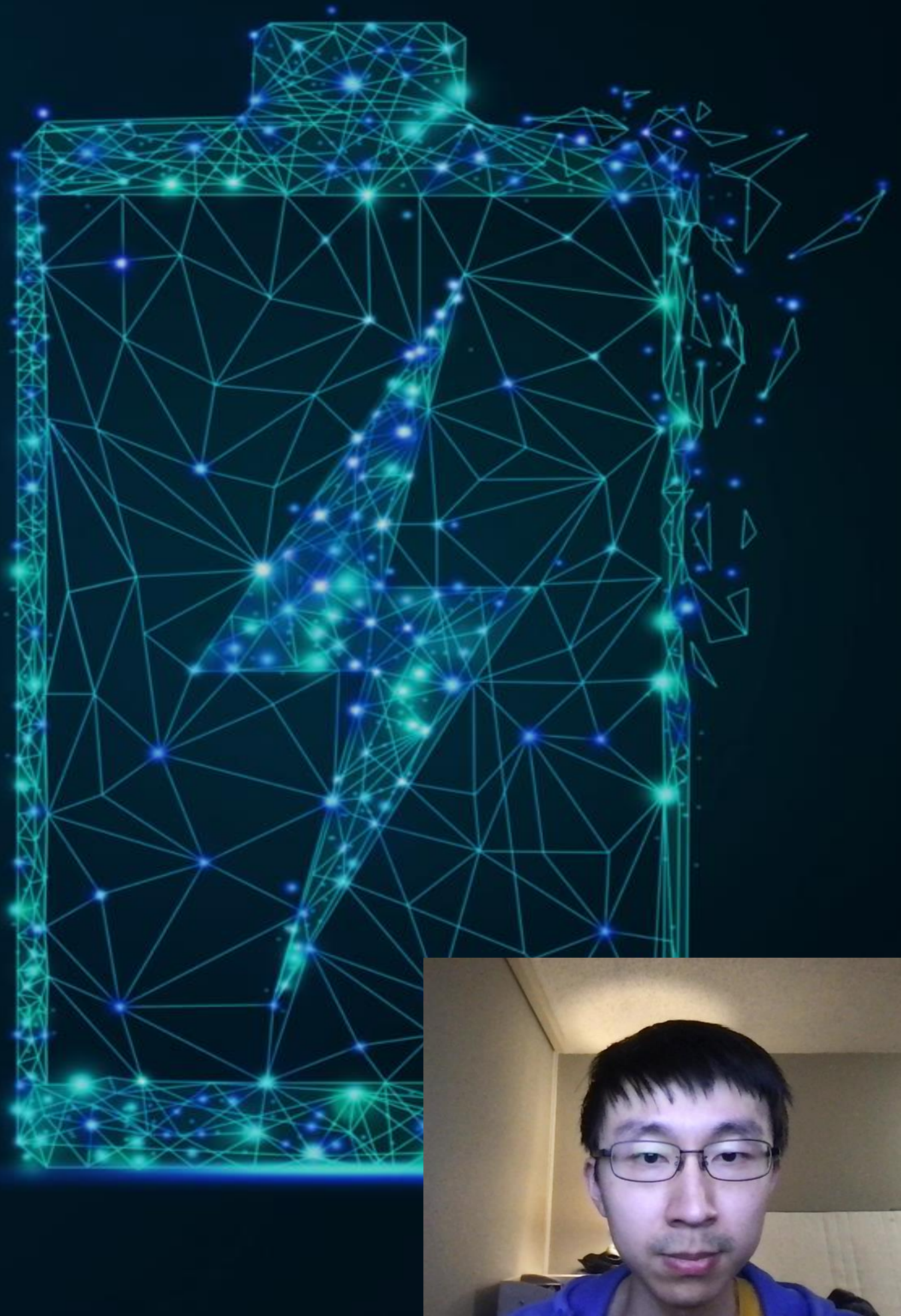
A single-salt, single-solvent, low-concentration electrolyte enables industrial anode-free pouch cells

Zhiao Yu
4th Year PhD Student
Recorded on 3/17/2021



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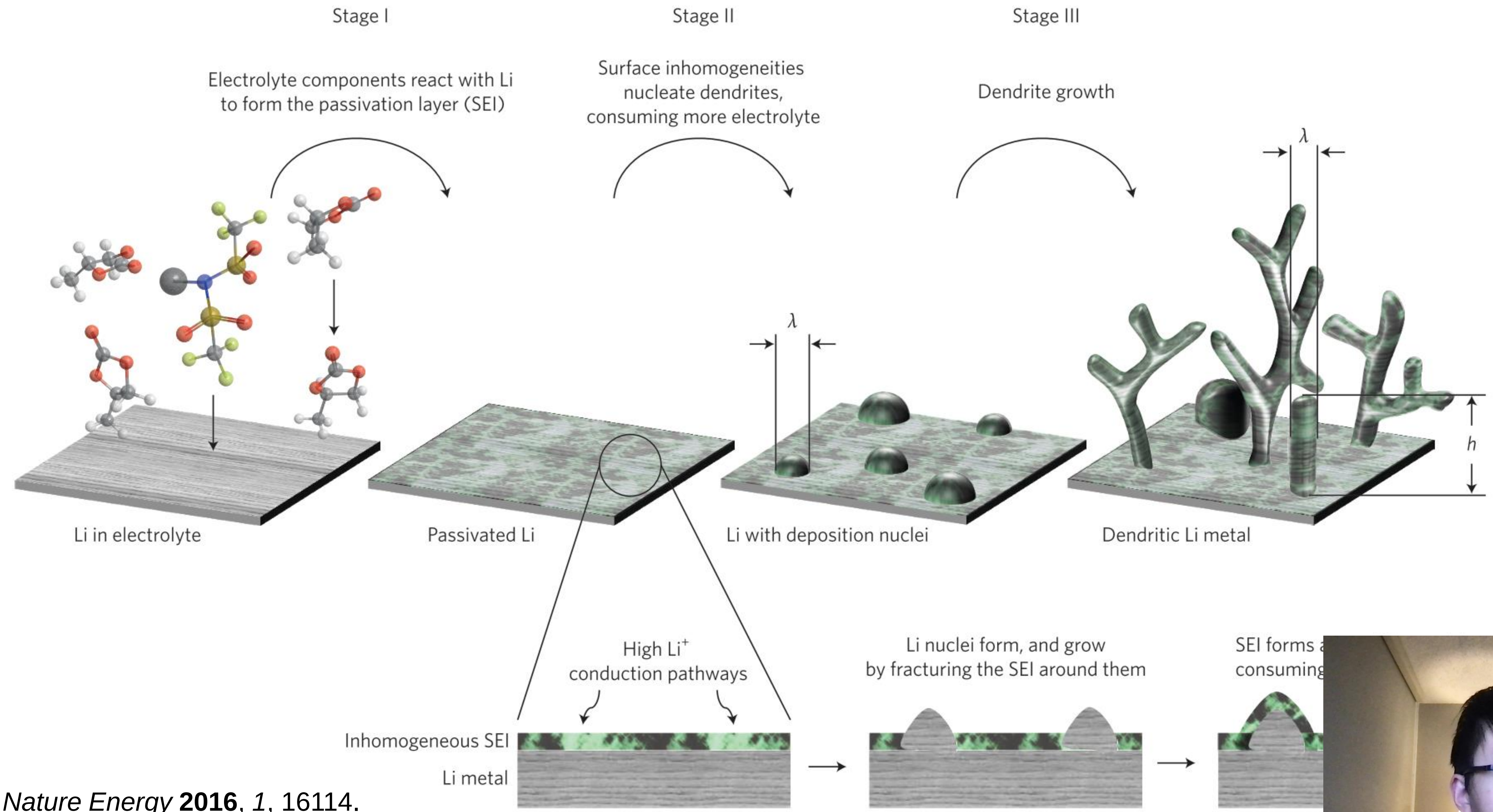
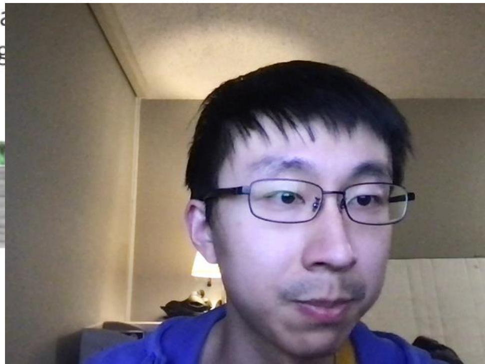
Drawbacks of Conventional Electrolytes

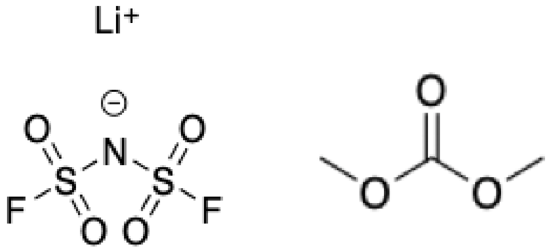


Nature Energy **2016**, *1*, 16114.



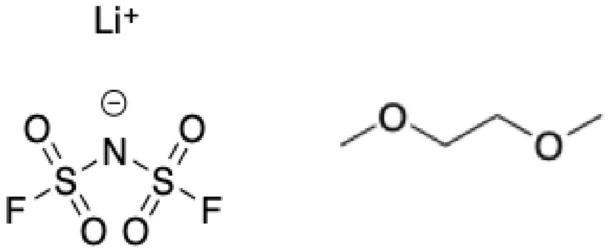
Electrolyte Engineering

1. High Concentration Electrolytes (HCEs)



10 M LiFSI in DMC

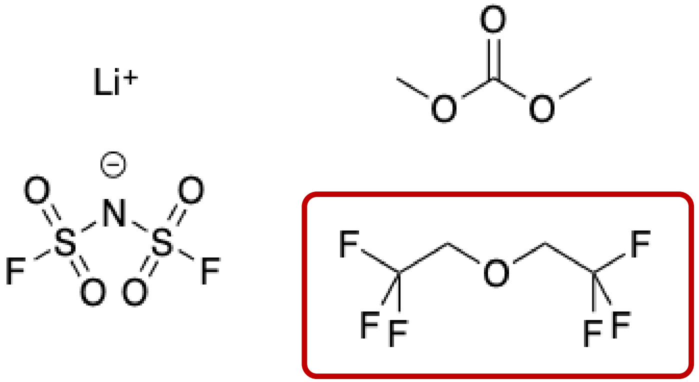
Chem **2018**, *4*, 174.



4 M LiFSI in DME

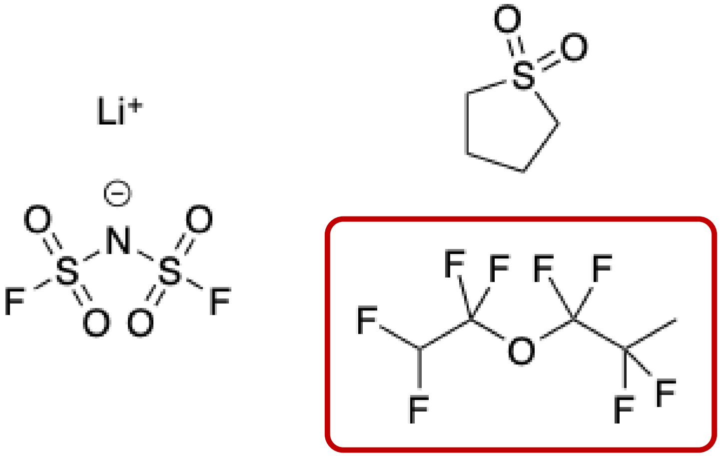
Nat. Comm. **2015,** *6***,** 6362.

2. Local High Concentration Electrolytes (LHCEs)



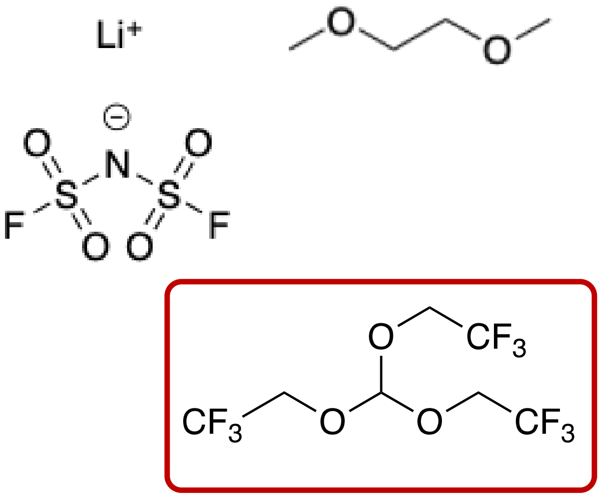
1.2 M LiFSI in DMC/BTFE (1:2)

Adv. Mater. **2018**, *30*, 1706102.



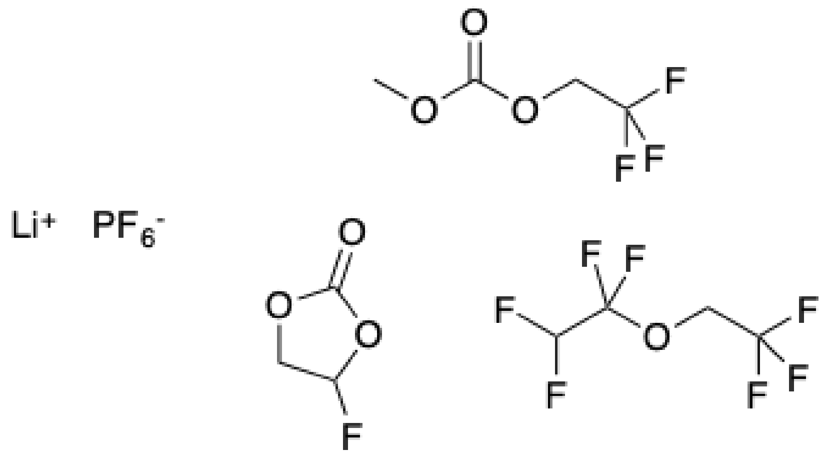
1 LiFSI + 3TMS + 3TTE

Chem **2018**, *4*, 1877.



Nat. Energ

3. Special Electrolytes



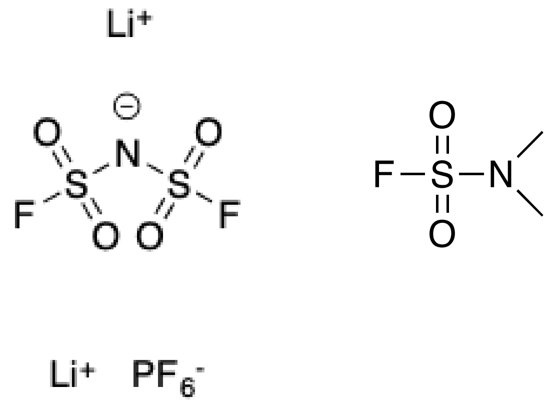
1 M $LiPF_6$ in FEC/FEMC/HFE (2:6:2)
LiFSI-FEC/FEMC/D2
LiBETI-FEC/DEC/M3

Nat. Nanotechnol. **2018**, *13*, 715.
Nat. Energy **2019**, *4*, 882.

LiTFSI in CH_3F/CO_2
LiTFSI in $MeCN/CH_3F/CO_2$
LiTFSI in $THF/CH_3F/CO_2$

Liquified gas electrolytes

Science **2017**, *356*, 1351.
Joule **2019**, *3*, 1986.
Energy Environ. Sci. **2020**, *14*, 112.

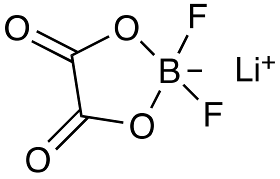


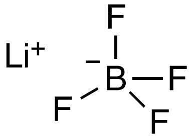
full fluorosulfonyl: 2.5 M LiFSI + 0.2 M $LiPF_6$ in FSA

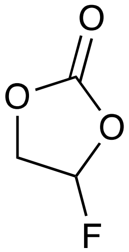
Energy Environ. S

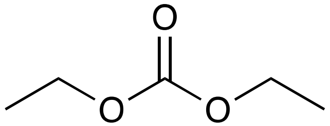
Electrolyte Engineering

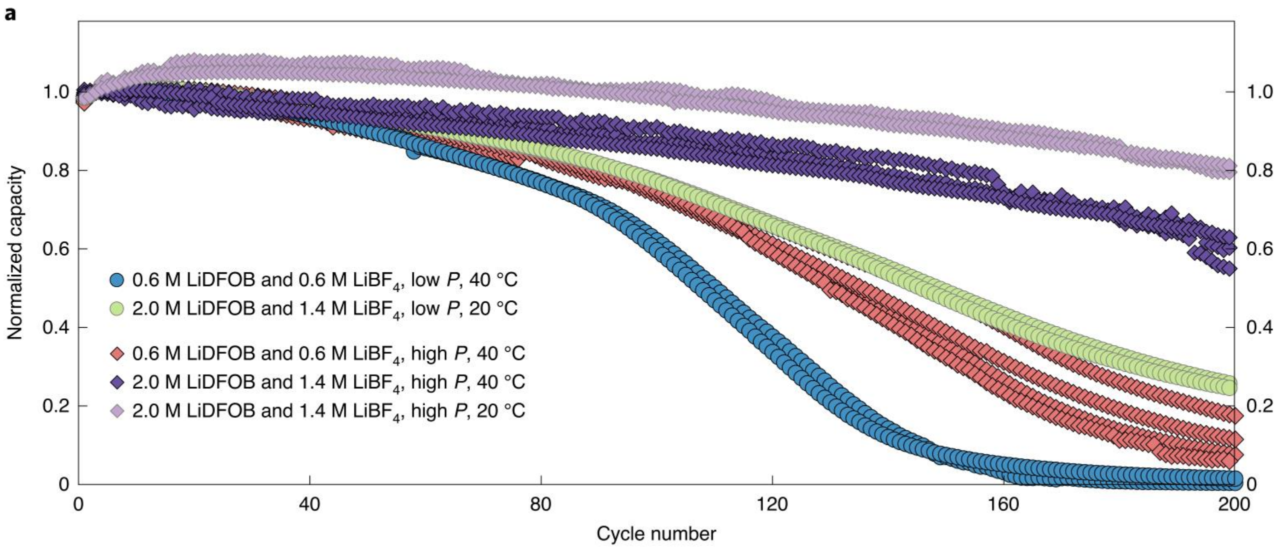
4. Dual-salt









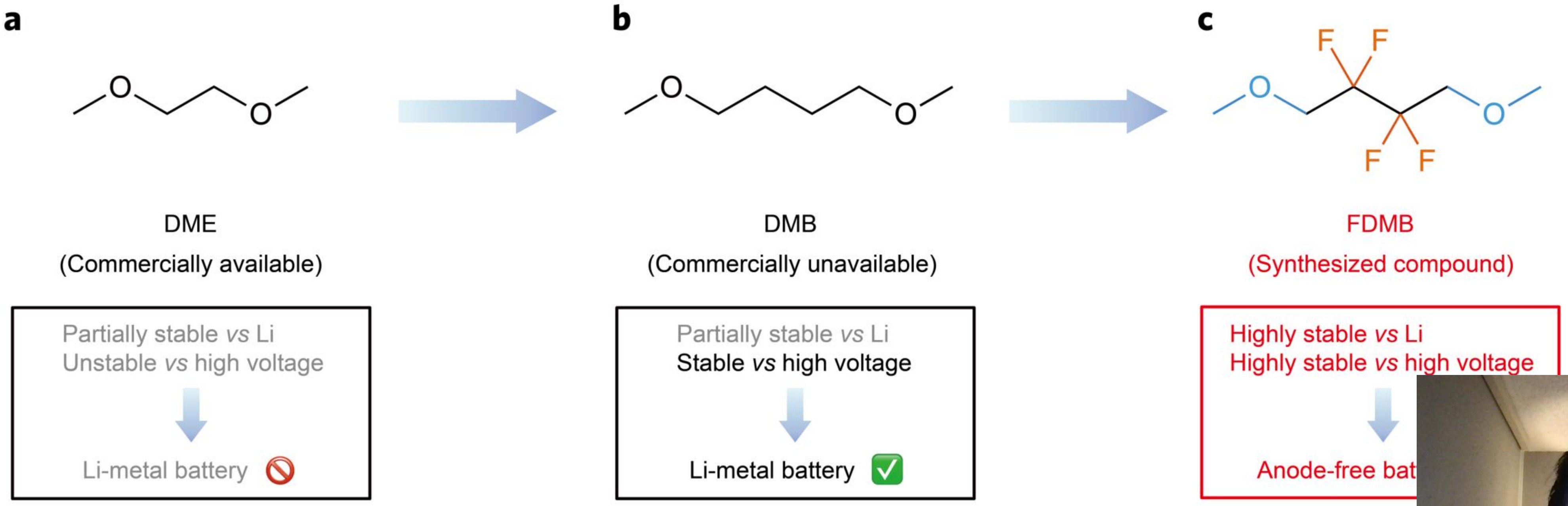


0.6 M LiDFOB + 0.6 M $LiBF_4$ in FEC/DEC (1:2)
2.0 M LiDFOB + 1.4 M $LiBF_4$ in FEC/DEC (1:2)

Nat. Energy **2019**, *4*, 683.
Nat. Energy **2020**, *5*, DOI: 10.1038/s41560-0

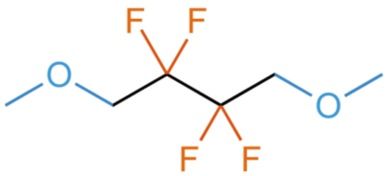
Design Principles

1. High performance yet low/standard concentration: 1 M
2. Compatible with both Li metal anodes and high-voltage cathodes
3. Single-salt, single-solvent for understanding structure-property relationships



Z. Yu, H. Wang, Y. Cui, Z. Bao et al. *Nature Energy*

Targets



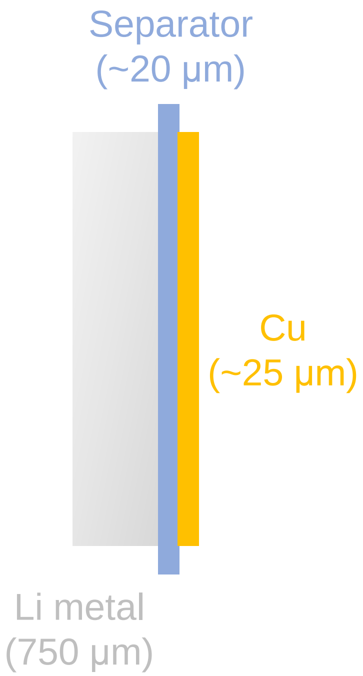
FDMB
(No CAS number)

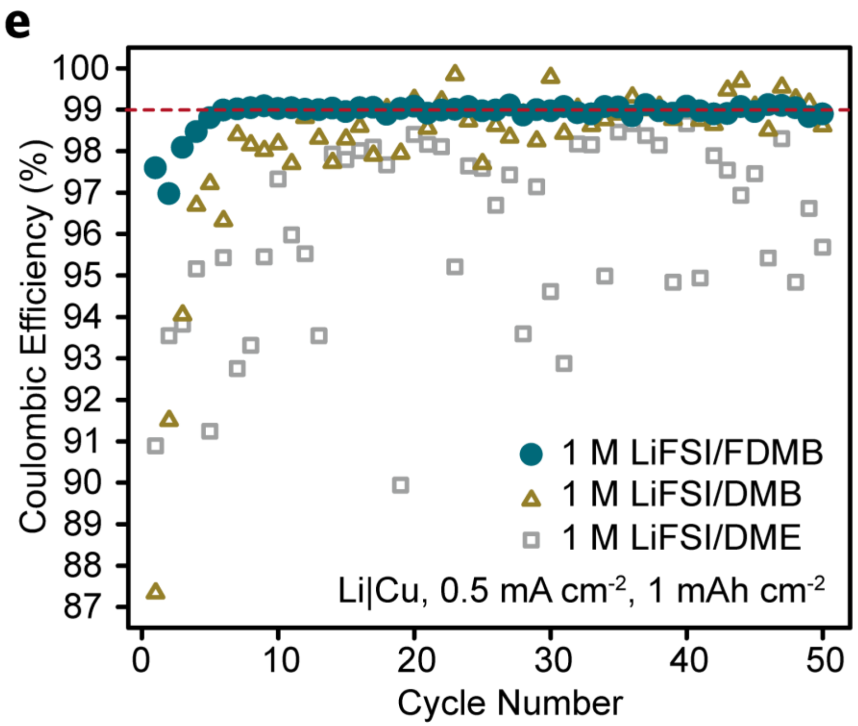
1. Consistently high CE to minimize Li loss, including in the initial cycles.
2. Functionality under lean electrolyte and limited-excess Li conditions.
3. Oxidative stability towards high-voltage cathodes.
4. Reasonably low salt concentration for cost-effectiveness.
5. High boiling point or even non-flammability for safety and processability.

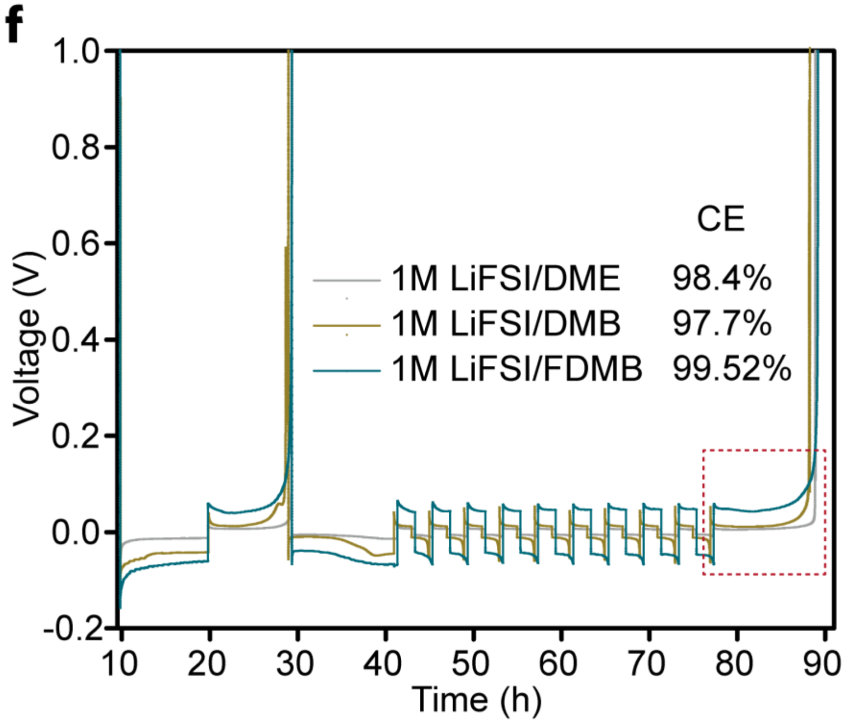
Battery Performance

1. Li metal anode compatibility
2. High-voltage cathode stability
3. Practical Li-metal full battery

Li Metal Compatibility: Li|Cu





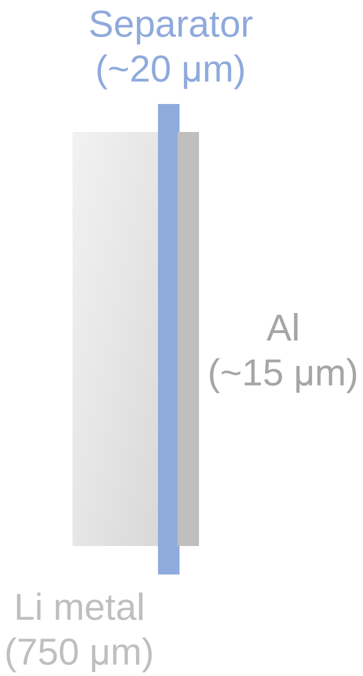


- Fast activation process: CE >99% within 5 cycles

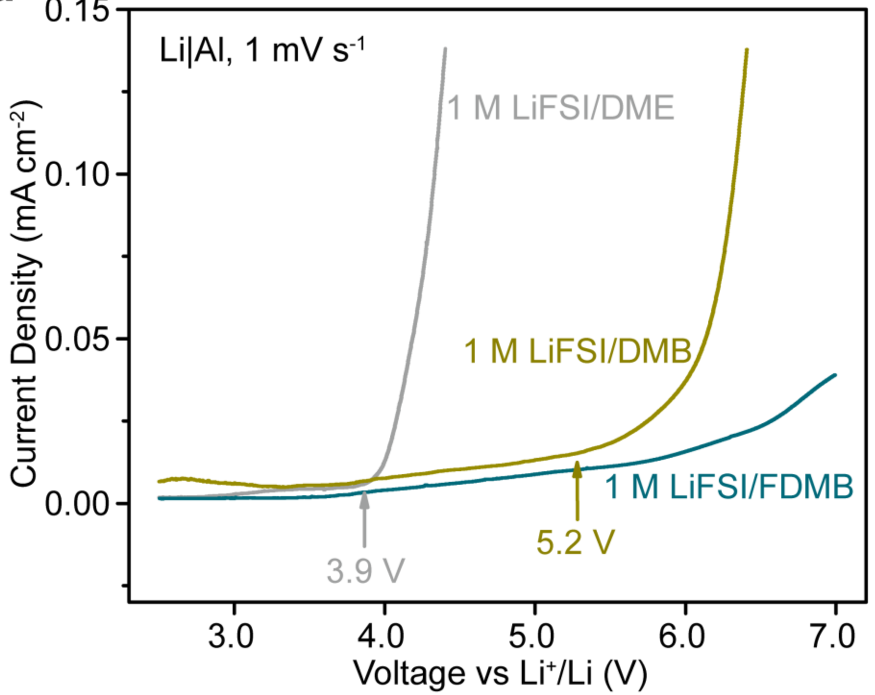
Note: J. Xiao et al. *Nat. Energy*

High-Voltage Stability: Li|Al

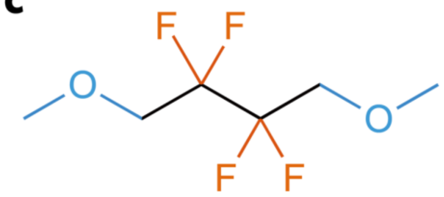
1. Oxidative stability of the solvent itself.
2. Solubility of $Al(anion)_x^{3-x}$ species in the electrolyte.
3. Ni^{3+} dissolution, stability of CEI/protection layer, etc.



a



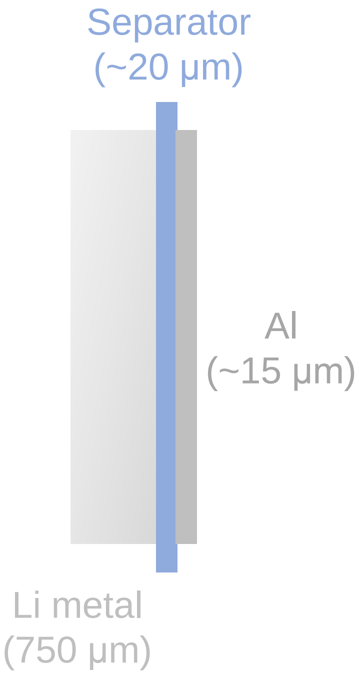
c



FDMB
(Synthesized compound)

➢ Stable vs high voltage until >6 V (conventional cathode chemistry

High-Voltage Stability: Li|Al

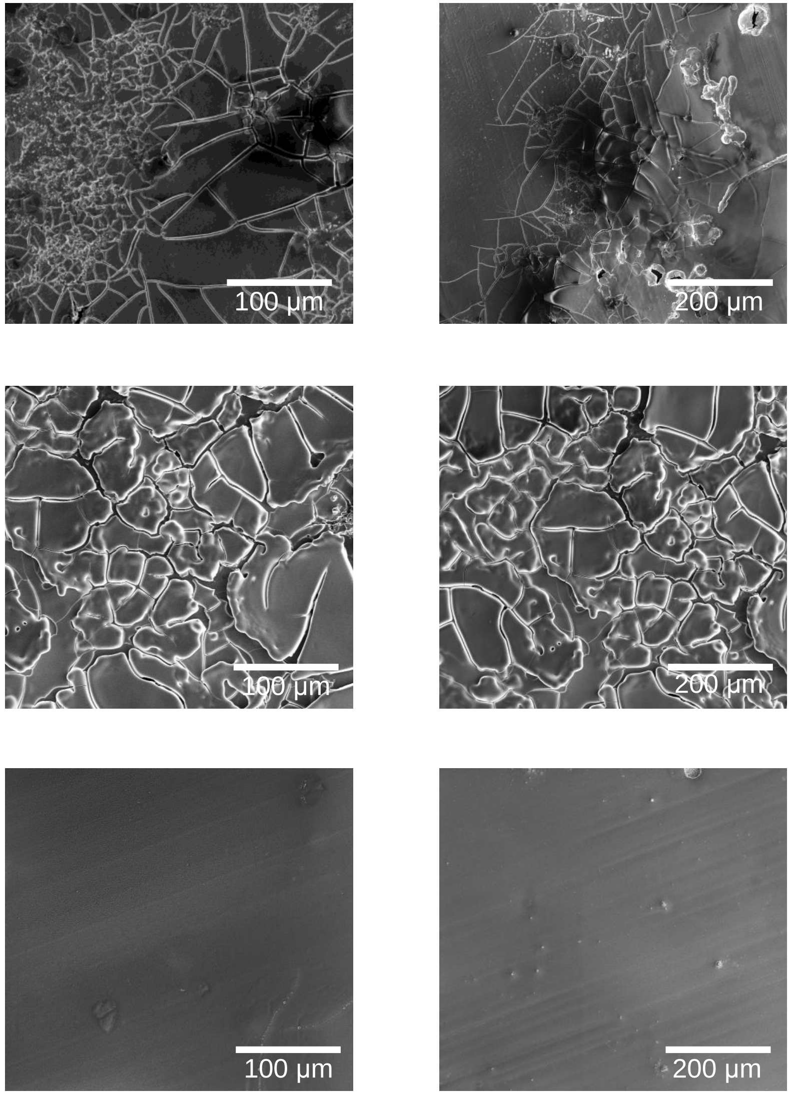


Hold at 5.5 V for 72 h.

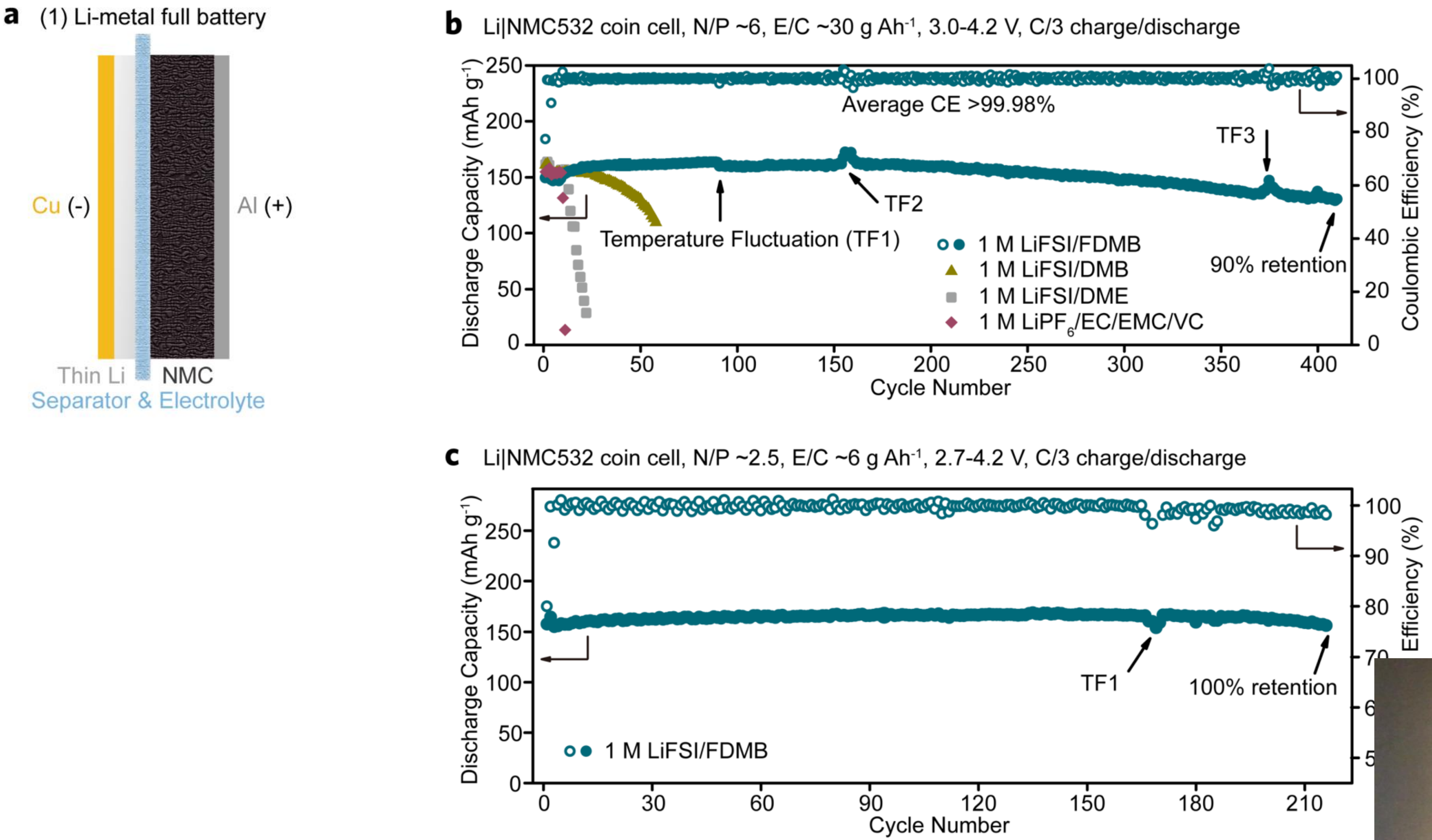
a) 1 M LiFSI/DME

b) 1 M LiFSI/DMB

c) 1 M LiFSI/FDMB

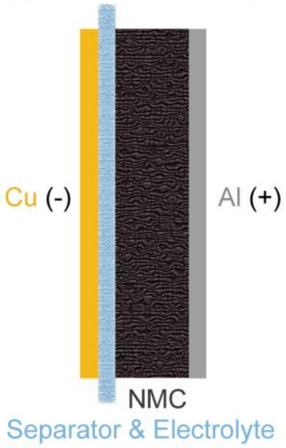


Li Metal Full Battery



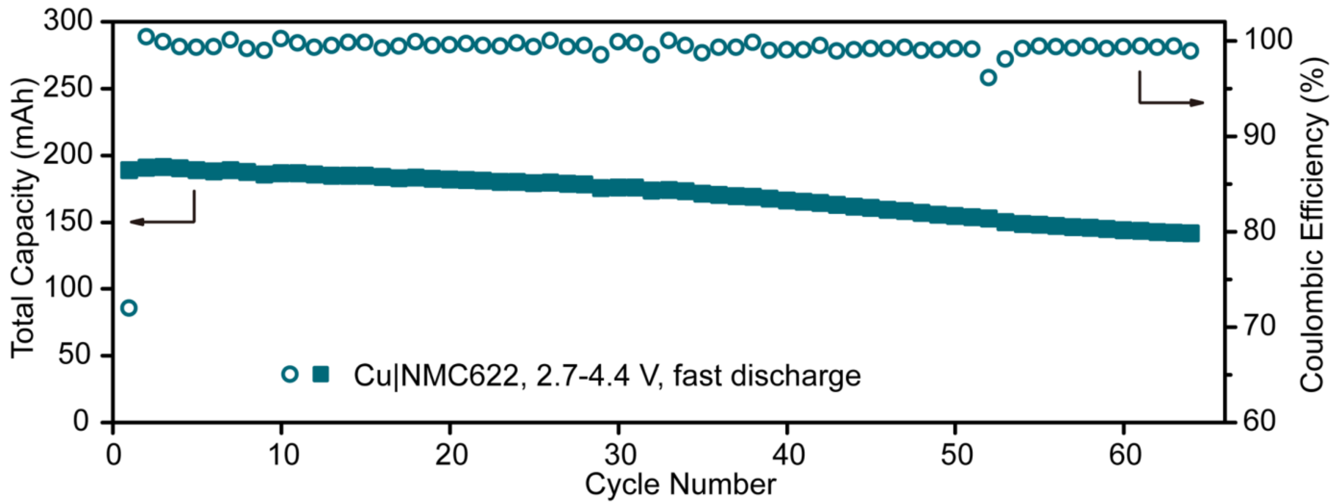
Anode-free Pouch Cell

(2) Anode-free battery



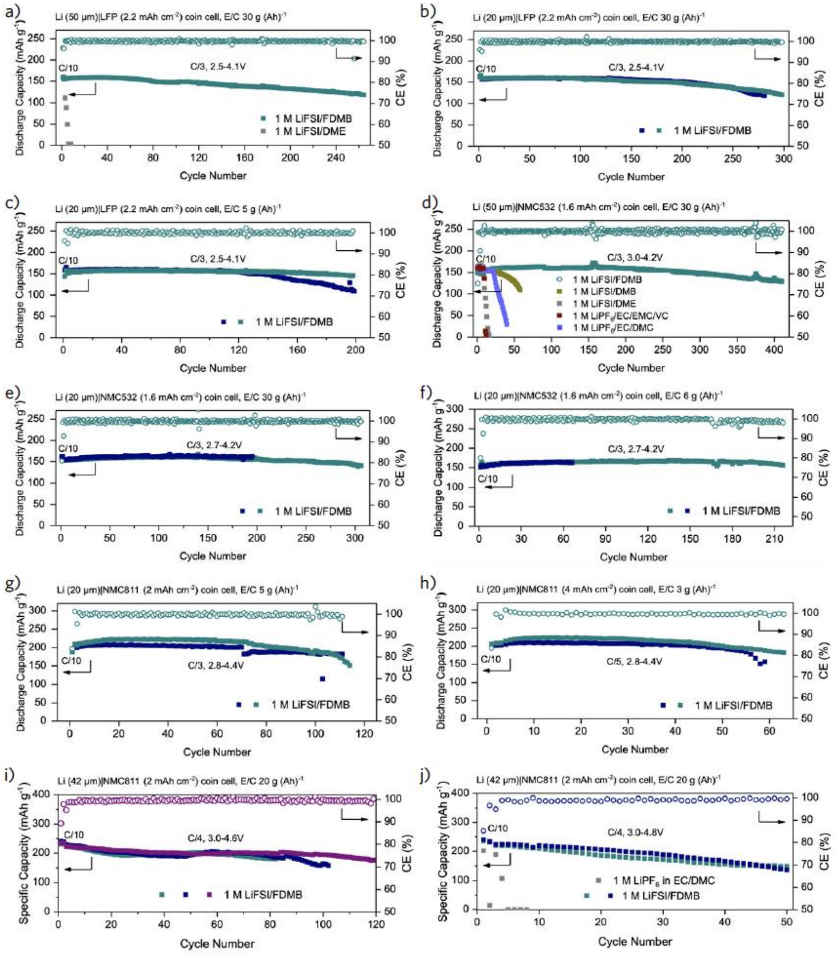
Parameters	Cu|NMC532	Cu|NMC622	Cu|NMC811
Areal capacity (mAh cm^{-2})	~3.0	~3.0	~3.9
NMC : carbon : binder	94.0 : 4.0 : 2.0	96.4 : 1.6 : 2.0	96.4 : 1.6 : 2.0
Cycling voltage range (V)	2.7-4.3	2.7-4.4	2.8-4.4
Cycling rate	C/5 charge, C/3 discharge		
External conditions	~300 kPa external pressure, 20-22 °C room temperature		
Total capacity (mAh)	~200	~220	~250
E/C ratio (g $(Ah)^{-1}$)	~2.6	~2.4	~2.2

e Anode-free pouch cell, cathode 3 mAh cm^{-2}, E/C ~2 g Ah^{-1}, 0.2C charge 2C discharge

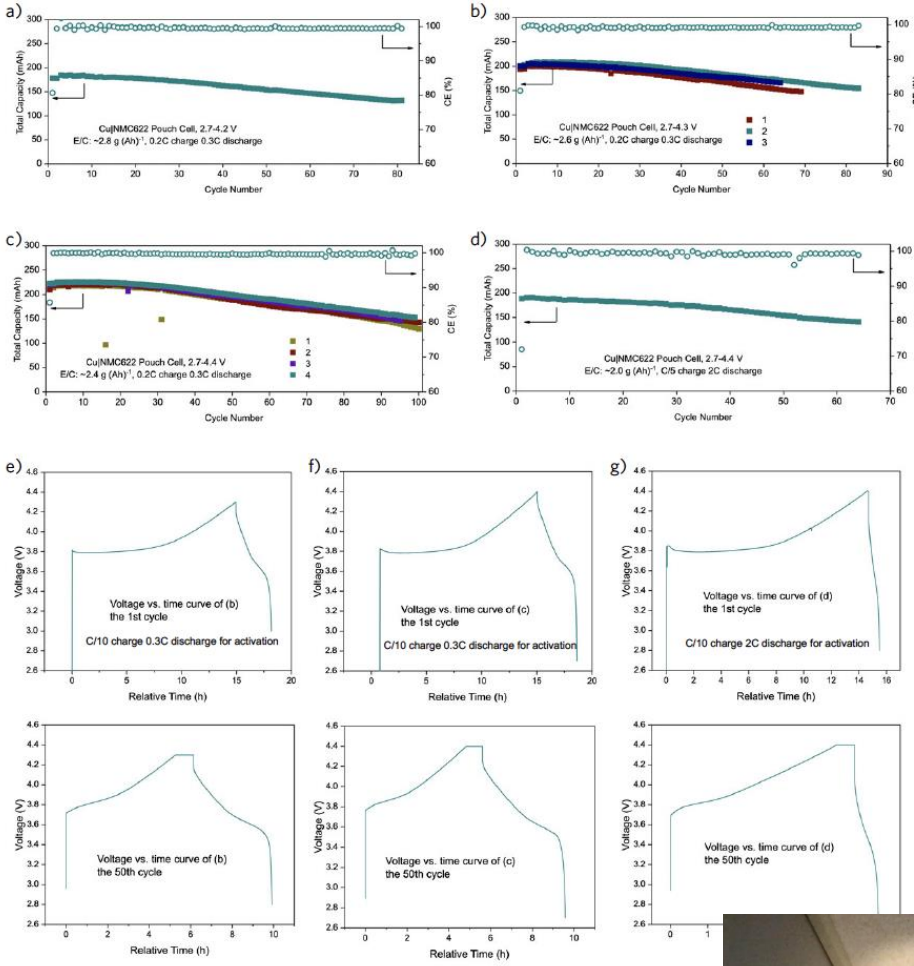


- Long anode-free battery cycling (Cu|PC-NMC532 >100 cycles)
- High energy density based on realistic chemistry (Cu|PC-NMC811 325

Repeated Battery Data



Supplementary Figure 14. Performance of Li-metal full coin cells (limited Li excess) with different cathodes, different areal loadings, different electrolyte amounts, and different cycling rates: (a) Li (50 µm)|LFP (2.2 mAh cm^{-2}), 30 g Ah^{-1}, C/3 cycling; (b) Li (20 µm)|LFP (2.2 mAh cm^{-2}), 30 g Ah^{-1}, C/3 cycling; (c) Li (20 µm)|LFP (2.2 mAh cm^{-2}), 5 g Ah^{-1}, C/3 cycling; (d) Li (50 µm)|NMC532 (1.6 mAh cm^{-2}), 30 g Ah^{-1}, C/3 cycling; (e) Li (20 µm)|NMC532 (1.6 mAh cm^{-2}), 30 g Ah^{-1}, C/3 cycling; (f) Li (20 µm)|NMC532 (1.6 mAh cm^{-2}), 6 g Ah^{-1}, C/3 cycling; (g) Li (20 µm)|NMC811 (2 mAh cm^{-2}), 5 g Ah^{-1}, C/3 cycling; (h) Li (20 µm)|NMC811 (4 mAh cm^{-2}), 3 g Ah^{-1}, C/5 cycling; (i) Li (42 µm)|NMC811 (2 mAh cm^{-2}), 20 g Ah^{-1}, 3.0-4.6 V, C/4 cycling; (j) Li (42 µm)|NMC811 (2 mAh cm^{-2}), 20 g Ah^{-1}, 3.0-4.8 V, C/4 cycling. For all cells, two pre-cycles at C/10 were conducted.



Supplementary Figure 18. Performance and selected voltage vs. relative time plots pouch cells with E/C ~2.4 g Ah^{-1}. Different colors in the same figure represent rep consistence of cycling performance.

Note: It is worth noting that fast discharge (~2C rate discharge, cathode loading at ~3 (Supplementary Figure 18d and g) and similar capacity retention trend was observed.

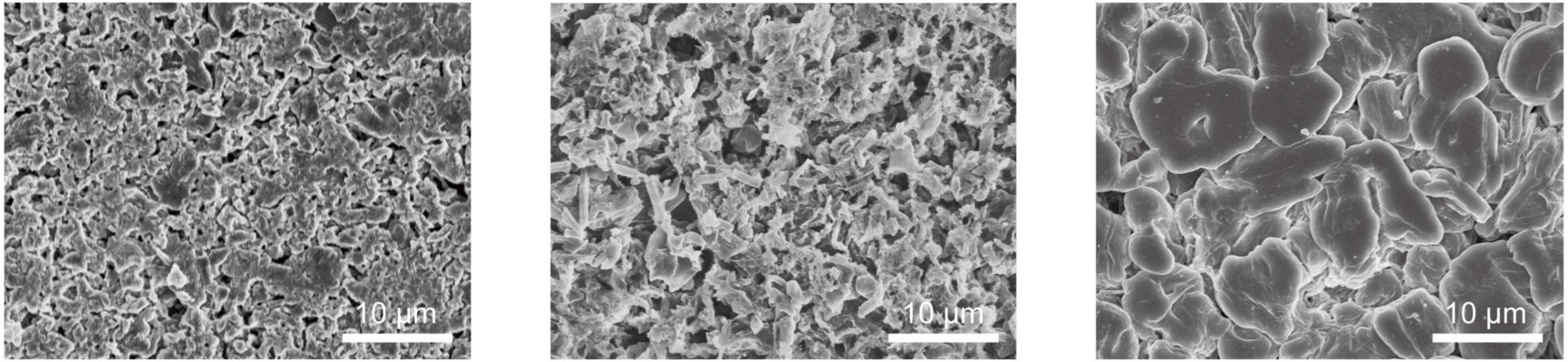
Mechanism:
Li Morphology and SEI

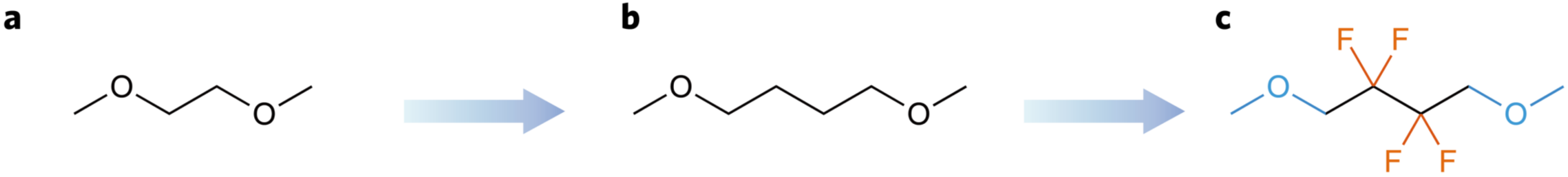
Li Deposition Morphology

a 1 M LiFSI/DME, Cu|NMC532, 10^{th} cycle after charging

b 1 M LiFSI/DMB, Cu|NMC532, 10^{th} cycle after charging

c 1 M LiFSI/FDMB, Cu|NMC532, 70^{th} cycle after charging





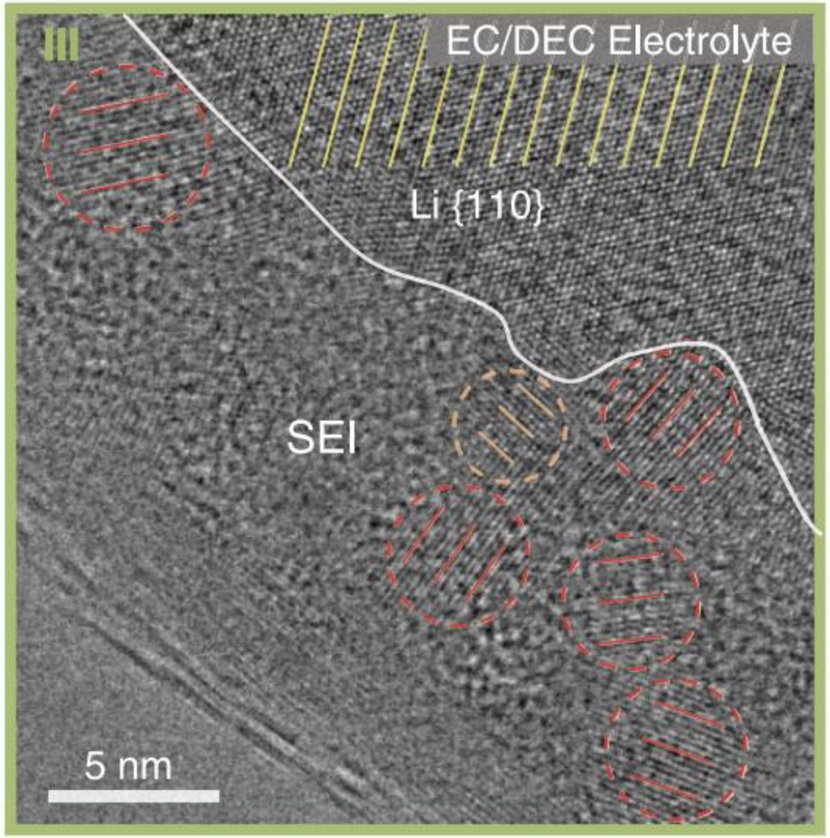
DME
(Commercially available)

DMB
(Commercially unavailable)

FDMB
(Synthesized con

* Anode-free coin cells, Li morphology on Cu side after cycling.

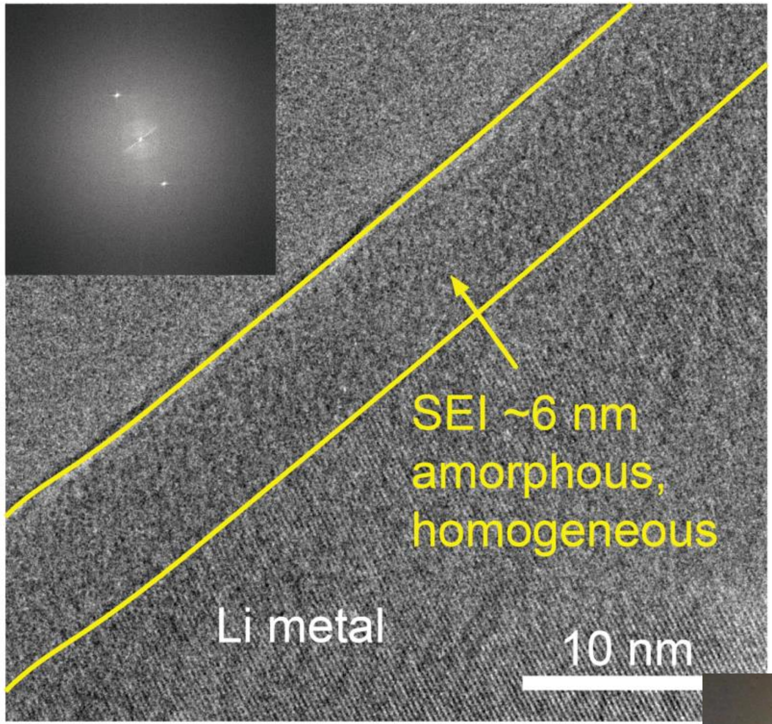
SEI: Cryo-TEM



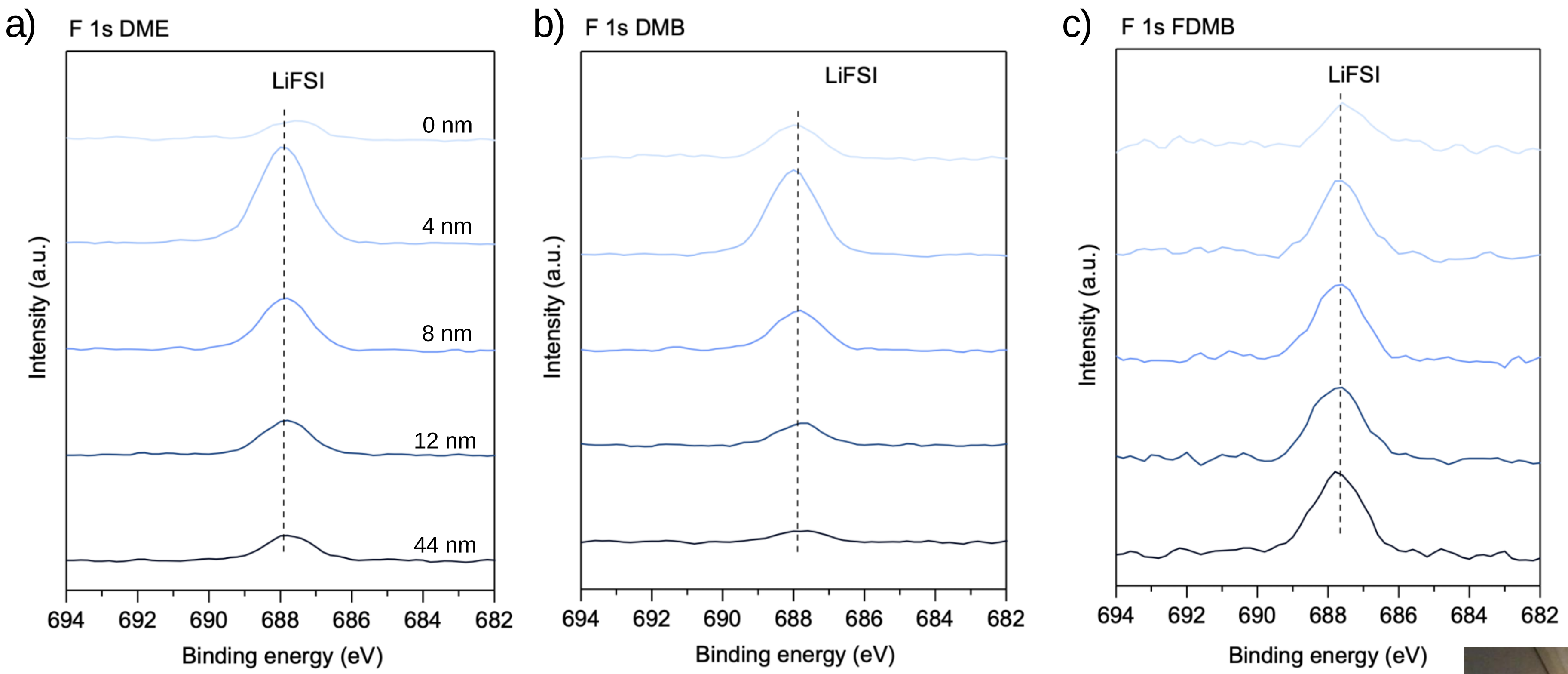
1 M $LiPF_6$ in EC/DEC
SEI thickness >20 nm, heterogenous

Science **2017**, *358*, 506.

f 1 M LiFSI/FDMB, SEI



SEI: XPS

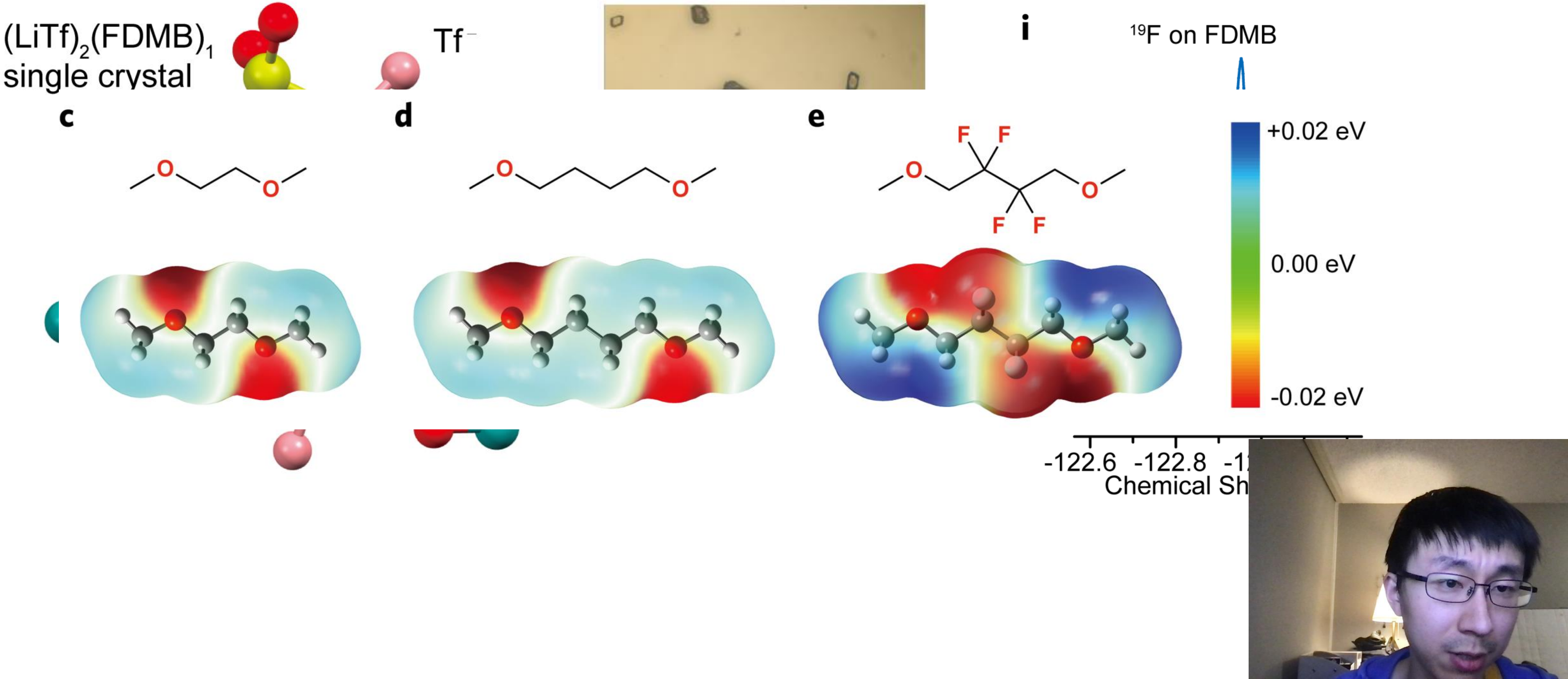


- Uniformity with depth profiling (similar results for other elements, please see

Beyond Performance: Chemistry Perspective

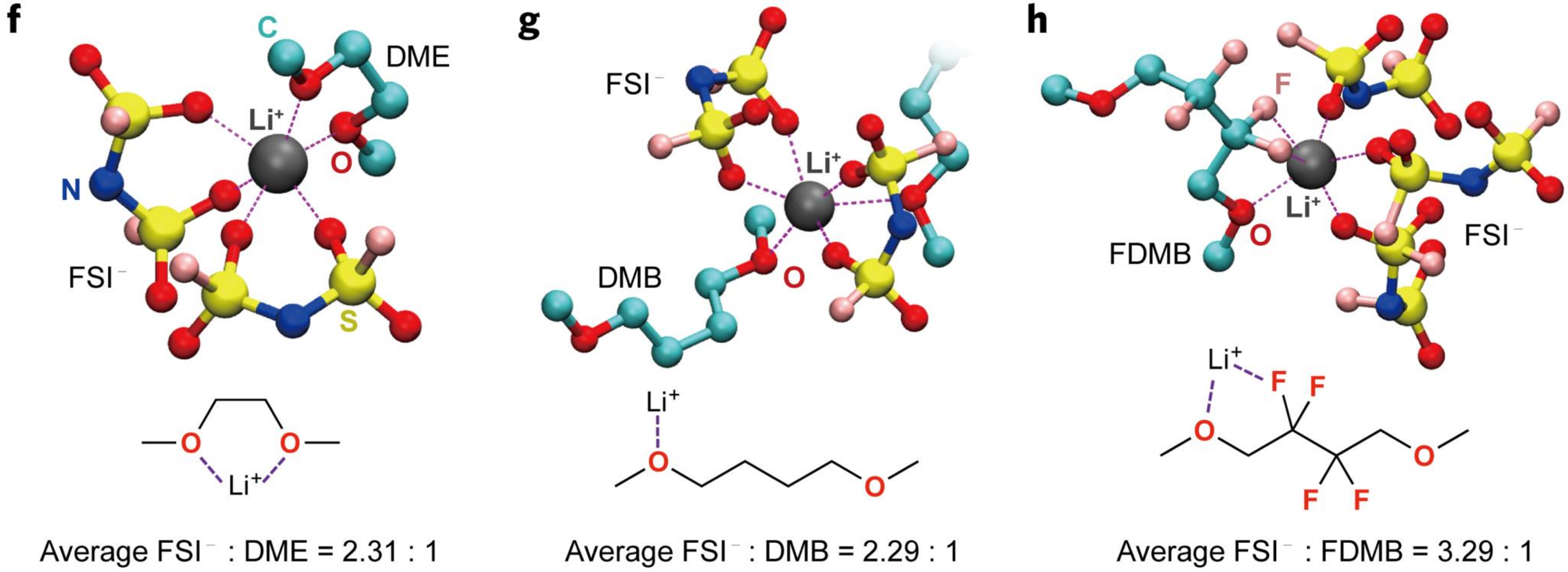
Special Li-F Interaction

- Special five-member ring, non-covalent interaction



Special Li-F Interaction

- High FSI/FDMB ratio in Li^+ solvation sheath: weak solvation ability of FDMB

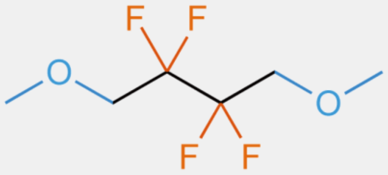


Summary: A New Electrolyte System

Anode

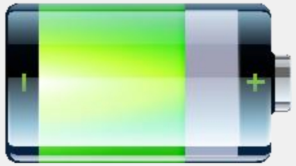
Thin Li metal, anode-free

Electrolyte



FDMB
(No CAS number)

Cathode



LFP, NMC…

1. Consistently high CE to minimize Li loss, including in the initial cycles.
2. Functionality under lean electrolyte and limited-excess Li conditions.
3. Oxidative stability towards high-voltage cathodes.
4. Reasonably low salt concentration for cost-effectiveness.
5. High boiling point or even non-flammability for safety and processability.

➢ Pursuing even better solvents… in progress.

Acknowledgements

- Prof. Zhenan Bao, Prof. Yi Cui, Prof. Jian Qin.
- Hansen, Xian, William.
- Yuchi, David, Kecheng, Xinchang, Wenxiao, Sneh, Yu, Chibueze, Samantha, Yuting, Eder.
- All Bao and Cui group members.
- Battery500 Consortium.

Thanks

Q & A