Lithium Dendrite Prevention for Lithium-Ion Batteries

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2016 DOE Vehicle Technologies Program Review
June 6-10, 2016

Project ID #ES275

Overview

Timeline

- Start date: Oct. 2012
- End date: Sept. 2017
- Percent complete: 80%

Barriers addressed

- Growth of lithium dendrites
- Low Coulombic efficiency
- Low charge current density

Budget

- Project funding
  - DOE share 100%
- Funding received in FY15: $400k
- Funding for FY16: $400k

Partners

- Argonne National Laboratory
- Lawrence Berkeley National Laboratory
- U.S. Army Research Laboratory

Relevance/Objectives

- Prevent lithium (Li) dendrite formation on Li-metal anodes in Li-metal batteries and on carbon anodes in Li-ion batteries.

- Enable Li metal to be used as an effective anode in rechargeable Li-metal batteries for long cycle life at a reasonably high current density.

- Explore various factors that affect the morphology of Li deposition, especially under high current density conditions.

Milestones

FY15

- ✓ Develop electrolytes to suppress Li dendrite growth on Li metal and graphite anode. (Dec. 2014) **Completed**
- ✓ Protect graphite electrode in PC-EC-based carbonate electrolytes with electrolyte additives. (March 2015) **Completed**
- ✓ Demonstrate over 300 cycles for 4-V Li-metal batteries without internal short circuiting, through optimized electrolyte formulation. (June 2015) **Completed**
- ✓ Achieve over 300 cycles for 4-V Li-metal batteries without internal short circuiting, through optimized electrolyte formulation. (Sept. 2015) **Completed**

FY16

- ✓ Develop mixed salts electrolytes to protect Al substrate and Li metal anode, and to maintain Li Coulombic efficiency over 98%. (Dec. 2015) **Completed**
- ✓ Demonstrate over 300 cycles for Li||LFP cells with high LFP loading and at high current density cycling. (March 2016) **Completed**
- ▪ Demonstrate over 100 cycles for 4-V Li-metal batteries with high cathode loading and at high current density cycling. (June 2016) **Ongoing**
- ▪ Achieve over 500 cycles for 4-V Li-metal batteries with high cathode loading and at high current density cycling. (Sept. 2016) **Ongoing**

Approach

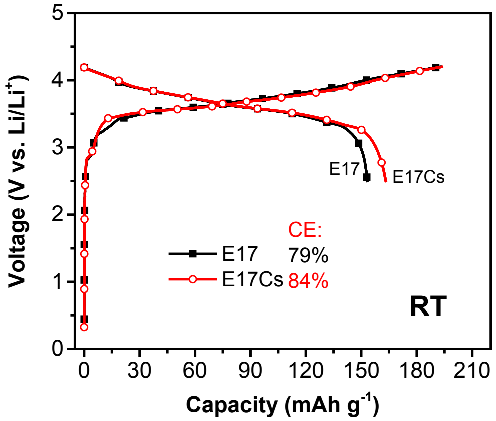
1. Use Cs^+ additive and EC-PC-based electrolytes to form high quality SEI layer to suppress Li dendrites on surfaces of Li-metal and graphite anodes while maintaining long-term operation of batteries.

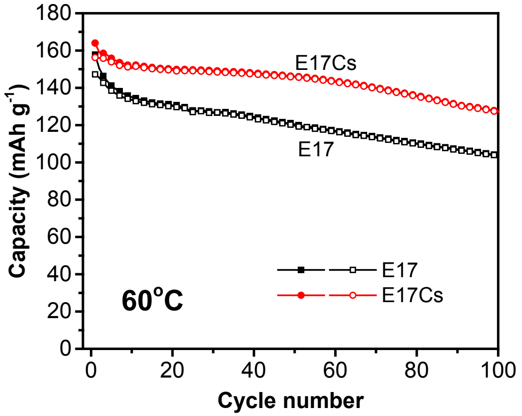
2. Use optimized charge/discharge protocol to form a transient high-concentration electrolyte layer on Li surface so as to protect Li metal anode and to enable sustainable operation of Li metal batteries.

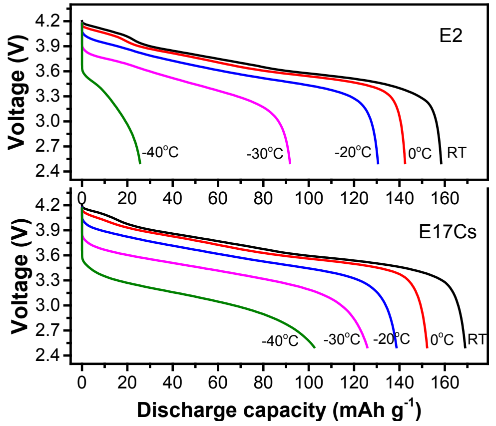
3. Use dual-salt electrolytes to form highly conductive SEI, protect Li metal, enable long cycle life and fast chargeability of Li metal batteries.

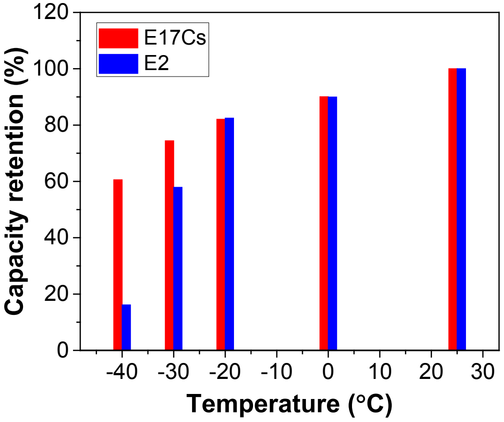
Technical Accomplishments

Performances of graphite||NCA full cells in a wide temperature range









E17:
1.0 M $LiPF_6$ in
EC-PC-EMC
(2:1:7 by wt.)

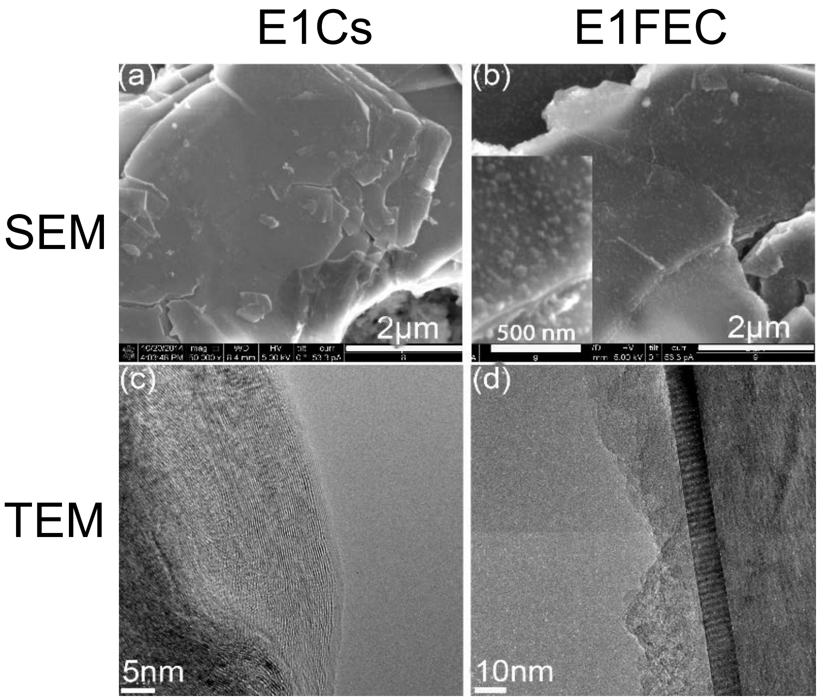
E17Cs:
E17 + 0.04 M
$CsPF_6$

E2:
1.0 M $LiPF_6$ in
EC/EMC (3:7
by vol.)

✓ Electrolytes with Cs^+ additive significantly enhance the cycling stability at elevated temperature and the low-temperature discharge performances of graphite||NCA full cells.

Technical Accomplishments

Characterization of graphite anodes after tested in full cells for 100 cycles at 60°C

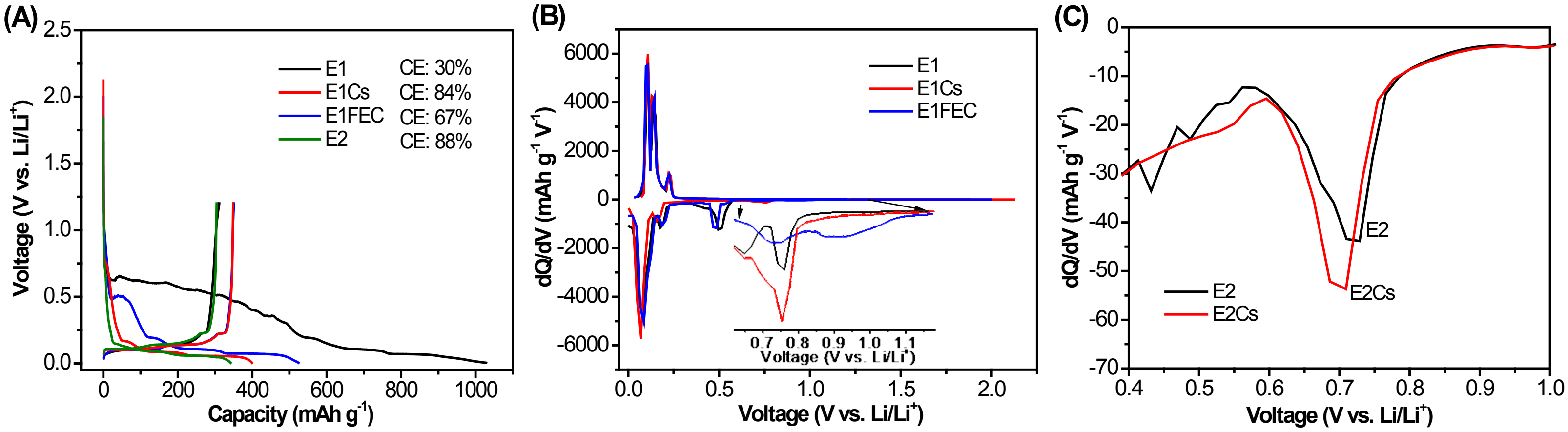


E1: 1.0 M $LiPF_6$ in EC-PC-EMC (5:2:3 by wt.)
E1Cs: E1 + 0.05 M $CsPF_6$
E1FEC: E1 + 2% FEC

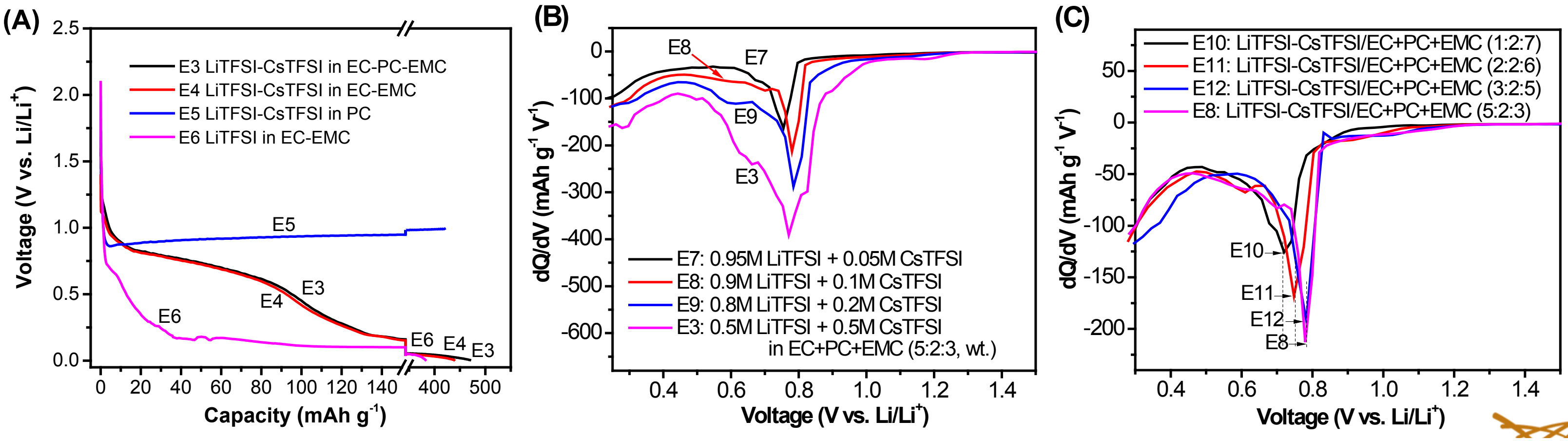
- ✓ The graphite anode from E1Cs appears to be clean (a), and the SEI layer is rather uniform with a thickness of <2 nm (c).
  - ✓ This is almost the same as the SEI thickness generated at 0.3 V following the first charge, indicating a stable and uniform interphasial morphology even at high temperature for long-term cycling.
- The SEI layer on the graphite tested in E1FEC contains many particles and the thickness is uneven (b), varying between 11 and 28 nm (d).

Technical Accomplishments

Electrochemical analysis on Cs$^+$-additive in Li||graphite cells



- Reduction potentials: FEC ~0.95 V, EC 0.75 V, PC 0.7–0.5 V
- Cs$^+$ induces slightly more EC decomposition.

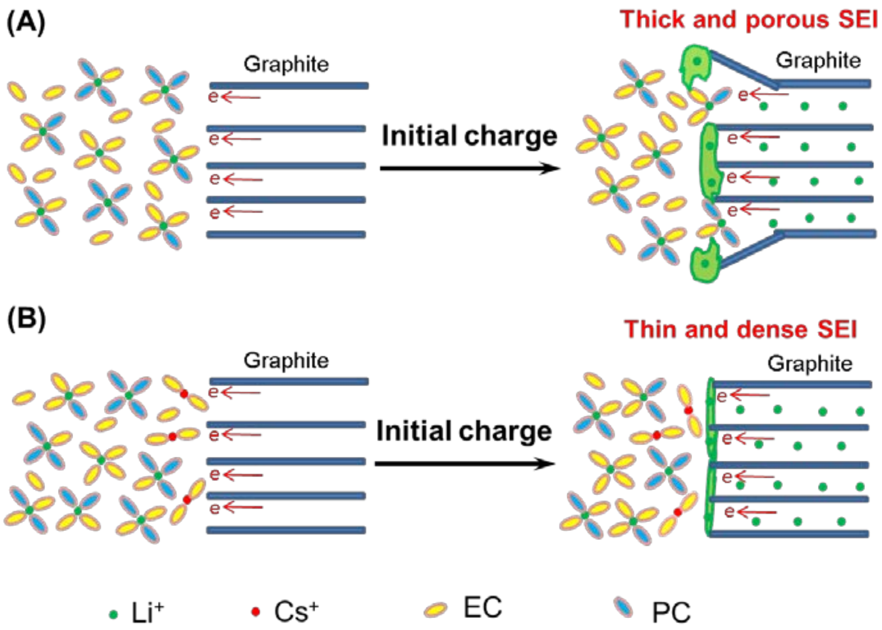


- Increasing Cs$^+$ content or EC content shifts the peak at 0.75 V to 0.8 V and increases the peak intensity.

➢ EC reduction enhanced by Cs$^+$ is responsible for the SEI formation.

Technical Accomplishments

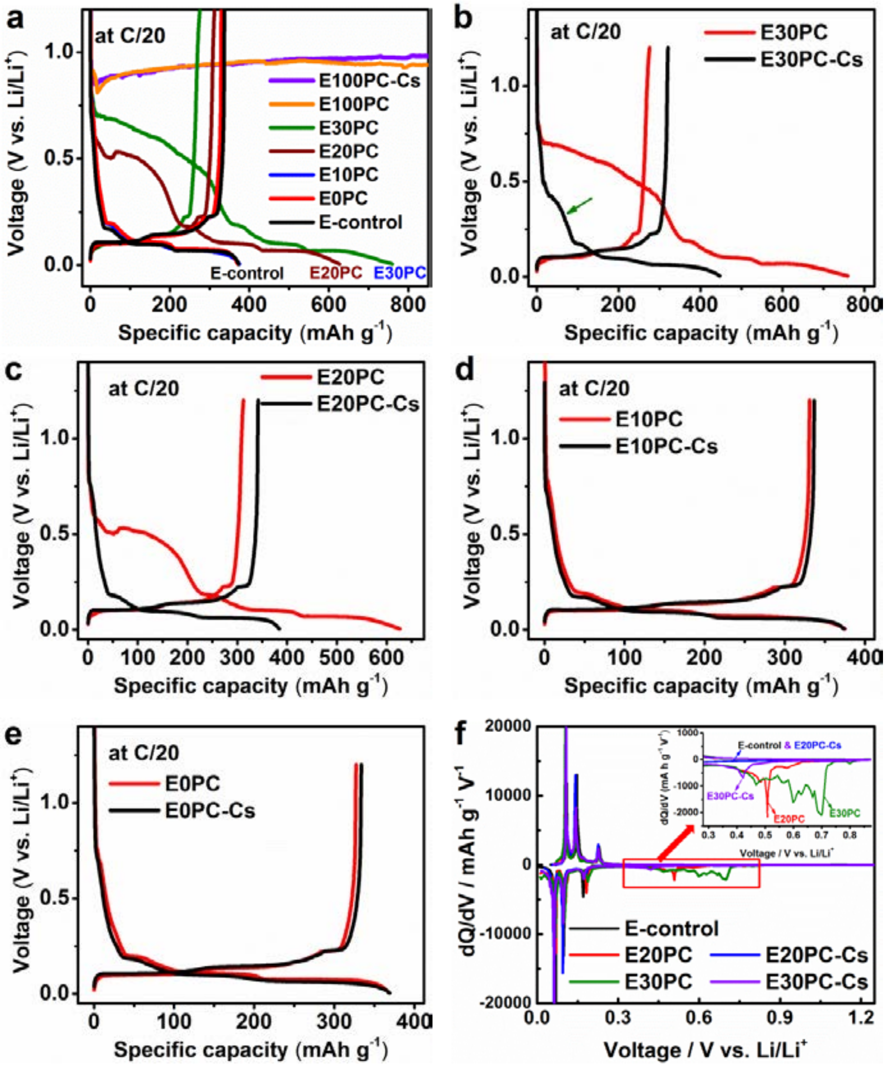
Protection mechanism of Cs^+-additive on graphite in PC-containing electrolytes

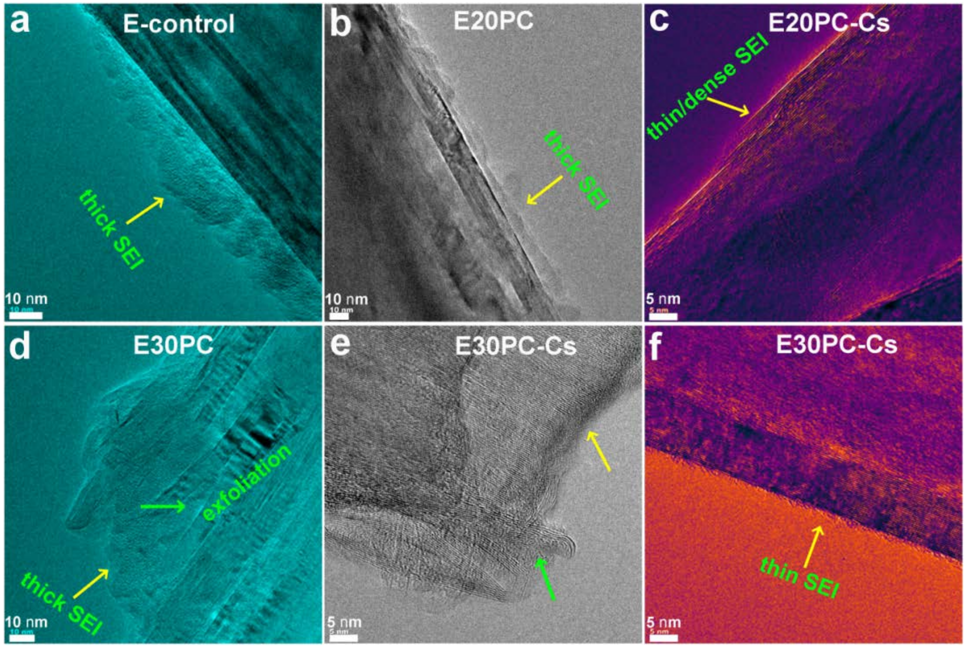


- Cs^+-$(EC)_m$ (m=1,2) solvates have planar structure, indicating possibly fast mobility and easy intercalation to graphite layers to decompose.
- Cs^+-$(EC)_m$ (m=1,2) solvates reduce earlier than Li^+-$(PC)_n$ (n=3,4).
- Cs^+ at 0.05 M has an effective redox potential of -3.103 V vs. SHE, lower than that of Li^+ at 1.0 M (-3.040 V vs. SHE).
- ✓ The formed SEI suppresses further solvent decomposition → Thin SEI layer.

Technical Accomplishments

Effect of PC content on graphite in half cells using electrolytes with and without Cs$^+$ additive

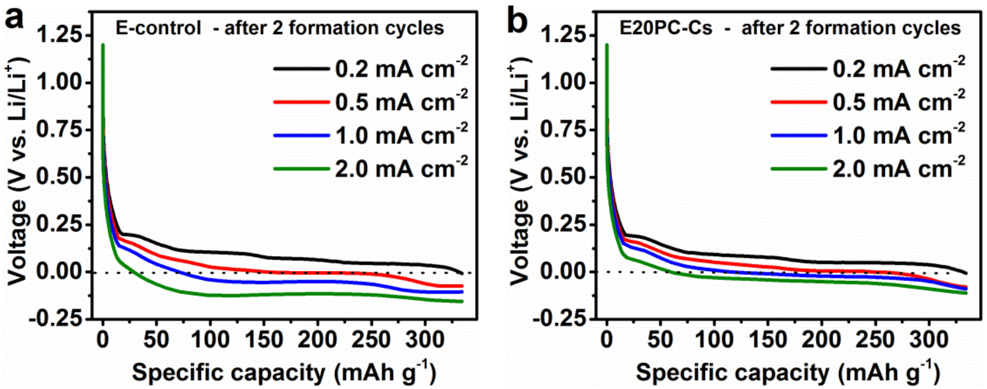




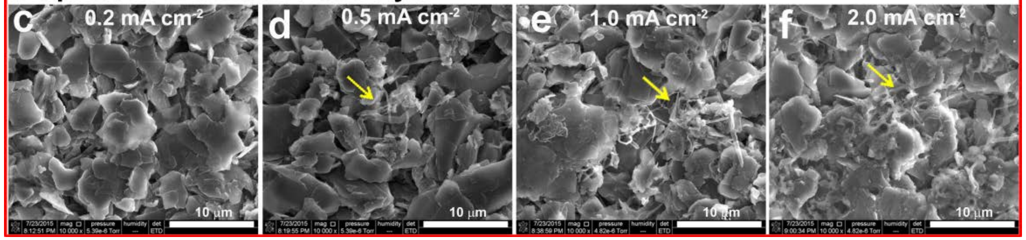
- ➢ Cs$^+$ has no effect in sole PC electrolyte.
- ✓ In EC-PC-EMC with 30 wt% EC and 20-30% PC, Cs$^+$ significantly suppresses PC co-intercalation.
- ➢ Without Cs$^+$ additive, the SEI is thick.
- ✓ Addition of Cs$^+$ significantly reduces SEI thickness.

Technical Accomplishments

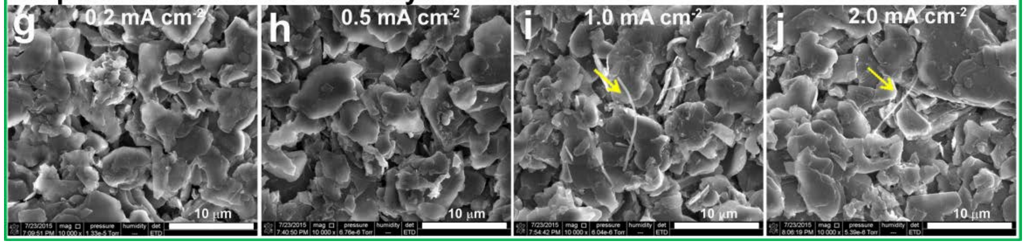
Effect of Cs$^+$-additive on Li dendrite formation on graphite anode at various current densities



Graphite in E-control electrolyte



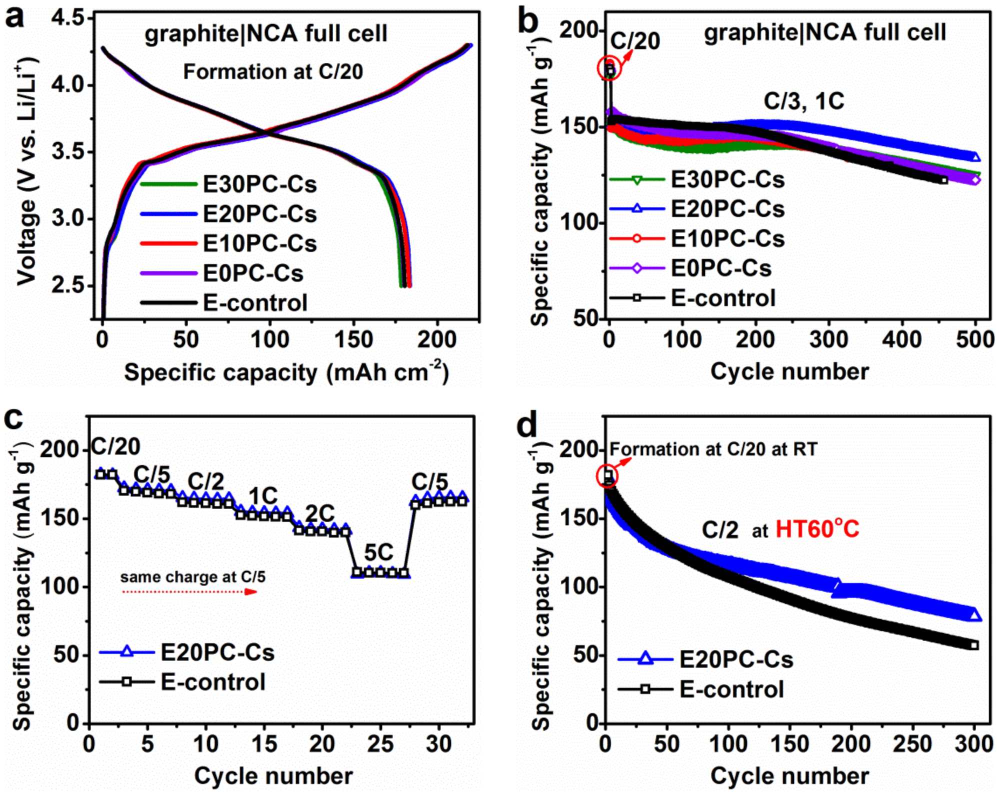
Graphite in E20PC-Cs electrolyte

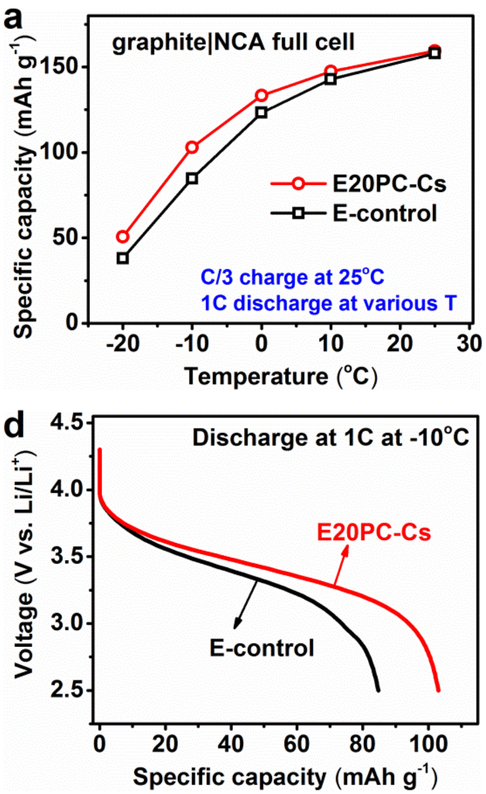


- ▪ 1.5 mAh/cm^2 graphite electrode
- ✓ E-control has slightly higher polarization than E20PC-Cs.
- ➢ For E-control, some Li dendrites form at lithiation current density of 0.5 mA/cm^2, and more Li dendrites form at higher current densities.
- ➢ For E20PC-Cs, no Li dendrites are found at lithiation current densities of 0.2 and 0.5 mA/cm^2, and much less Li dendrites are observed at current densities of 1.0 and 2.0 mA/cm^2.
- ✓ Cs$^+$ additive can suppress Li dendrite formation on graphite anode surface even at relatively high lithiation current densities.

Technical Accomplishments

Electrochemical performances of graphite||NCA full cells using Cs^+-electrolytes with various PC contents

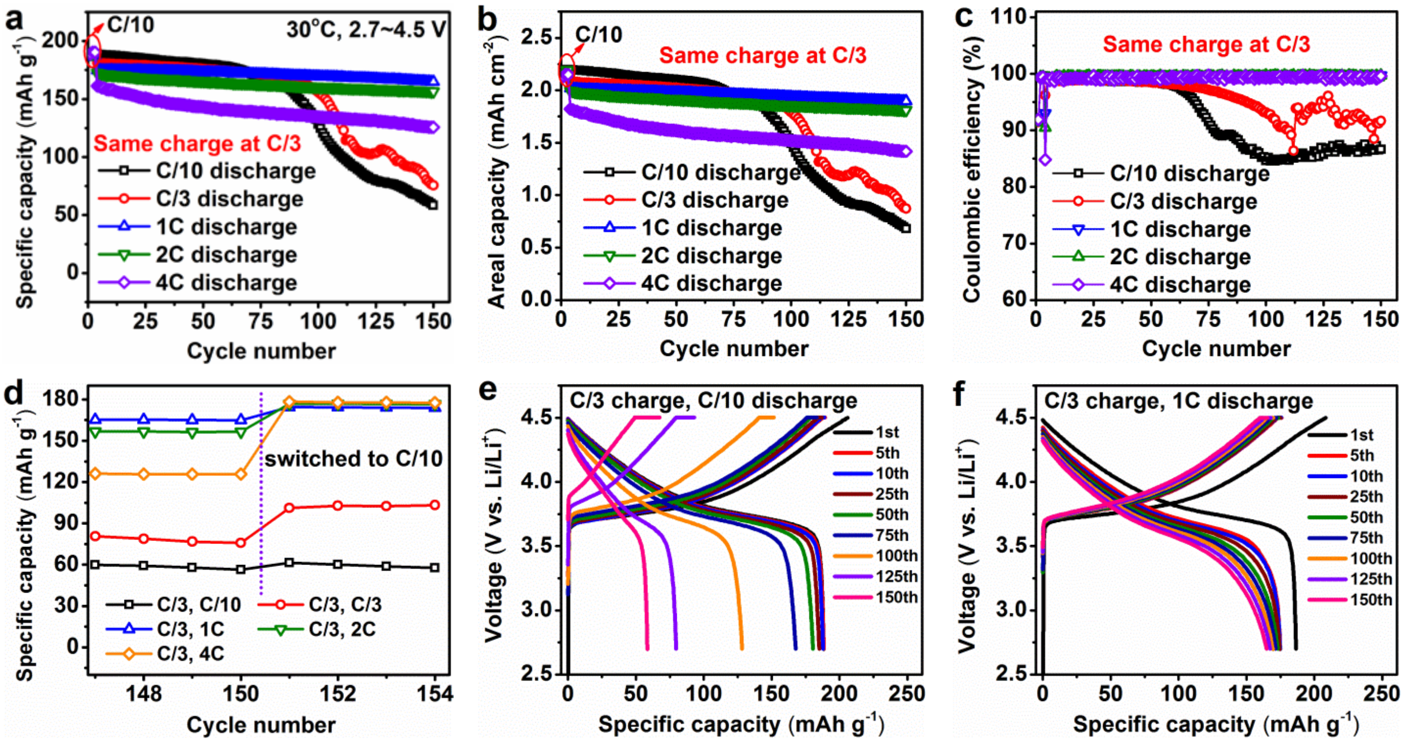




- 1C rate = 1.5 mA/cm^2
- ➢ E20PC-Cs shows better cycling stability at RT and 60°C and low-temperature discharge than E-control.
- ➢ Both E20PC-Cs and E-control show nearly the same rate capability.
- ✓ E20PC-Cs can replace the conventional electrolyte for Li-ion batteries.

Technical Accomplishments

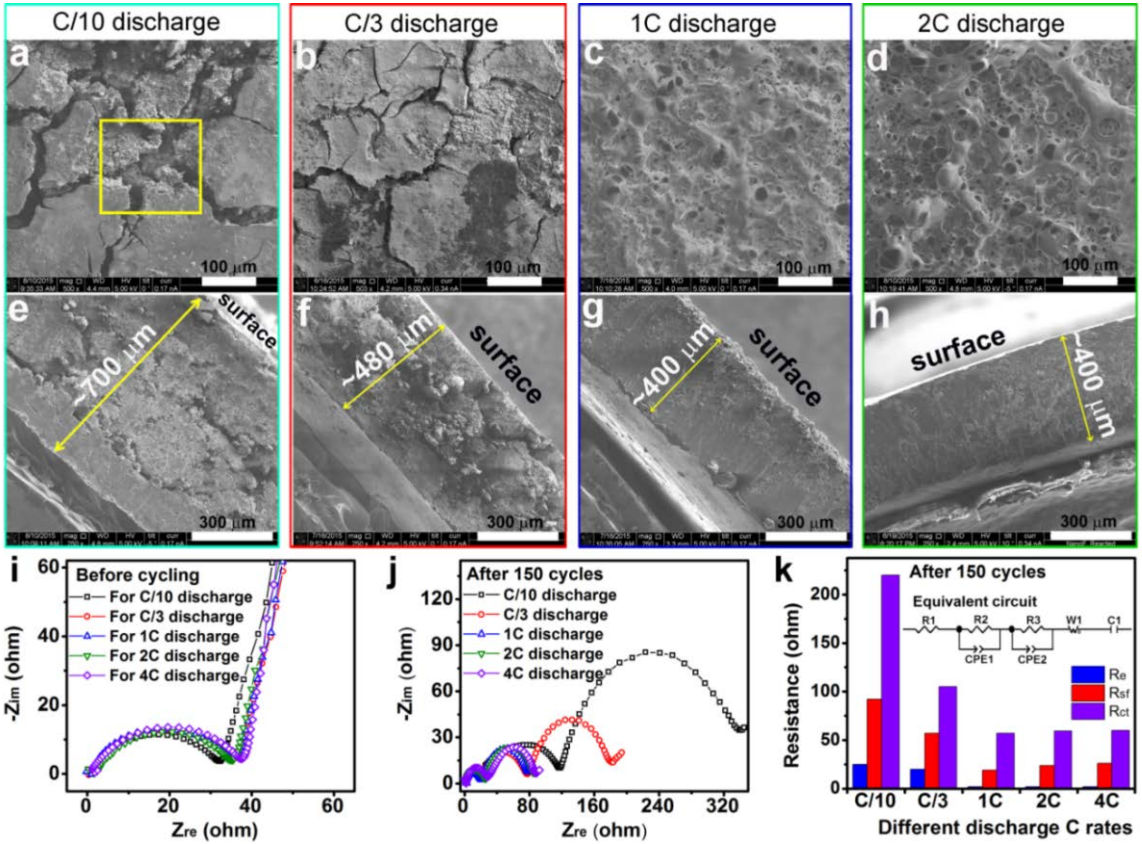
Effect of discharge rate on electrochemical performances of Li||NMC cells at 30°C



- NMC areal loading is 2.0 mAh/cm^2 so 1C rate = 2.0 mA/cm^2
- Conventional 1.0 M $LiPF_6$/EC-DMC (1:2 v/v) electrolyte
- Discharge rate has significant effect on cycling stability of Li metal cells.
- At the same charge rate, certain discharge rates (1C~2C or 2.0~4.0 mA/cm^2) lead to stable and long cycling performance of Li metal batteries.

Technical Accomplishments

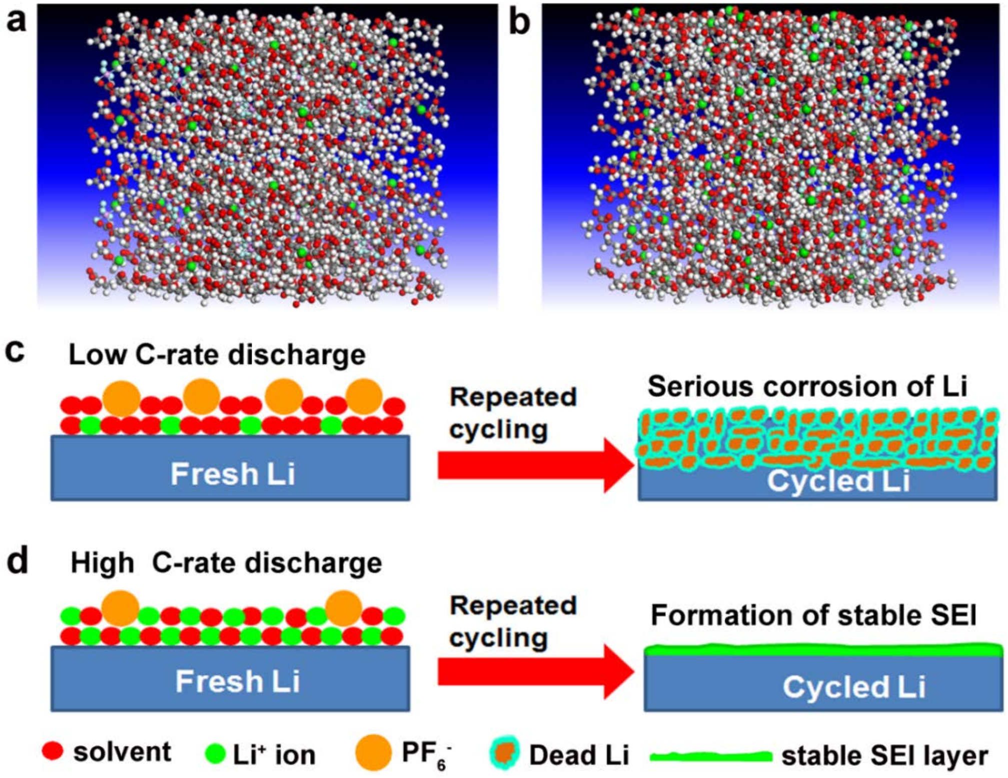
Effect of discharge rate on Li anode morphology and cell impedance of Li||NMC cells after 150 cycles at 30°C

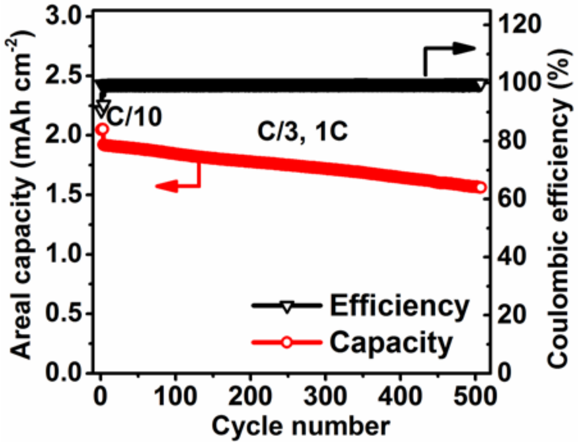


- Lower discharge rate results in more serious corrosion to Li metal anode, thicker SEI and higher cell impedance.
- Discharge at 1C and 2C leads to much less Li corrosion, nearly no change in Li thickness and low cell impedance.

Technical Accomplishments

Ab initio MD simulations of electrolyte conditions at Li anode surface and schematic illustration of SEI evolution



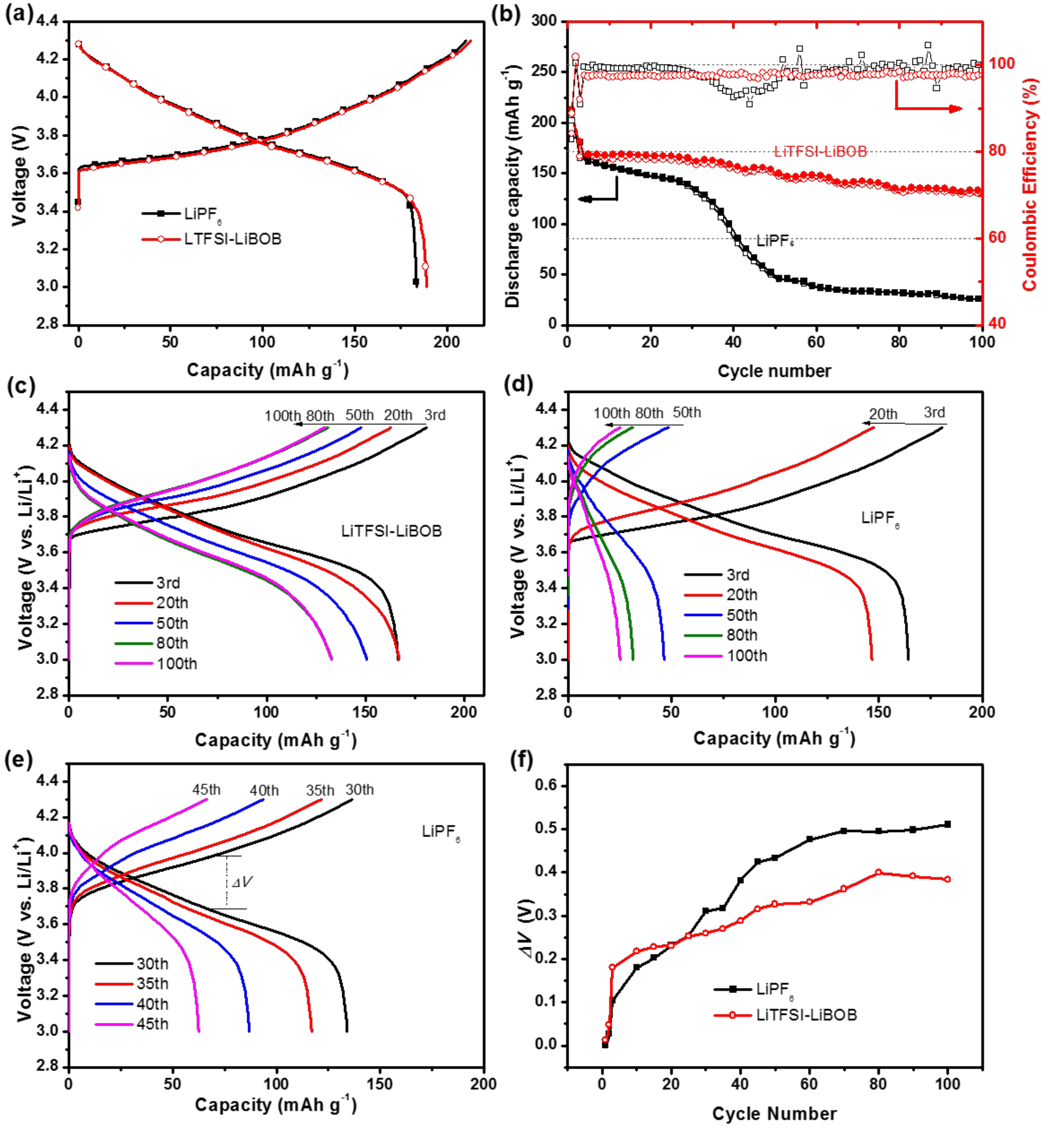


At C/3 charge and 1C discharge rate (2 mA cm^{-2}), Li||NMC cell has 81.6% capacity retention after 500 cycles and the Coulombic efficiency as high as 99.8%.

- Fast discharge results in high concentration of Li$^+$ at Li surface which reduces free solvent molecules in contact with Li metal → Alleviate parasitic reactions between Li and solvents and salt anion → Form stable SEI and protect Li metal anode during long-term cycling.

Technical Accomplishments

Effect of LiTFSI-LiBOB dual-salt/carbonate solvent electrolyte on fast chargeability of Li||NCA cells



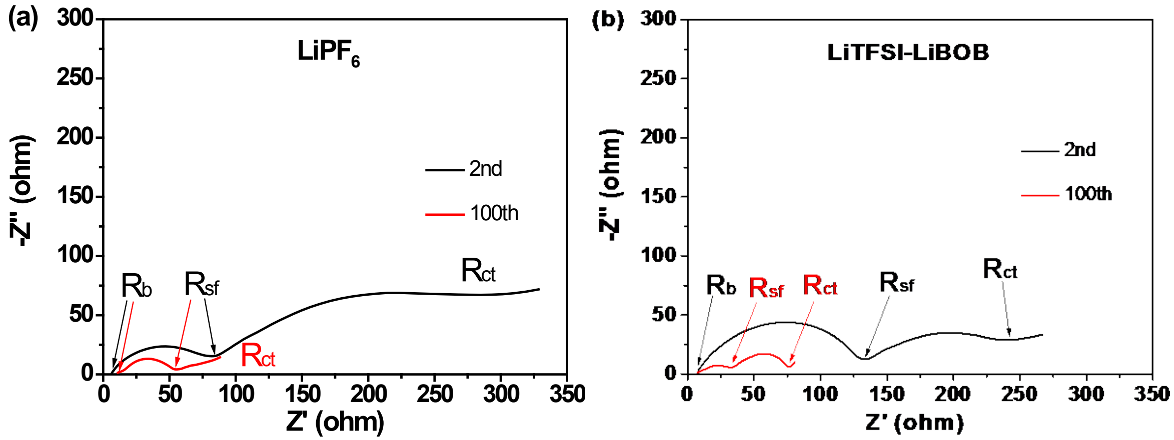
- NCA loading 1.5 mAh/cm^2
- 1C rate = 1.5 mA/cm^2
- After 2 formation cycles at C/10, the cells were cycled at 1C charging and discharging.

➢ LiTFSI-LiBOB electrolyte outperforms LiPF$_6$ electrolyte.

- Higher 1st cycle Coulombic efficiency (88.7% vs. 86.7%).
- Much better cycling stability at 1C charging and discharging.
- Much slower capacity fading.
- Higher capacity retention after 100 cycles (80% vs. 15%).
- Lower polarization between charging and discharging.

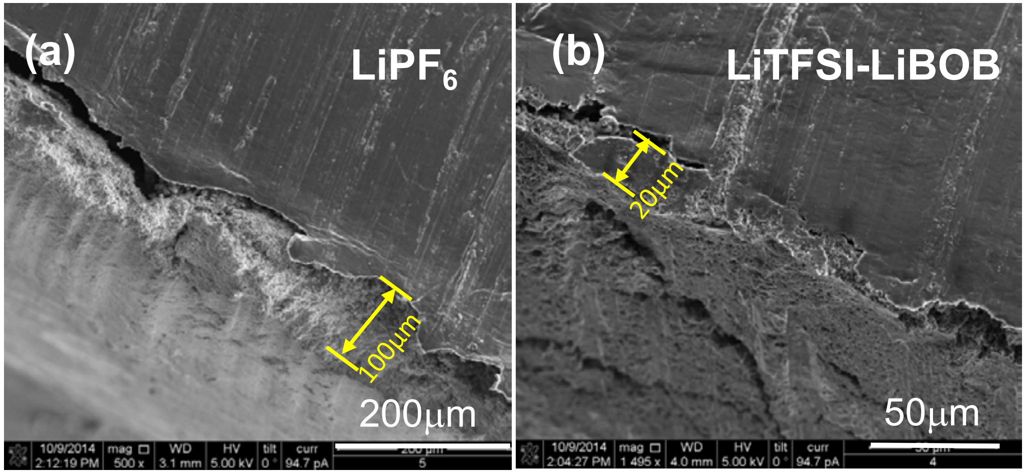
Technical Accomplishments

Analyses of cell impedance and Li morphology after cycling in $LiPF_6$ and LiTFSI-LiBOB electrolytes



- Bulk electrolyte resistance (R_b) for $LiPF_6$ cell increases after 100 cycles while that for LiTFSI-LiBOB keeps stable → The dual-salt forms compact SEI and prevent continuous electrolyte decomposition.

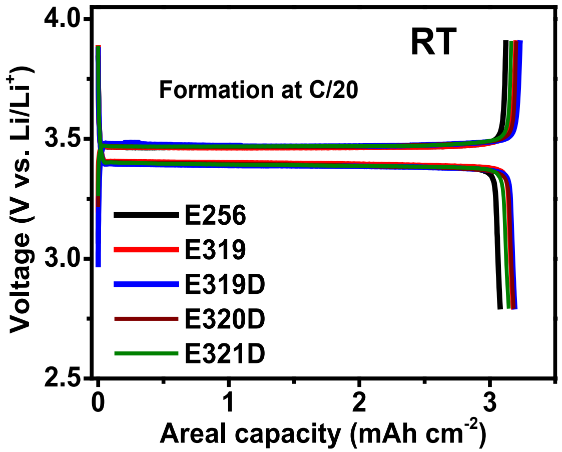
SEM images of Li metal anodes after 100 cycles

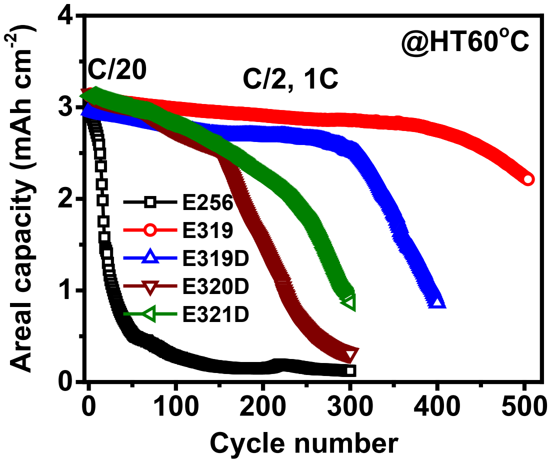


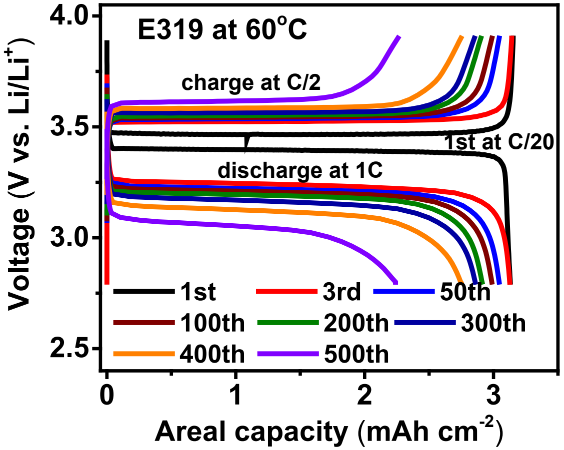
- LiTFSI-LiBOB electrolyte leads to much smaller R_{sf} and R_{ct} → More ionic conductive SEI formed.
- LiTFSI-LiBOB electrolyte forms much thinner SEI layer on Li anode.

Technical Accomplishments

Dual-salt electrolytes for long-term cycling of Li||LFP cells with a high areal loading LFP cathode at 60°C







- High areal loading LFP electrode of 3.0 mAh/cm^2 from LBNL.
- The dual-salt electrolytes show slightly higher capacity than the $LiPF_6$-based control electrolyte (E256).
- E319 electrolyte shows better cycling stability than other electrolytes at high charging rate (1.5 mAh/cm^2) and at elevated temperatures in high loading Li||LFP cells — 70% capacity retention after 500 cycles.

Collaboration and Coordination with Other Institutions

Partners:

- Argonne National Laboratory: Provided coated NCA cathode and graphite anode sheets for testing.

- Lawrence Berkeley National Laboratory: Provided coated LFP cathode for testing.

- Army Research Laboratory: Conducted EFM and ESI-MS analyses.

Remaining Challenges and Barriers

- Low Coulombic efficiency of Li metal anode during cycling.
- Cycling stability of Li metal batteries with high loading cathodes.
- Li metal dimension or volume change during charging and discharging cycles.

Future Work - FY2016/17

- Continue to evaluate electrolytes in 4-V Li-metal batteries with high cathode loading and at high current density cycling to achieve over 500 cycles.
- Develop ionic conductive protection layer on Li metal anode to reduce parasitic reactions between Li metal and electrolytes and improve Li Coulombic efficiency.
- Develop 3D substrates to maintain Li metal dimension during charging and discharging cycles.

Summary

1. Investigated the mechanism of Cs^+/PC on improved performances of graphite anode and Li dendrite suppression
    - Cs^+ additive and appropriate PC content in electrolytes have synergistic effects to form an ultrathin, uniform, compact and robust SEI layer on graphite surface.
    - This high quality SEI layer suppresses Li dendrites on graphite anode and enhances long-term operation of Li-ion full cells.
2. Optimized the charge/discharge protocol for the improved performance of Li metal batteries
    - The optimized cycling protocol of slow charge and fast discharge can form a transient high-concentration electrolyte layer on Li surface to protect Li metal anode and to enable sustainable operation of Li metal batteries.
3. Developed dual-salt electrolytes to improve charge rate and long-term cycling stability of Li metal batteries
    - LiTFSI-LiBOB and other dual-salt electrolytes with or without additives can form highly conductive SEI, protect Li metal, enable long cycle life and fast chargeability of Li metal batteries.

Acknowledgments

- ✓ Support from the DOE/OVT/BMR program is greatly appreciated.

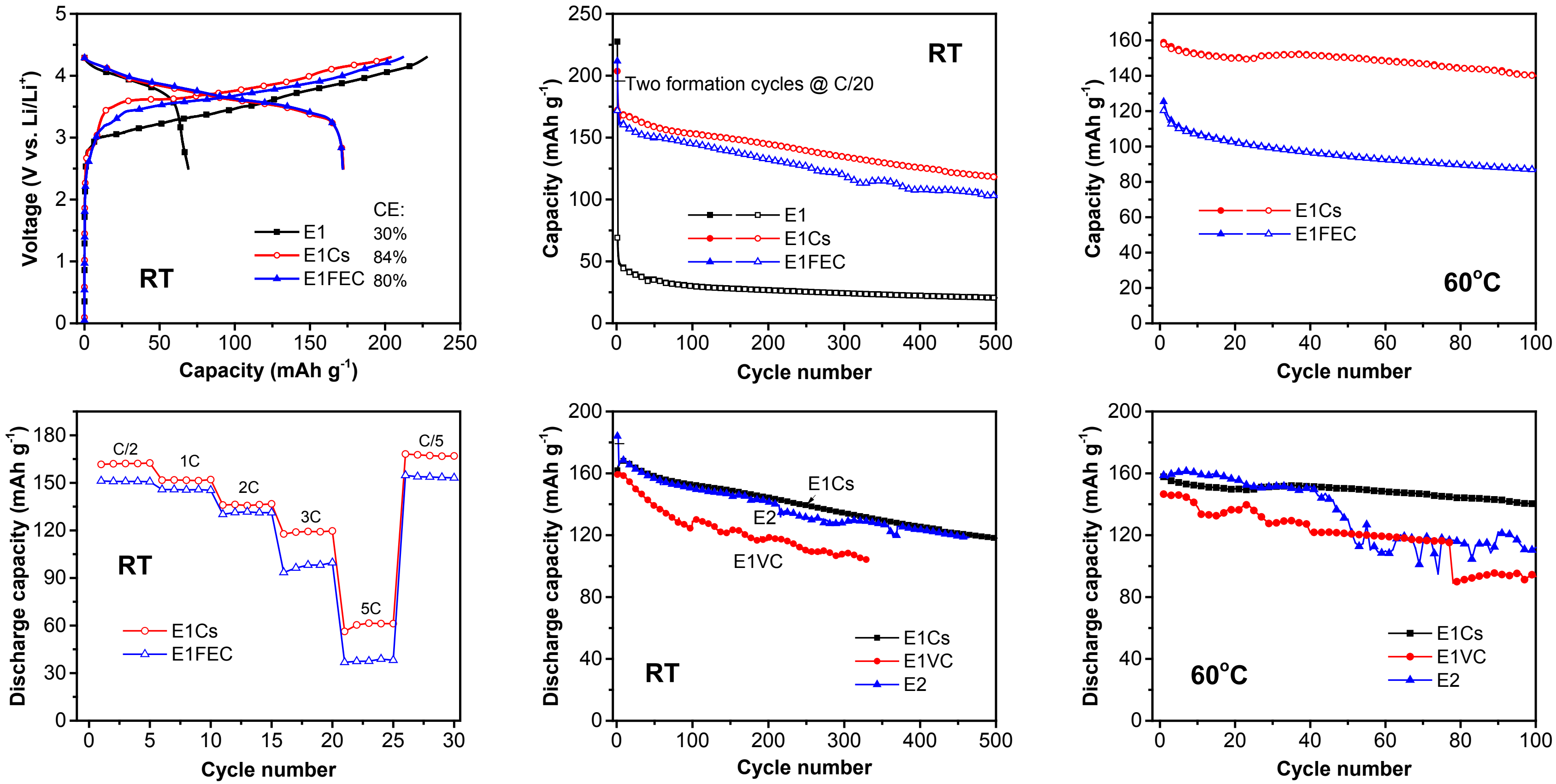
- ✓ Team Members:

  Hongfa Xiang, Jianming Zheng, Donghai Mei,
  Pengfei Yan, Liang Xiao, Ruiguo Cao, Jiangfeng Qian,
  Priyanka Bhattacharya, Chongmin Wang, Mark Bowden,
  Mark Engelhard, Sarah Burton, Zihua Zhu

Technical Backup Slides

Technical Accomplishments

Electrochemical performances of graphite||NCA full cells with various electrolytes

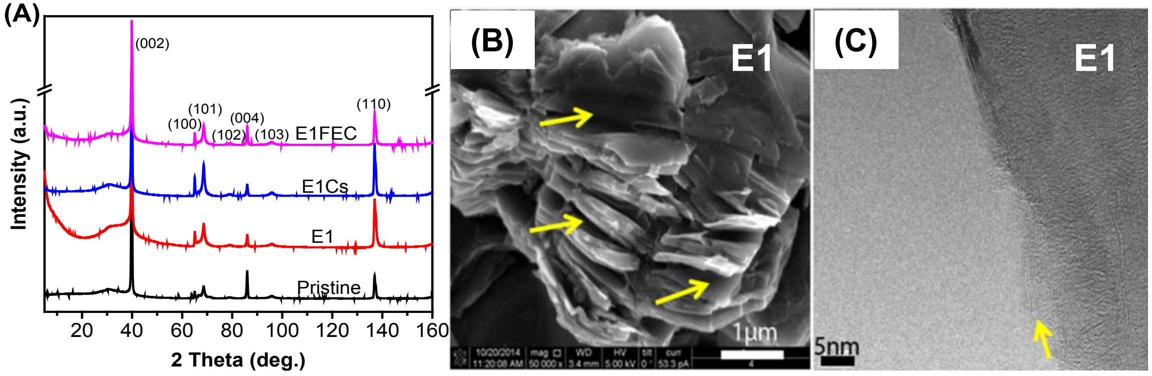


E1 = 1.0 M $LiPF_6$ in EC-PC-EMC (5:2:3 by wt.)   E2 = 1.0 M $LiPF_6$ in EC-EMC (3:7 by vol.)

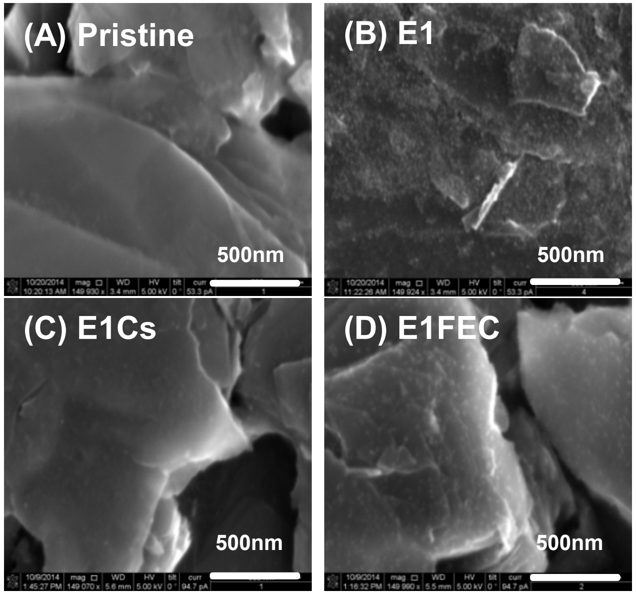
- ✓ Cs^+ additive enhances the performances of graphite||NCA full cells even with PC in electrolyte.

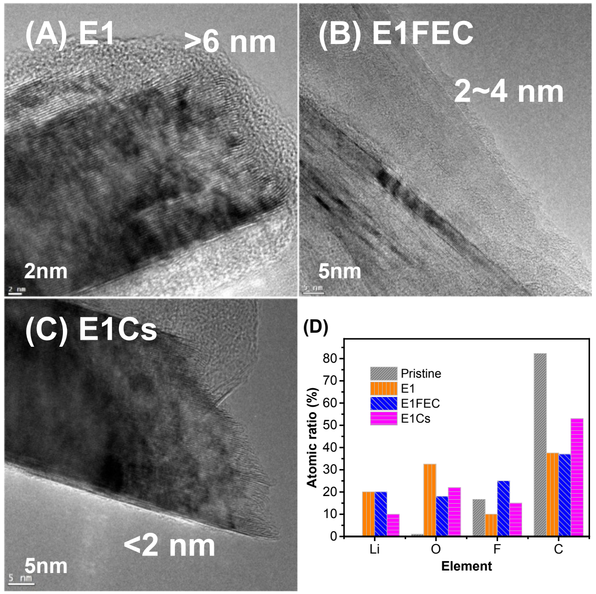
Technical Accomplishments

Characterization of graphite anodes from half cells after charging to 0.3 V at the 1st formation cycle



- Broad peak below 20° in XRD for graphite from E1 suggests partial exfoliation of graphite at the edges of the particles.
- Yellow arrows in SEM and TEM also indicate partial exfoliation of graphite at the edges.

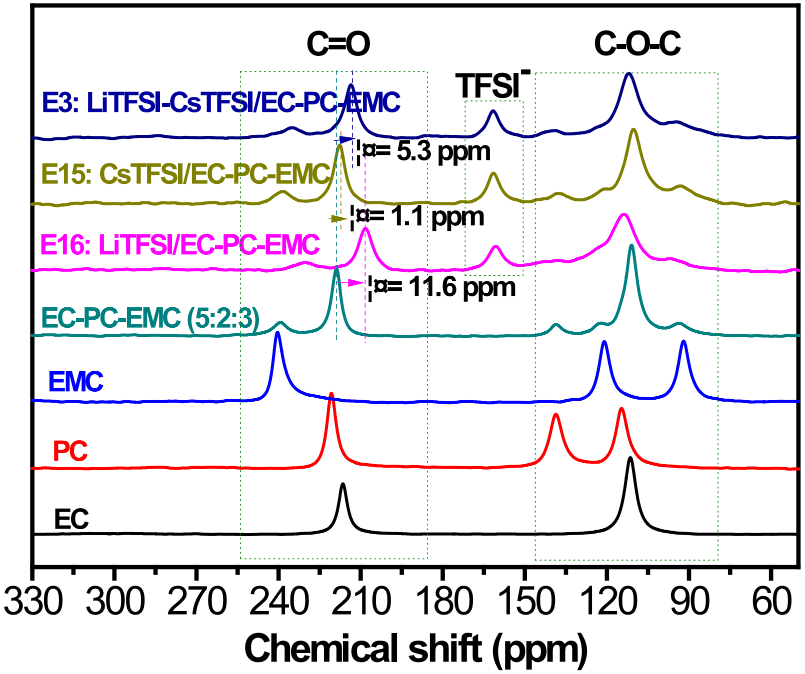




- ✓ **Cs⁺-containing electrolyte E1 forms an ultrathin and uniform SEI on graphite, which contains more organic species.**
- Electrolytes without additive or with FEC form thicker SEI with small sports.

Technical Accomplishments

^{17}O NMR characterization of Li^+ and Cs^+ solvation in electrolytes

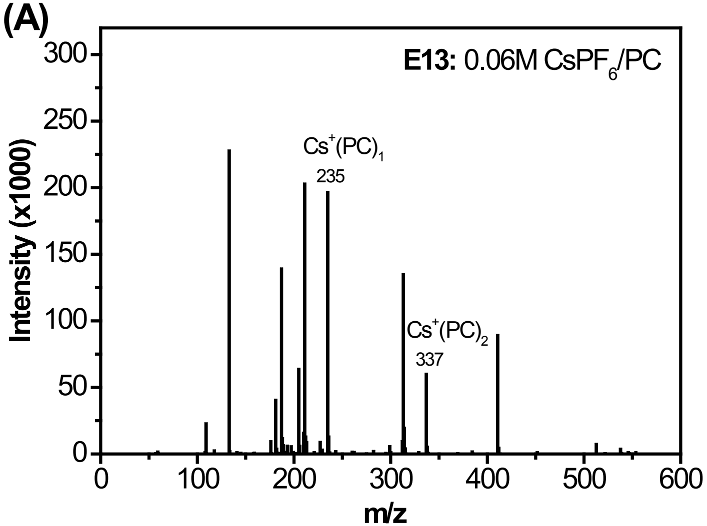


- Cs^+ causes much less displacement in the C=O chemical shift ($\Delta\delta$ = 1.1 ppm) than does Li^+ ($\Delta\delta$ = 11.6 ppm).
- ➢ Cs^+ acts as a much weaker Lewis acid, and its solvation number with cyclic carbonate solvents should be lower than that of Li^+,
- Consistent with literature reports that the coordination number for Li^+ in nonaqueous solvents is normally ~4 and for Cs^+ is <2.
- ✓ Li^+ is more like to be solvated by cyclic carbonate molecules than Cs^+.

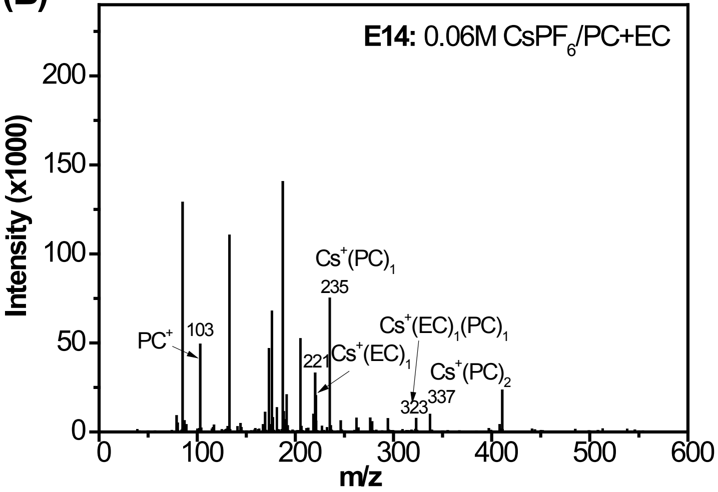
Technical Accomplishments

ESI-MS characterization of Li^+ and Cs^+ solvation in electrolytes

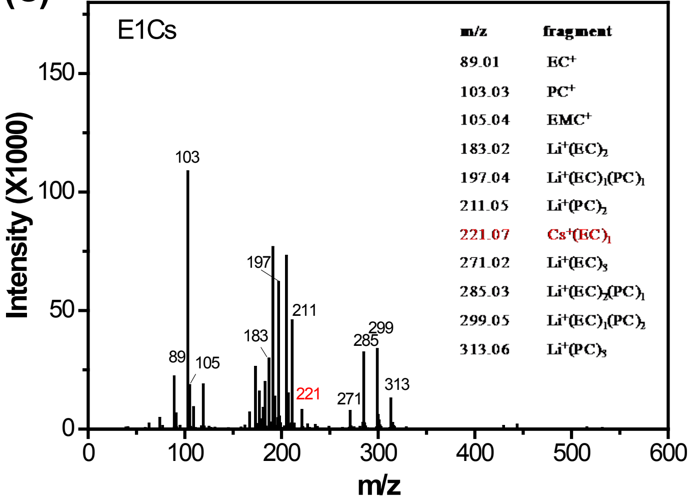
(A)



(B)



(C)

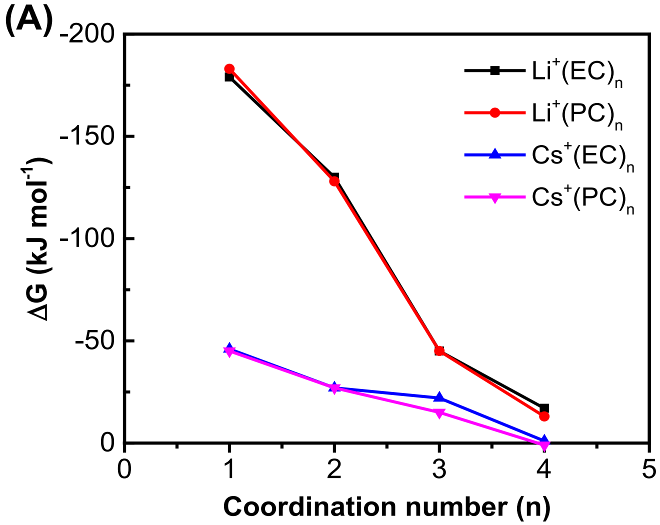


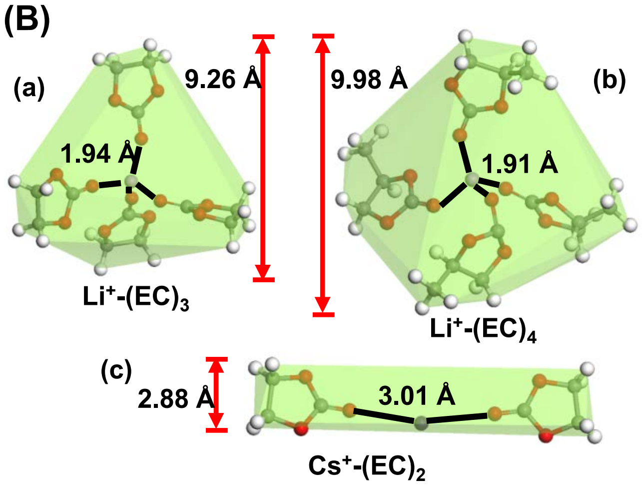
m/z	fragment
89.01	EC^+
103.03	PC^+
105.04	EMC^+
183.02	$Li^+(EC)_2$
197.04	$Li^+(EC)_1(PC)_1$
211.05	$Li^+(PC)_2$
221.07	$Cs^+(EC)_1$
271.02	$Li^+(EC)_3$
285.03	$Li^+(EC)_2(PC)_1$
299.05	$Li^+(EC)_1(PC)_2$
313.06	$Li^+(PC)_3$

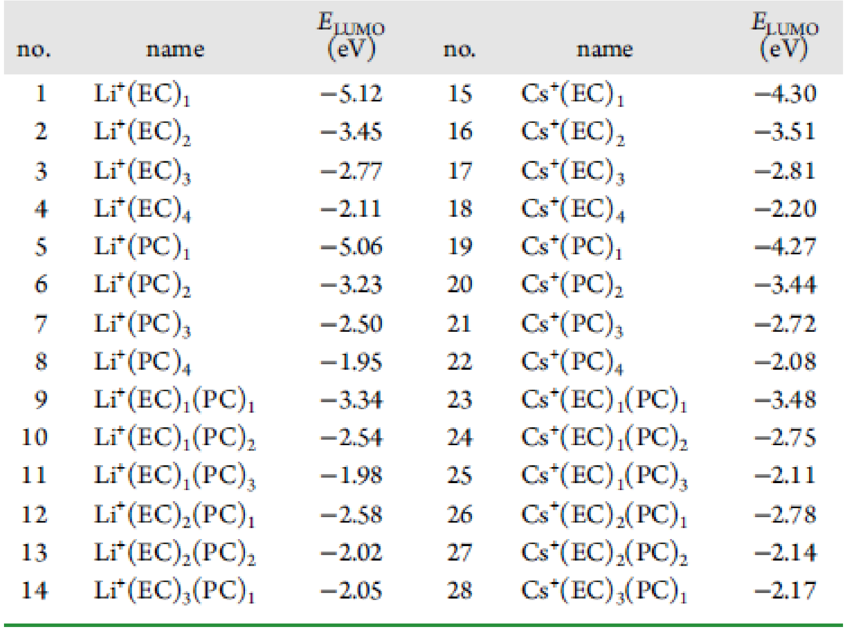
- ESI-MS: Electrospray ionization mass spectroscopy.
- ▪ Literature reports that Li^+ prefers to coordinate with PC over EC. Cs^+ has the same trend.
- ▪ In E1Cs, Cs^+-$(EC)_1$ of m/z 221 exists but no Cs^+-$(PC)_1$ and Cs^+-$(PC)_2$ are present.
- ➢ PC molecules are scavenged by Li^+ coordination.
- ✓ Cs^+ is passively “preferably” solvated by EC molecules to for Cs^+-$(EC)_1$ and Cs^+-$(EC)_2$.

Technical Accomplishments

Computational calculations on molecular energies and structures of Li$^+$- and Cs$^+$-solvates







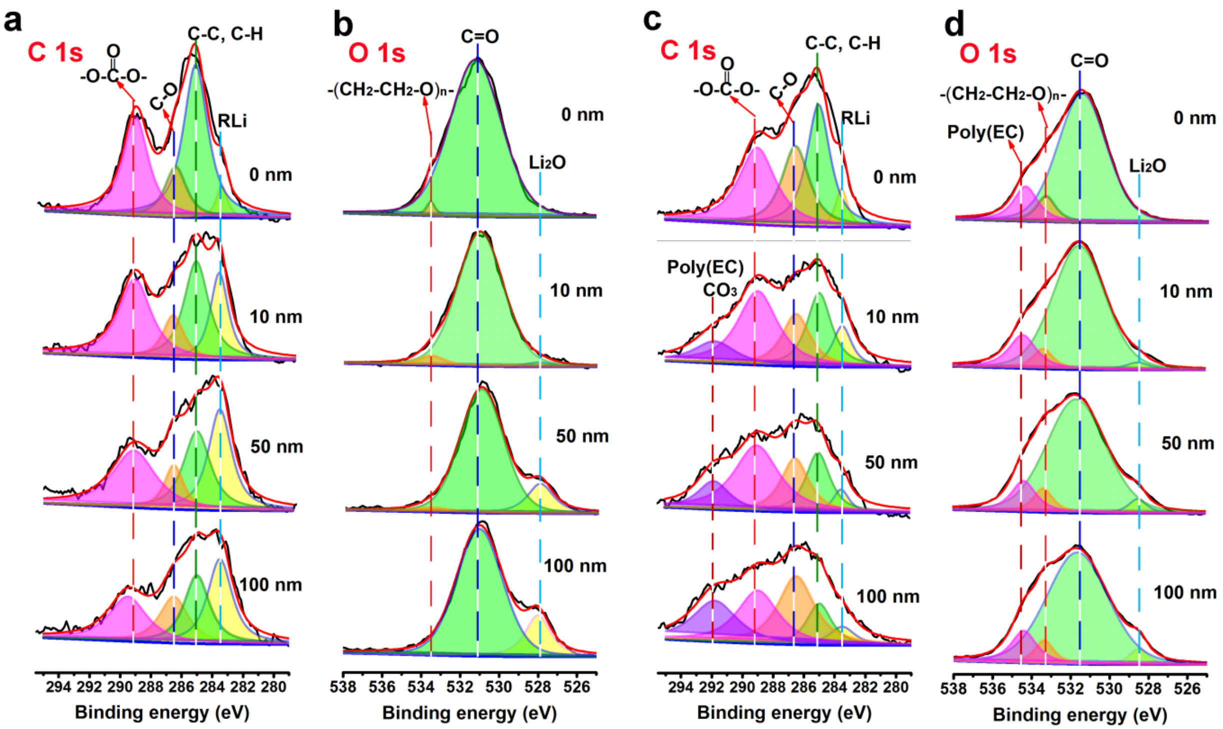
no.	name	E_{LUMO} (eV)	no.	name	E_{LUMO} (eV)
1	Li$^+$(EC)$_1$	−5.12	15	Cs$^+$(EC)$_1$	−4.30
2	Li$^+$(EC)$_2$	−3.45	16	Cs$^+$(EC)$_2$	−3.51
3	Li$^+$(EC)$_3$	−2.77	17	Cs$^+$(EC)$_3$	−2.81
4	Li$^+$(EC)$_4$	−2.11	18	Cs$^+$(EC)$_4$	−2.20
5	Li$^+$(PC)$_1$	−5.06	19	Cs$^+$(PC)$_1$	−4.27
6	Li$^+$(PC)$_2$	−3.23	20	Cs$^+$(PC)$_2$	−3.44
7	Li$^+$(PC)$_3$	−2.50	21	Cs$^+$(PC)$_3$	−2.72
8	Li$^+$(PC)$_4$	−1.95	22	Cs$^+$(PC)$_4$	−2.08
9	Li$^+$(EC)$_1$(PC)$_1$	−3.34	23	Cs$^+$(EC)$_1$(PC)$_1$	−3.48
10	Li$^+$(EC)$_1$(PC)$_2$	−2.54	24	Cs$^+$(EC)$_1$(PC)$_2$	−2.75
11	Li$^+$(EC)$_1$(PC)$_3$	−1.98	25	Cs$^+$(EC)$_1$(PC)$_3$	−2.11
12	Li$^+$(EC)$_2$(PC)$_1$	−2.58	26	Cs$^+$(EC)$_2$(PC)$_1$	−2.78
13	Li$^+$(EC)$_2$(PC)$_2$	−2.02	27	Cs$^+$(EC)$_2$(PC)$_2$	−2.14
14	Li$^+$(EC)$_3$(PC)$_1$	−2.05	28	Cs$^+$(EC)$_3$(PC)$_1$	−2.17

- Cs$^+$-(EC)$_1$ and Cs$^+$-(EC)$_2$ have planar structure.
- Li$^+$-(PC)$_3$ and Li$^+$-(PC)$_4$ have tetrahedron structure.
- Cs$^+$-(EC)$_1$ and Cs$^+$-(EC)$_2$ have lower LUMO energies than Li$^+$-(PC)$_3$ and Li$^+$-(PC)$_4$.

✓ Cs$^+$-(EC)$_m$ (m=1,2) solvates reduce earlier than Li$^+$-(PC)$_n$ (n=3,4)

Technical Accomplishments

XPS analysis on cycled Li anode surfaces from Li||NMC cells discharged at two rates



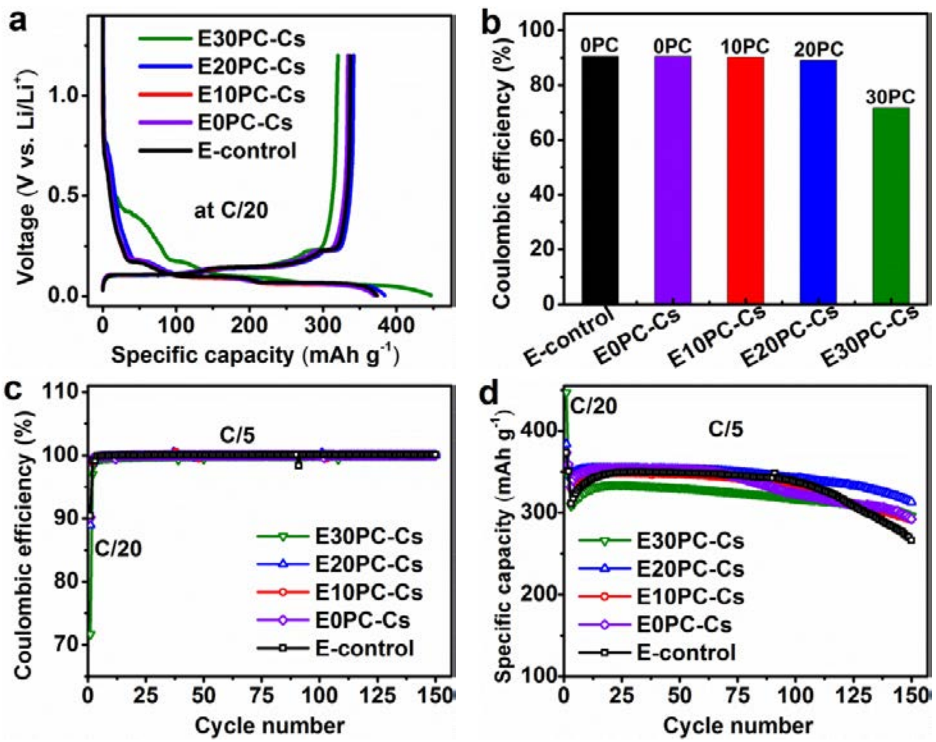
C/3 charge, C/10 discharge

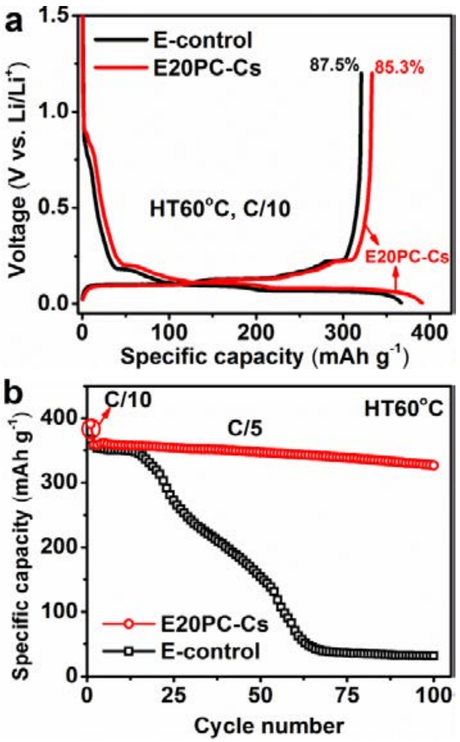
C/3 charge, 2C discharge

- The SEI formed at slow discharge rate (C/10) contains mainly lithium alkylcarbonate, Li_2O, LiF and $LiPF_x$.
- The SEI formed at fast discharge rate (2C) mainly contains poly(ethylene carbonate) from EC polymerization and less C/F/P contents (i.e. less electrolyte decompositions.

Technical Accomplishments

Effect of PC content on graphite in half cells using electrolytes with Cs+ and various PC contents



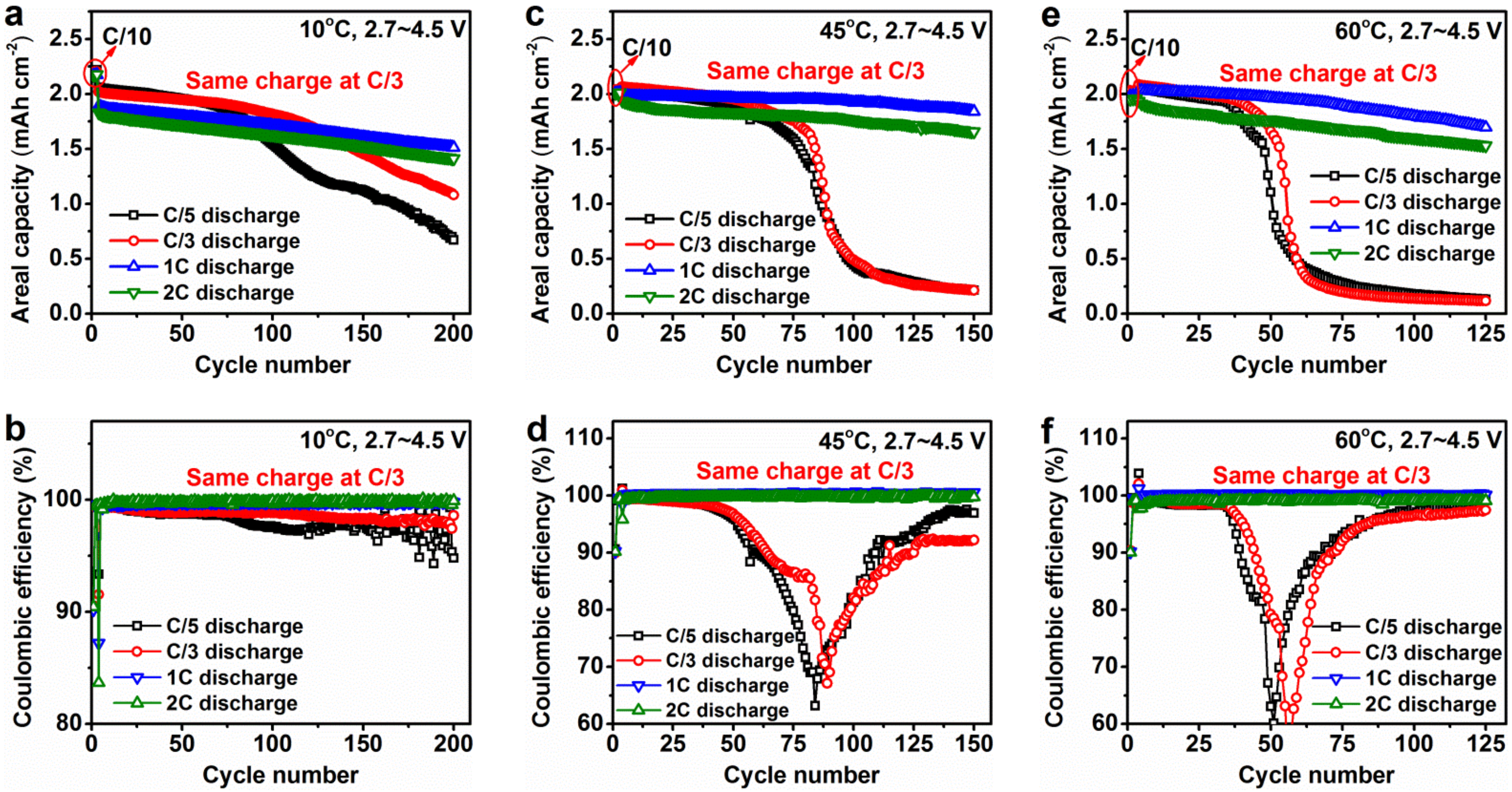


- ➢ 20% PC in solvent mixture is the optimal content in EC-PC-EMC with 30 wt% EC.
- ➢ E20PC-Cs allows graphite anode to show the best RT cycling in Li||graphite half cells.

- ➢ E20PC-Cs (with 30EC-20PC-50EMC) leads graphite anode to cycle stably in Li||graphite half cells.

Technical Accomplishments

Effect of discharge rate on electrochemical performances of Li||NMC cells at other temperatures

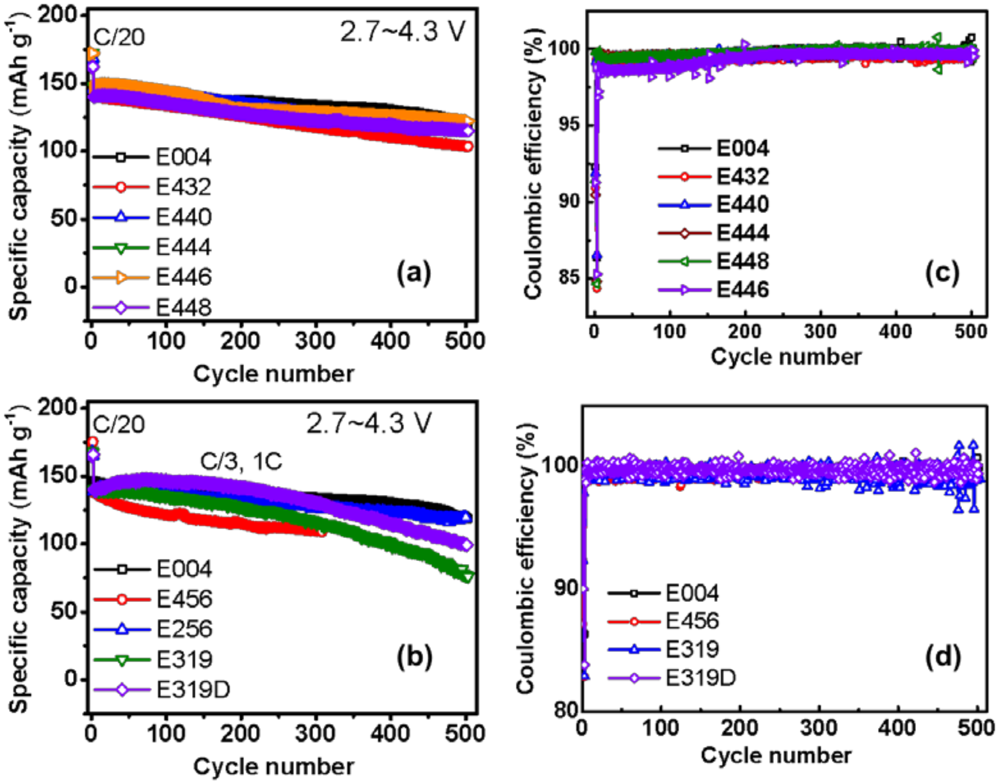


- ➢ Same as cycling at 30°C, discharge at 1C~2C rate also results in stable and long cycling performance of Li metal batteries at other temperatures from 10 to 60°C.
- ➢ 1C discharge rate is good for discharge at elevated temperatures.
- ➢ Increasing temperature leads to shorter cycle life due to increased side reactions.

Technical Accomplishments

Long-term cycling stability of Li||NMC442 cells using different electrolytes

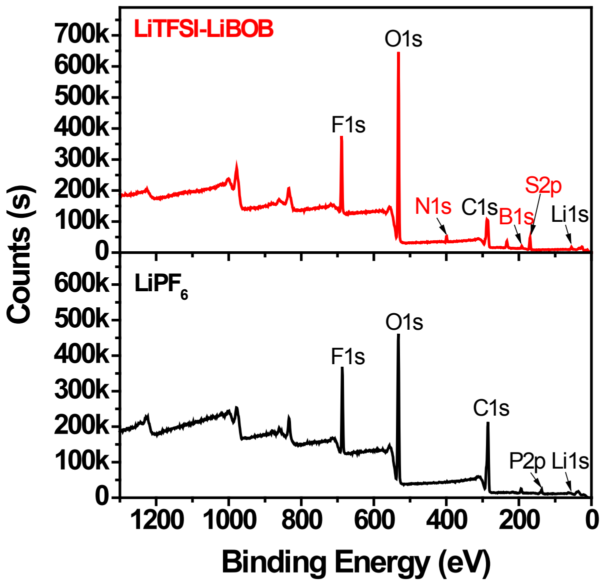
- Areal loading of NMC442 electrode is 2.0 mAh/cm^2 – medium high
- 1C rate = 2.0 mA/cm^2
- Control electrolytes – E004, E256 and E448 based on LiPF$_6$ in EC/EMC
- E432, E440, E444 and E446 are LiPF$_6$ + CsPF$_6$ in EC/PC/EMC
- E319, E319D and E456 are based on dual-salts or other additives

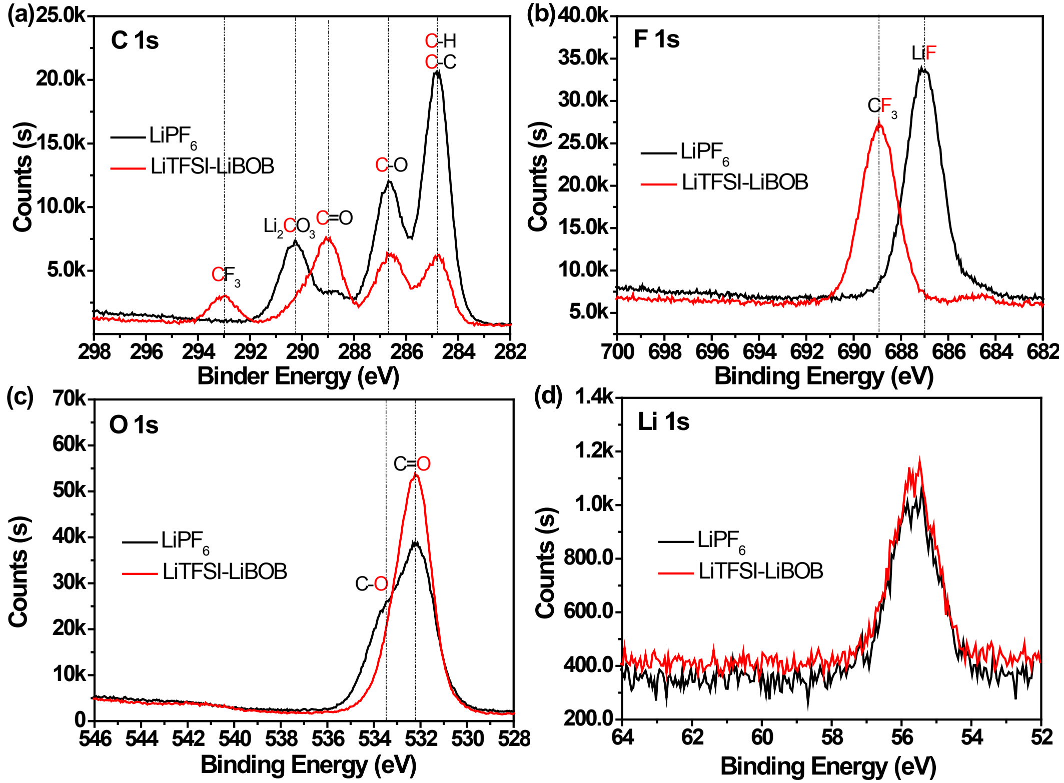


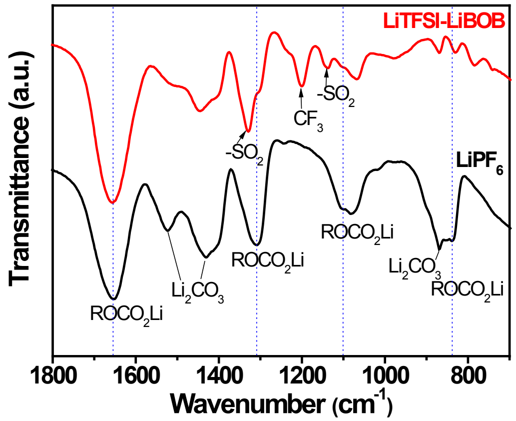
- ➢ Two control electrolytes (E004 and E256) and two studied electrolytes (E446 and E448) show stable cycling for 500 cycles before the capacity retention reaches 80%.
- ➢ Nearly all of these electrolytes have Coulombic efficiencies above 98% after the first two formation cycles.

Technical Accomplishments

Characterization of SEI layers on cycled Li metal anodes from two electrolytes by XPS and FTIR







- The SEI from LiTFSI-LiBOB electrolyte contains different components than that from $LiPF_6$.
- Mainly from the decompositions of the salt anions BOB^- and $TFSI^-$.