Supporting Information

Stable Lithium Metal Plating/Stripping in a Localized High-Concentration Cyclic Carbonate-Based Electrolyte

Yuta MAEYOSHI,*[,§] Kazuki YOSHII,[§] and Hikari SAKAEBE[§§]

Research Institute of Electrochemical Energy, Department of Energy and Environment, National Institute of Advanced Industrial Science and Technology (AIST), 1-8-31 Midorigaoka, Ikeda, Osaka 563-8577, Japan

**Corresponding Author: y.maeyoshi@aist.go.jp*

§ ECSJ Active Member

§§ ECSJ Fellow

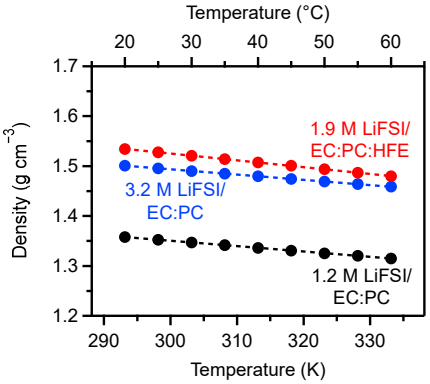

Figure S1. Temperature dependence of density for LiFSI/EC:PC and LiFSI/EC:PC:HFE electrolytes. Linear dependence of density on temperature was observed for all the electrolytes. The density (ρ) was fitted using the following equation:

$$\rho = a + bT$$

where a is a density at 0 K (g cm^{-3}), b is a coefficient of volume expansion (g cm^{-3} K^{-1}), and T is the absolute temperature (K). The parameters fitted by the least-square method are summarized in Table S1 with the coefficient of determination (R^2) for the fitting.

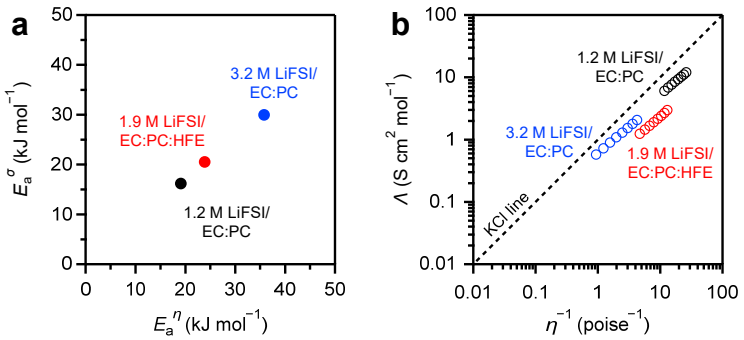

Figure S2. (a) Relationship between the activation energy for ionic conductivity (E_a^{σ}) and viscous flow (E_a^{η}) for LiFSI/EC:PC and LiFSI/EC:PC:HFE electrolytes. (b) Walden plots at 25–60 °C for the electrolytes. Walden plots show the relationship between the molar conductivity (Λ) and the viscosity (η) of the electrolytes.

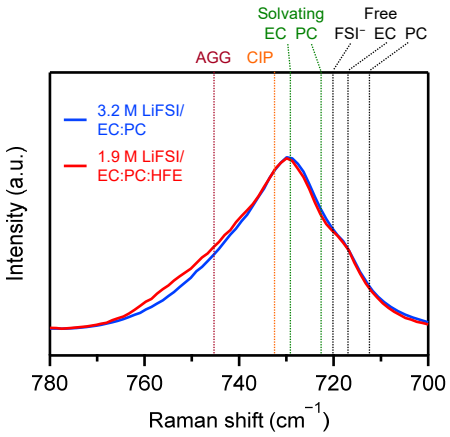

Figure S3. Raman spectra of 3.2 M LiFSI/EC:PC and 1.9 M LiFSI/EC:PC:HFE electrolytes for a wavenumber range of 780–700 cm^{-1} (corresponding to peaks related to the S–N stretching mode of FSI^- and the ring-bending modes of PC and EC). Free PC and EC show ring-bending bands at 712 and 717 cm^{-1}.[1] These bands respectively shift to around 722 and 729 cm^{-1} when PC and EC solvate Li^+.[1] The S–N stretching band of free FSI^- (~720 cm^{-1}) shifts to higher wavenumbers when the ion-pairing of FSI^- and Li^+ is intensified to form contact ion pairs (~732 cm^{-1}, CIPs, one FSI^- coordinating one Li^+) and aggregates (higher than 745 cm^{-1}, AGGs, one FSI^- coordinating two or more Li^+).[2]

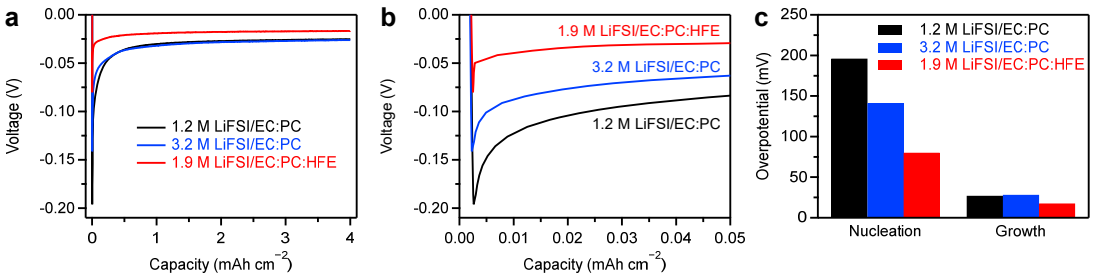

Figure S4. (a) Voltage vs. capacity of Li plating in Cu|Li half-cells using 1.2 M LiFSI/EC:PC, 3.2 M LiFSI/EC:PC, and 1.9 M LiFSI/EC:PC:HFE electrolytes at a current density of 0.5 mA cm^{-2} and a deposition capacity of 4.0 mAh cm^{-2}. (b) Magnified view of the panel (a). (c) Overpotential for the Li nucleation (the voltage spike at the onset of Li deposition) and the Li growth (the voltage plateau after Li nucleation) processes. The values of the Li growth overpotential are at a deposition capacity of 2.0 mAh cm^{-2}.

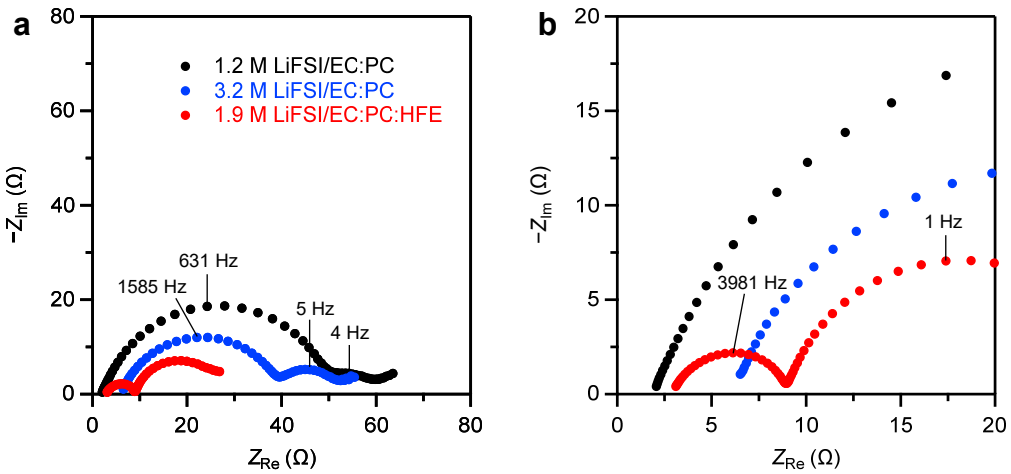

Figure S5. (a) Nyquist plots of electrochemical impedance spectroscopy measurements for Li|Li symmetric cells using 1.2 M LiFSI/EC:PC, 3.2 M LiFSI/EC:PC, and 1.9 M LiFSI/EC:PC:HFE electrolytes. The cells were measured at 25 °C after 1 cycle of Li plating/stripping at a current density of 0.5 mA cm^{-2} and a capacity of 1.0 mAh cm^{-2}. (b) Magnified view of the panel (a).

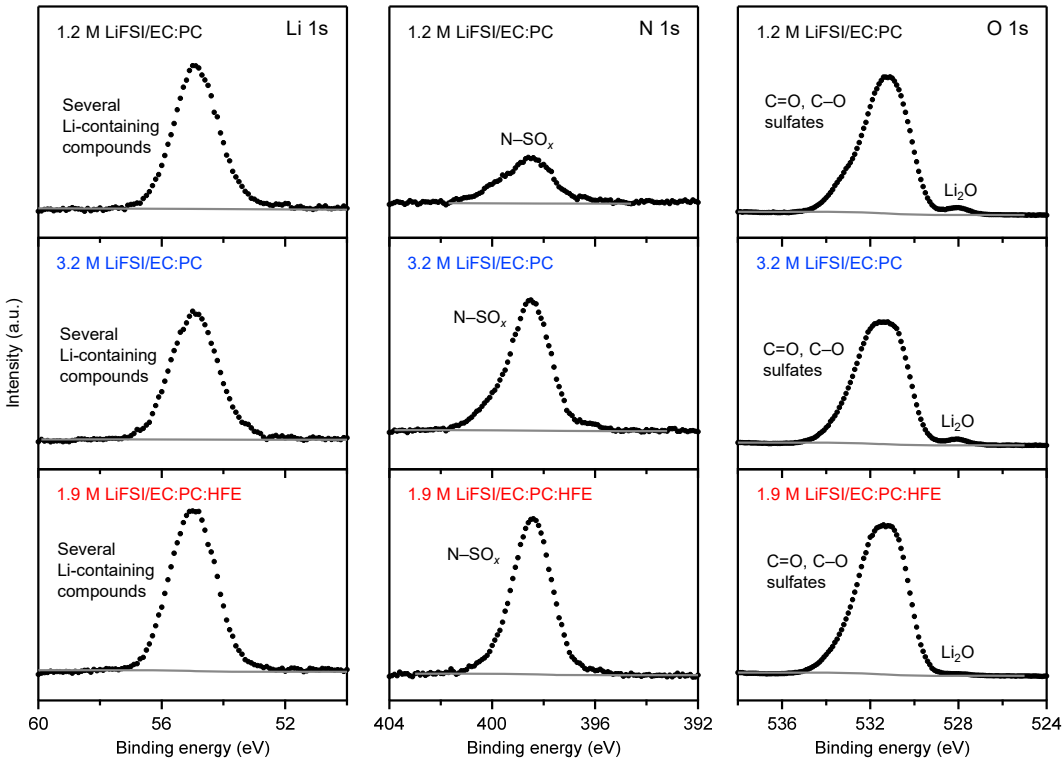

Figure S6. Li 1s, N 1s, and O 1s XPS spectra of the SEI layers on Cu foil after 10 cycles of Li plating/stripping in 1.2 M LiFSI/EC:PC, 3.2 M LiFSI/EC:PC, and 1.9 M LiFSI/EC:PC:HFE electrolytes.

Table S1. Fitting parameters for density of LiFSI/EC:PC and LiFSI/EC:PC:HFE electrolytes.

Electrolytes	a (g cm^{-3})	b (g cm^{-3} K^{-1})	R^2
1.2 M LiFSI/EC:PC	1.672	1.074×10^{-3}	0.99
3.2 M LiFSI/EC:PC	1.810	1.054×10^{-3}	0.99
1.9 M LiFSI/EC:PC:HFE	1.933	1.359×10^{-3}	0.99

Table S2. Fitting parameters for viscosity of LiFSI/EC:PC and LiFSI/EC:PC:HFE electrolytes.

Electrolytes	A_η (mPa s)	E_a^η (kJ mol^{-1})	R^2
1.2 M LiFSI/EC:PC	3.97×10^{-3}	19.1	0.99
3.2 M LiFSI/EC:PC	5.57×10^{-5}	35.8	0.99
1.9 M LiFSI/EC:PC:HFE	1.35×10^{-3}	23.9	0.99

Table S3. Fitting parameters for ionic conductivity of LiFSI/EC:PC and LiFSI/EC:PC:HFE electrolytes.

Electrolytes	A_σ (mS cm^{-1})	E_a^σ (kJ mol^{-1})	R^2
1.2 M LiFSI/EC:PC	5.04×10^3	16.2	0.99
3.2 M LiFSI/EC:PC	3.38×10^5	30.0	0.99
1.9 M LiFSI/EC:PC:HFE	9.47×10^3	20.5	0.99

References

1. J. L. Allen, O. Borodin, D. M. Seo, and W. A. Henderson, *J. Power Sources*, **267**, 821 (2014).
2. J. Wang, Y. Yamada, K. Sodeyama, C. H. Chiang, Y. Tateyama, and A. Yamada, *Nat. Commun.*, **7**, 12032 (2016).