Lithium-Metal Anodes: Problems and Multiple Solutions Based on Hosts, Interphase, and Electrolytes

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Pacific Northwest National Laboratory

2021 DOE VTO Annual Merit Review

June 21-24, 2021

Project ID #bat362

Overview

Timeline

- Project start date: Oct. 2016
- Project end date: Sep. 2021
- Percent complete: 90%

Budget

- Total project funding $50M
  - DOE share 100%
- Funding received in FY21: $10M

Barriers

- Low Coulombic efficiency
- Li dendrite growth
- Large volume change

Partners

- Stanford University/SLAC
- University of California San Diego
- Idaho National Laboratory
- University of Washington
- Binghamton University
- UT Austin
- Brookhaven National Laboratory
- Texas A&M University

Relevance/Objectives

- Develop stable electrolytes to improve the CE of Li metal anode.
- Enable operation of thin Li metal anode in lean electrolyte conditions.
- Develop protective layers/separator to protect Li metal against dendrite growth.
- Develop efficient host for Li metal to minimize volume change of Li based anode.
- Enable high efficiency and safe utilization of Li metal anode for high energy density Li metal batteries required for long range EV applications.

Milestones

1. Benchmark Li-anode architecture with 50-μm thick lithium anode using protocols for 350 Wh/kg cells, and achieve over 200 cycles in coins. (Q1, FY 2021; Completed)
2. Optimize pressure effect for Li-S from coin cells. (Q2, FY 2021; Completed)
3. Provide new electrolyte formulation for Li-S (PNNL). (Q3, FY 2021; In progress)
4. Demonstrate 350 Wh/kg pouch cell with > 450 cycles; 400 Wh/kg > 100 cycles; and > 450 Wh/kg pouch cell. Demonstrate good cycling of Li-S pouch cell 300 Wh/kg. (Q4, FY 2021; In progress)

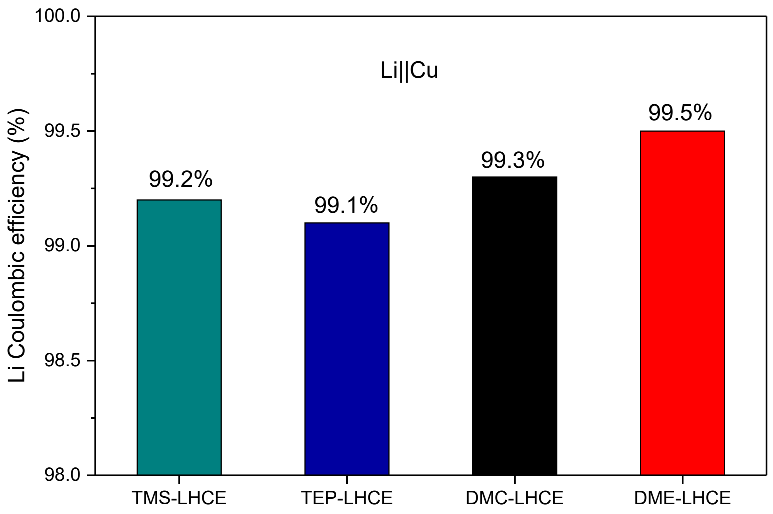
Approaches (PNNL)

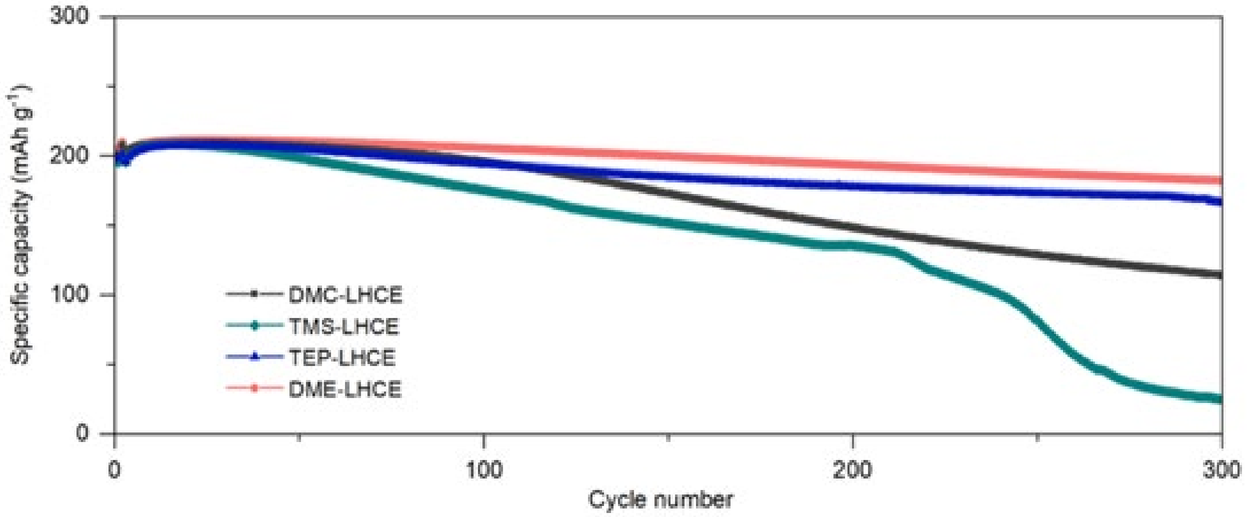
- Improve CE by using Localized High Concentration Electrolytes (LHCE)
- Tune LHCEs for high loading, lean electrolytes pouch cell applications
- Use fluorinated orthoformate-based electrolytes to extend long term calendar life of LMBs

Technical Accomplishments and Progress

1. Comparative studies on solvating solvents in LHCE

LHCE	Molar ratio	Mole concentration (M)	Ionic conductivity at 25 °C (mS cm^{-1})	Viscosity 25 °C (cP)	Density (g mL^{-1})
LiFSI-DMC-TTE	1 : 2.2 : 3	1.38	0.96	4.8	1.49
LiFSI-TMS-TTE	1 : 3 : 3	1.22	2.03	14.1	1.51
LiFSI-TEP-TTE	1 : 1.4 : 3	1.26	0.93	5.0	1.44
LiFSI-DME-TTE	1 : 1 : 3	1.52	1.59	3.7	1.48





- ➢ DME-LHCE exhibits the best Li –CE (99.5%) and leads to the best cycling stability of Li||NMC811 cells.

X. Ren, P. Gao, J. Zhang & W. Xu, et al., *PNAS*, 2020, **46**, 28603-28613

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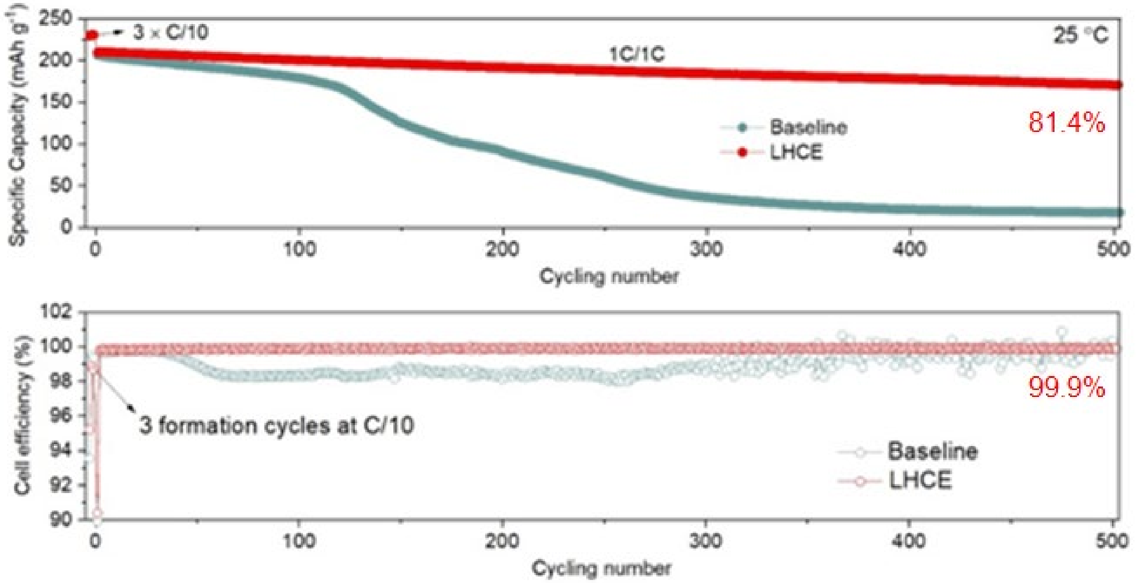
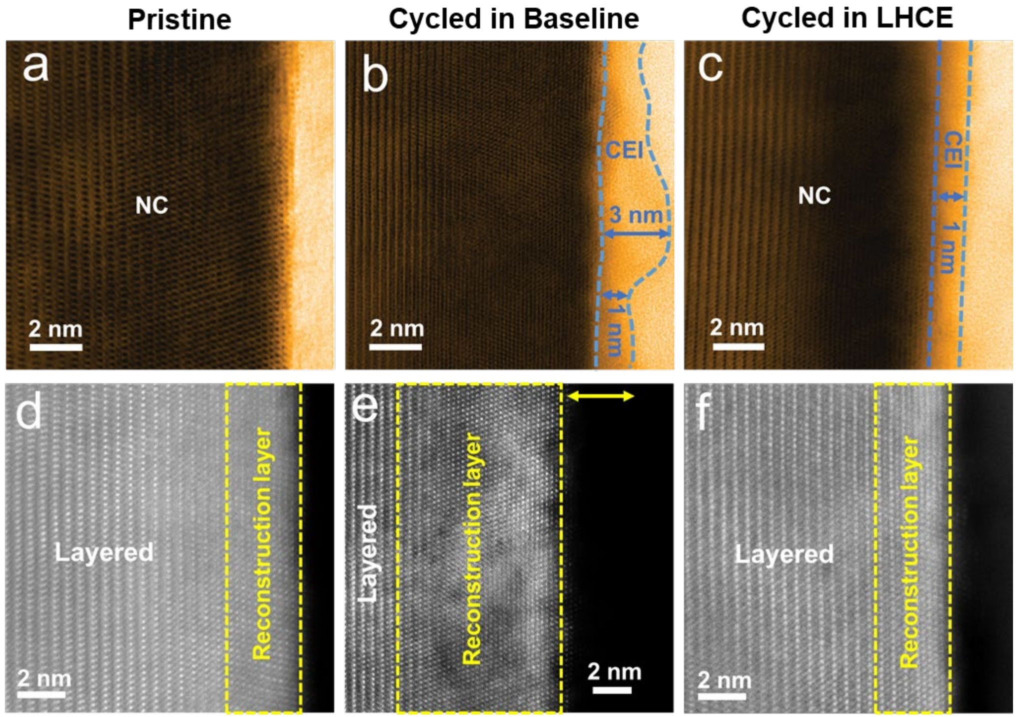
Technical Accomplishments and Progress

Cycling performance and structures of surface layers on $LiNi_{0.94}Co_{0.06}O_2$ (NC) after 500 cycles at 4.4 V and RT

- $Li||LiNi_{0.94}Co_{0.06}O_2$ (NC) coin cells, 2.8-4.4 V, 1C = 1.5 mA/cm^2
- Baseline=1M $LiPF_6$/EC-EMC+2wt%VC
- LHCE=LiFSI-1.2DME-3TT (by mol)





- ➢ LiFSI/DME-TTE based LHCE significantly improved cycling stability at 25 °C of ultrahigh-Ni cathode (NC) at 4.4 V.
- ➢ DME-LHCE formed uniform and ultrathin CEI on NC even after 500 cycles at 4.4 V and RT.
- ➢ DME-LHCE did not lead to extra rock salt layer as the baseline did.

BATTERY 500 CONSORTIUM

X. Zhang, W. Xu, et al., *Mater. Today*, 2021, DOI:10.1016/j.mattod.2021.01.013

In collaboration with Prof.
A. Manthiram of UT Austin

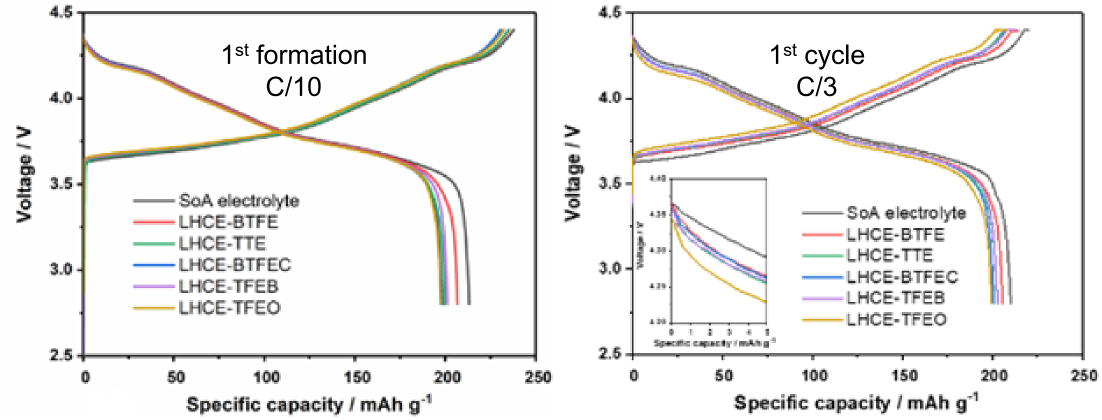
Technical Accomplishments and Progress

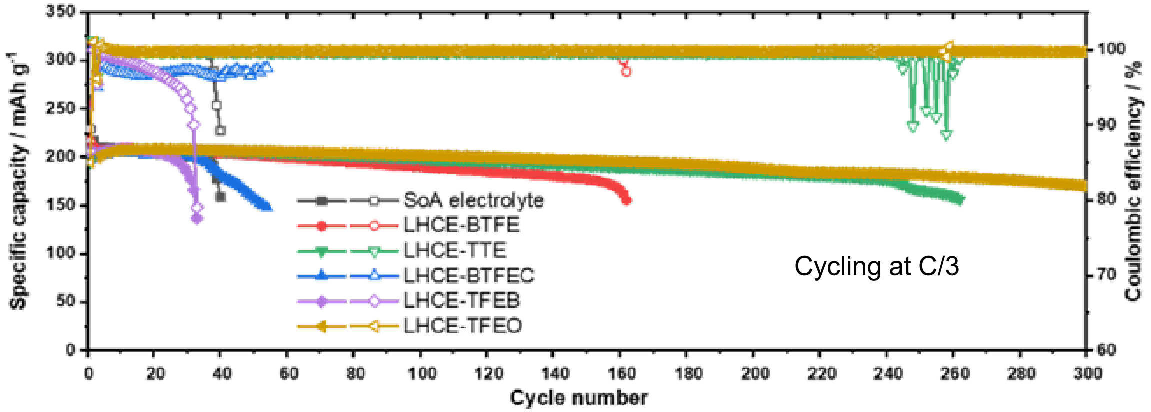
2. Comparative studies on diluent in LHCE

Diluent	BTFE (D1)	TTE (D2)	BTFEC (D3)	TFEB (D4)	TFEO (D5)
D – Molecular weight / g mol^{-1}	182.06	232.07	226.07	307.91	310.11
D – Boiling point / °C	62–63	93.2	117–118	120–123	144–146
D – Freezing point / °C	1	27.5	-	43	60
D – Density / g mL^{-1}	1.4	1.53	1.51	1.43	1.46
D – Viscosity @ 25 °C/ cP	0.7	1.43	1.69	1.18	1.97
D – Fluorine:hydrogen ratio	1.5	2	1.5	1.5	1.5
D – HOMO / eV	−8.76	−9.31	−9.28	−9.27	−8.84
D – LUMO / eV	−0.5	−0.5	−0.6	−0.47	−0.4
E – Salt concentration / M	1.65	1.49	1.49	1.17	1.15
E – Density / g mL^{-1}	1.39	1.48	1.45	1.43	1.41
E – Viscosity @ 25 °C/ cP	2.86	4.92	4.06	2.84	4.86
E – Conductivity @ 25 °C/ mS cm^{-1}	4.88	2.44	2.64	1.88	1.61

- Five fluorinated solvents barely dissolve LiFSI.
- The physical properties of the LHCEs containing different diluents are similar.

- Li||NMC811 coin cells.



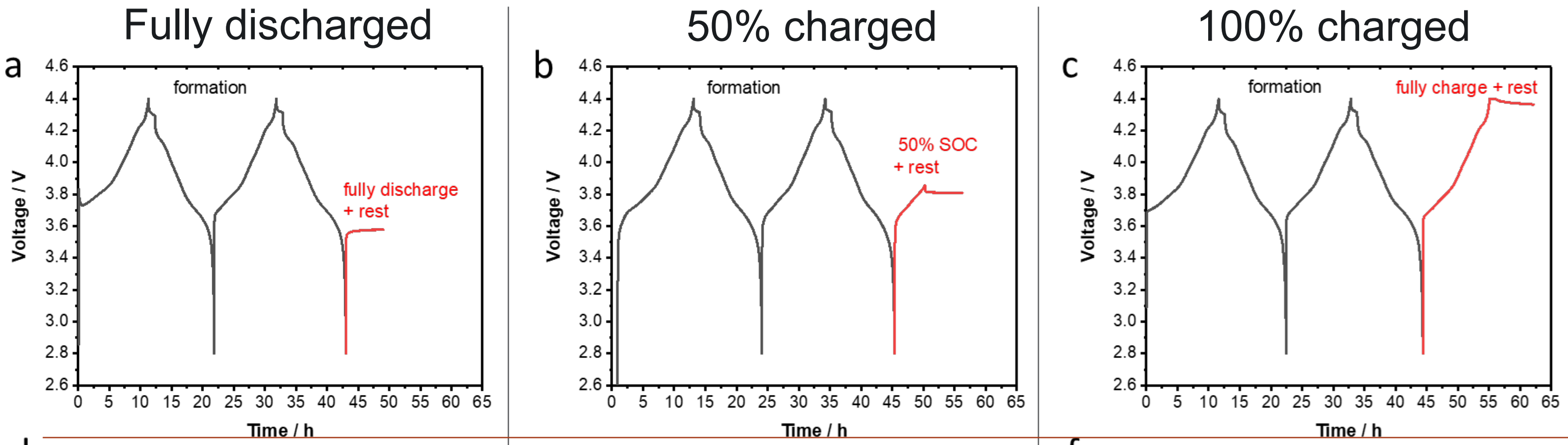


- TFEO based LHCE leads to the best cycling stability in the coin cells with flooded electrolytes

X. Cao, P. Gao, W. Xu, J.-G. Zhang, et al., *PNAS*, **2021**, *118* (9) e2020357118

Technical Accomplishments and Progress

3. Long-term (18 month) calendar life investigation on Li||NMC811 cells using TFEO based LHCE electrolyte

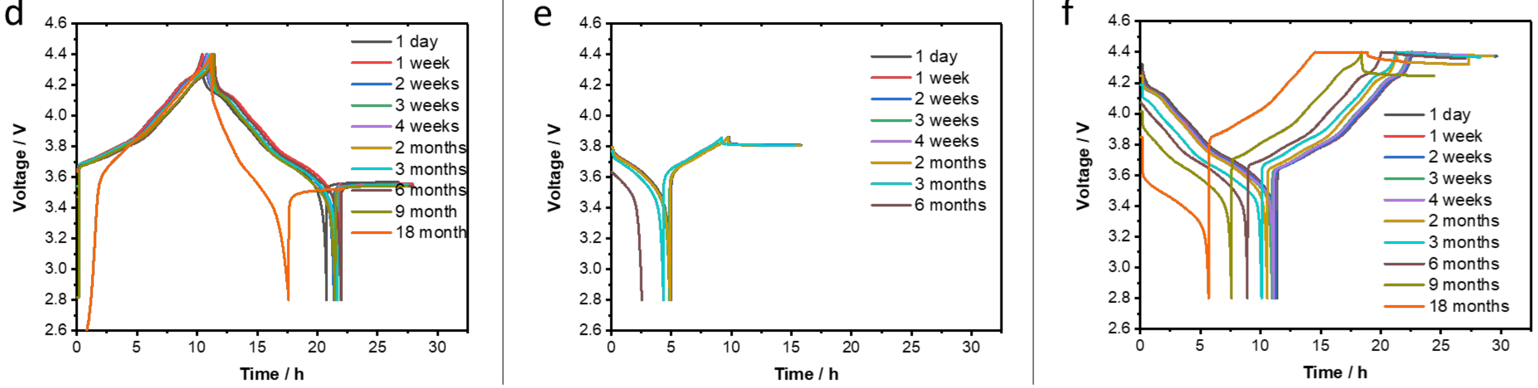


Voltage profiles of the cells before long term storage:

(a) The cell rested at fully discharge state

(b) The cell charged to 50% SOC

(c) The cell charged to 100% SOC



Voltage profiles of the cells at different times during 18-month storage

(d) The cell rest at fully discharge state

(e) The cells charged to 50% SOC

(f) The cell charged to 100% SOC

- ➢ Fully charged cells can still retain 53% of the original capacity after 9-months storage.

Technical Accomplishments and Progress

Self-discharge and capacity recovery of Li||NMC cells at different stages during 18-month storage

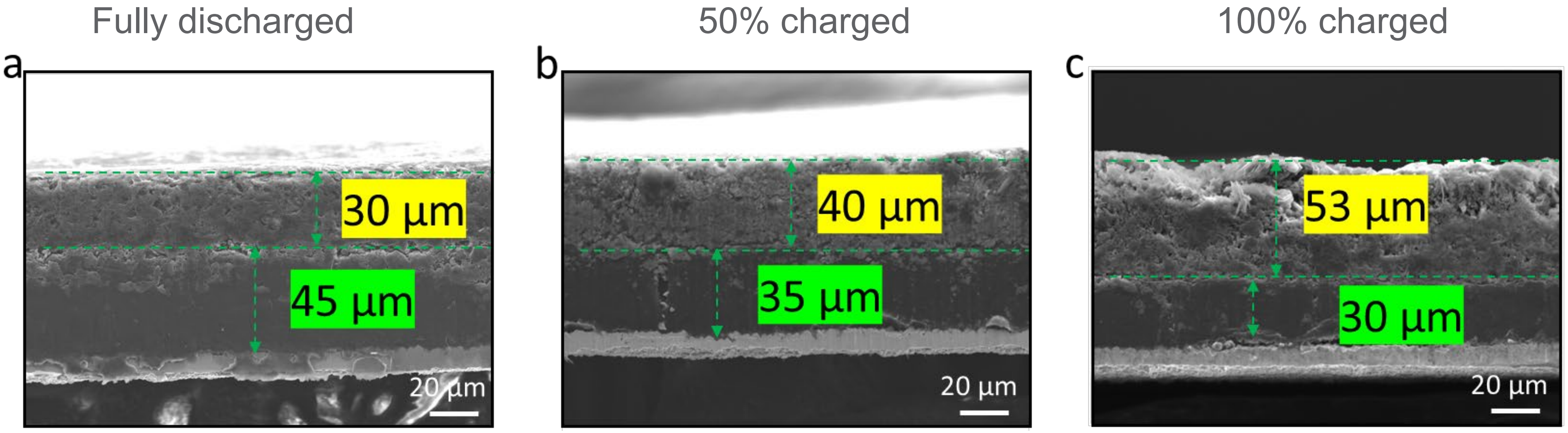
Time frame	Time gap	Capacity recovery at fully discharge state		Self-discharge at 50% SOC				Self-discharge at fully charged state			
		Discharge capacity / mAh g^{-1}	Capacity recovery / %	Discharge capacity / mAh g^{-1}	Charge capacity / mAh g^{-1}	Self-discharge capacity loss / mAh g^{-1}	Self-discharge rate/ % day^{-1}	Discharge capacity / mAh g^{-1}	Charge capacity / mAh g^{-1}	Self-discharge capacity loss / mAh g^{-1}	Self-discharge rate/ % day^{-1}
Initial capacity		203			97				218.9		
1 day	1 day	206.8	101.9	96.2	97	0.8	0.82	224.4	227.5	0	--
1 week	1 week	208.7	102.8	94.2	97	2.8	0.41	221.8	228.3	5.7	0.36
2 weeks	1 week	211.7	104.3	94.9	97	2.1	0.31	221	229	7.3	0.46
3 weeks	1 week	212.1	104.5	94.6	97	2.4	0.35	219.4	229.7	9.6	0.6
4 weeks	1 week	212.8	104.8	93.7	97	3.3	0.48	215.8	228.2	13.9	0.86
2 months	1 month	211.8	104.3	83.7	97	13.3	0.46	198.8	227.6	29.4	0.43
6 months	4 months	210.2	103.5	56.4	-	40.6	0.35	164.5	226.7	63.1	0.23
9 months	3 months	202.5	99.8	-	97	-	-	148.4	216.8	78.3	0.38
18 months	9 months	181.9	89.6	21.3		75.7	0.43	114		102.8	0.26

- Self-discharge at fully charge state is only 47% after 9-months storage.
- Cells stored at fully discharged state can recover ~90% capacity after 18-months.

Technical Accomplishments and Progress

Structural and CEI properties of the NMC811 cathodes in Li||NMC811 cells after 18-month storage at different SOC

Charge condition during 18-month storage :



Cross-section views of SEM images of Li metal electrodes collected from cells

- Corrosion of Li metal anode increases with increasing SOC during storage

Proposed Future Work

1. Further improve the stability of electrolytes at elevated temperature to ensure safety and long-term calender life of LMBs.
2. Investigate calendar life of LMBs using pouch cells to eliminate the possible corrosion of stainless-steel coin-cell case by LiFSI salt.
3. Apply uniform pressure on pouch cells to minimize the surface of Li anode during storage and improve cycle and calendar life of LMBs.

Any proposed future work is subject to change based on funding levels.

Summary

1. Ether based LHCEs enable LMBs to show excellent long-cycle-life at voltages up to 4.5 V on different cathode materials.
2. Fluorinated Orthoformate based LHCE electrolyte (LiFSI in DME/TFEO) can enable long-term cycle life and good calendar life of LMBs.
3. Self-discharge of a fully charged LMBs is only 47% of the original capacity after 9-month storage.
4. Fully discharged LMBs are most stable during long term storage (~90% capacity recovery after 18-months).
5. Calendar life of LMBs increases with decreasing SOC of batteries during storage.

Acknowledgements

✓DOE/VTO/Battery500 program

✓PNNL Team Members: Xia Cao, Xiaodi Ren, Xianhui Zhang, Peiyuan Gao, Lianfeng Zou, Mark H. Engelhard, Bethany E. Matthews, Jiangtao Hu, Chaojiang Niu, Chongmin Wang, Kim, Jumyeong, Jie Xiao, Jun Liu

✓University of Maryland: Xinzi He and Chunsheng Wang

✓Battery 500 PIs and team members

Responses to Previous Year Reviewers' Comments

Q1: "Are there a better way to screen them other than cycling. Perhaps leakage current can be monitored at a fixed potential or the thickness of the SEI as a function of time at a fixed potential can be measured to determine if the Li-metal SEI is stable."

A1: The leak current measurement is a very effective way to check leak current and project calendar life in a static conditions which is dominated by chemical stability of electrolyte/electrode, but it is not the best way to check CE and cycling stability that are mainly depends on the electrochemical stability of Li in the given electrolyte. We have developed a method to screen the electrolyte by measuring the average CE in ten cycles in a Li||Cu cell instead of long-term cycling (Zhang et al., Adv. Energy Mater. 2017, 1702097.)

Q2: "At 99.3% CE means the cell with twice the excess Li is dead in 100 cycles or so...Keep the final goal in mind: 99.9% CE or higher."

A2: We agree that a Li CE >99.9% is required for long-term cycling of LMBs. We have improved the Li CE to be more than 99.5%. By adding a uniform pressure to cell and select the appropriate testing protocol, we can also increase the Li CE to be 99.8%. More work will be done to further increase Li CE.

Q3: "Cost has not been discussed other than at a very high level."

A3: Cost of LHCE electrolytes strongly depends on the scale of the production. We are working with industry partners to scale up the state-of-the-art LHCE to reduce the cost in the near future.

Q4: "The team also needs to provide calendar life and low-temperature data using the LHCE."

A4: New data reported in this presentation has demonstrated the LMBs using the LHCE has a reasonable calender life (cells stored at fully discharged state can recover ~90% capacity after 18-months) although it needs to be further improved.

Q5: "The project needs some way to quantitatively predict whether an electrolyte-anode combination will produce dendrites or not and they need to be detected early.

A5: The post mortal analysis of our cycled cells indicates that dendrite growth need to be suppressed by the combination of the multiple approaches, including a high CE electrolyte, appropriate operating pressure, well controlled cell assembly procedure, and operating conditions.

Collaboration and Coordination with Other Institutions

Partners:

- Stanford University: Coating and host for Li metal anode, cryo-electron microscopy
- SLAC: In situ X-ray characterization of Li metal anode
- University of California San Diego: Protective coating and in situ cryo-TEM characterization
- Idaho National Laboratory: Pressure effect on Li cycling and test of PNNL-made pouch cell
- University of Washington: Simulation of Li metal batteries
- UT Texas: Solid state electrolytes
- Brookhaven National Laboratory: Characterization of electrodes
- Texas A&M University: Simulation
- Binghamton University: Thermal stability

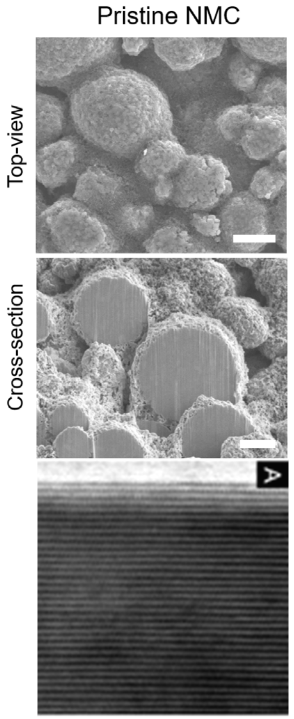
Remaining Challenges/Barriers

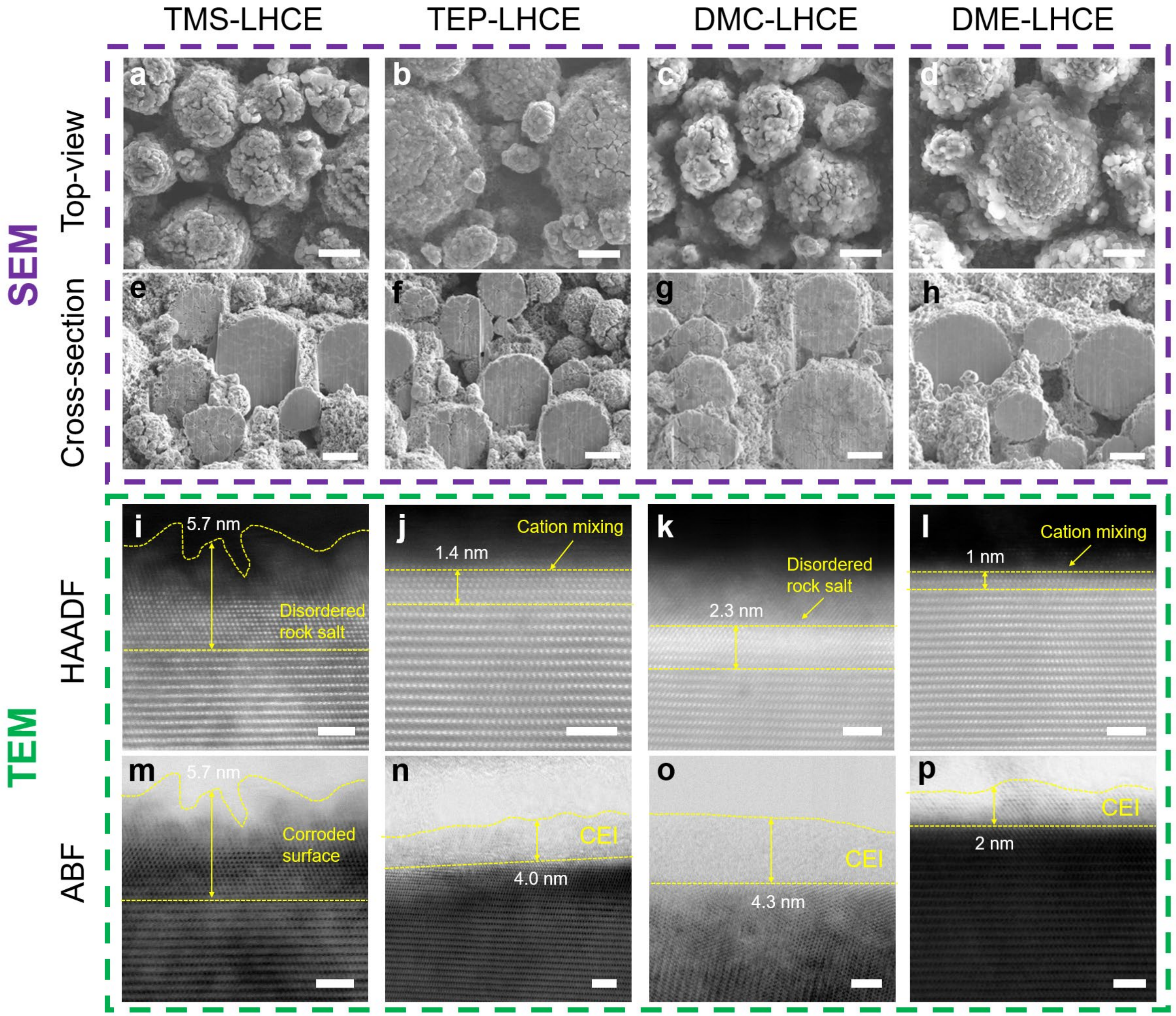
- The thermal stability of the electrolyte as well as the full cells need to be improved, especially when operating at realistic conditions.
- Calendar life of LMBs needs to be improved.
- Li CE need to be increase to more than 99.9%

Technical Backup Slides

Technical Accomplishments and Progress

Morphologies of NMC811 cathodes and CEI structures after 100 cycles in four LHCEs





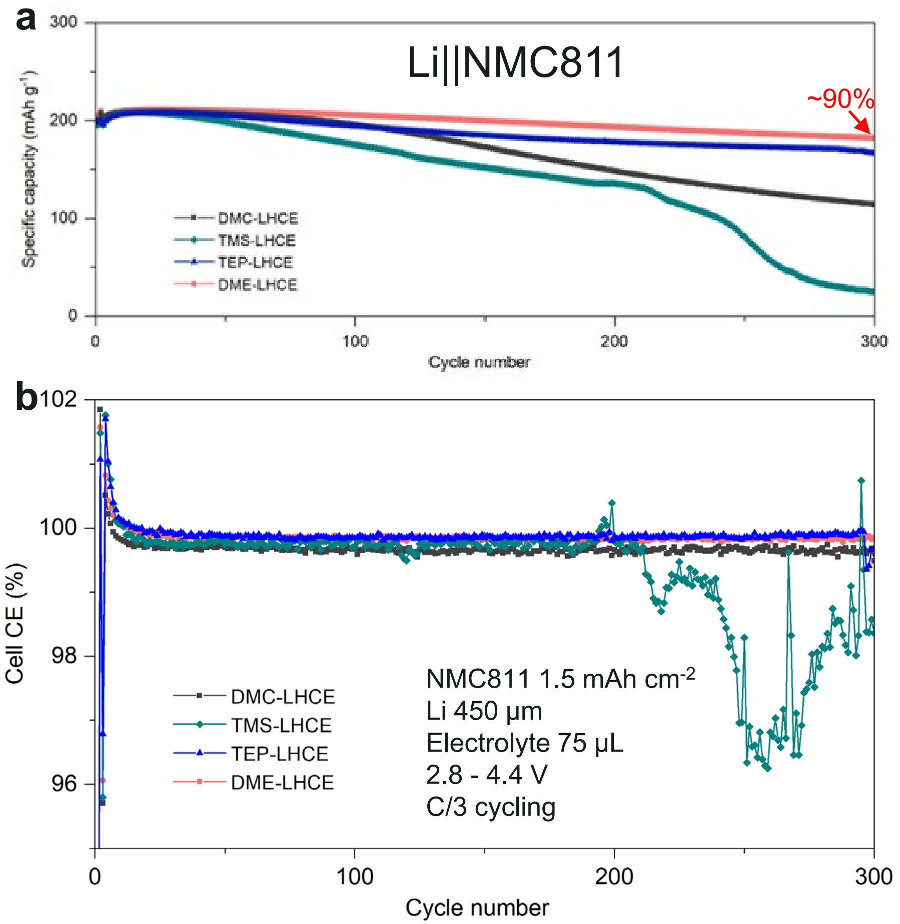
- Crack inside secondary particles TMS-LHCE > DMC-LHCE > TEP-LHCE > DME-LHCE.
- Rock-salt layer: TMS-LHCE > DMC-LHCE > TEP-LHCE > DME-LHCE.
- CEI layer: TMS-LHCE > DMC-LHCE > TEP-LHCE > DME-LHCE.

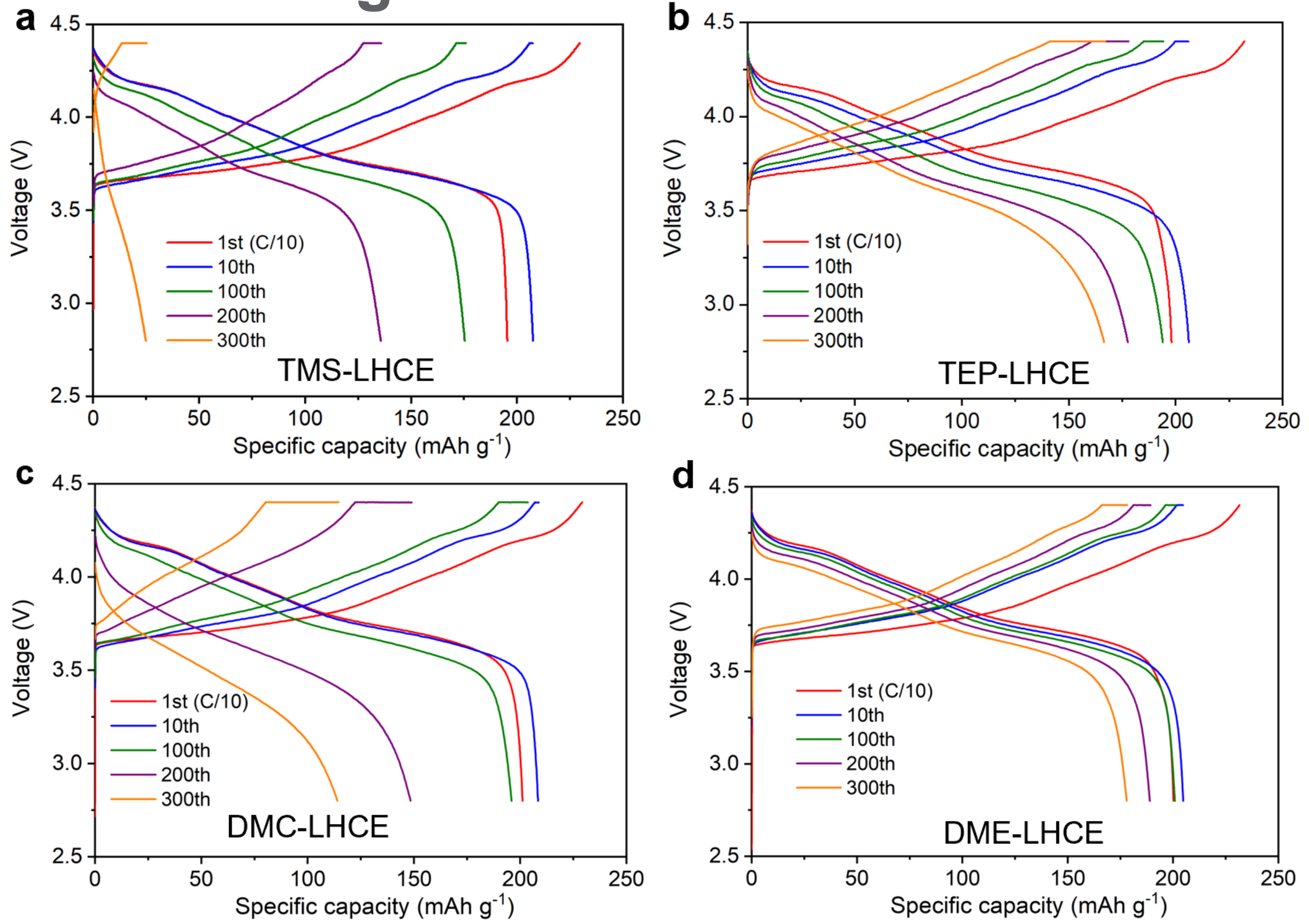
➢ DME-LHCE leads to the most stable cathode structure and much thinner CEI layer than other electrolytes.

X. Ren, P. Gao, J. Zhang & W. Xu, et al., *PNAS*, 2020, **46**, 28603-28613

Technical Accomplishments and Progress

Comparative studies on solvating solvents in LHCE





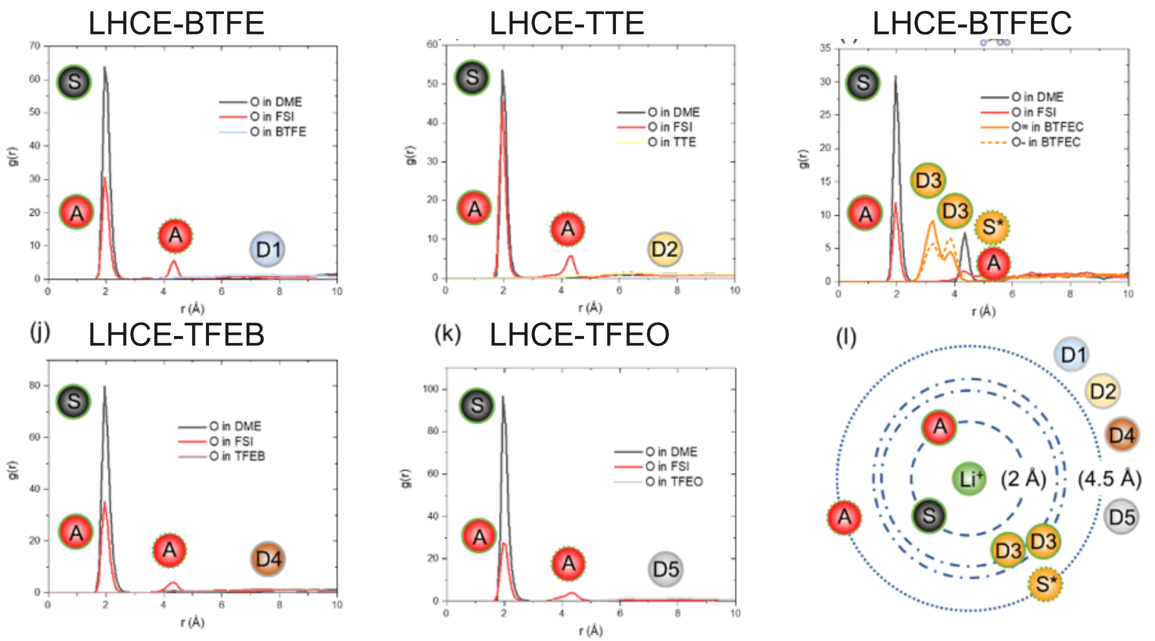
- ➢ DME-LHCE leads to the best cycling stability.
- ➢ DME-LHCE leads to smallest voltage fade and capacity loss.

X. Ren, P. Gao, J. Zhang & W. Xu, et al., *PNAS*, 2020, **46**, 28603-28613

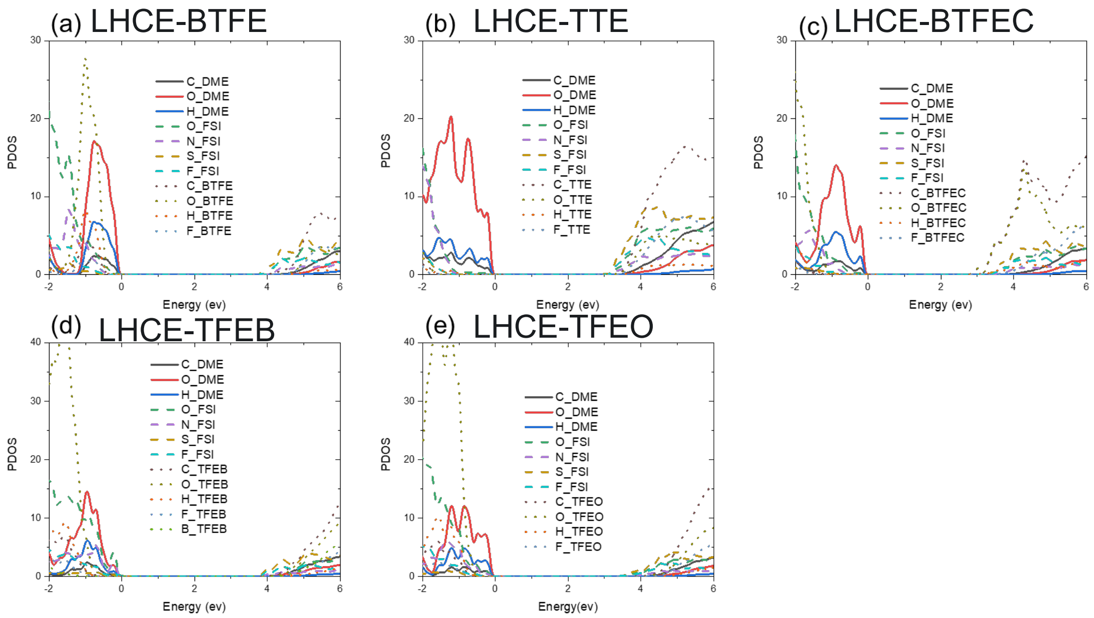
Technical Accomplishments and Progress

Comparative studies on diluent in LHCE

Radical distribution functions



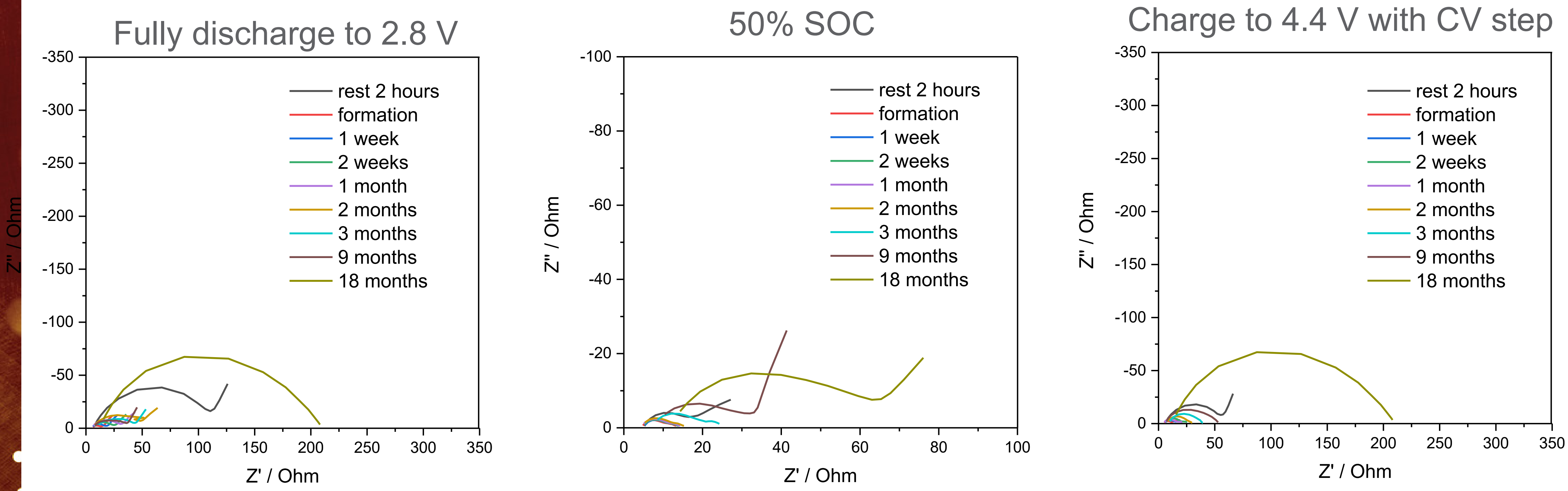
Projected density of states (PDOS) of LHCEs



- Salt anion and solvating solvent form inner solvation sheath.
- BTFE, TTE, TFEB and TFEO exist in outer space of this inner sheath.
- BTFEC coordinates to Li^+ in the second shell, which destroys the HCE clusters.
- The conduction band minimum (CBM) in the LHCE-BTFEC is on BTFEC while the CBMs in the other LHCEs are on the FSI^- anion.

X. Cao, P. Gao, W. Xu, J.-G. Zhang, et al., *PNAS,* **2021**, *118* (9) e2020357118

Resistance evolution upon storage at 30 °C



- ➢ Resistance changes is very small in the first 9 months.
- ➢ Resistance changes accelerate after 9 months storage.
- ➢ Accelerated resistance change maybe related to the corrosion of S.S. can of coin-cells.