Electronic Supplementary Information

Structural and electrochemical study of lithium-ion battery electrolytes using an ethylene sulfite solvent: from dilute to concentrated solutions

Kenzo Suzuki,[a,‡] Saki Sawayama,[a,‡] Yuna Deguchi,[a] Ryansu Sai,[a] Jihae Han,[a] and Kenta Fujii [a],*

[a] Graduate School of Sciences and Technology for Innovation, Yamaguchi University, 1-16-2 Tokiwadai, Ube, Yamaguchi 755-8611, Japan.

[*] To whom correspondence should be addressed. E-mail: k-fujii@yamaguchi-u.ac.jp

Fraction of the FSA species: c_f/c_T, c_b/c_T, and c_{agg}/c_T.

The integrated intensity (I_f) of the free FSA anion is given as $I_f = \varepsilon_f c_f$, where ε_f is the molar extinction coefficient, and c_f is the concentration of the free FSA anion in the LiFSA/ES solutions. Here, we note that no coordination of FSA anions to Li-ions occurs in the dilute solutions (<2.0 mol dm^{-3}). Thus, all of the FSA anions exist as a free FSA in the bulk, resulting in the relation: c_{Li} = c_f to determine the ε_f value (= I_f/c_f). In the c_{Li}-range of 2.0–2.5 mol dm^{-3}, the Li ions coexist as two types of mononuclear Li-ion complexs, i.e., [Li(ES)$_4$]$^+$ and contact ion-pair [Li(ES)$_n$(FSA)$_m$] as described in the manuscript. The c_b (concentration of the bound FSA) is thus calculated by c_b = $c_T - c_f$, where c_T is the total concentration of FSA anions in solutions, and then the ε_b can be determined from the relation, $I_b = \varepsilon_b c_b$. At ≥3.0 mol dm^{-3}, the aggregate FSA coexists with both free and bound FSA species in the solutions. The concentration of aggregate FSA (c_{agg}) is thus obtained as follows, $c_{agg} = c_T - c_f + c_b$. The fraction of free, bound (CIP), and aggregate FSA species in the solutions are thus calculated by c_f/c_T, c_b/c_T, and c_{agg}/c_T, respectively.

Table S1. Molar ratio (salt: solvent), concentrations of LiFSA salt (c_{Li}), ES (c_{ES}), density (d), and refractive index (n_2) for LiFSA/ES solutions.

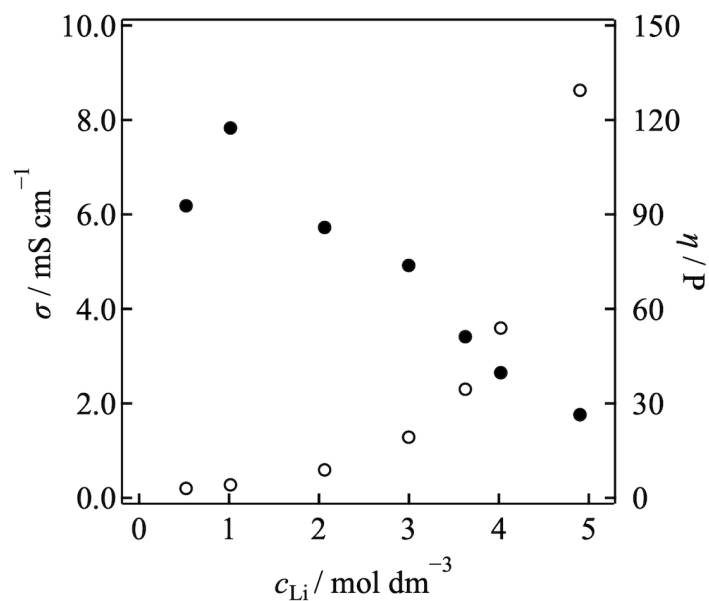| LiFSA/ES system				
LiFSA : ES	c_{Li} / mol dm^{-3}	c_{ES} / mol dm^{-3}	d / g cm^{-3}	n_2
–	0	13.2	1.430	1.44
1 : 52.5	0.25	12.9	1.441	1.44
1 : 24.1	0.5	12.8	1.465	1.44
1 : 16.0	0.75	12.3	1.480	1.44
1 : 12.0	1.0	12.1	1.495	1.44
1 : 5.24	2.0	10.8	1.557	1.44
1 : 4.02	2.5	10.3	1.586	1.44
1 : 3.24	3.0	9.7	1.610	1.44
1 : 2.50	3.6	9.1	1.644	1.44
1 : 2.11	4.0	8.5	1.668	1.43
1 : 1.50	4.9	7.4	1.713	1.43

Figure S1. c_{Li} dependences of ionic conductivity (filled circles) and viscosity (open circles) for LiFSA/ES solutions at 298 K.
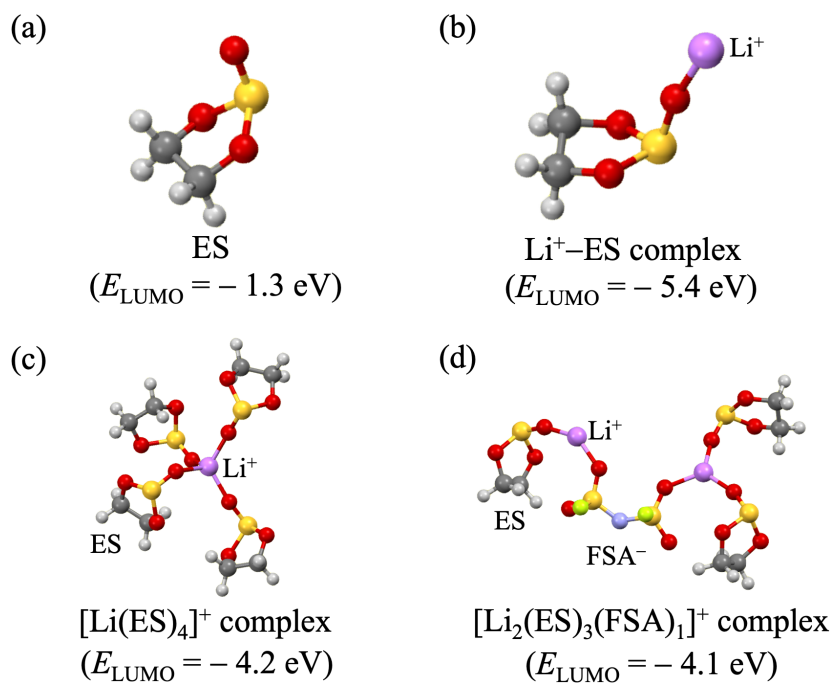

(a)

ES
($E_{LUMO} = -1.3$ eV)

(b)

Li$^+$

Li$^+$–ES complex
($E_{LUMO} = -5.4$ eV)

(c)

ES

Li$^+$

[Li(ES)$_4$]$^+$ complex
($E_{LUMO} = -4.2$ eV)

(d)

Li$^+$

ES

FSA$^-$

[Li$_2$(ES)$_3$(FSA)$_1$]$^+$ complex
($E_{LUMO} = -4.1$ eV)

Figure S2. The optimized geometries of (a) isolated ES, (b) Li$^+$-ES complex, (c) [Li(ES)$_4$]$^+$ complex, and (d) [Li$_2$(ES)$_3$(FSA)$_1$]$^+$ complex and their LUMO energies obtained from DFT calculations.

ES

Li⁺

FSA⁻

$[Li_2(ES)_3(FSA)_1]^+$ complex

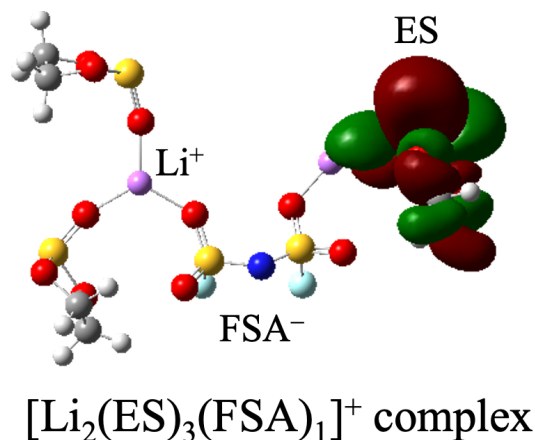**Figure S3.** The location of LUMOs on the optimized $[Li_2(ES)_3(FSA)_1]^+$ complex using DFT calculations.
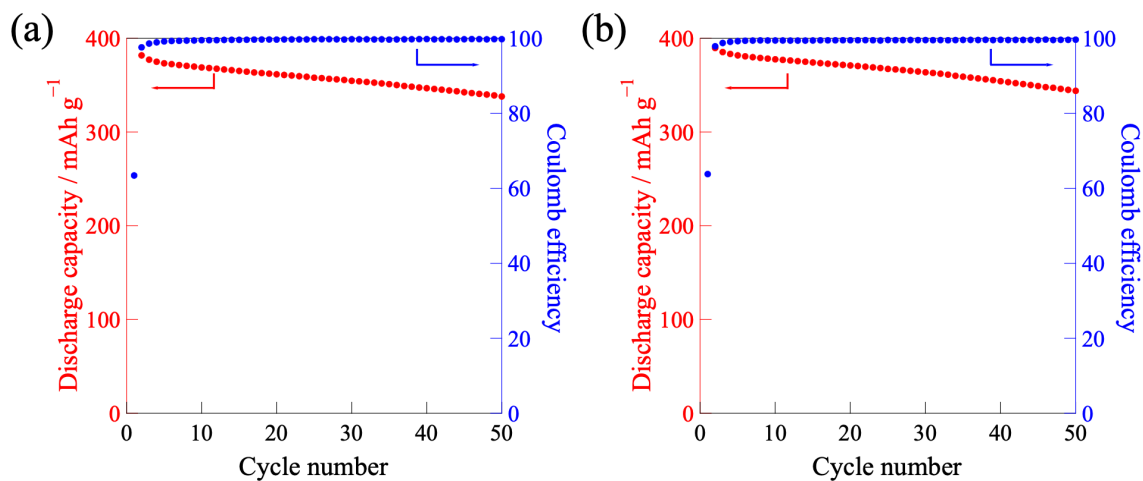

Figure S4. Cycling performance (red, left axis) and coulomb efficiency (blue, right axis) of the (a) 3.6 mol dm^{-3} and (b) 1.0 mol dm^{-3} LiFSA/ES solutions. The coulombic efficiencies at the initial cycle are 63.4% and 63.8% for the 3.6 and 1.0 mol dm^{-3} solutions, respectively.