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Electrolyte Design For Fast-Charging Li-ion Batteries

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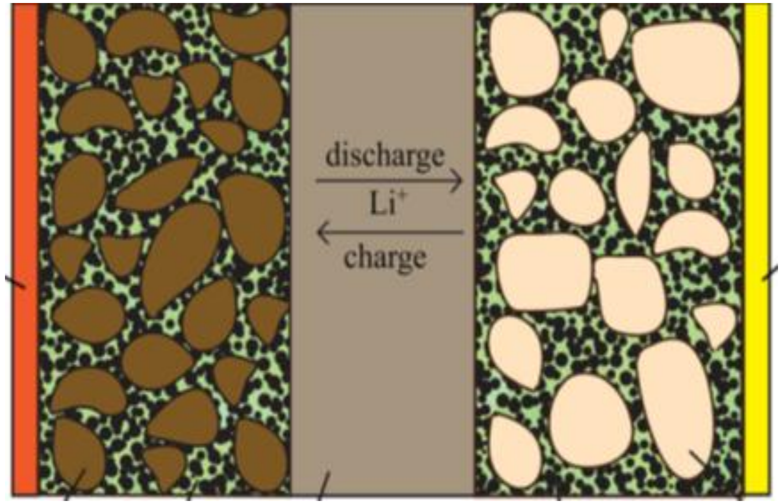
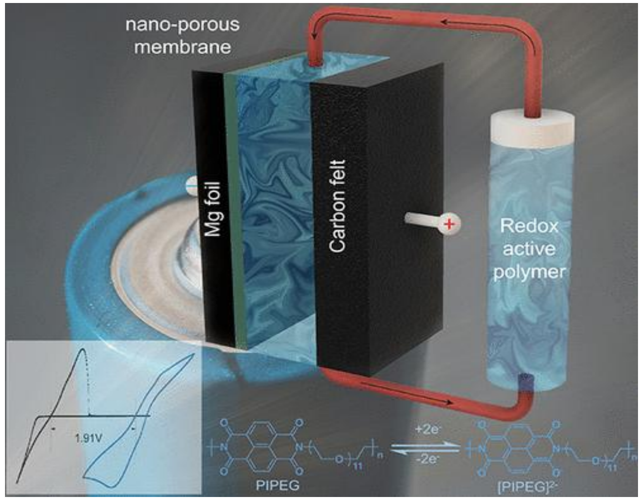
Multi-scale Electrochemical Engineering Lab

ME2 Lab

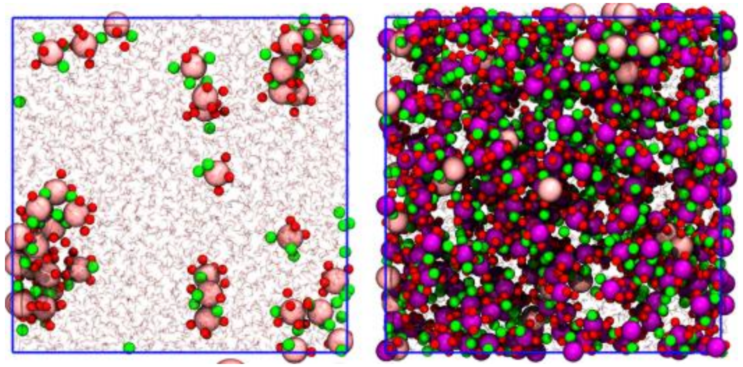
Li-ion batteries



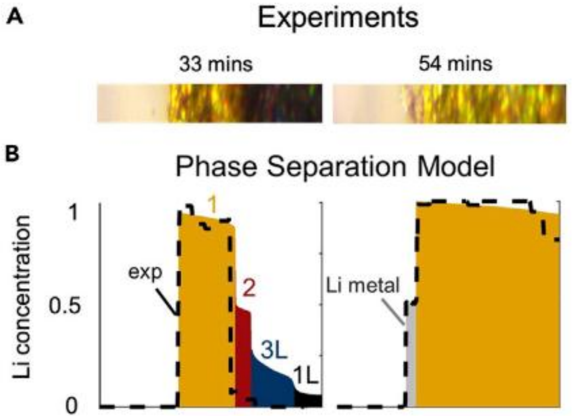
Flow batteries



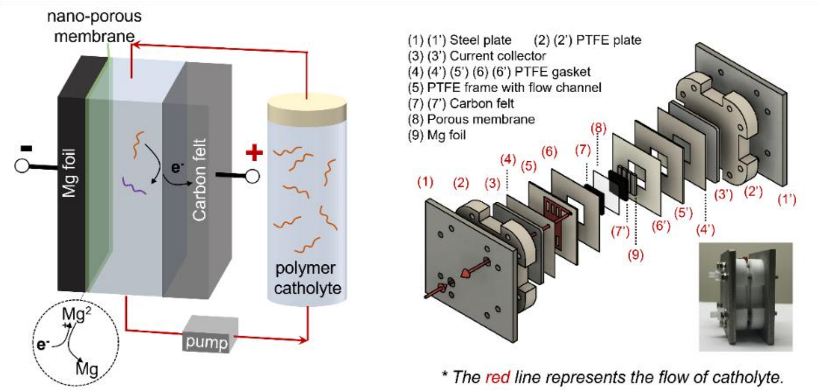
Atomic/molecular scale | Meso-scale | Device scale



Structure-property of electrolytes



Reaction, diffusion and phase transformation



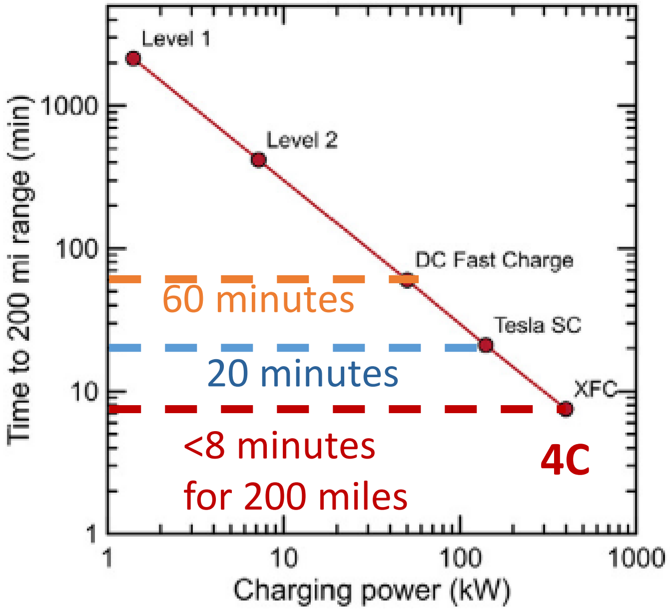
** The red line represents the flow of catholyte.*

New device or process

Motivation

- Many US households do not have at-home charger
- Long-distance travel: limited by EV charging time
- Taxis requires fast turn-around for business operation

Tesla model S: 100 kWh

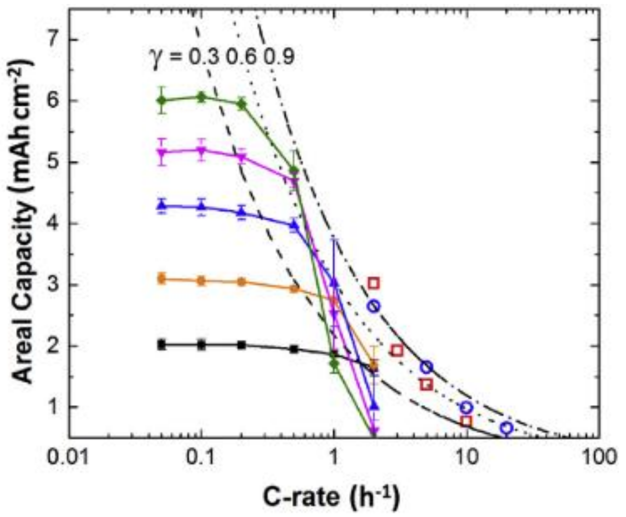


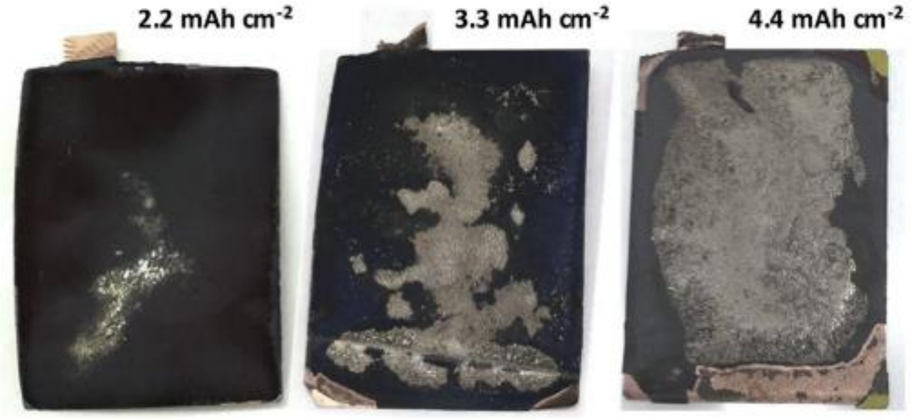
Logan, E. R. and Dahn, J. R. (2020) ‘Electrolyte Design for Fast-Charging Li-Ion Batteries’, *Trends in Chemistry*, 2(4), pp. 354–366.

US DOE, ARPA-e, *ELECTRIC VEHICLES FOR AMERICAN LOW-CARBON LIVING (EVs4ALL) program FOA*

Challenges for Fast-Charging Li-ion Batteries

- Reduced capacity utilization
  - Ohmic overpotential
  - Interfacial overpotential (charge transfer, SEI)
  - Concentration overpotential
- Accelerated degradation
  - Anode: Li plating
  - Cathode: Particle crack and fracture

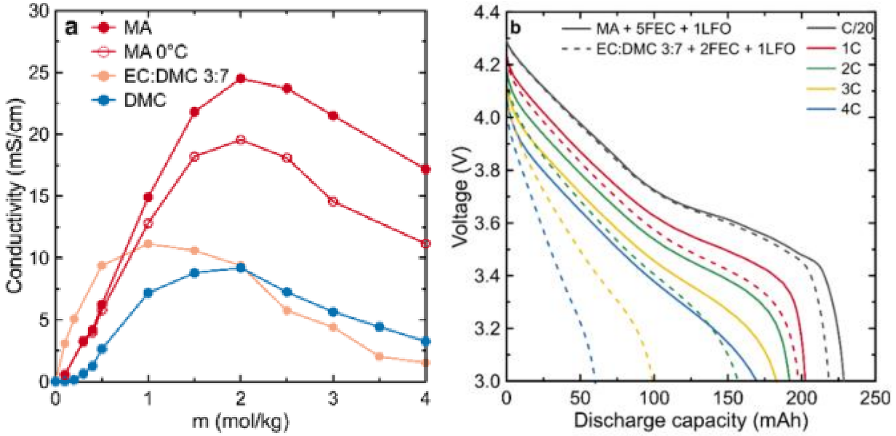


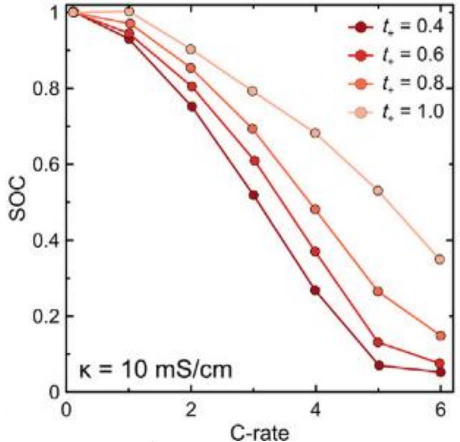


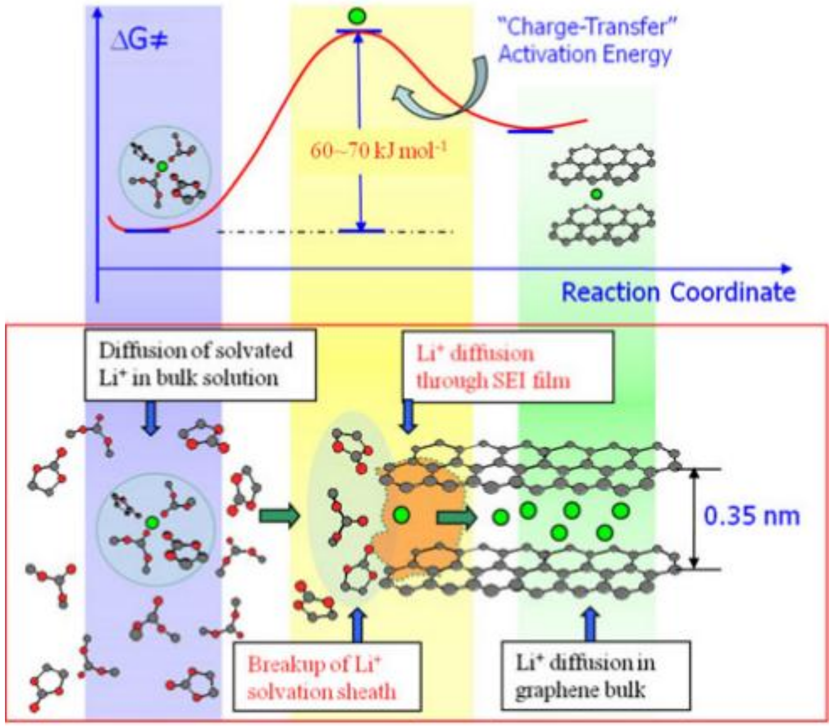
Ahmed, S., Bloom, I., Jansen, A. N., Tanim, T., Dufek, E. J., Pesaran, A., Burnham, A., Carlson, R. B., Dias, F., Hardy, K., Keyser, M., Kreuzer, C., Markel, A., Meintz, A., Michelbacher, Mohanpurkar, M., Nelson, P. A., Robertson, D. C., Scoffield, D., … Zhang, J. (2017). Enabling fast charging – A battery technology gap assessment. *Journal of Power Sources*, *367*, 250–262.

Criteria for electrolyte capable of fast-charging

- Transport properties
  - High Li^+ diffusivity (conductivity)
  - High Li^+ transference number
- Interfacial properties
  - Low SEI resistance
  - Low charge transfer resistance
    - Low de-solvation energy







Logan, E. R., Hall, D. S., Cormier, M. M. E., Taskovic, T., Bauer, M., Hamam, I., Hebecker, H., Molino, L., & Dahn, J. R. (2020). Ester-Based Electrolytes for Fast Charging of Energy Dense Lithium-Ion Batteries. *Journal of Physical Chemistry C*, *124*(23), 12269–12280.

Liu, Y., Zhu, Y., & Cui, Y. (2019). Challenges and opportunities towards fast-charging battery materials. *Nature Energy*, *4*(7), 540–550.

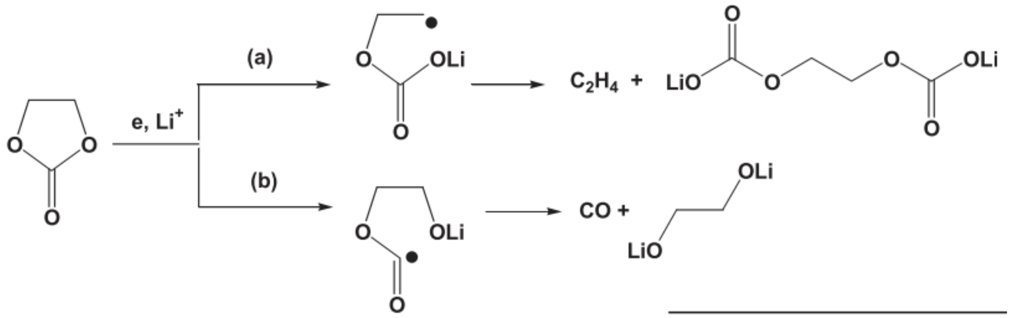
Xu, K. and Von Wald Cresce, A. (2012) 'Li+-solvation/desolvation dictates interphasial processes on graphitic anode in Li ion cells', *Journal of Materials Research*, 27(18), pp. 2327–2341.

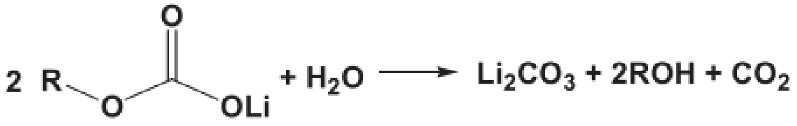
Carbonate-based electrolyte has high interfacial resistance

In commercial carbonate electrolytes

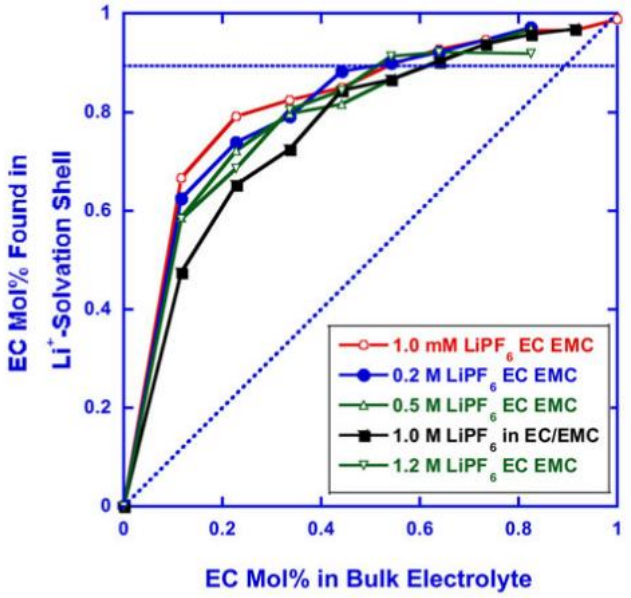
(e.g., 1M $LiPF_6$ EC DMC)

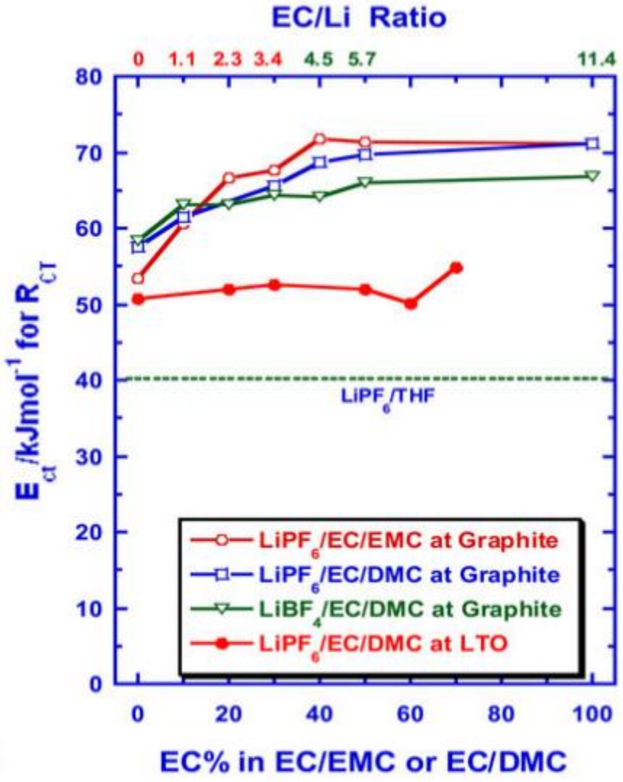
- Li^+ preferential solvated by EC
- EC strongly binds Li^+
- Energy barrier for intercalation: 50-70 kJ/mol
  - De-solvation dominates: 50 kJ/mol
- SEI dominated by EC decomposition
  - Alkyl carbonate, Li_2CO_3 and etc.





$$2\ R{-}O{-}C({=}O){-}OLi + H_2O \longrightarrow Li_2CO_3 + 2ROH + CO_2$$

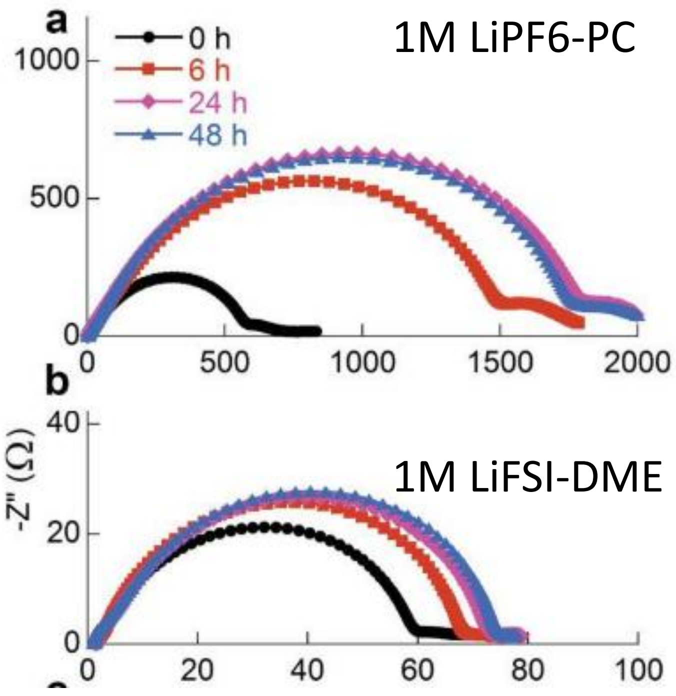




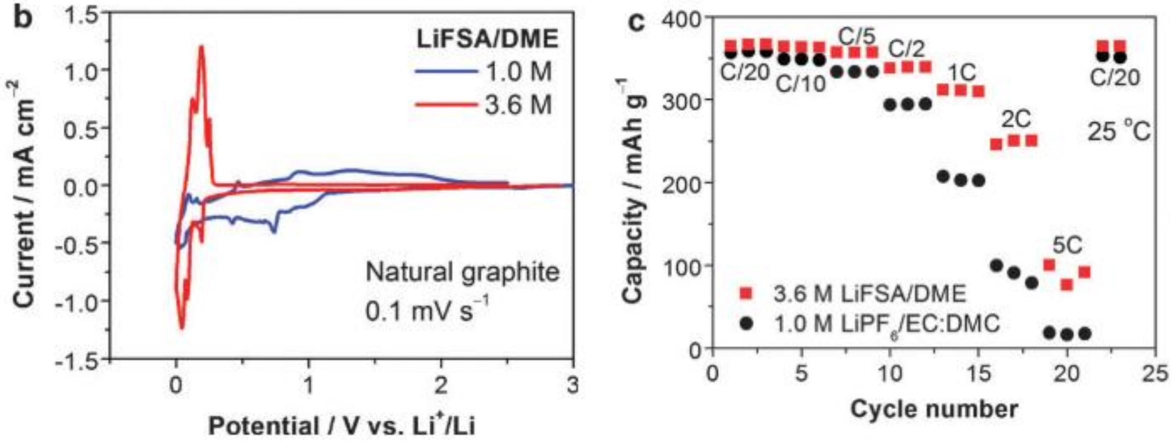
Xu, K. and Von Wald Cresce, A. (2012) 'Li+-solvation/desolvation dictates interphasial processes on graphitic anode in Li ion cells', *Journal of Materials Research*, 27(18), pp. 2327–2341.

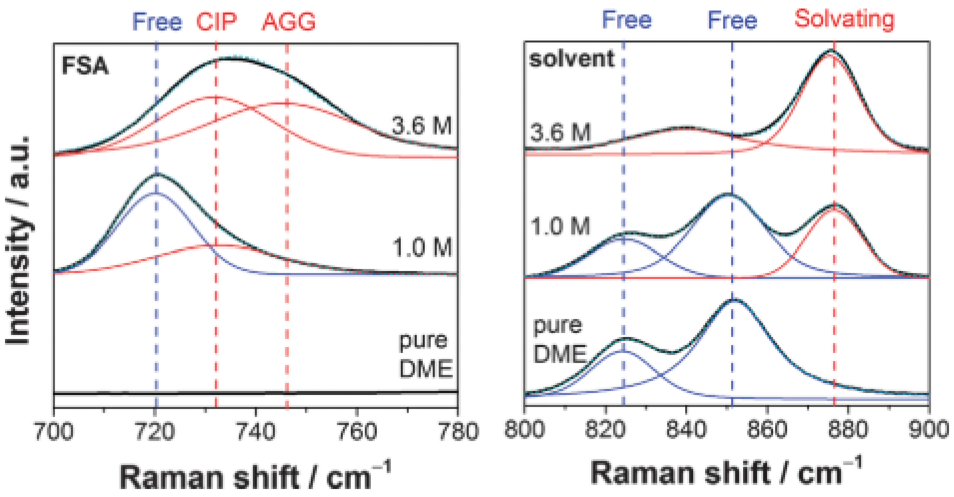
Ether-based electrolyte has much lower interfacial resistance

EIS of Li|Li symmetric cell



Interfacial resistance:
> one order lower





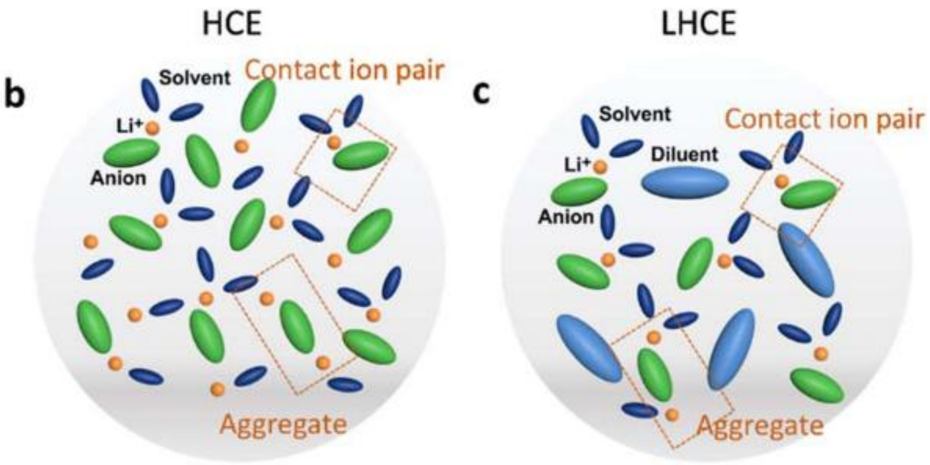
solvent co-intercalation unless in concentrated electrolyte

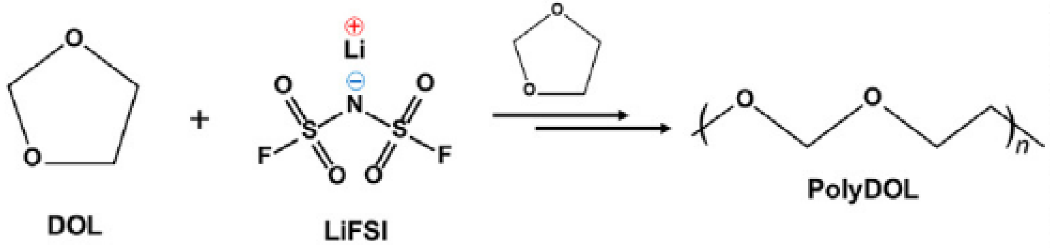
- No free DME
- No free FSI-
- FSI- enters Li+ solvation sheath

Qian, J. *et al.* (2015) ‘High rate and stable cycling of lithium metal anode’, *Nature Communications*, 6, p. 6362.
Yamada, Y. *et al.* (2013) ‘A superconcentrated ether electrolyte for fast-charging Li-ion batteries’, *Chemical Communications*, 49(95), pp. 11194–11196.

Can we lower salt concentration in concentrated LiFSI-DME?

- Concentrated electrolyte (HCE)
    - High viscosity, low conductivity, poor wettability, high cost
- Localized high-concentration electrolyte (LHCE)
    - Dilute HCE with non-solvating solvents
    - But fluorinated solvents are expensive
- Can we dilute concentrated LiFSI-DME with cheaper and more common solvents ?
    - Reduce salt concentration, electrolyte viscosity, increase conductivity
    - Maintain its compatibility with graphite
    - DOL: LiTFSI-DME-DOL commonly used in low voltage Li battery, such as Li-S, Li-O_2





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Cao, X. *et al.* (2021) 'Review—Localized High-Concentration Electrolytes for Lithium Batteries', *Journal of The Electrochemical Society*, 168(1), p. 010522.

Cheng, H. *et al.* (2021) 'In situ initiator-free gelation of highly concentrated lithium bis(fluorosulfonyl)imide-1,3-dioxolane solid polymer electrolyte for high performance lithium-metal batteries', *Materials Today Energy*, 20, p. 100623.

LiTFSI can stabilize DOL and prevent polymerization

A=10 m LiFSI-DME (~5M)
B=1.34 m LiTFSI-DOL

A:B(vol)

1:2
1:3
1:4
1:6

More Diluent
Less concentrated

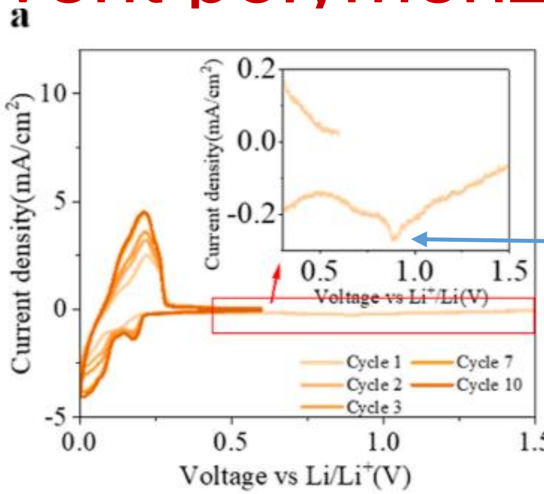
Gel

No Gel

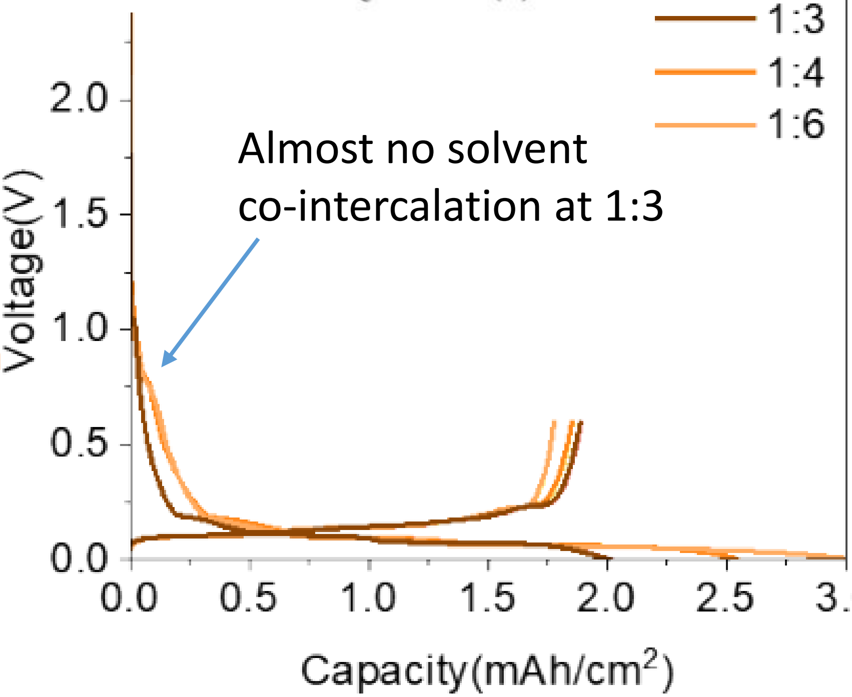
no
co-intercalation

co-intercalation

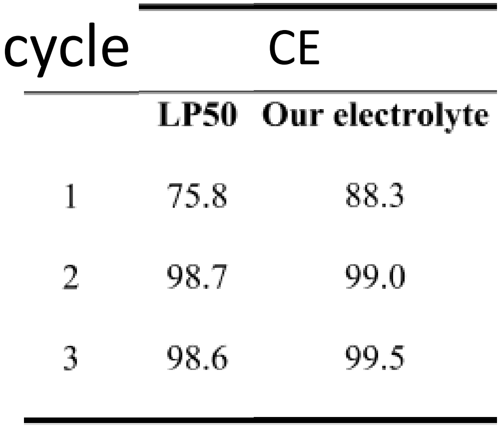
A:B=1:3, effective salt concentration 1.9M



FSI decompose at ~0.9V*



Almost no solvent co-intercalation at 1:3



cycle	CE	
	LP50	**Our electrolyte**
1	75.8	88.3
2	98.7	99.0
3	98.6	99.5

Li, Z. ***Gao, T***. (2022) ‘Enhancing the Charging Performance of Lithium-Ion Batteries by Reducing SEI and Charge Transfer Resistances’, *ACS Applied Materials & Interfaces*.

*Jiang, L. L. *et al.* (2021) ‘Inhibiting Solvent Co-Intercalation in a Graphite Anode by a Localized High-Concentration Electrolyte in Fast-Charging Batteries’, *Angewandte Chemie - International Edition*, 60(7), pp. 3402–3406.

Fast-charging in Li-Graphite half-cells

LP50
1M LiPF$_6$ EC-EMC

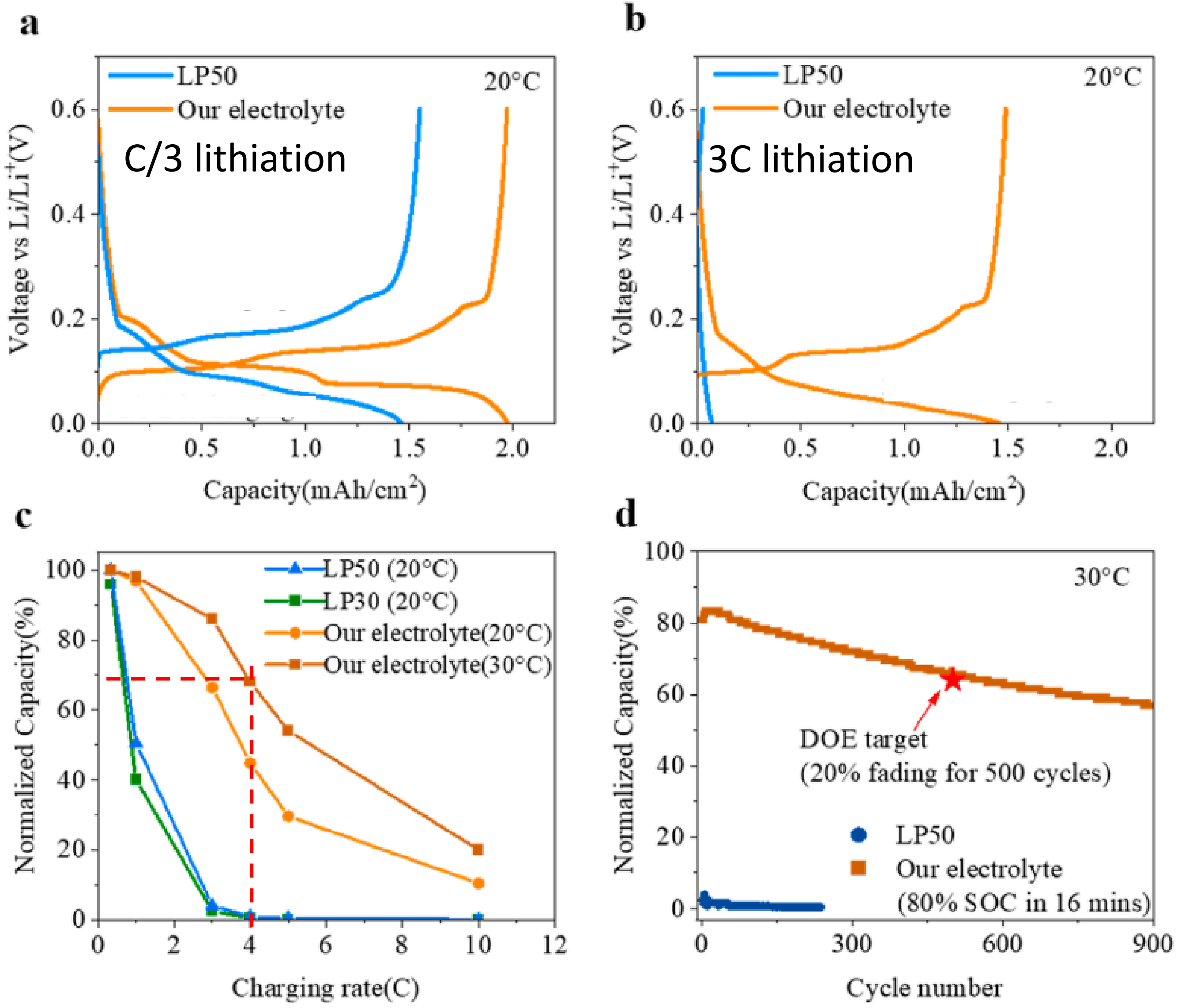
LP30
1M LiPF6 EC-DMC

C/3 de-lithiation

Graphite:
2.1 mAh/cm2

~70% SOC
in 10.5 minutes
（4C and 30 °C）

- 175 miles in 8 minutes



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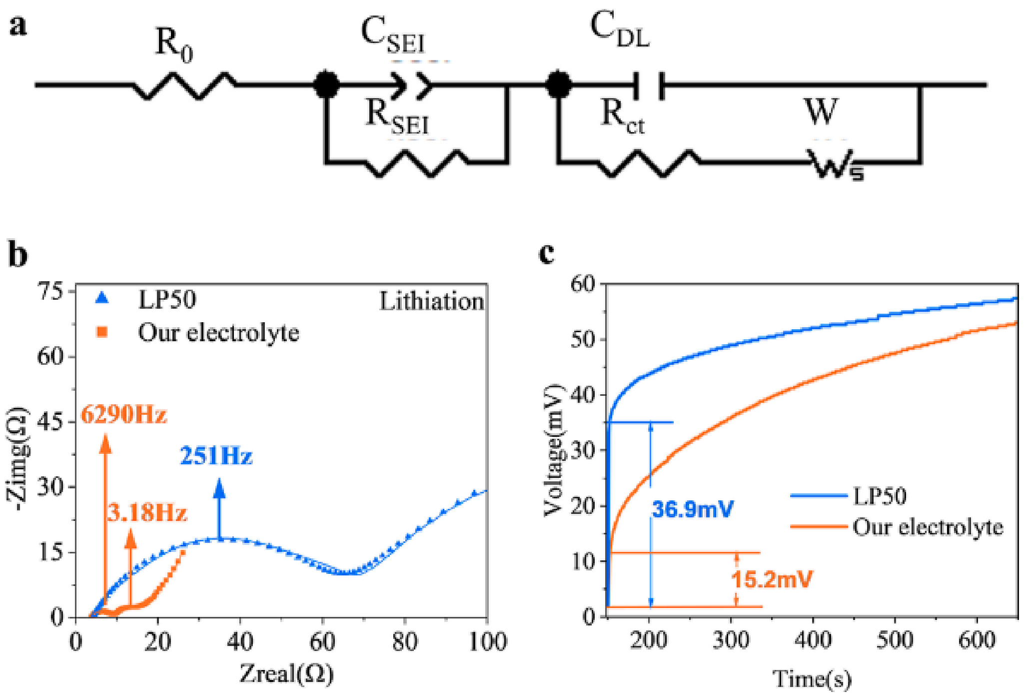
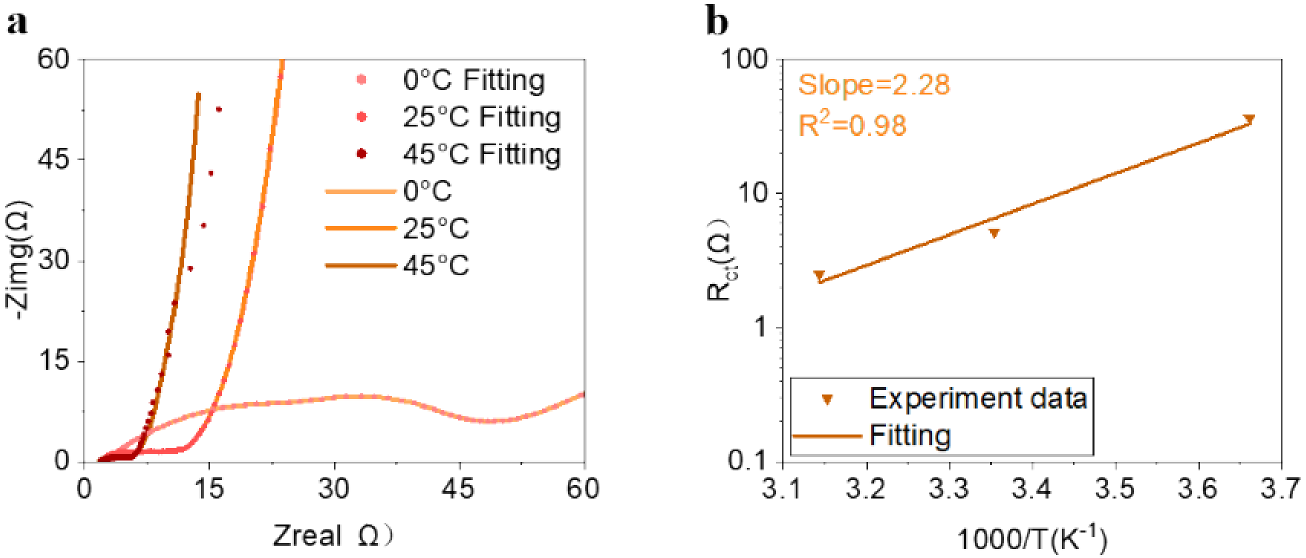
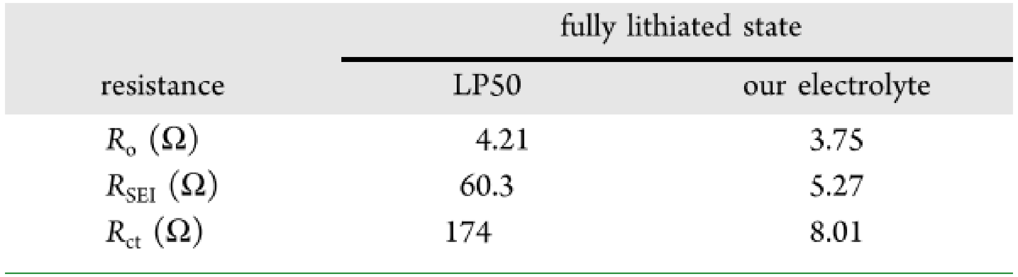
Reduced Interfacial Resistance







	fully lithiated state	
resistance	LP50	our electrolyte
R_o (Ω)	4.21	3.75
R_{SEI} (Ω)	60.3	5.27
R_{ct} (Ω)	174	8.01

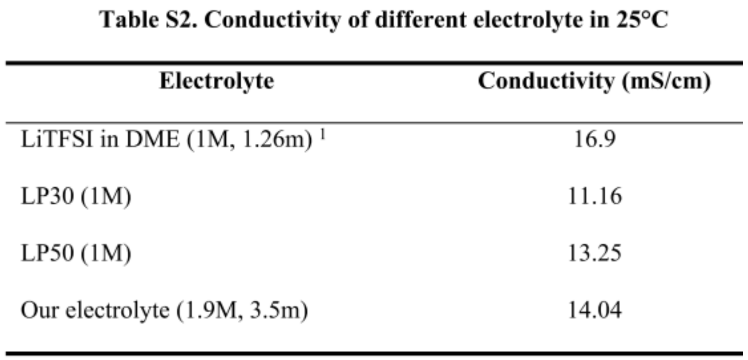


Table S2. Conductivity of different electrolyte in 25°C

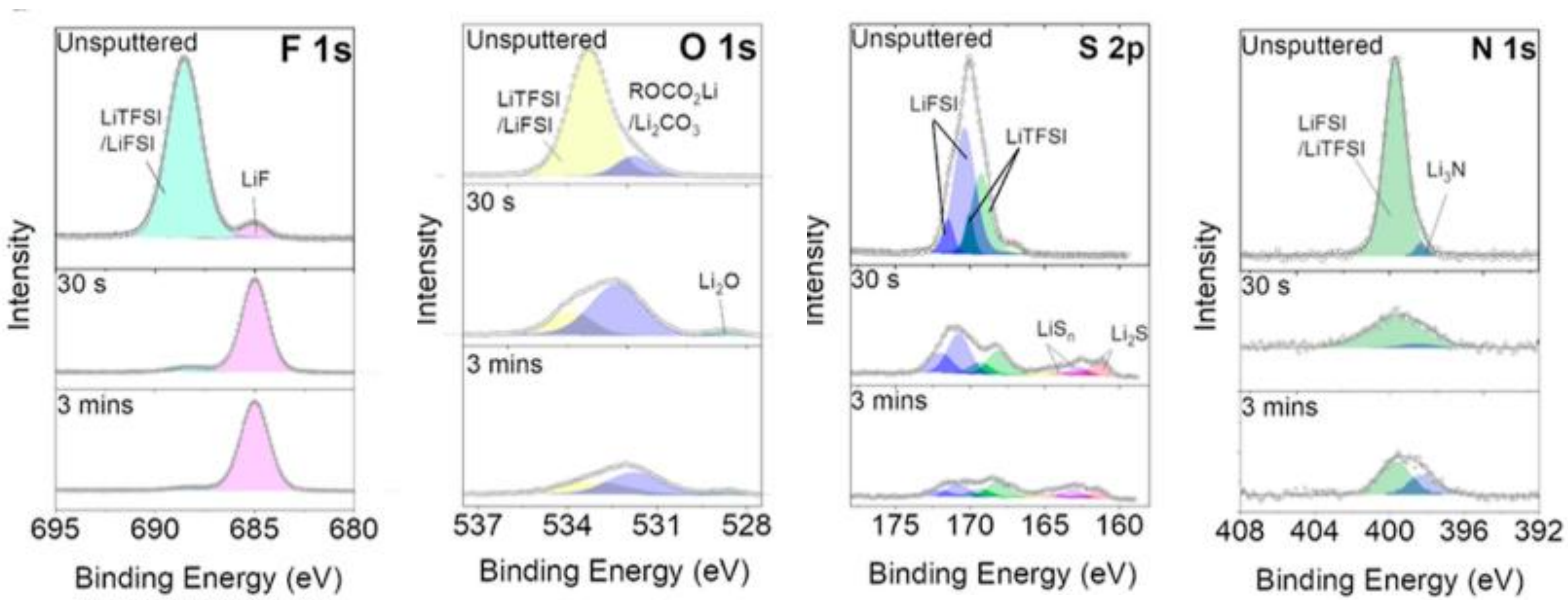
Electrolyte	Conductivity (mS/cm)
LiTFSI in DME (1M, 1.26m) [1]	16.9
LP30 (1M)	11.16
LP50 (1M)	13.25
Our electrolyte (1.9M, 3.5m)	14.04

Energy barrier for charge transfer reaction:
19 kJ/mol

Carbonate:
50-70 kJ/mol

Li, Z. ***Gao, T***. (2022) ‘Enhancing the Charging Performance of Lithium-Ion Batteries by Reducing SEI and Charge Transfer Resistances’, *ACS Applied Materials & Interfaces*.

SEI dominated by LiF



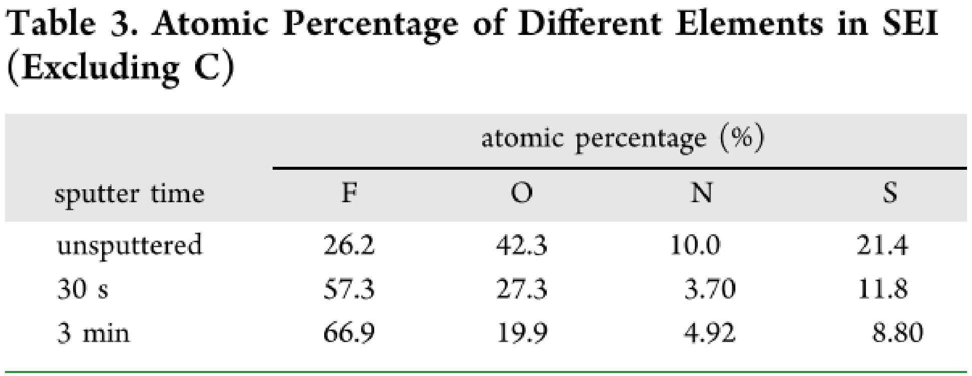


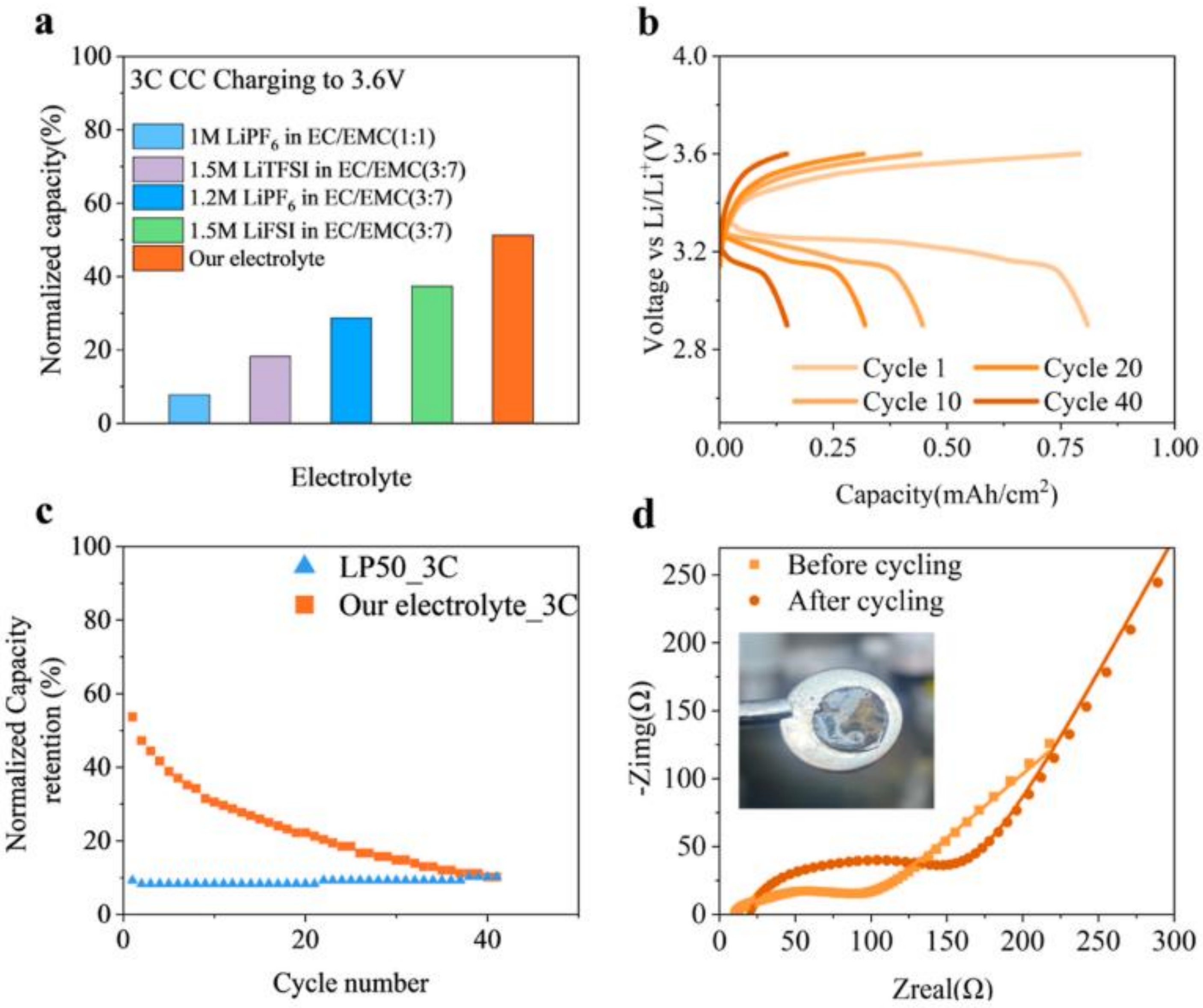
Table 3. Atomic Percentage of Different Elements in SEI (Excluding C)

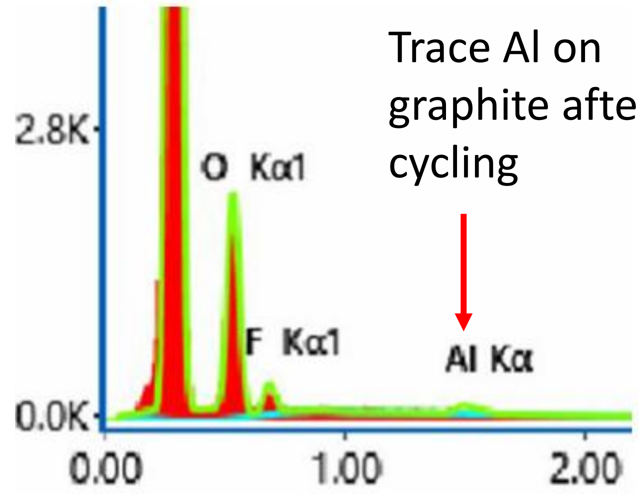
	atomic percentage (%)			
sputter time	F	O	N	S
unsputtered	26.2	42.3	10.0	21.4
30 s	57.3	27.3	3.70	11.8
3 min	66.9	19.9	4.92	8.80

SEI mostly LiF
A small amount of Li_2CO_3, Li_2S_x, Li_3N

Li, Z. ***Gao, T***. (2022) ‘Enhancing the Charging Performance of Lithium-Ion Batteries by Reducing SEI and Charge Transfer Resistances’, *ACS Applied Materials & Interfaces*.

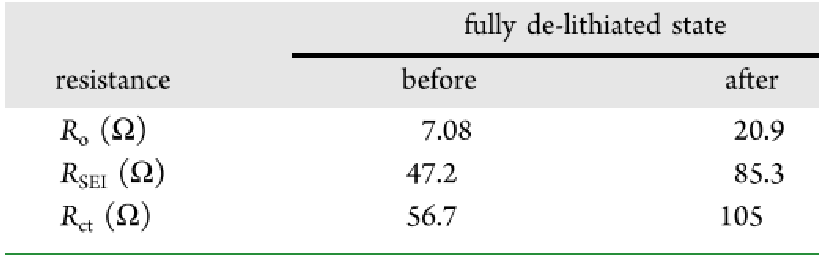
Fast-charging in LFP-graphite full-cells





Trace Al on graphite after cycling

- Better fast-charging than other electrolytes
- But capacity fades quickly
  - Electrolyte gels during cycling
  - Impedance grows during cycling
- Corrosion of Al CC by LiTFSI and/or LiFSI*
  - Could trigger DOL polymerization**



	fully de-lithiated state	
resistance	before	after
R_o (Ω)	7.08	20.9
R_{SEI} (Ω)	47.2	85.3
R_{ct} (Ω)	56.7	105

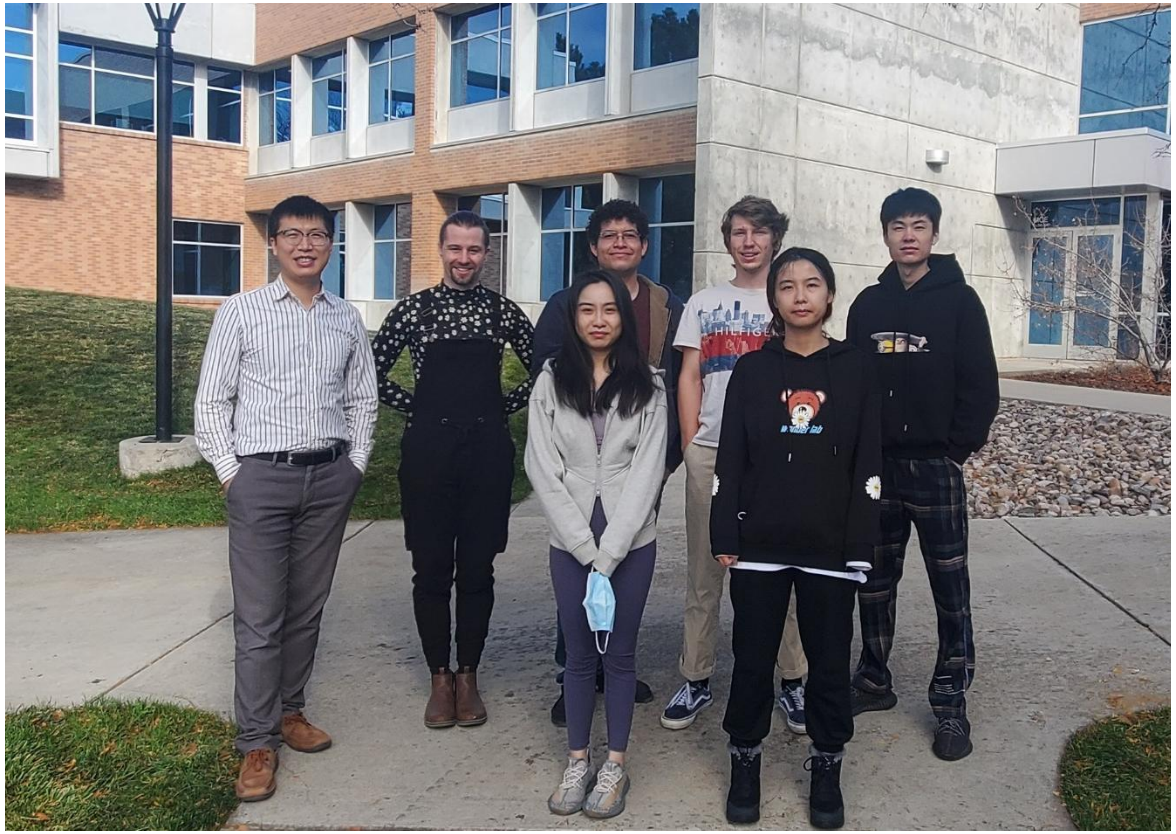
**Sahadeo, E. *et al.* (2020) ‘Mg2+ ion-catalyzed polymerization of 1,3-dioxolane in battery electrolytes’, *Chemical Communications*, 56(33), pp. 4583–4586.

*Dahbi, M. *et al.* (2011) ‘Comparative study of EC/DMC LiTFSI and LiPF6 electrolytes for electrochemical storage’, *Journal of Power Sources*, 196(22), pp. 9743–9750.

Conclusion

- EC-based electrolyte: large interfacial resistance
- Ether-based electrolytes: a potential solution due to the significantly reduced interfacial resistance
  - > 10X smaller $R_{SEI,}$ > 10 X smaller $R_{ct,}$ 1/3 of de-solvation energy
  - 70% charge in 10.5 minutes for Li/graphite cell at 2.1 mAh/cm2. LP50 fails to charge at this condition
- Solvent co-intercalation: can be addressed at a reasonably low concentration (1.9M), by diluting concentrated LiFSI-DME with LiTFSI-DOL
- Stable cycling in Li/graphite half cells for >500 cycles
- However, compatibility with oxide cathode requires more study
  - Gelation of DOL
  - Anodic stability

Acknowledgement



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