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Cycle performance of lithium anodes in fluoroethylene carbonate-based electrolytes for lithium-sulfur battery

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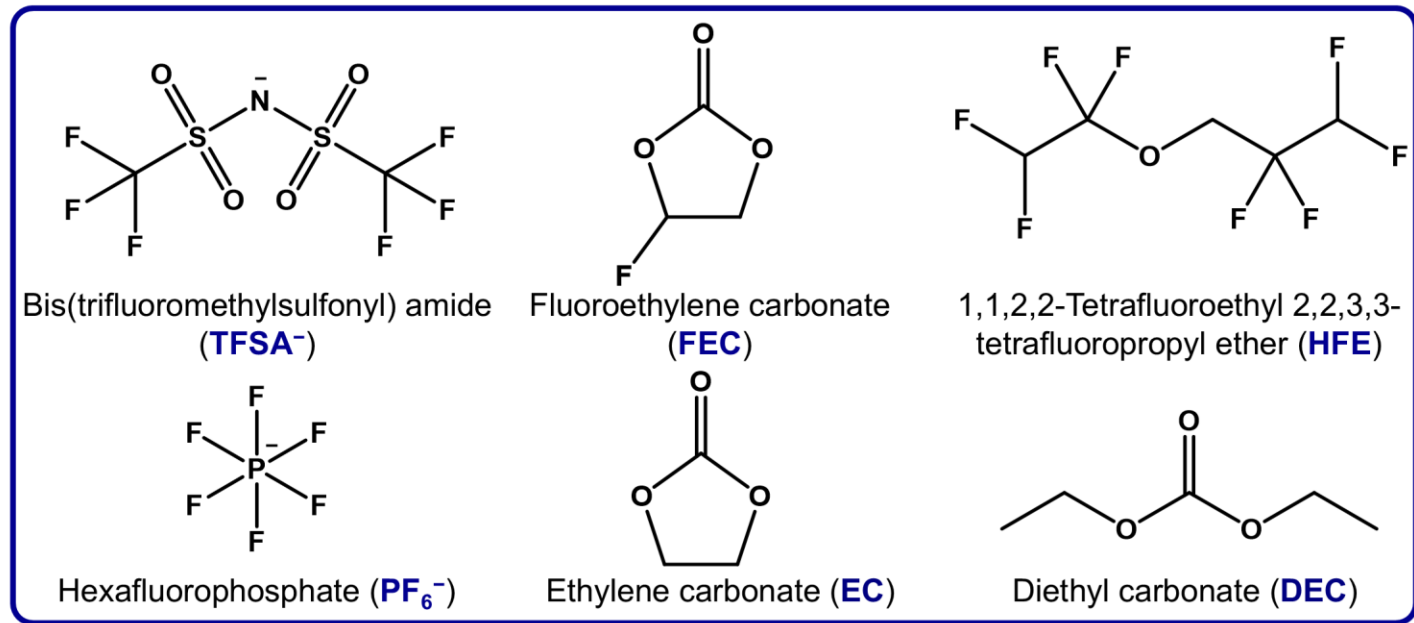
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Electrolyte for Li-S battery

- Previous reports on HFE-diluted solutions of LiTFSA
 - Low Li_2S_x solubility[1].
 - HFE leads to Li ion-solvent coordination structure in smaller clusters. The local Li-ion coordination structure is maintained[1].
- Previous reports on FEC-based electrolytes
 - SEI formed by FEC for the suppression of Li_2S_x reaction at Li anode[2].
- We are studying **1 M LiTFSA/FEC+HFE (1:1 vol)** [3] as an electrolyte for Li-S batteries

Aims of this Study

- Investigate the lithium deposition/dissolution processes and SEI formation in this electrolyte, and compare with a typical Li-ion battery electrolyte, **1 M LiPF_6 /EC+DEC (1:1 vol)**. Other combinations of salt/solvent are also compared.



	EC/DEC (1:1 vol)	FEC/HFE (1:1 vol)
1 M LiPF_6	(a)	(c)
1 M LiTFSA	(b)	(d)

- [1] A. Nakanishi, *et al.*, *J. Phys. Chem. C*, **123**, 14229 (2019).
 [2] J. Song, *et al.*, *J. Electrochem. Soc. A*, **160**, A873 (2013).
 [3] M. Ishikawa, *et al.*, *J. Phys. Chem. C*, **127**, 15069 (2023).

➤ Deposition/Dissolution of Li

CC, 0.5 mA cm^{-2} , 3.2–3.6 V, 25 °C

Electrolyte: (a) 1 M $\text{LiPF}_6/\text{EC}+\text{DEC}$ (1:1 vol)
(b) 1 M $\text{LiTFSA}/\text{EC}+\text{DEC}$ (1:1 vol)
(c) 1 M $\text{LiPF}_6/\text{FEC}+\text{HFE}$ (1:1 vol)
(d) 1 M $\text{LiTFSA}/\text{FEC}+\text{HFE}$ (1:1 vol)

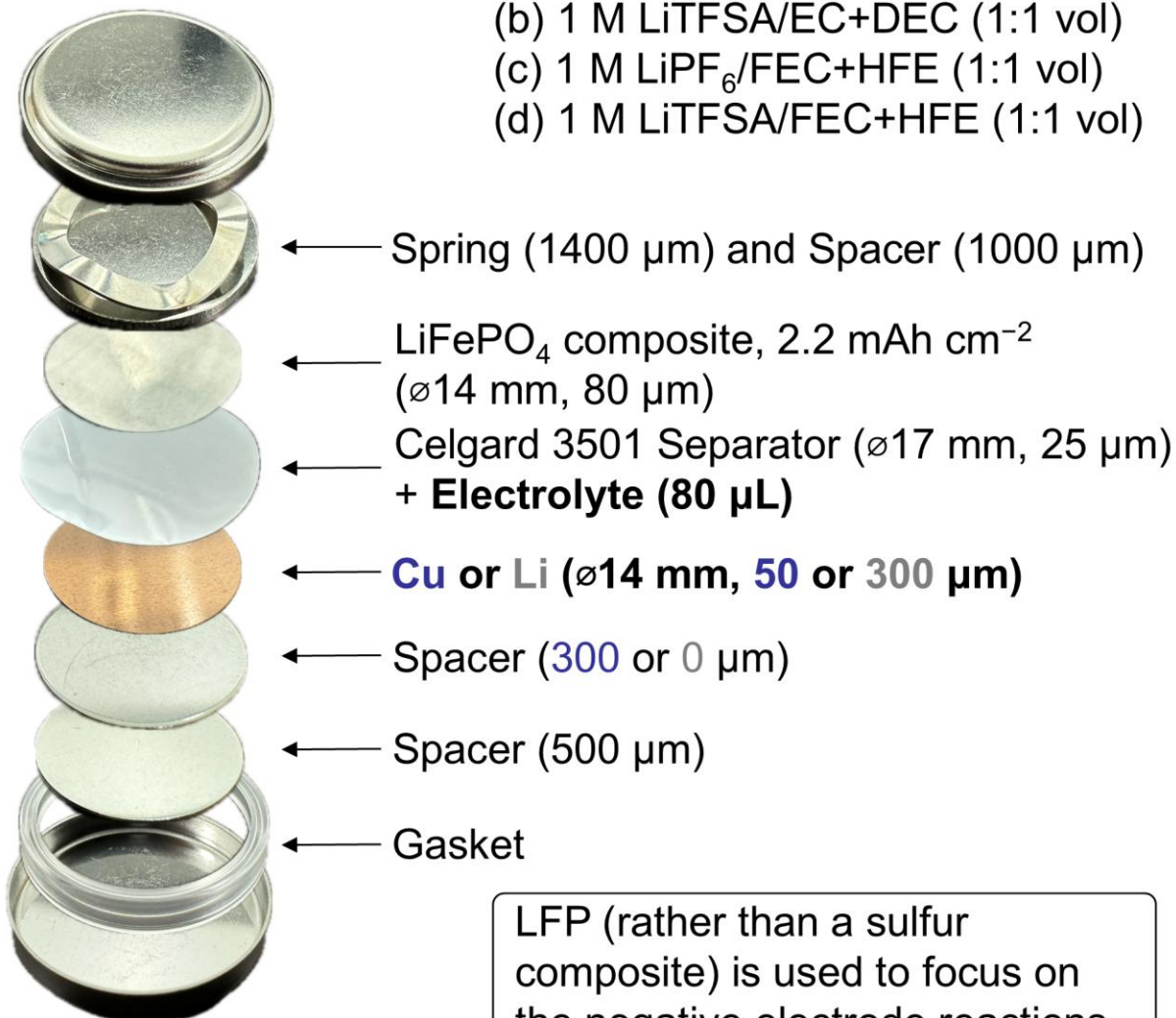


Fig. Schematic of coin cell.

➤ Negative electrode pre-treatment

Li: surface polishing (diamond)

Cu: electrolytic polishing, electrolytic degreasing, etching

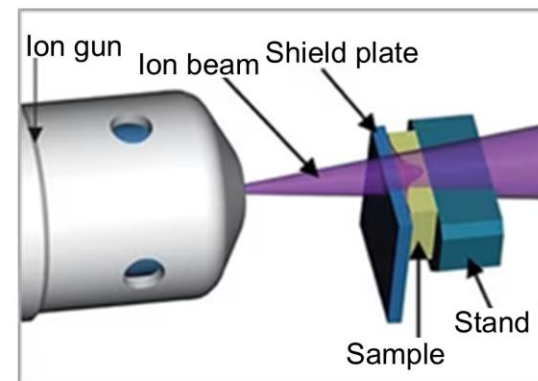
➤ Analysis

Scanning electron microscopy (SEM)

X-ray photoelectron spectroscopy (XPS)

(without air exposure)

➤ Ion Milling for Cross-sectional SEM



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Condition

- Sample temperature: $-80 \text{ }^{\circ}\text{C}$
- Processing time: 1 h
- Accelerating voltage: 6 kV
- Discharge voltage: 1.5 kV
- Sample stage:
3 round trip / min, 30°

Irradiate the Ar beam from the deposited Li side.



Deposition/Dissolution of Li (Li|LFP)

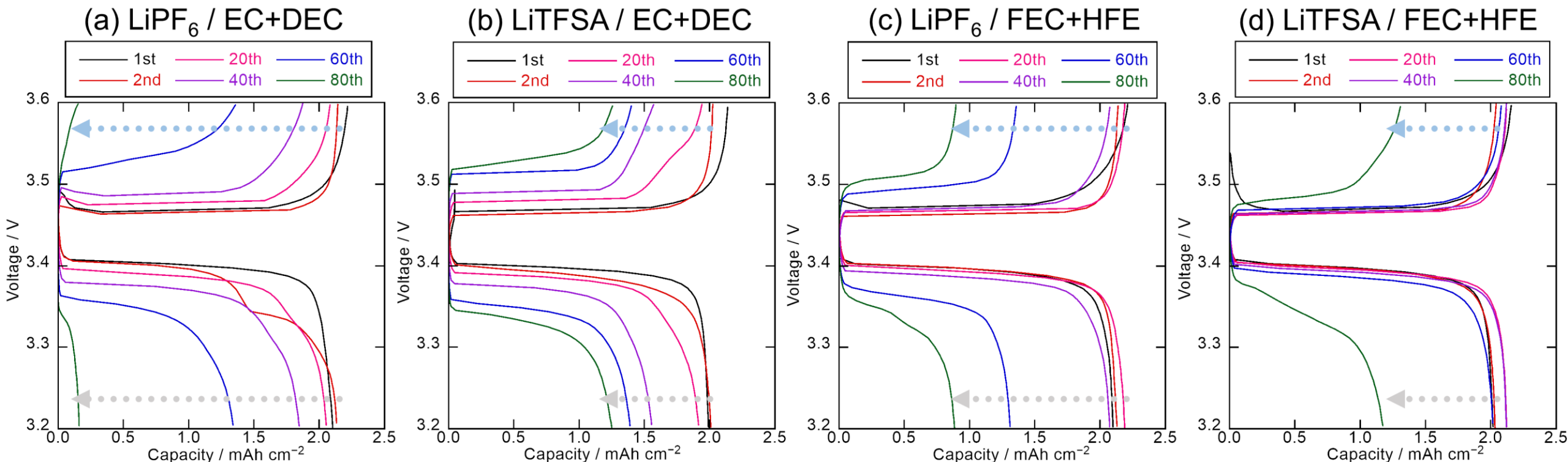
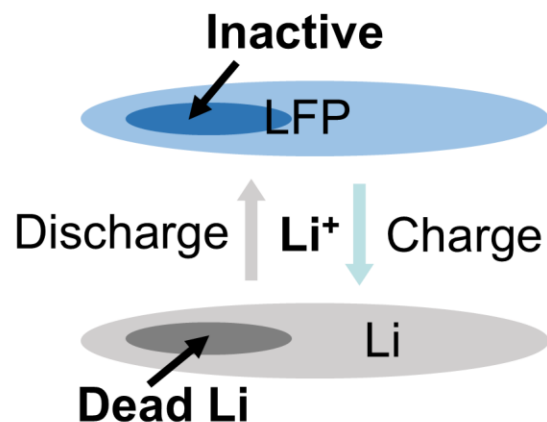


Fig. Charge-discharge curves of Li|LFP coin cells using (a) 1 M LiPF₆/EC+DEC (1:1 vol), (b) 1 M LiTFSA/EC+DEC (1:1 vol), (c) 1 M LiPF₆/FEC+HFE (1:1 vol), and (d) 1 M LiTFSA/FEC+HFE (1:1 vol) at 25 °C. Current density: 0.5 mA cm⁻².



- Formation of dead Li
- Inactivation of LFP
- Decrease in the effective electrode surface area

Decrease in charge/discharge capacity
Increase in overpotential

Deposition/Dissolution of Li (Li|LFP)

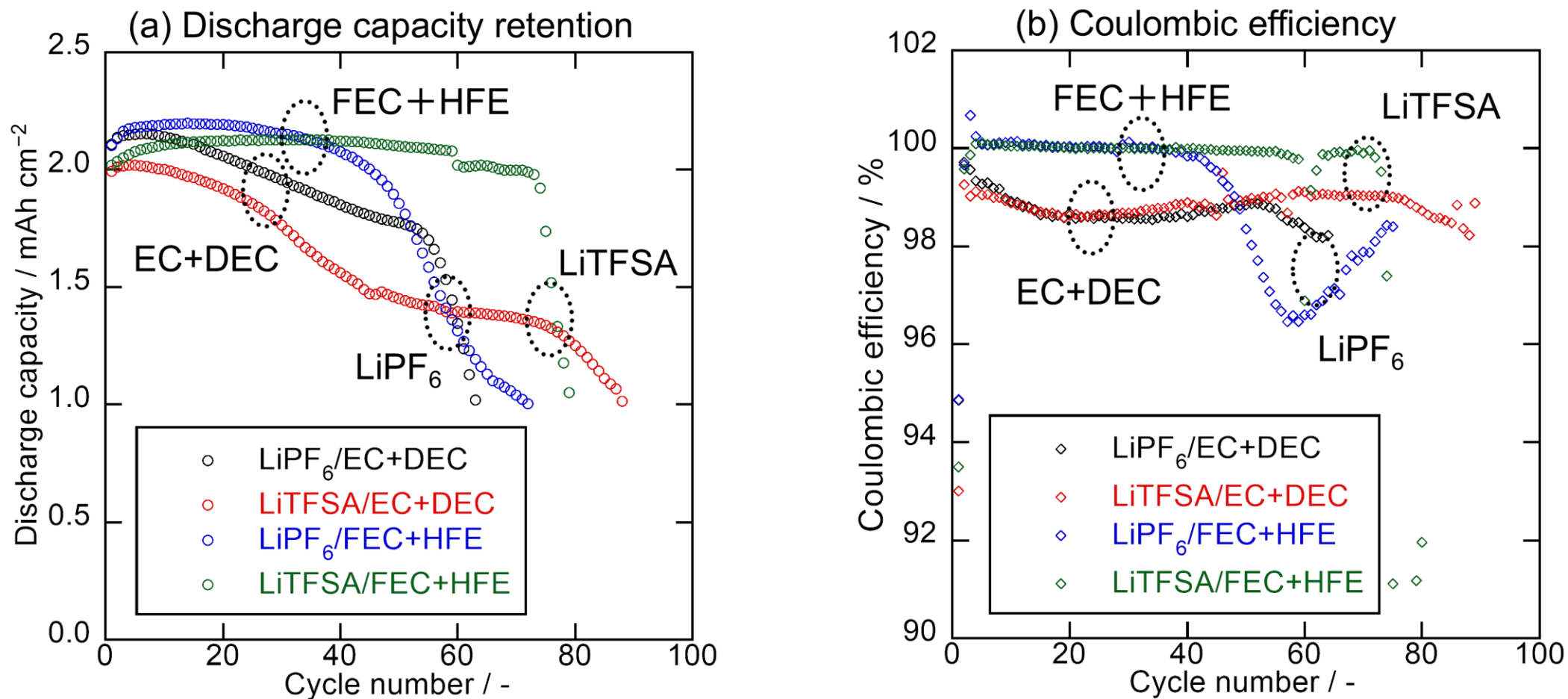


Fig. Cycle dependence of the (a) capacity retention and (b) coulombic efficiency of Li|LFP coin cells using 1 M LiPF₆/EC+DEC (1:1 vol), 1 M LiTFSA/EC+DEC (1:1 vol), 1 M LiPF₆/FEC+HFE (1:1 vol), and 1 M LiTFSA/FEC+HFE (1:1 vol) at 25 °C. Current density: 0.5 mA cm⁻².

- Even with 1 M LiTFSA/FEC+HFE (1:1 vol), capacity decreased rapidly around 80 cycles.
- The influence of the solvent is significant up to around 50 cycles. (FEC+HFE > EC+DEC)
- After around 50 cycles, the influence of the lithium salt becomes more significant. (LiTFSA > LiPF₆)

Deposition/Dissolution of Li (Cu|LFP)

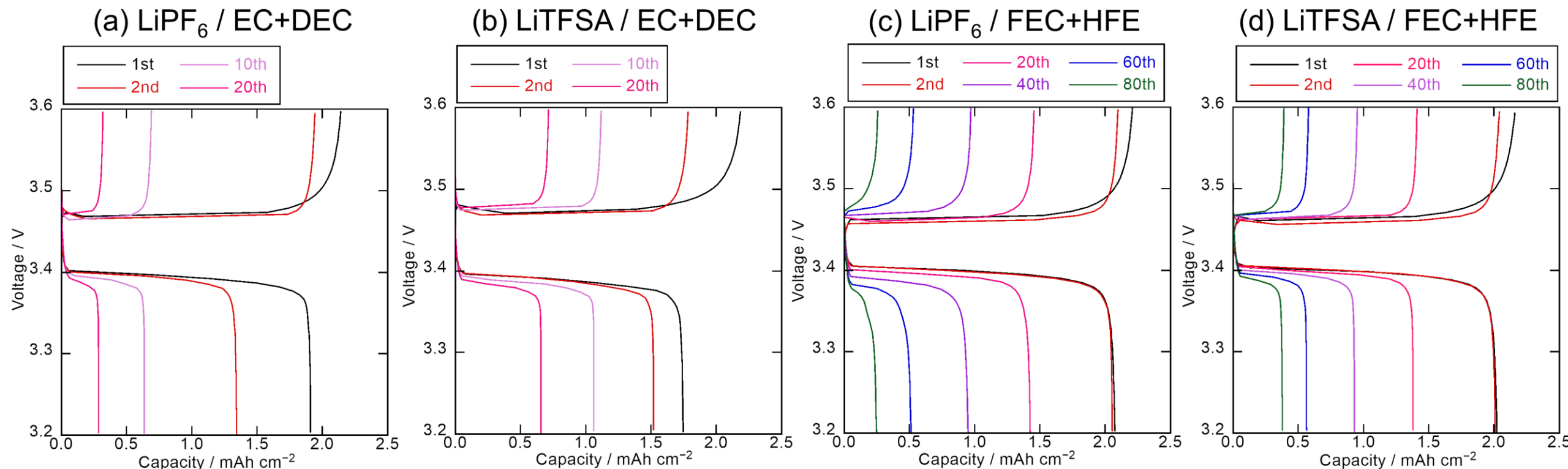
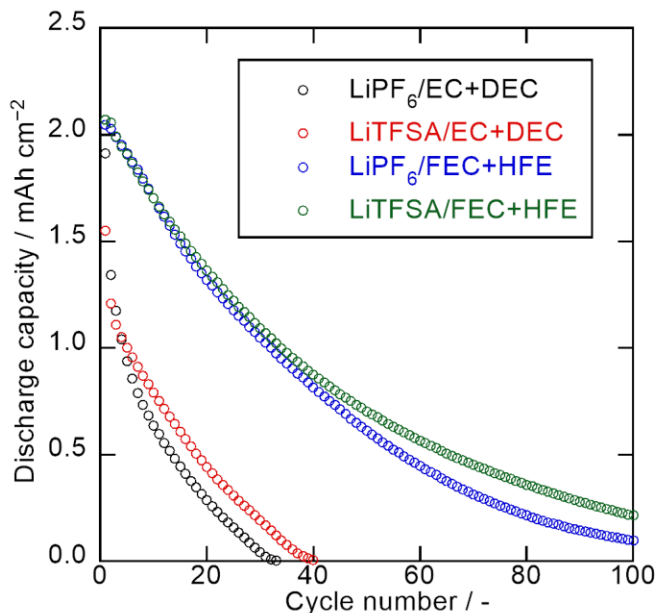


Fig. Charge-discharge curves of Cu|LFP coin cells using (a) 1 M LiPF₆/EC+DEC (1:1 vol), (b) 1 M LiTFSA/EC+DEC (1:1 vol), (c) 1 M LiPF₆/FEC+HFE (1:1 vol), and (d) 1 M LiTFSA/FEC+HFE (1:1 vol) at 25 °C. Current density: 0.5 mA cm⁻².

- Unlike the results with a Li negative electrode, with Cu the increase in overpotential is negligible.
→The lithium was consumed during cycling as a result of reactions with the electrolyte.

Deposition/Dissolution of Li (Cu|LFP)

(a) Discharge capacity retention



(b) Coulombic efficiency

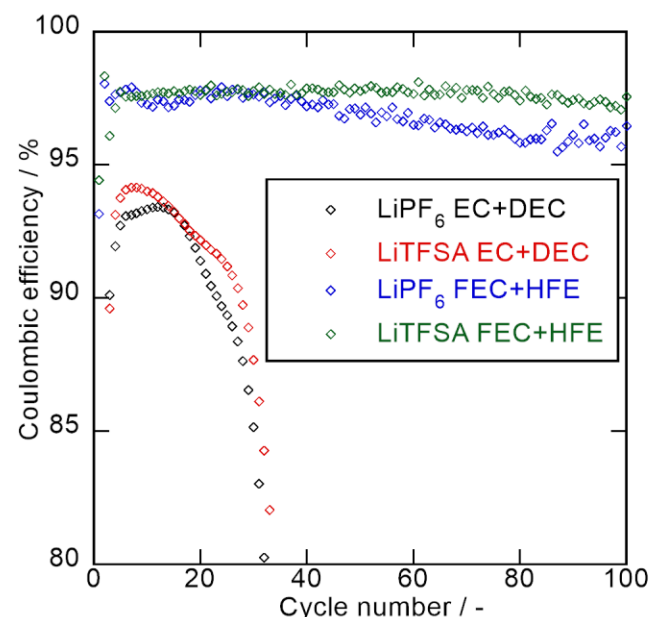
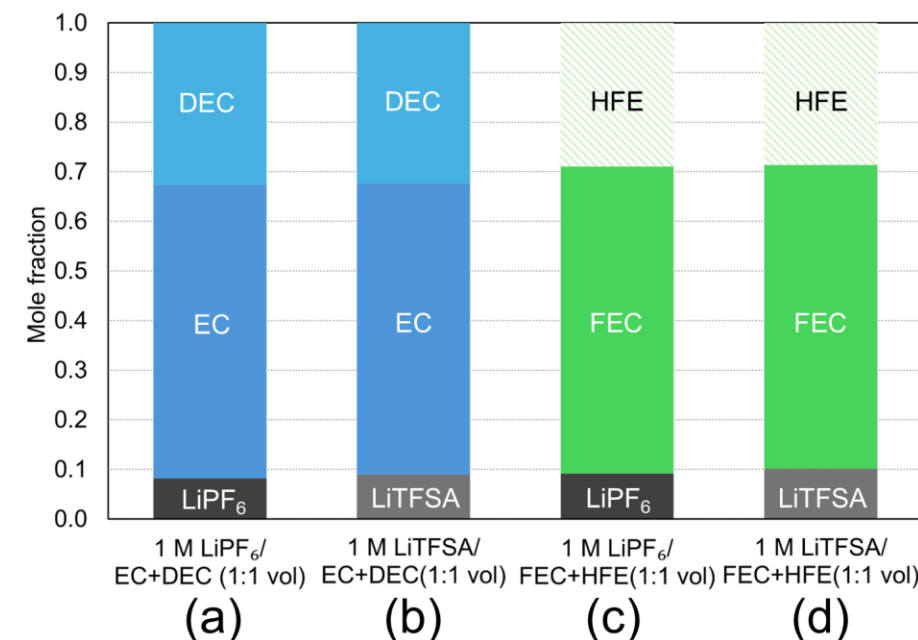


Fig. Cycle dependence of the (a) capacity retention and (b) coulombic efficiency of Cu|LFP coin cells using 1 M LiPF₆/EC+DEC (1:1 vol), 1 M LiTFSA/EC+DEC (1:1 vol), 1 M LiPF₆/FEC+HFE (1:1 vol), and 1 M LiTFSA/FEC+HFE (1:1 vol) at 25 °C. Current density: 0.5 mA cm⁻².

- The influence of the **solvent** is significant. (FEC+HFE > EC+DEC)
→ EC + DEC has a higher reactivity with Li than FEC + HFE
because carbonate-based solvents are more easily reduced than ether-based solvents.

Electrolyte composition
and molar ratio

- (a) 1 M LiPF₆/EC+DEC (1:1 vol)
1.0 : 7.2 : 4.0
(b) 1 M LiTFSA/EC+DEC (1:1 vol)
1.0 : 6.5 : 3.6
(c) 1 M LiPF₆/FEC+HFE (1:1 vol)
1.0 : 6.7 : 3.2
(d) 1 M LiTFSA/FEC+HFE (1:1 vol)
1.0 : 6.0 : 2.8



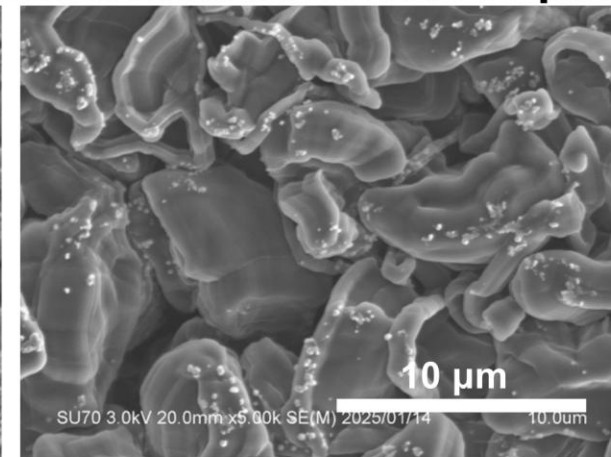
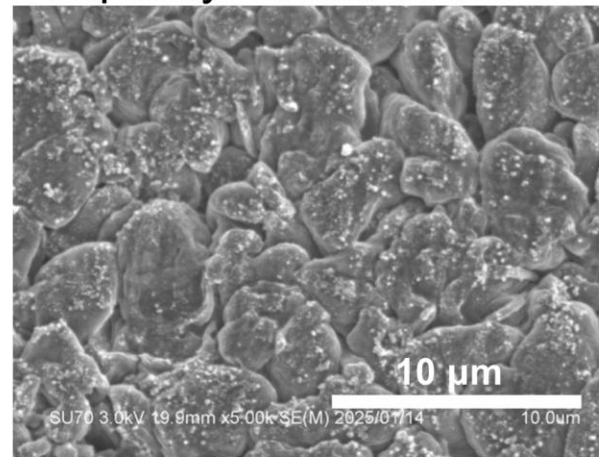
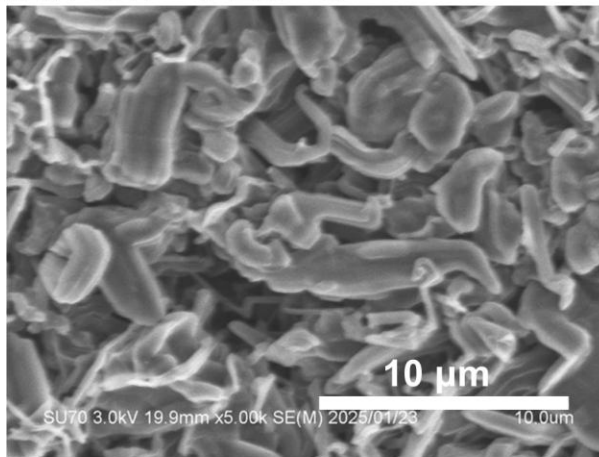
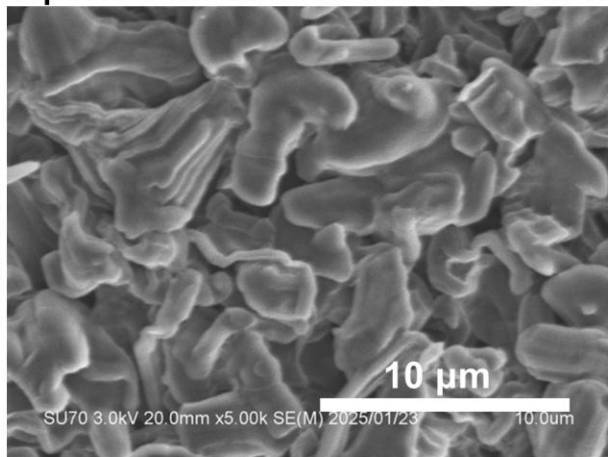
- The influence of the **lithium salt** is LiTFSA > LiPF₆, when the same solvent is used.

SEM images of deposited Li (1st deposition)

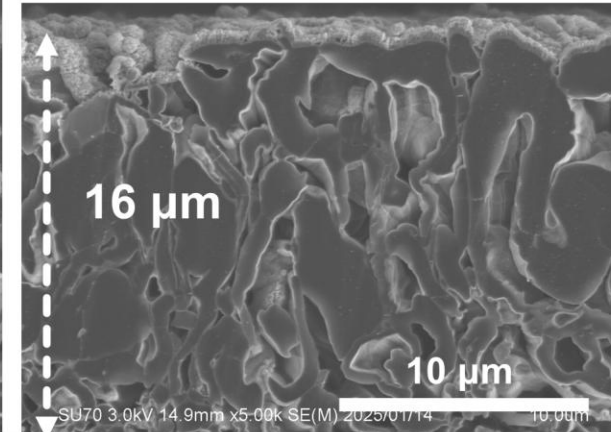
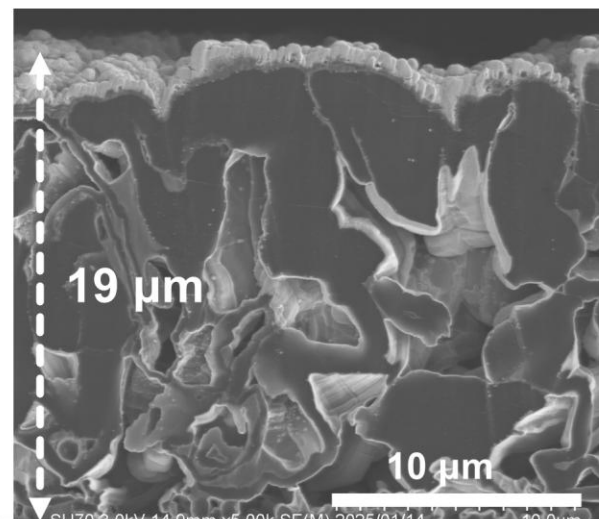
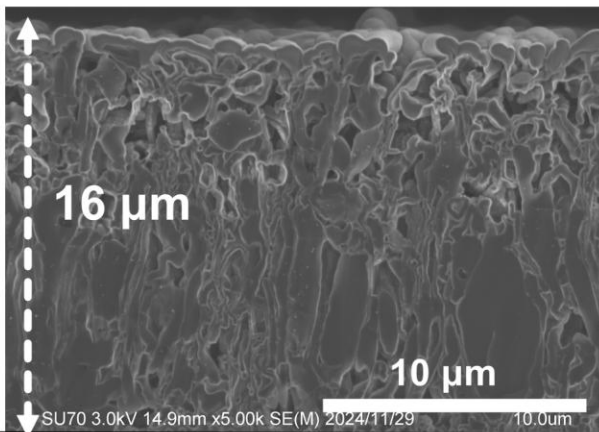
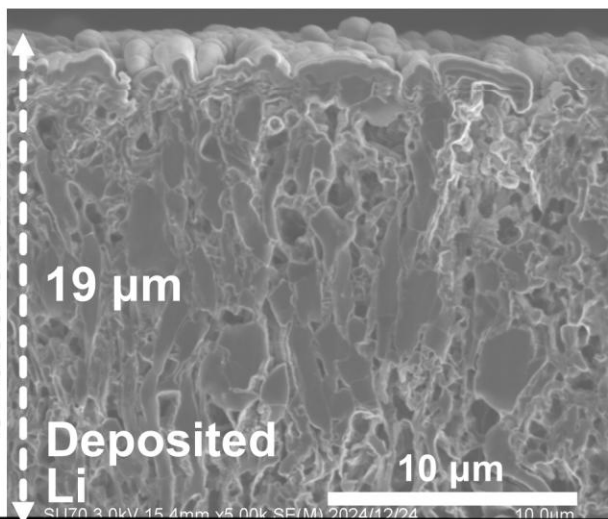
Deposition 0.5 mA cm⁻² / 2.2 mAh cm⁻² / 25 °C

Capacity: 2.2 mAh cm⁻² → Theoretical thickness: 11 μm

Surface



Cross-section



(a) LiPF₆ / EC+DEC

(b) LiTFSA / EC+DEC

(c) LiPF₆ / FEC+HFE

(d) LiTFSA / FEC+HFE

Small domain

Large domain

Fig. Surface and cross-sectional SEM images of Li on Cu electrode after 1st deposition in (a) 1 M LiPF₆/EC+DEC (1:1 vol), (b) 1 M LiTFSA/EC+DEC (1:1 vol), (c) 1 M LiPF₆/FEC+HFE (1:1 vol), and (d) 1 M LiTFSA/FEC+HFE (1:1 vol).

XPS analysis of deposited Li (1st deposition)

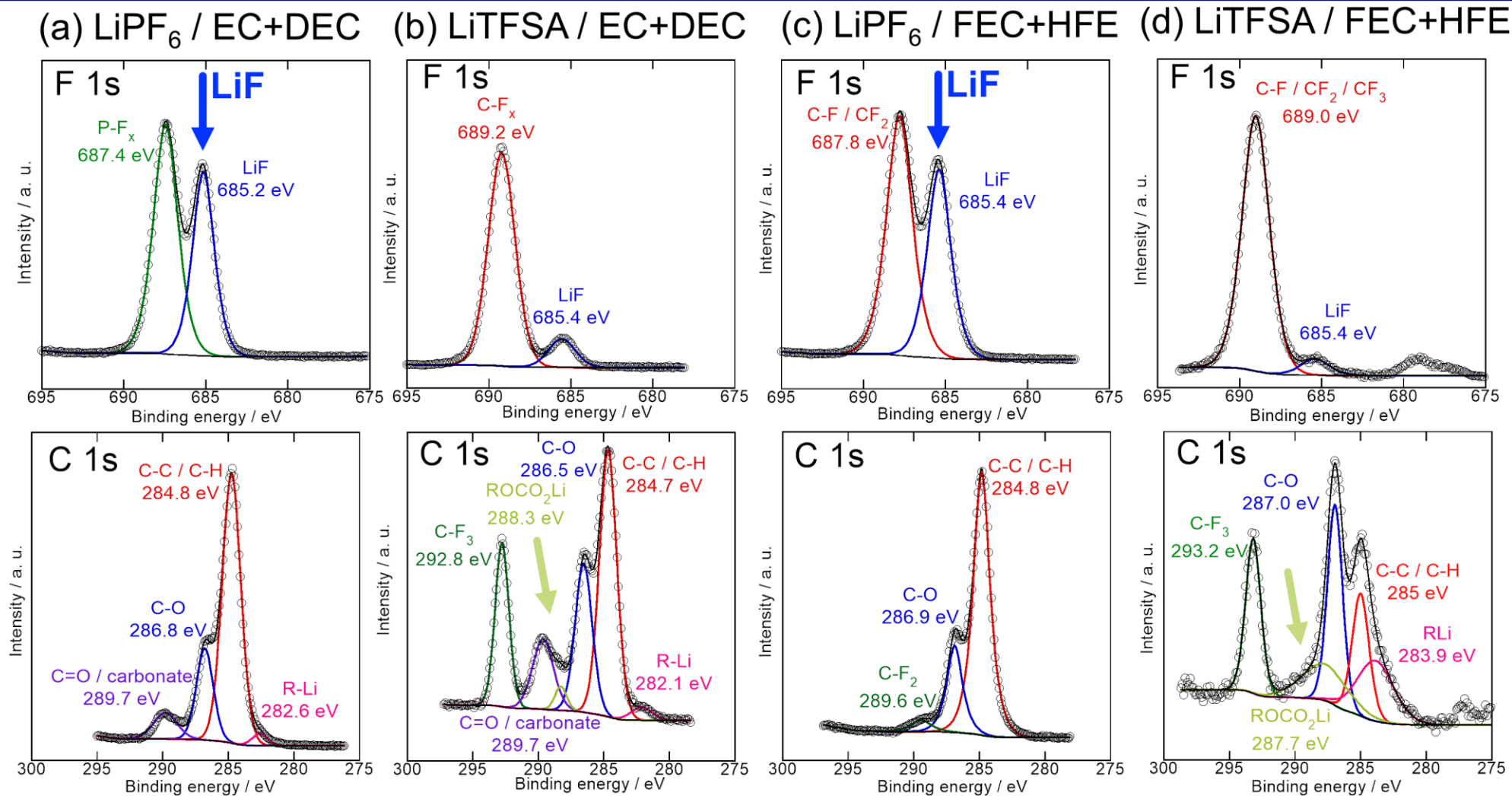
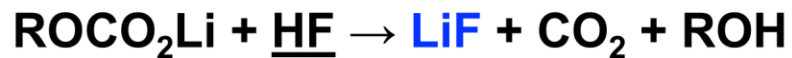


Fig. C 1s and F 1s XPS spectra of Li on Cu foil after 1st deposition in (a) 1 M LiPF₆/EC+DEC (1:1 vol), (b) 1 M LiTFSA/EC+DEC (1:1 vol), (c) 1 M LiPF₆/FEC+HFE(1:1 vol), and (d) 1 M LiTFSA/FEC+HFE (1:1 vol) at 25 °C. Current density: 0.5 mA cm⁻², Electric charge: 2.2 mAh cm⁻².



Hydrolysis products of LiPF₆ [1]

[1] U. Heider, R. Oesten, and M. Jungnitz, *J. Power Sources*, **81**, 119 (1999).

➤ Electrodes

Working electrode (WE): Pt disk ($\phi 3$ mm)

Reference electrode (RE): Li foil

Counter electrode (CE): Li foil

➤ Electrolytes

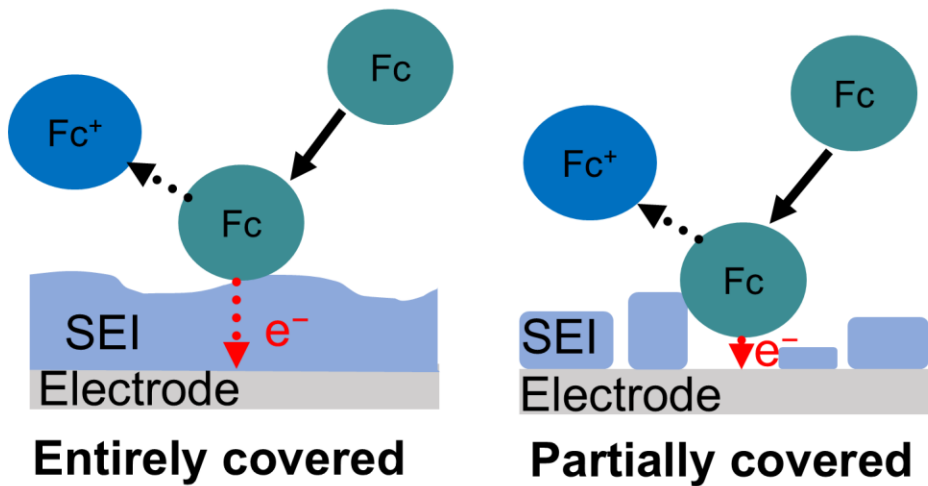
(a) 1 M $\text{LiPF}_6/\text{EC}+\text{DEC}$ (1:1 vol) containing **10 mM Fc**

(b) 1 M $\text{LiTFSA}/\text{EC}+\text{DEC}$ (1:1 vol) containing **10 mM Fc**

(c) 1 M $\text{LiPF}_6/\text{FEC}+\text{HFE}$ (1:1 vol) containing **10 mM Fc**

(d) 1 M $\text{LiTFSA}/\text{FEC}+\text{HFE}$ (1:1 vol) containing **10 mM Fc**

➤ Observation of SEI formation[1]



➤ Measurement

Cyclic voltammetry (CV)

Potentiostatic cathodic reduction

Open circuit potential (OCP)

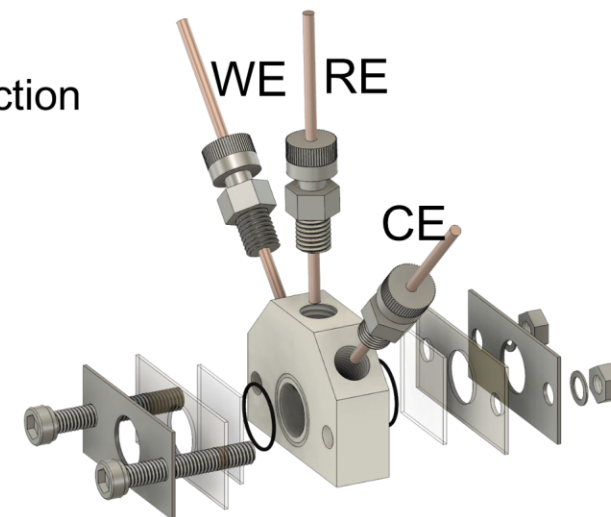
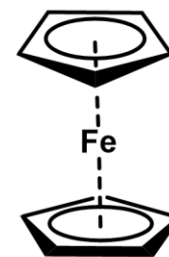


Fig. Schematic illustration of cell

For an electrically non-conductive SEI:

- If the electrode is **entirely** covered by the SEI.
⇒ **Peak potential shift**
→ Elongation of tunnelling distance, decreased standard rate constant.
- If the electrode is **partially** covered by the SEI.
⇒ **No peak potential shift**

Redox Probe (SEI Formation)

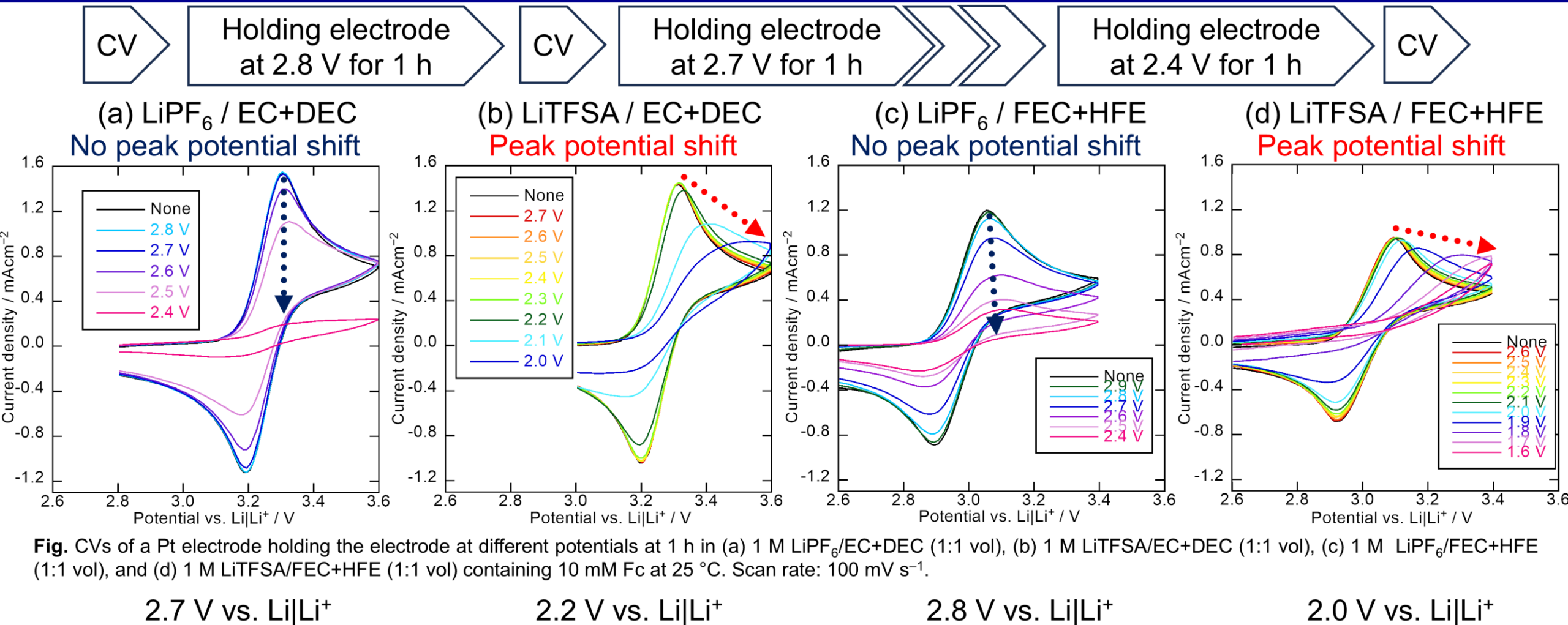


Fig. CVs of a Pt electrode holding the electrode at different potentials at 1 h in (a) 1 M LiPF_6 /EC+DEC (1:1 vol), (b) 1 M LiTFSA /EC+DEC (1:1 vol), (c) 1 M LiPF_6 /FEC+HFE (1:1 vol), and (d) 1 M LiTFSA /FEC+HFE (1:1 vol) containing 10 mM Fc at 25 °C. Scan rate: 100 mV s^{-1} .

- A **peak potential shift** and a decrease in current density occurred with LiTFSA .
→ **Entirely covered** and SEI with no electronic conductivity
- No **peak potential shift** and a decrease in current density occurred with LiPF_6 .
→ **Partially covered** and SEI with no electronic conductivity

Redox Probe (SEI Breakdown)

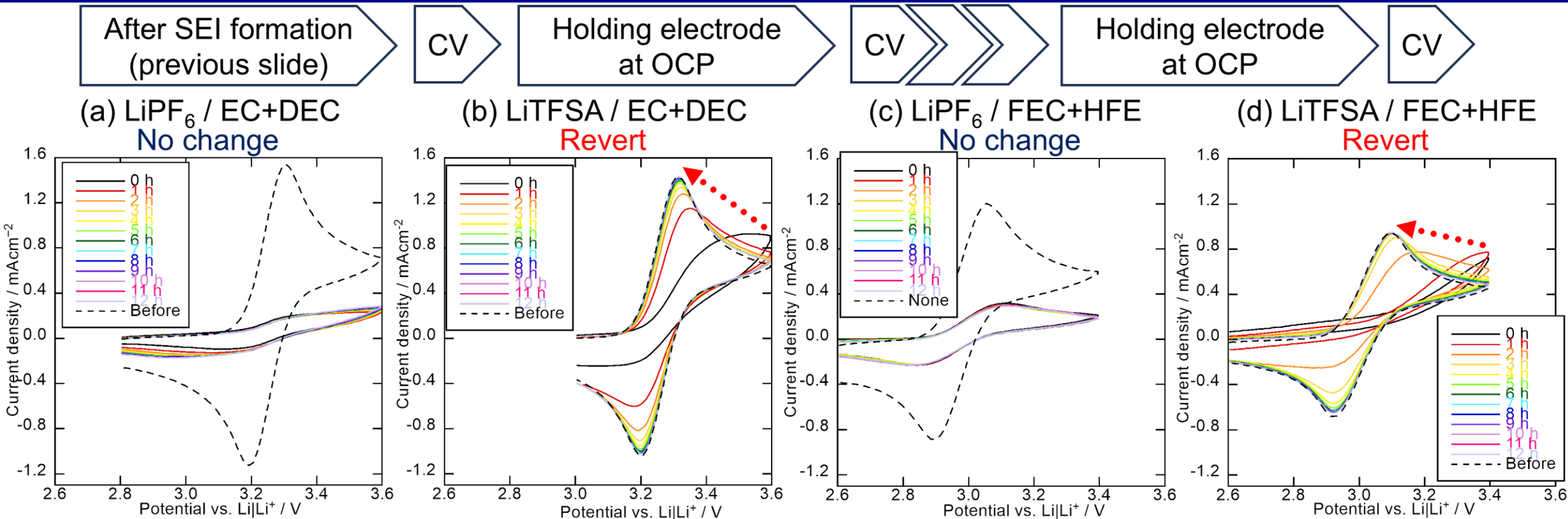
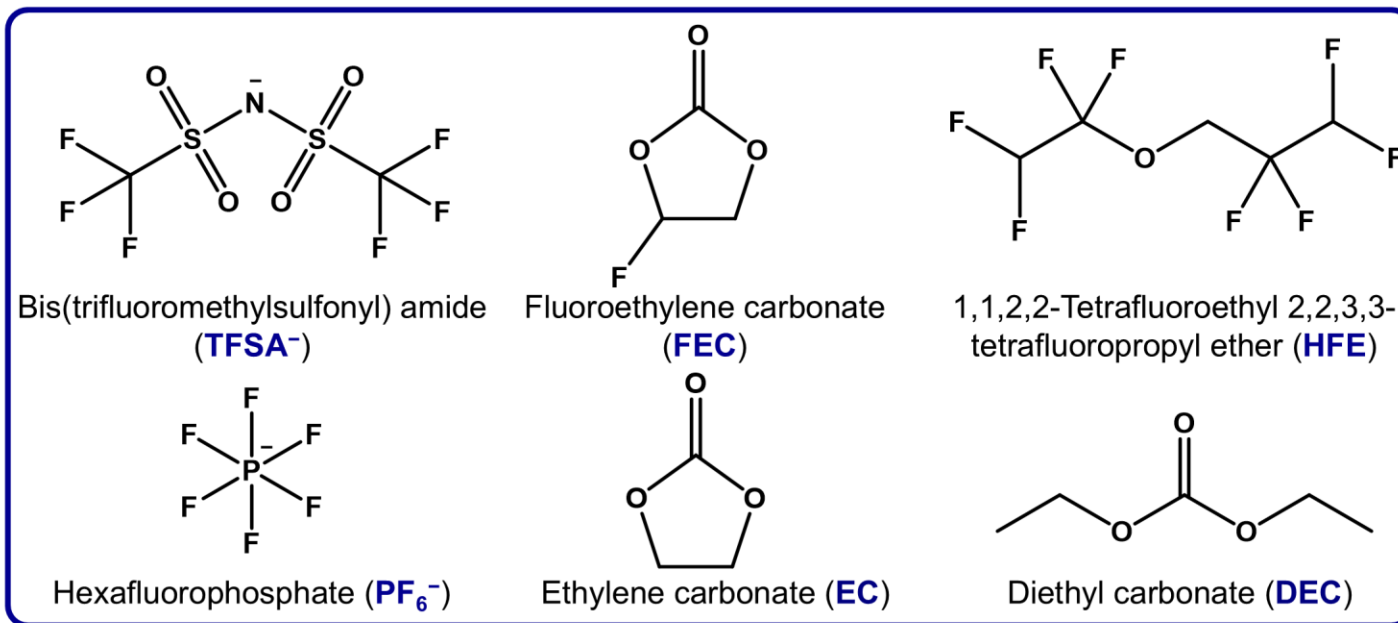


Fig. CVs of a Pt electrode at different standing periods after the SEI formation in (a) 1 M LiPF_6 /EC+DEC (1:1 vol), (b) 1 M LiTFSA /EC+DEC (1:1 vol), (c) 1 M LiPF_6 /FEC+HFE (1:1 vol), and (d) 1 M LiTFSA /FEC+HFE (1:1 vol) containing 10 mM Fc at 25 °C. Scan rate: 100 mV s⁻¹.

- ✓ CV shape **reverted** in LiTFSA -containing electrolyte → SEI disappeared → Gel-like SEI
- ✓ CV shape **unchanged** in LiPF_6 -containing electrolyte → SEI remained → Rigid SEI

With LiPF_6 , the formation of an uneven SEI (LiF) with very low electrical and ionic conductivity[1] increased the effective current density, promoting the deposition of Li in dendritic and whisker-like forms.

Summary



	EC/DEC (1:1 vol)	FEC/HFE (1:1 vol)
1 M LiPF ₆	(a)	(c)
1 M LiTFSA	(b)	(d)

- ❑ Discharge capacity decreased rapidly around 80 cycles in 1 M LiTFSA/FEC+HFE (1:1 vol).
- ❑ FEC+HFE may have a lower reactivity with Li than EC+DEC because the electrolyte contains a lower proportion of carbonate-based solvents.
- ❑ LiTFSA may suppress the formation of dead Li compared to LiPF₆ because LiPF₆ leads to the formation of an uneven SEI while LiTFSA forms a uniform SEI.

Acknowledgment

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