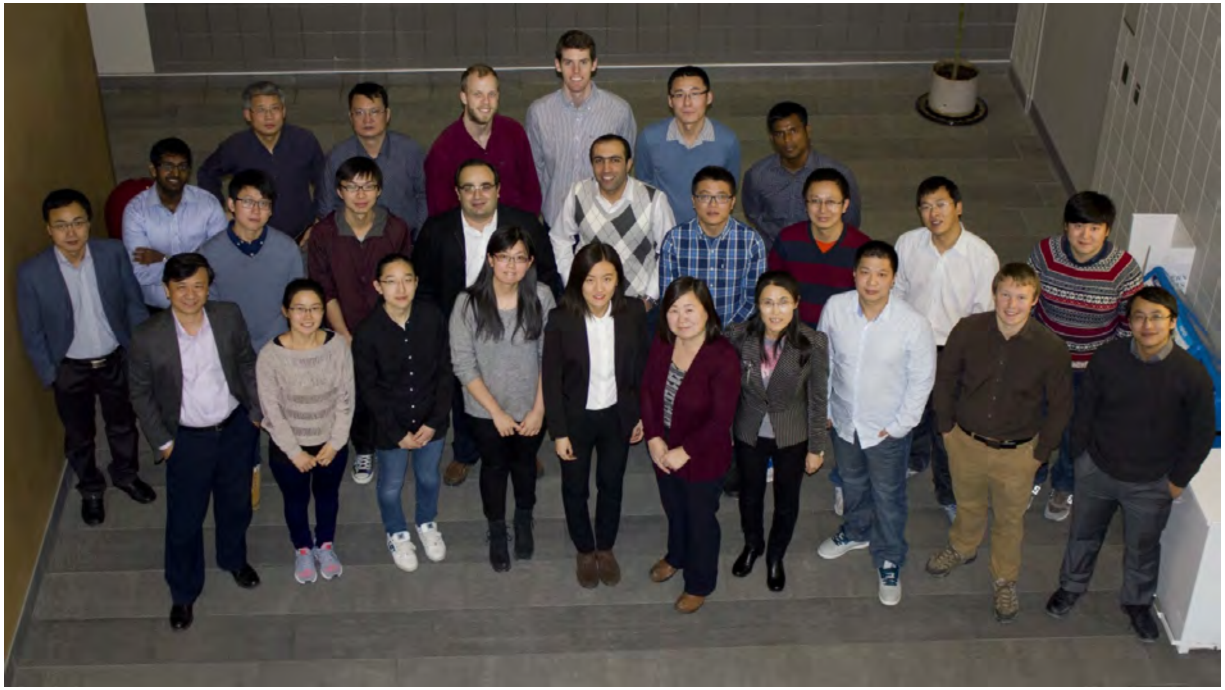

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