Dendrite Prevention in Li metal and Li Ion Batteries

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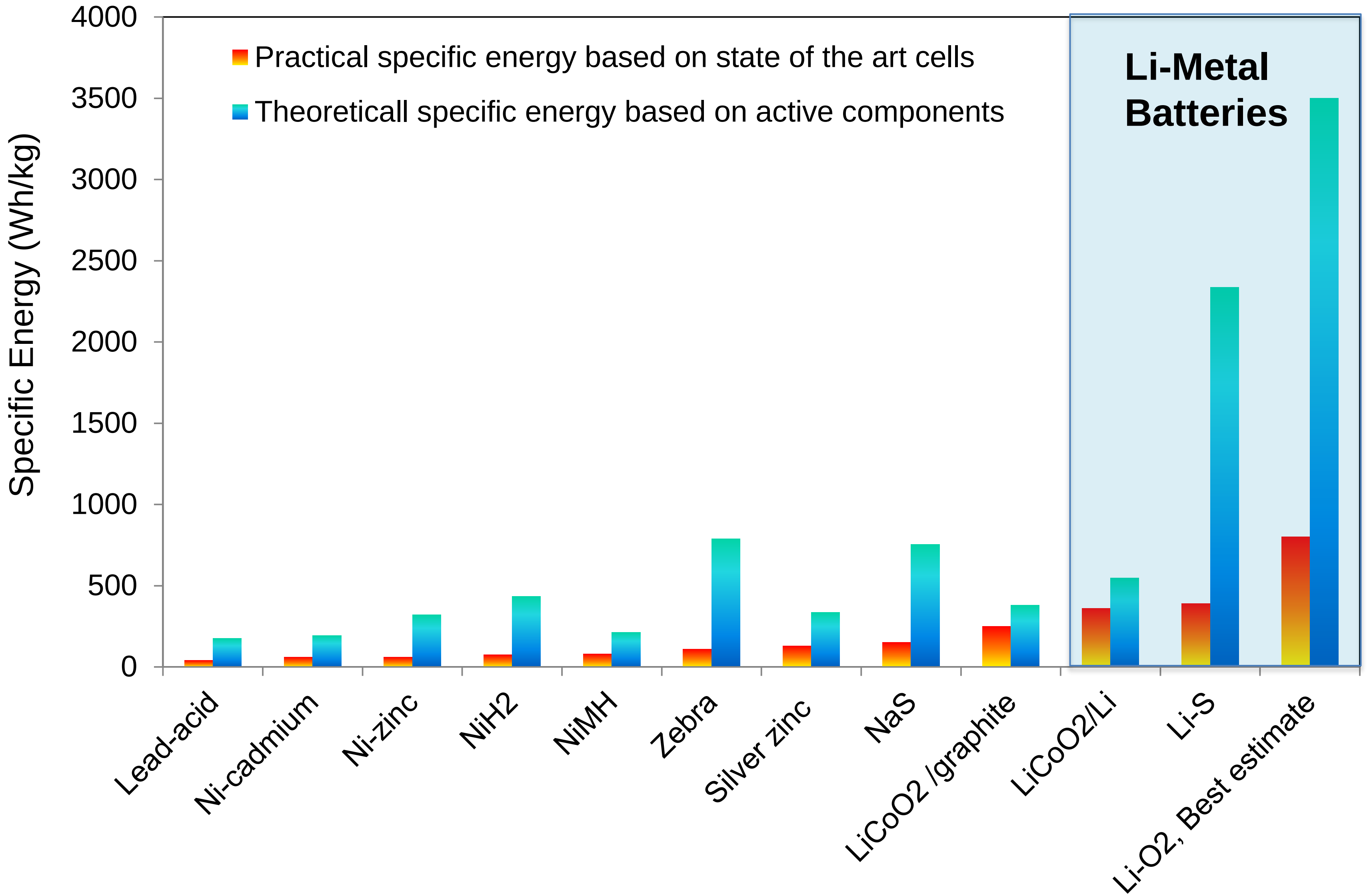
Outline

1. Introduction
2. Self-Healing Electrostatic Shield (SHES) Mechanism
3. Effects of Cs^+ Additive on Li Deposition
4. Dendrite-Free Li Deposition with High Coulombic Efficiency
5. Summary

1. Introduction

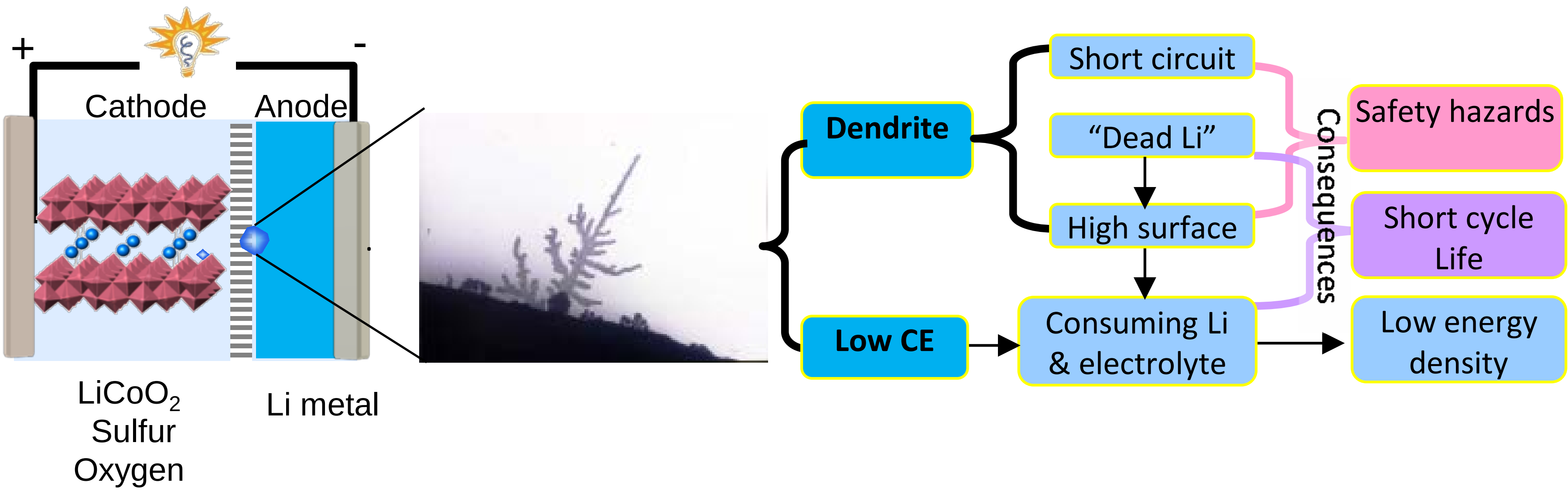
Comparison of Specific Energy of Various Batteries



Challenges on Li Metal Batteries

Two main barriers :

1. Dendrite growth; 2. Low Coulombic efficiency



(a) Li metal batteries

(b) The typical morphology of Li dendrite (Chianelli,1976)

(c) Main problems related with dendrite and low Coulombic efficiency.

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2. Self-Healing Electrostatic Shield (SHES) Mechanism

Foundation: Nernst Equation $\boldsymbol{E_{Red} = E^{\emptyset}_{Red} - \frac{RT}{zF} ln \frac{\alpha_{Red}}{\alpha_{Ox}}}$

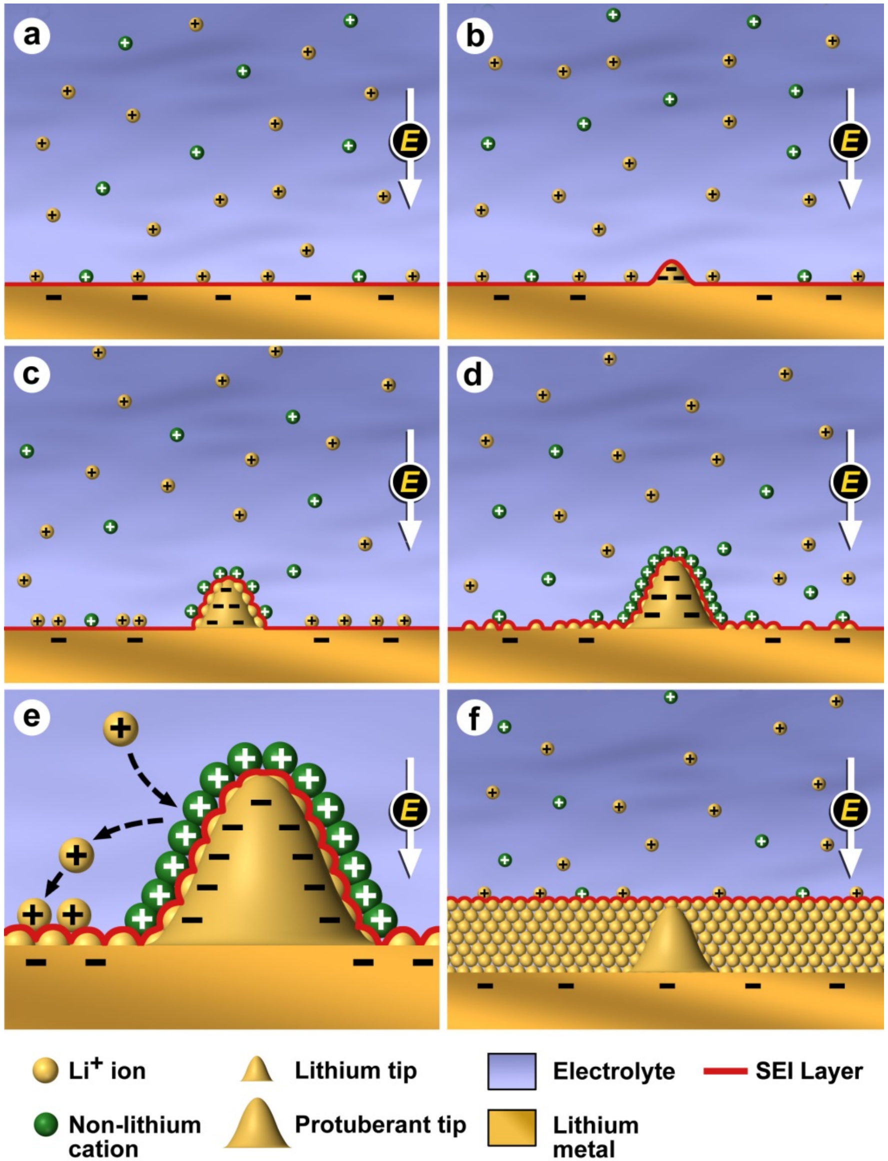
The effective reduction potentials of selected cations

	Li^+	Cs^+	Rb^+
Stand reduction potential (1M)	-3.040 V	-3.026 V	-2.980 V
Effective reduction potential at 0.05M*	-	-3.103 V	-3.06 V
Effective reduction potential at 0.01M*	-	-3.144 V	-3.098 V

*Assume the activity coefficient of additive species equals 1 at dilute condition.

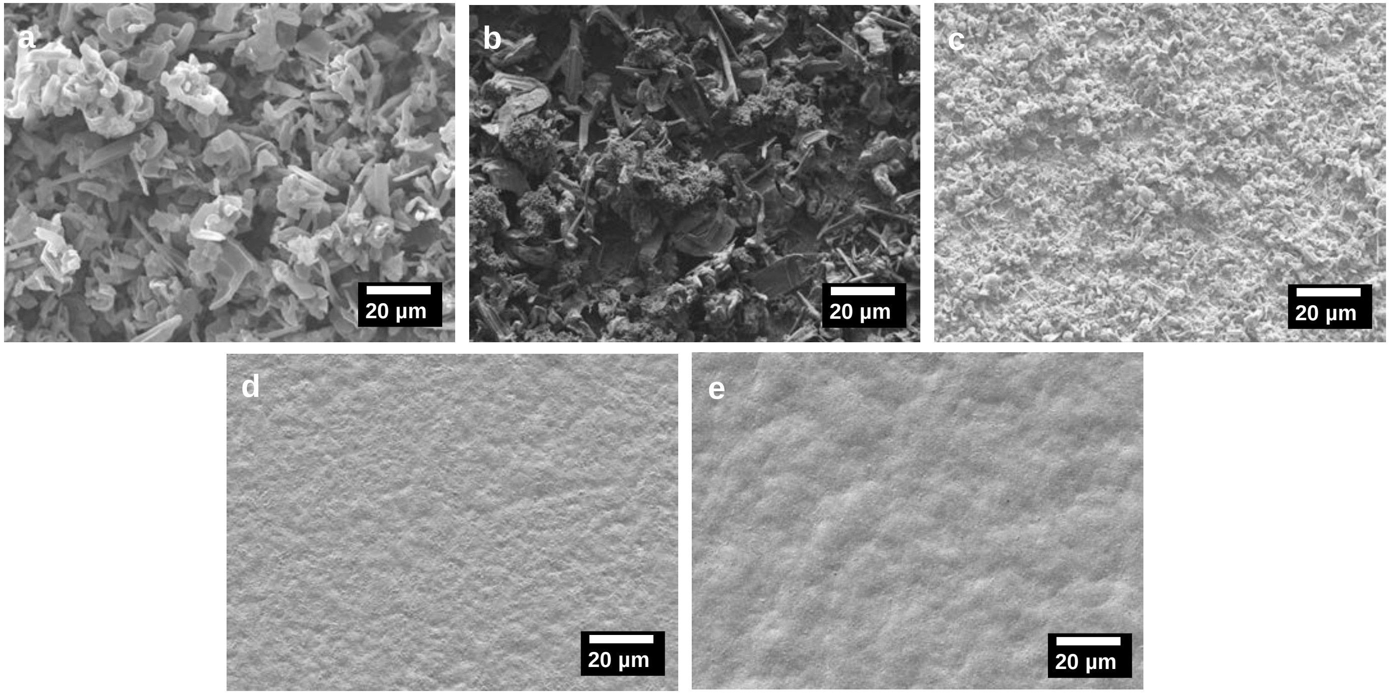
- **An cation may have an E_{Red} lower than those of Li^+.**

Self-Healing Electrostatic Shield (SHES) Mechanism



- SEI layer will form once Li metal contact liquid electrolyte.
- Li ions can diffuse through SEI layer and deposit on Li surface
- SHES additives (such as Cs ions) will stay outside of SEI layer
- Formation and stability of SEI layer are the main factors affecting the Coulombic efficiency of Li deposition/stripping processes.

3. Effect of $CsPF_6$ Additive on The Morphology of Li Deposition

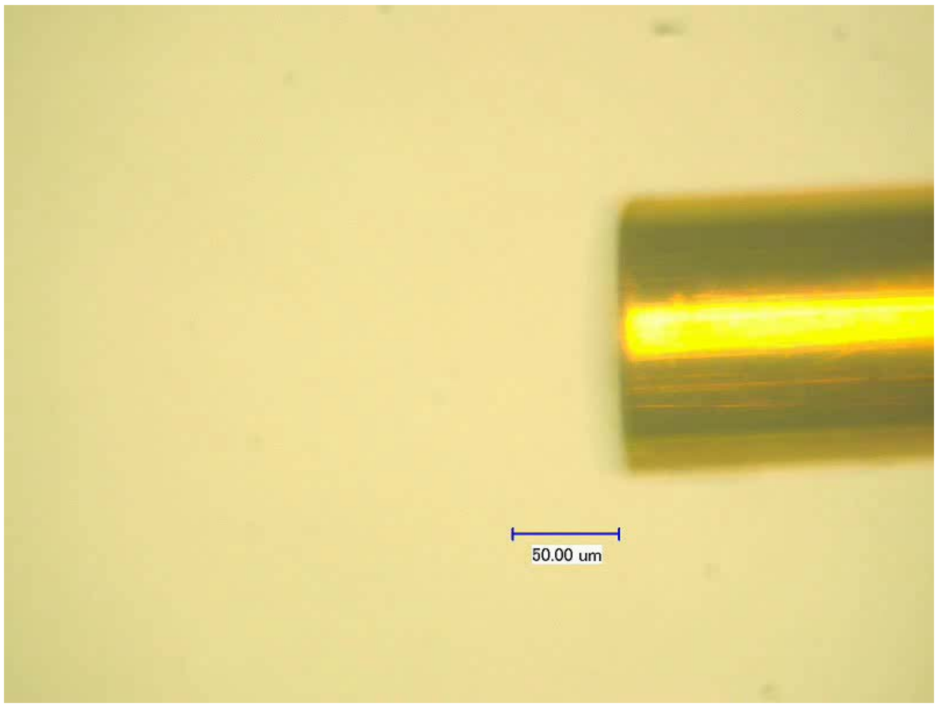


- Control electrolyte: 1 M $LiPF_6$ in PC.
- $CsPF_6$ concentration in the electrolyte: (**a**) 0 M, (**b**) 0.001 M, (**c**) 0.005 M, (**d**) 0.01 M, and (**e**) 0.05 M.

➢ **Cs^+ additive can effectively suppress Li dendrite growth.**

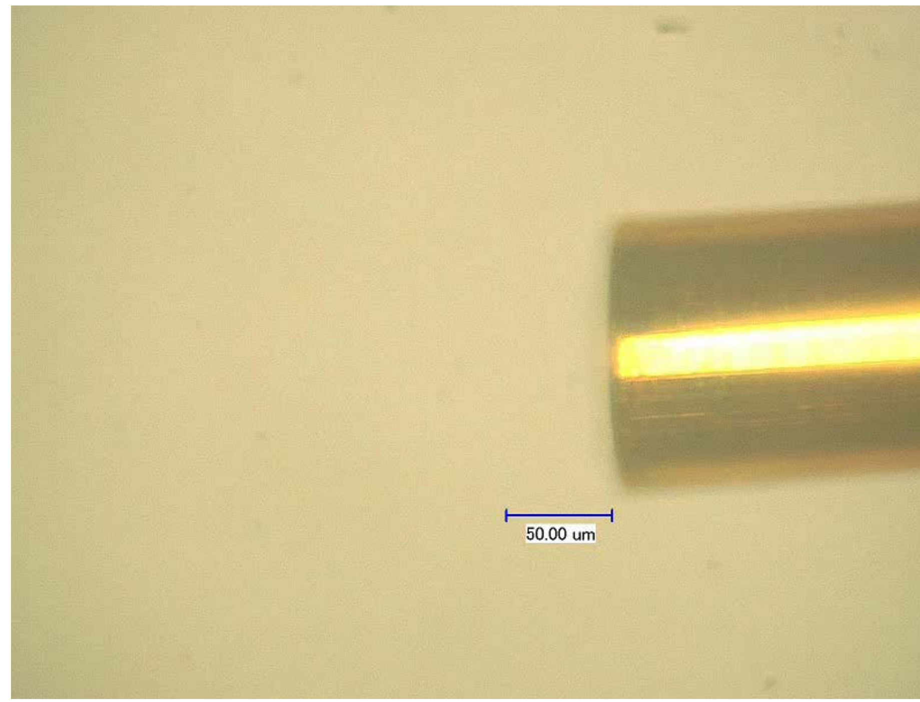
In-Situ Observation of Li Deposition

Li deposition without additive
(1M $LiPF_6$ in PC)



➢ Needle-like dendritic growth perpendicular to the surface

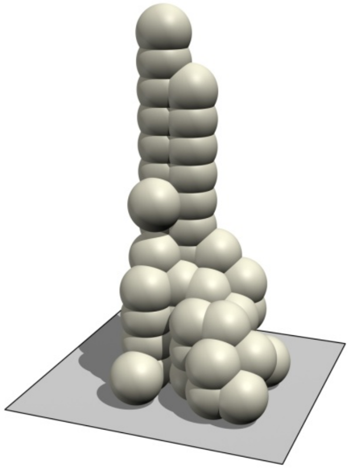
Li deposition with additive
(1M $LiPF_6$ in PC with 0.05M $CsPF_6$)



➢ Dense film growth

Simulation of Li Growth in Different Electrolyte

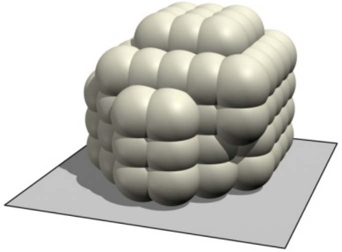
1M $LiPF_6$ solution in PC



➢ Needle-like dendritic growth

Li_deposition_no_add.avi

1M $LiPF_6$ + 0.05M $CsPF_6$ solution in PC



➢ Dense film growth

Li_deposition_Cs.avi

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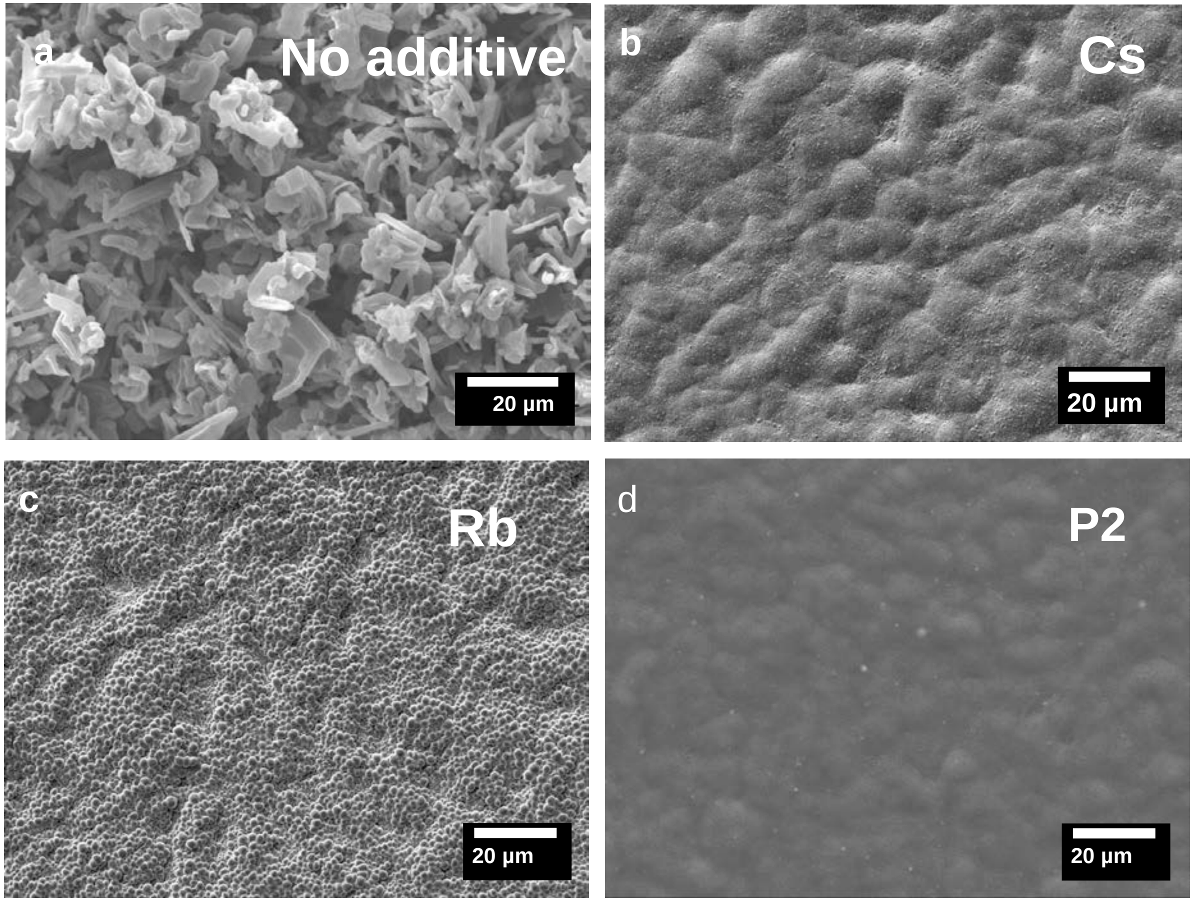
Effects of Other Additives: Rb^+, P1 and P2



- **SHES mechanism is effective for Cs, Rb, and P2.**

1M $LiPF_6$ in PC without or with 0.05 M additive

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Long Term Cycling Stabilities of Li-Metal Batteries

ICP Analysis on the Deposited Lithium Films

Sample	Element	
	Li	Additive
Deposited Li film from 1 M $LiPF_6$/PC	0.035 M	-
Deposited Li film from 0.05 M $CsPF_6$ in 1 M $LiPF_6$/PC	0.014 M	Cs: 0
Deposited Li film from 0.05 M $RbPF_6$ in 1 M $LiPF_6$/PC	0.056M	Rb: < detection limit (~10 μM)

- **The SHES additives can be used for long term cycling.**

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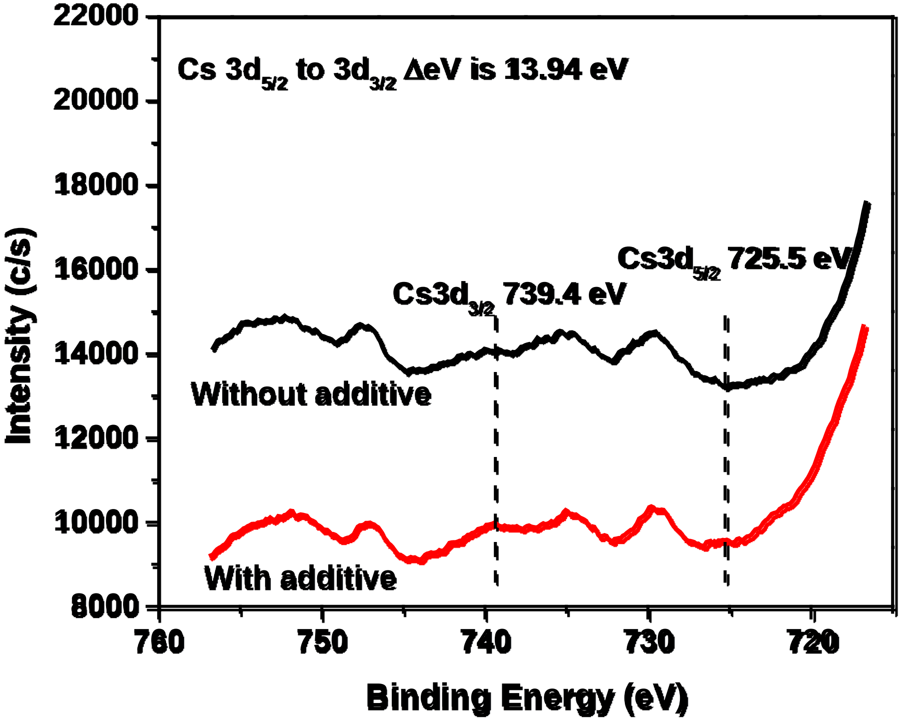
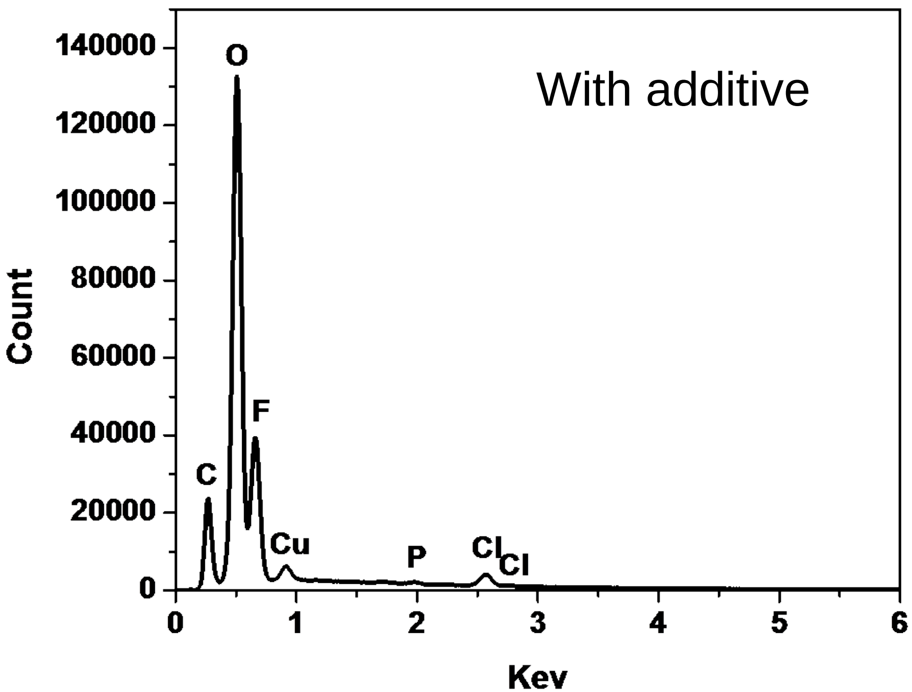
XPS and EDX Analysis on the Deposited Lithium Films

XPS Spectra



EDX Spectra



- No Cs can be identified (within the detectable limit) in the film deposited in an electrolyte containing Cs.

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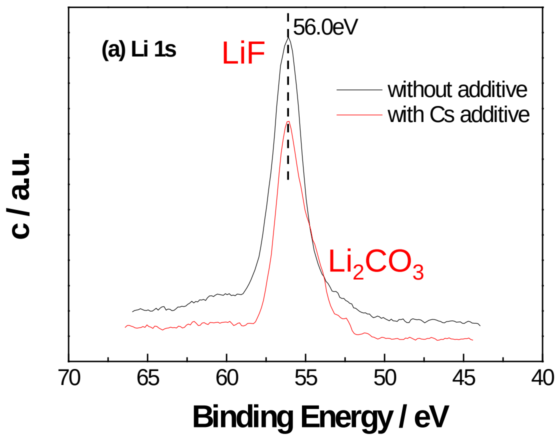
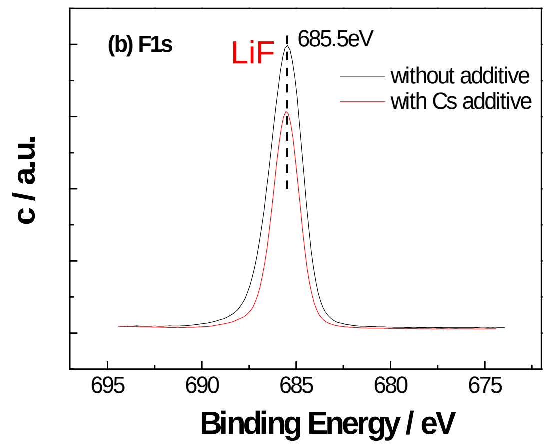
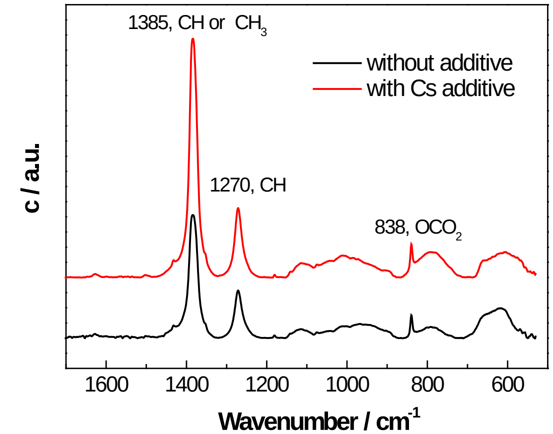
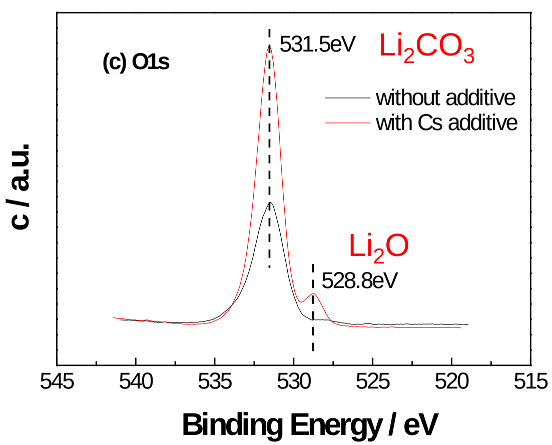
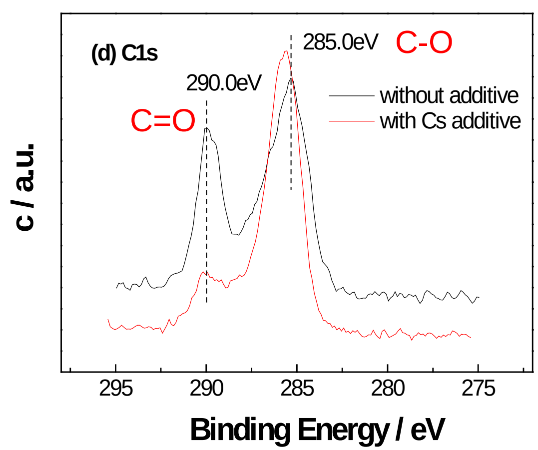
XPS Analyses on Li Surface Films









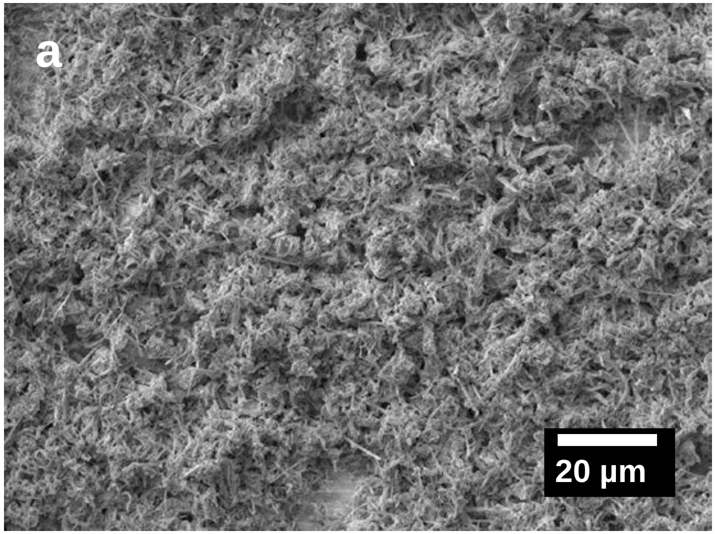


- ➢ Main components and structure of SEI films from electrolytes with and without Cs^+-additive are very close.
- ✓ Cs^+-additive does not participate in the SEI film-forming process.

Morphology Evolution during Repeated Li-Deposition/striping

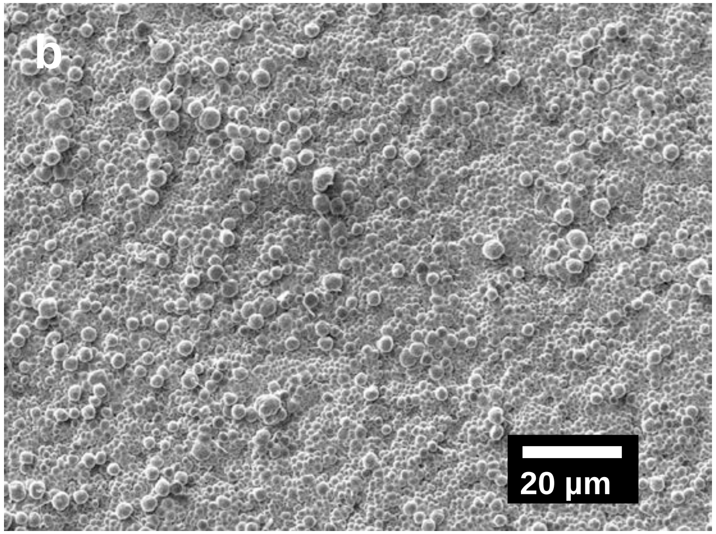
Self-amplification of chaotic/dendritic growth

Self-healing of ordered/smooth growth



(a) 1 hr deposition in the control electrolyte.

Significant Li dendrite was formed.



(b) Additional 14 hr in the electrolyte with Cs^+ additive.

All Li dendrite was soothed.

- **Cs^+ additive can effectively smooth the existing dendrite.**

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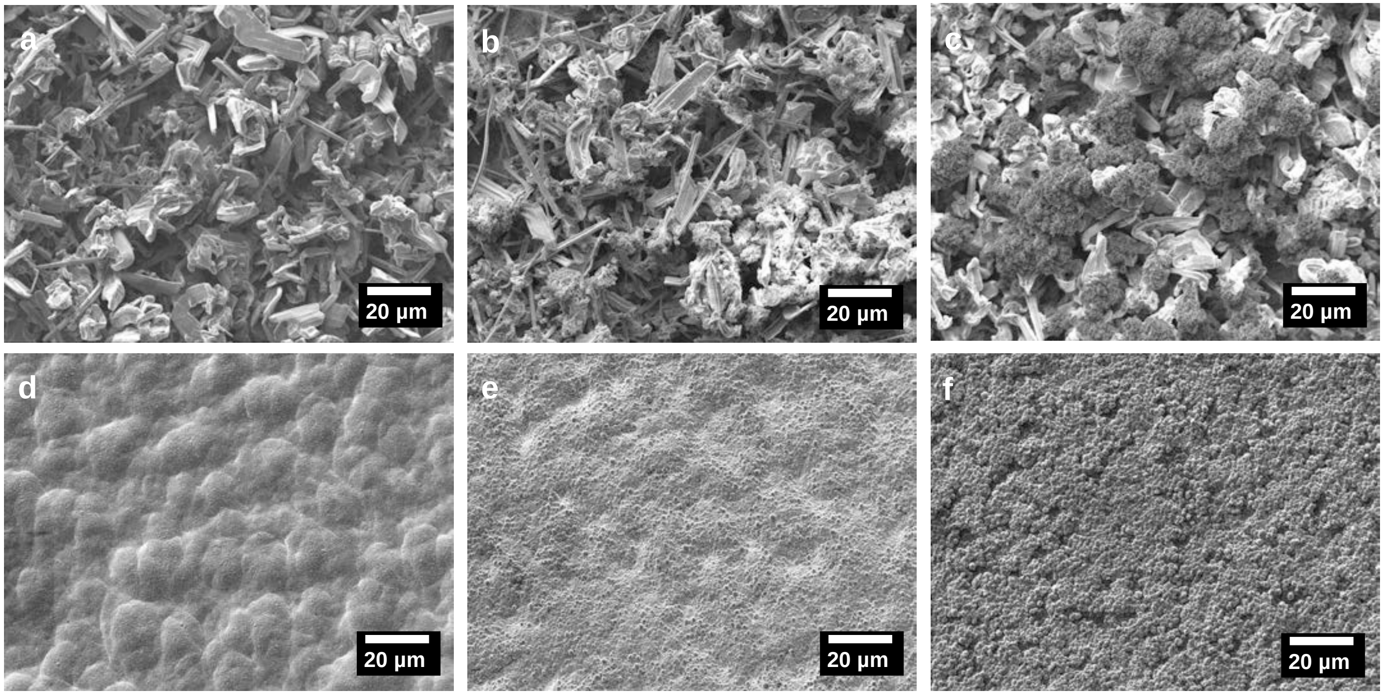
Effect of Cs$^+$ on Morphologies of Deposited Li Films After Cycling

Li films deposited on Cu foils after repeated deposition/stripping cycles in <u>beaker cells (no pressure effect)</u>.

2th deposition | 3th deposition | 10th deposition

No additive

With Cs$^+$ additive



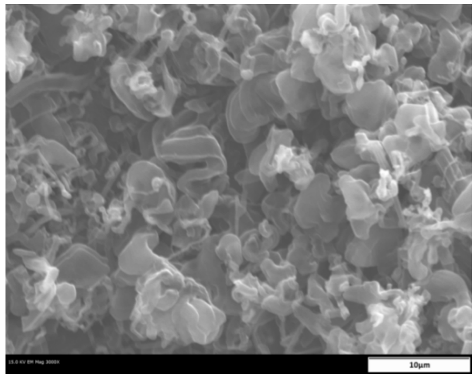
➢ **SHES mechanism is effective for cycling.**

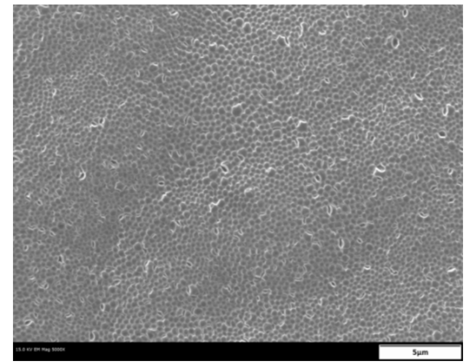
SEM Images on the Cross Section of Li Films

1 M $LiPF_6$ in PC

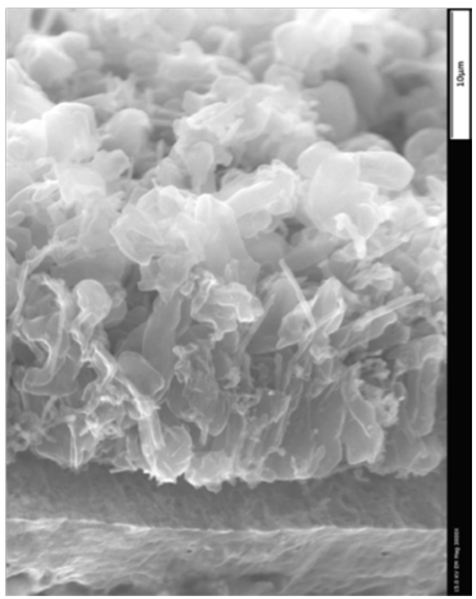
1 M $LiPF_6$ in PC+ 0.05 M $CsPF_6$

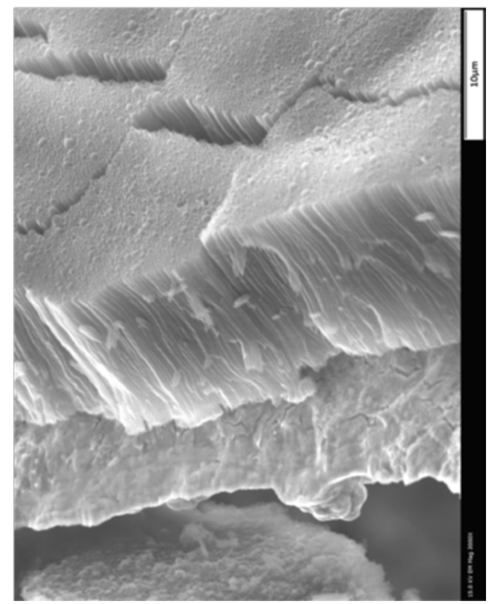
Surface





Cross section

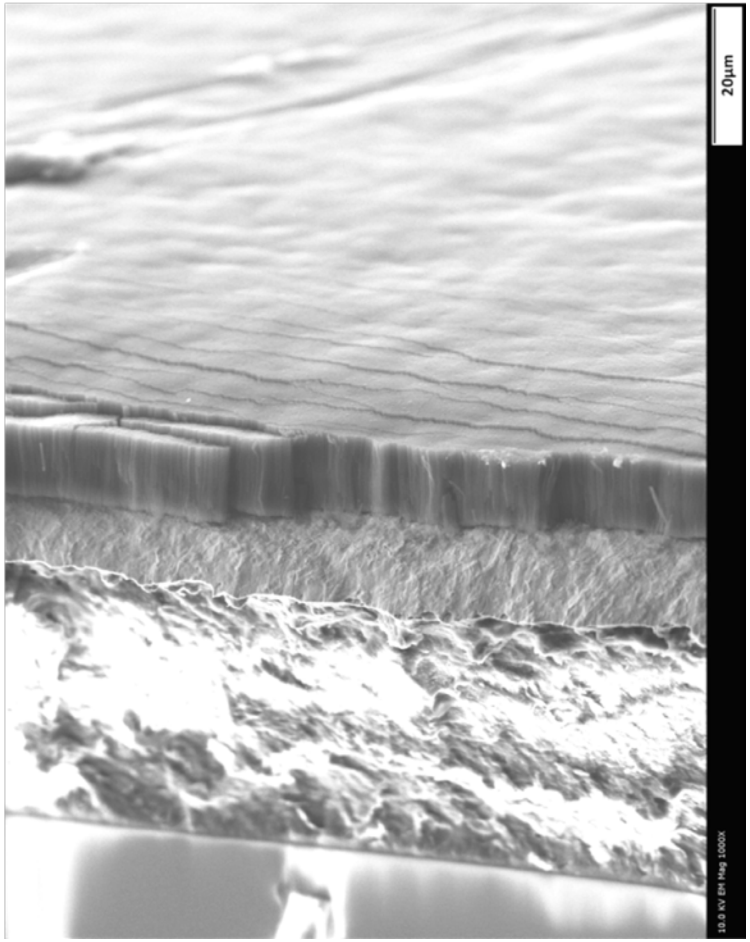


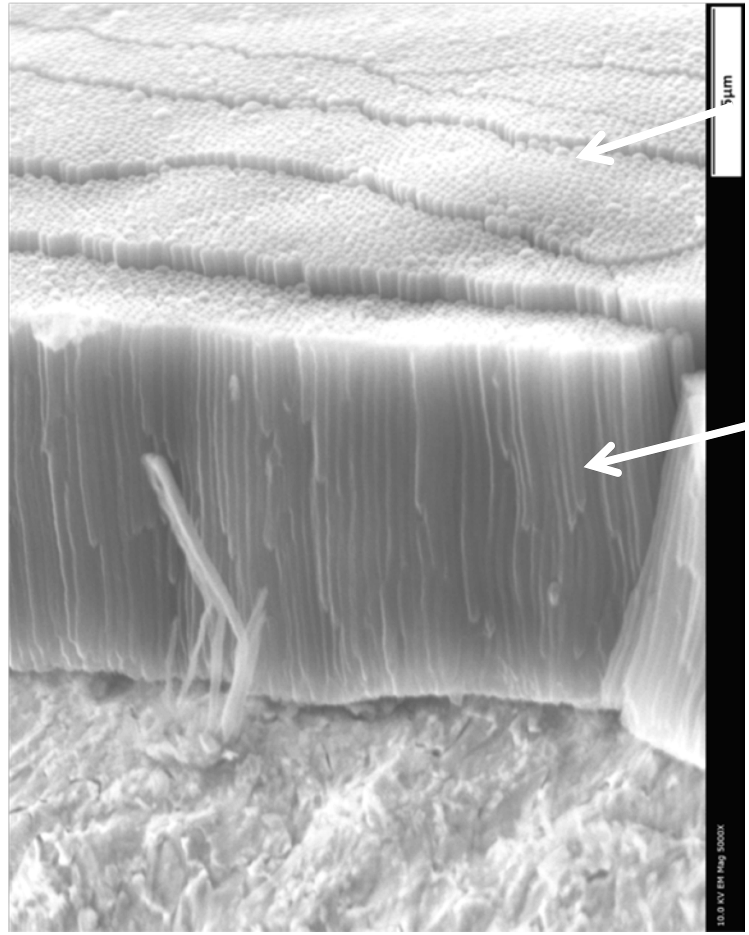


- Dendritic surface
- Random growth

- Smooth surface
- Highly ordered growth

Dendrite-Free Li Deposition with High CE





Smooth surface with small bumps

Cross section

Uniform growth of dense Li films. The growth pattern can be controlled by electrolyte

CE=96.42%

4. Dendrite-Free Li Deposition with High Coulombic Efficiency

Main Challenges:

1. **Li Dendrite Growth**
   - Cs or Rb additives based on the SHES mechanism can effectively prevent dendrite growth when PC is used as the solvent.

2. **Low Coulombic Efficiency**
   - Li will react with PC during cycling and lead to lower efficiency (~76%).

- **Electrolyte solvents and salts need to be optimized to obtain <u>both</u> dendrite-free Li deposition and high Coulombic efficiency.**

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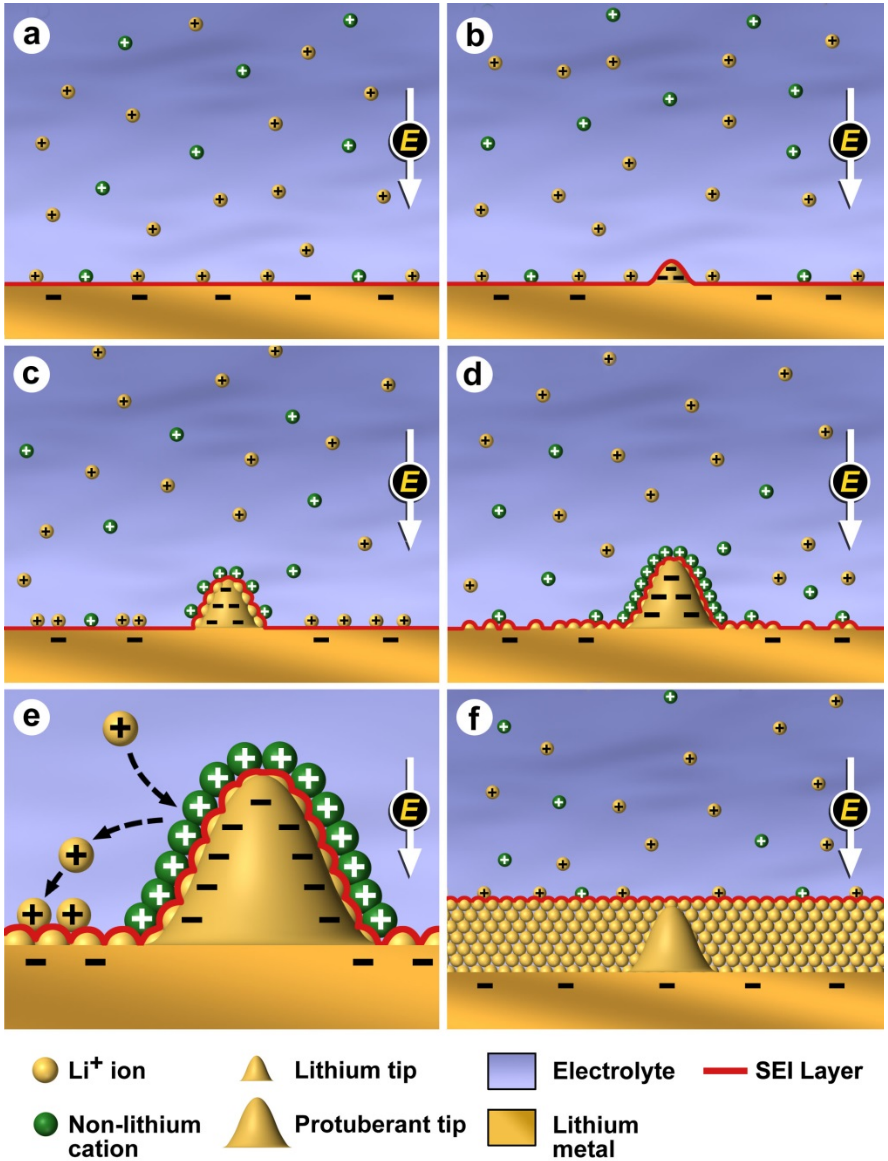
Self-Healing Electrostatic Shield (SHES) Mechanism



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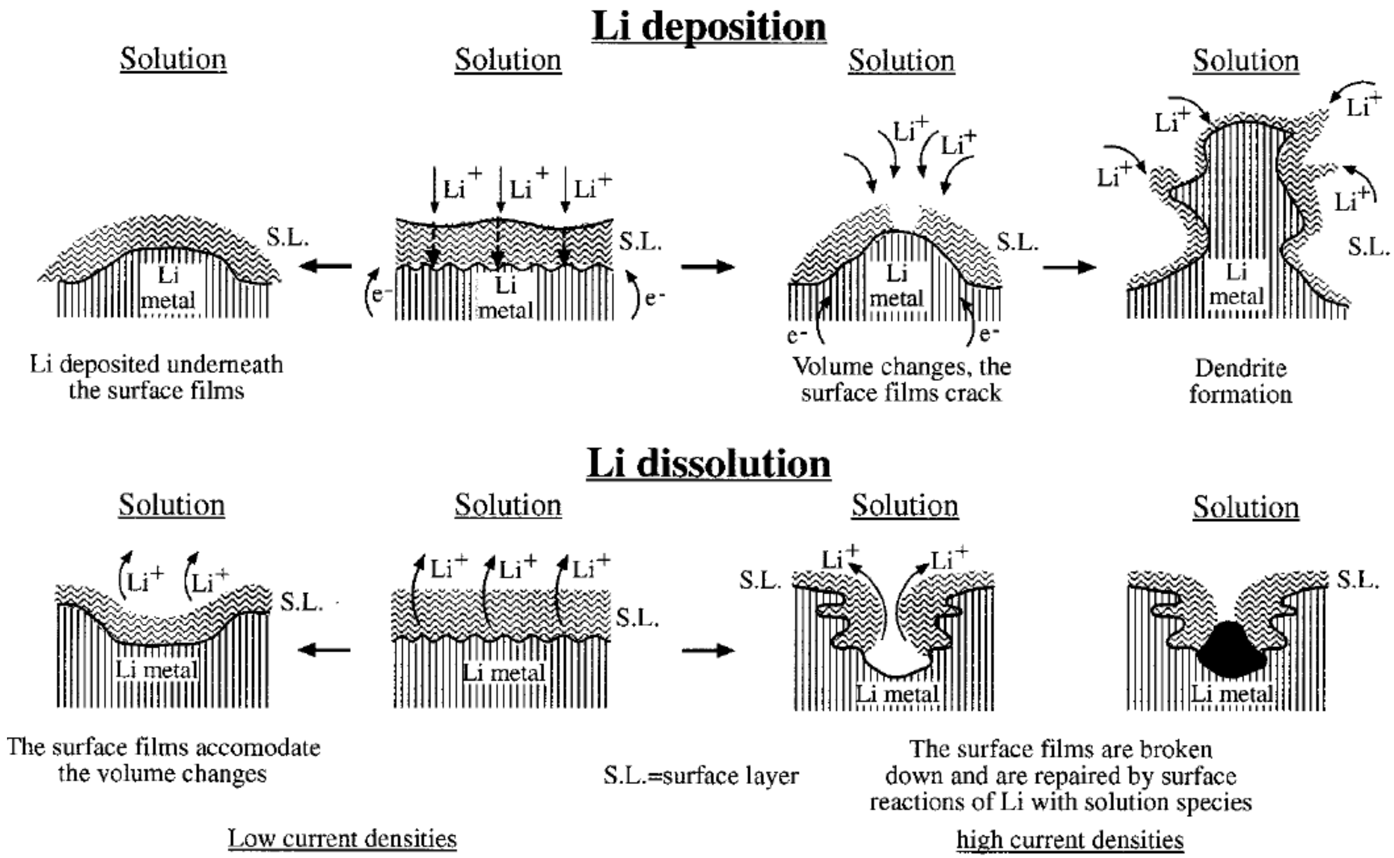
The morphology and failure mechanism of Li electrodes during Li deposition and dissolution



Y. S. Cohen, Y. Cohen and D. Aurbach, *The Journal of Physical Chemistry B*, 2000, **104**, 12282-12291.

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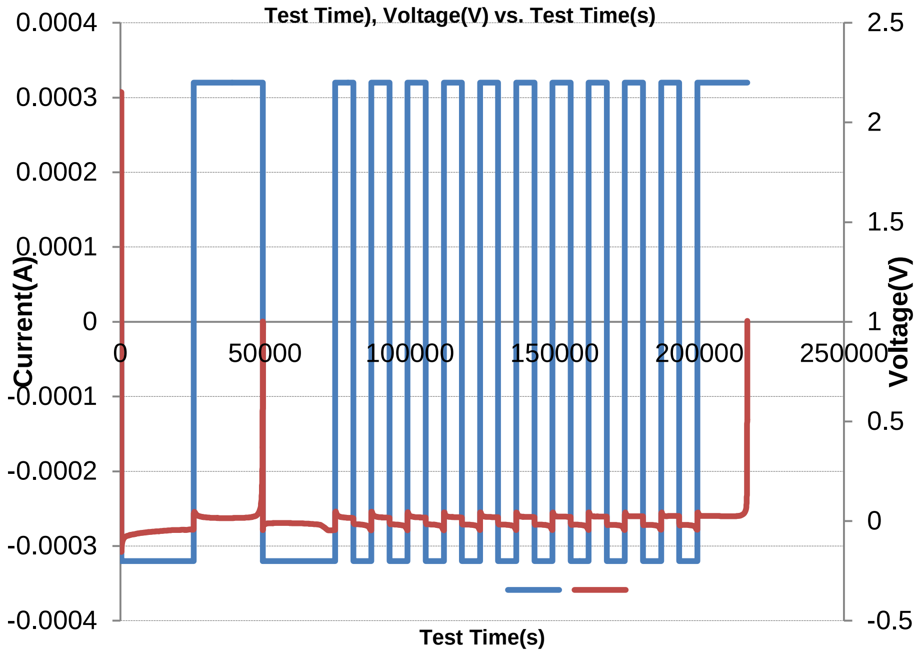
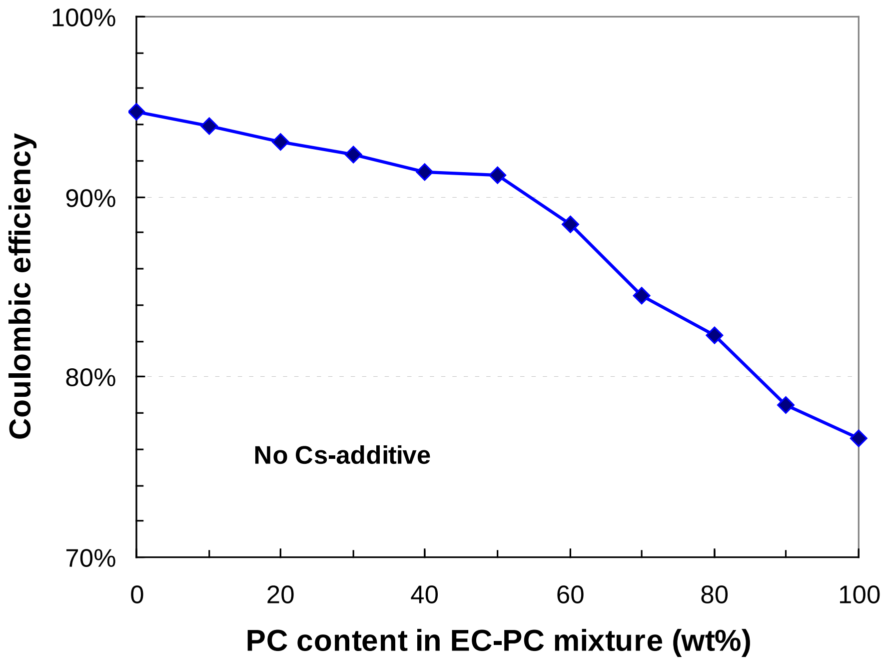
Improving Li Cycling Efficiency by Adding EC in PC





- Coin cell configuration: Li | 1M $LiPF_6$ in EC-PC | Cu

✓ **The average Coulombic efficiency of Li anode is significantly improved by using EC-PC with high EC contents.**

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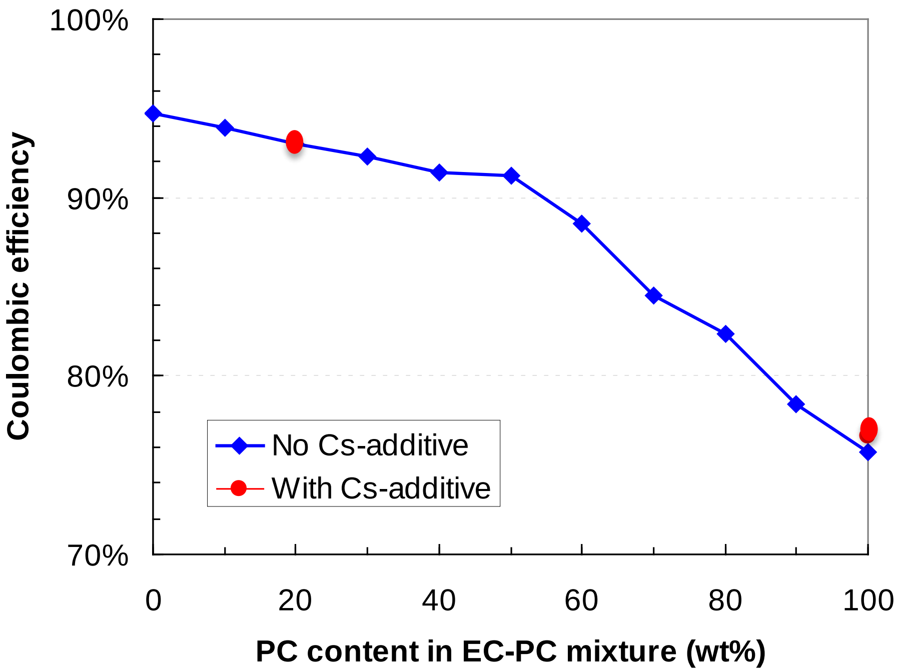
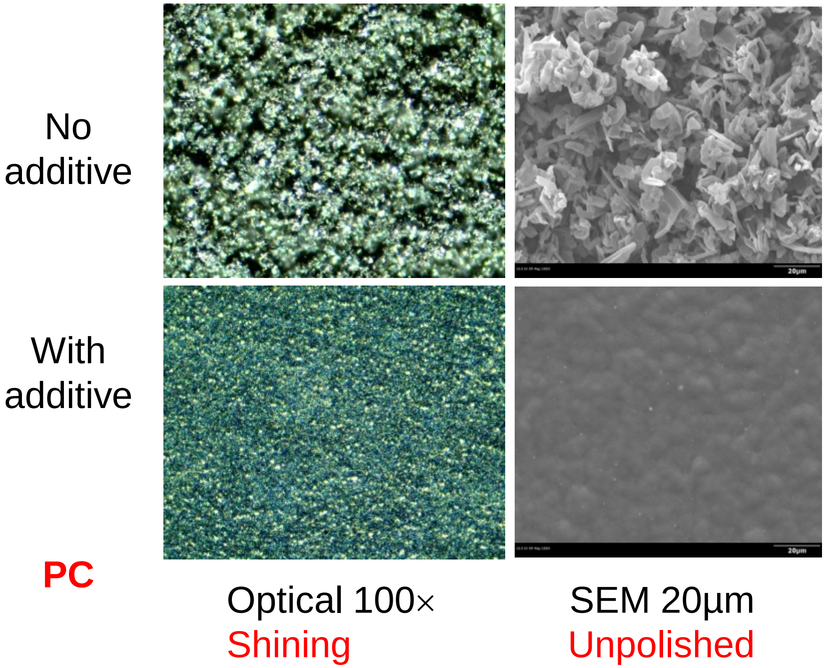
Effect of Cs-Additive on Li Cycling Efficiency & Morphology in EC-PC





- Coin cell configuration: Li | Cu with 1M $LiPF_6$ w. or w/o 0.05M $CsPF_6$ in EC-PC

✓ **New electrolyte with Cs-additive demonstrates both high Coulombic efficiency and dendrite free morphology.**

- Without Cs-additive: Li films are not shining when deposited in either PC or EC-PC (8:2) electrolytes.

✓ **With Cs-additive: Both Li films show metallic shining.**

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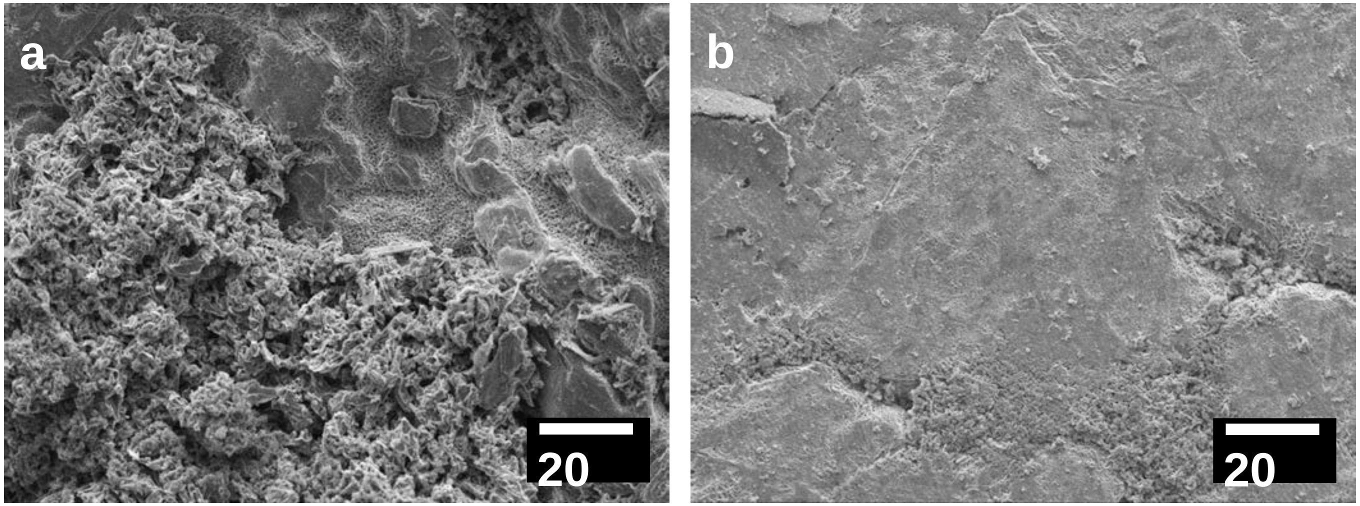
Effect of Carbonate Solvents on Li Coulombic Efficiency

Carbonate solvent	Average lithium Coulombic efficiency	
	Without $CsPF_6$	With 0.05 M $CsPF_6$
PC	76.5%	76.6%
EC	94.8%	
EC-PC (8:2 wt)	93.1% with dendrite	**93.1%, dendrite-free**
DMC	23.6%	
EMC	7.3%	
VC	97.1%	
VEC	97.6%	
FEC	98.2%	
EL1	**98.0%**	**97.5%, dendrite-free**

- Tested in Li |Cu cells.
- Li Coulombic efficiency is greatly affected by carbonate solvent. Cyclic carbonates give high efficiency while linear carbonates result in very poor efficiency.
- Dendrite-free Li deposition with >98% CE obtained.

4. Li Metal Batteries with SHES Additives

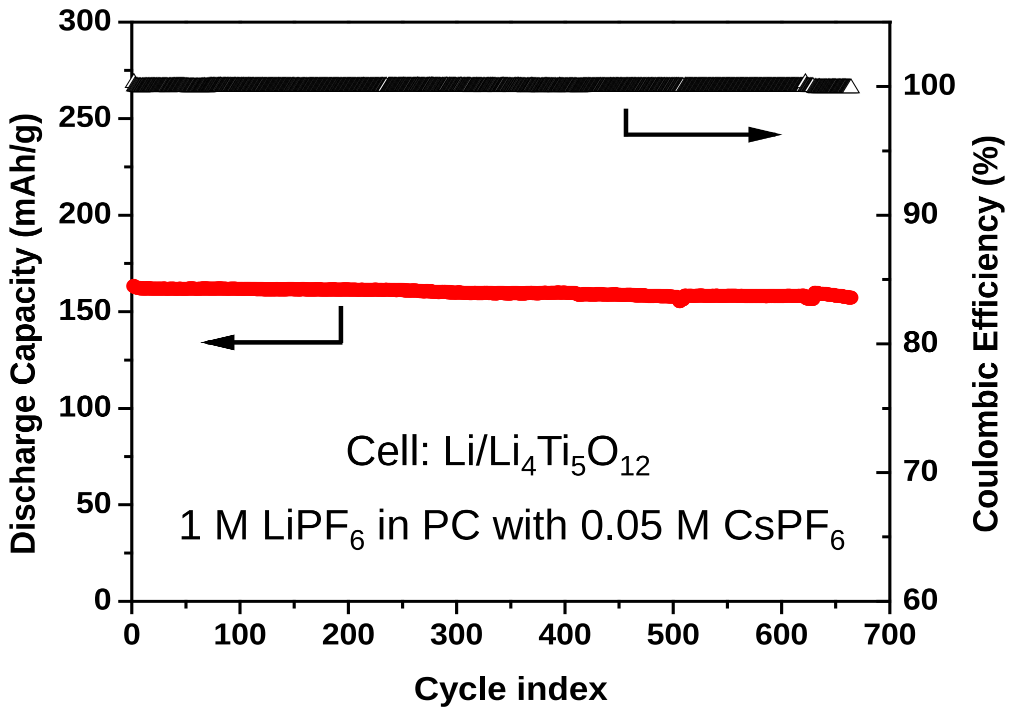
Morphology Changes During Long Term Cycling of Li Electrode in Li/LTO Cells



Surface morphologies of Li electrodes after 100 cycles in coin cells of Li|$Li_4Ti_5O_{12}$ system containing electrolytes without (a) and with (b) Cs^+-additive.

➢ **SHES mechanism is effective during long term cycling.**

Long Term Stability of Li-Metal Batteries Using Cs^+ Additive



- **Columbic efficiency of the full cell: 99.97% (with excess Li)**
- **Cycling stability of the full cell: Only 3.3% capacity fade in 660 cycles**

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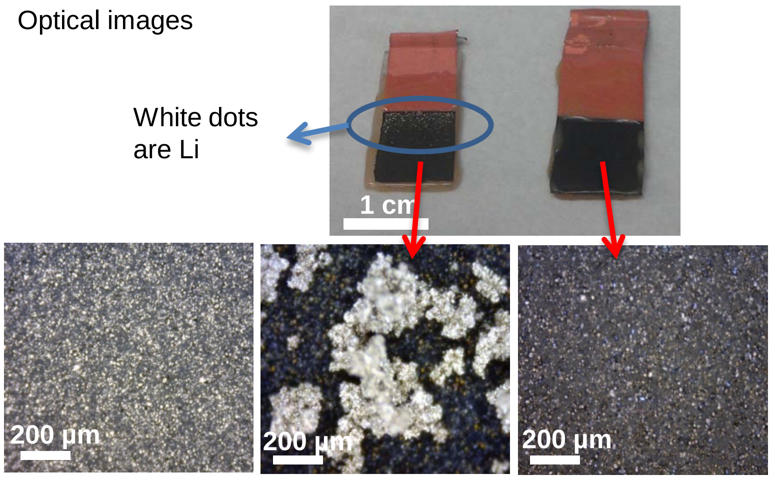
SHES Additive Prevents Li Dendrites on Overcharged Carbon Electrodes

100% overcharge (i.e. overcharged to 200% of the nominal capacity)

Optical images

White dots are Li



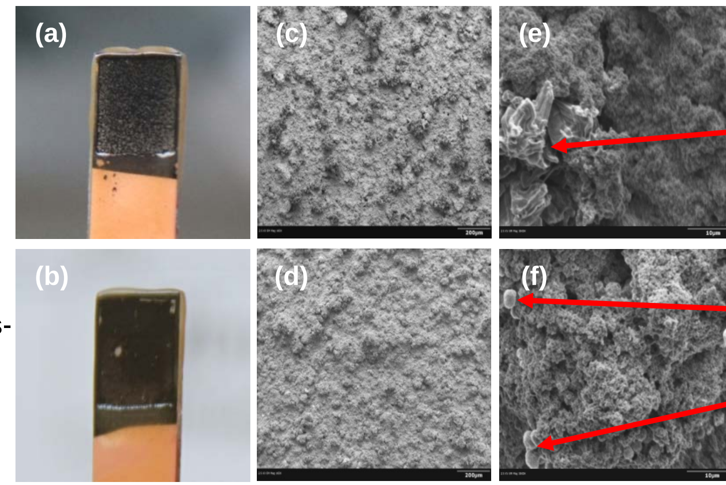
Pristine HC electrode | Without additive | With Cs-additive

200% overcharge (i.e. overcharged to 300% of the nominal capacity)

Optical | SEM

Without additive

With Cs-additive



Dendritic Li was deposited on the surface

Spherical Li was deposited on the surface

Cs Additive can prevent Li dendrite growth on overcharged carbon electrodes

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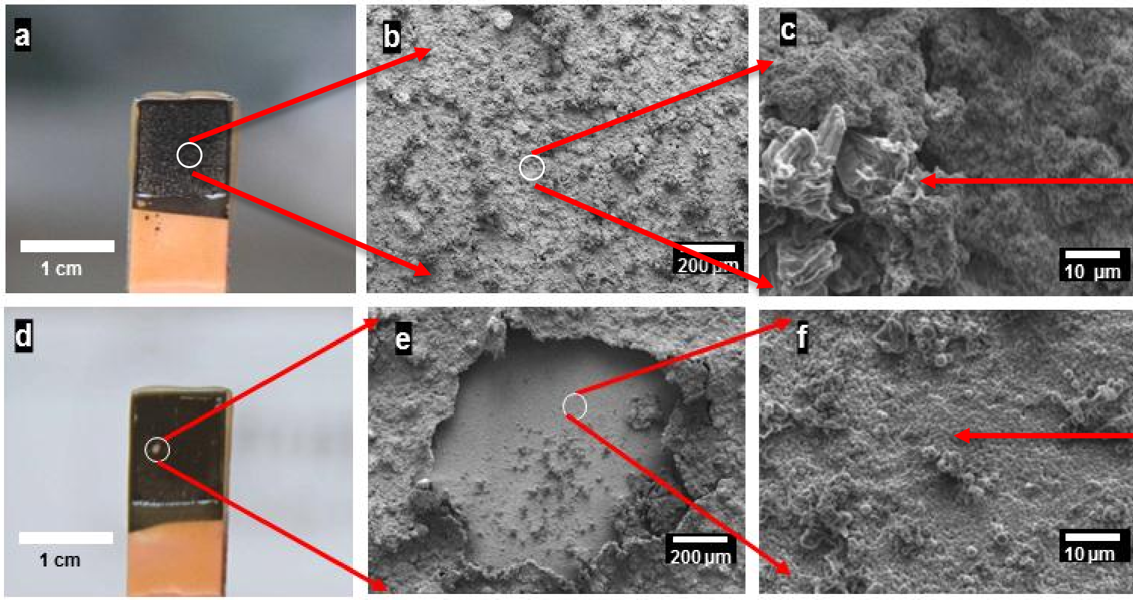
SHES Effect on Li-ion Batteries

Without additive



Li was deposited on the surface

With additive

Li was deposited on the bottom

Optical and SEM images of the surface morphologies of the hard carbon electrodes after charged to 300% of the regular capacity in the control electrolyte (a, b, c) and in an electrolyte with 0.05 M $CsPF_6$ additive added in the control electrolyte (d, e, f).

New Additive can prevent Li dendrite growth on overcharged carbon electrodes

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5. Summary

- The Self-Healing Electrostatic Shield (SHES) mechanism has been proposed to suppress Li dendrite growth.
- Novel additives (Cs, Rb, etc.) based on the SHES mechanism can effectively suppress Li dendrite growth on Li metal batteries.
- High Coulombic efficiency (>98%) can be obtained if the appropriate solvent is used.
- The SHES mechanism may also be used to prevent dendrite growth during other metal depositions.

Acknowledgments

Contributors:

Wu Xu, Fei Ding, Gordon L. Graff, Jian Zhang, Yaohui Zhang, Maria L. Sushko, Xilin Chen, Yuyan Shao, Mark H. Engelhard, Zimin Nie, Thomas A. Blake, Jie Xiao, Xingjiang Liu, Peter V. Sushko, Jun Liu

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