Supporting Information:

Conductometric Analysis of Ion Equilibrium in Li⁺/F⁻ and Mg²⁺/F⁻ Hybrid Electrolyte Solutions

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1 Concentration dependence of the molar ionic conductivity

The concentration dependence of the molar conductivity, Λ_I, confirmed Kohlrausch's square root law over the concentration range measured for each salt solution: LiFSA, LiTFSA, CsTFSA, CsF and Mg(TFSA)$_2$ (Fig. S1). The molar conductivity of infinite dilution, Λ_I^∞, and concentration parameter, S_I, are calculated from the slope and the intercept of Fig. S1, and shown in Table S1. The values of the molar ionic conductivity, λ_i, at a given ion concentration, c_i, were evaluated with Λ_I^∞, S_I, and the cation transport number of LiFSA solution, $t_{+,\mathrm{LiFSA}}$. First, λ_{Li^+} and λ_{FSA^-} were obtained as follows:

$$\lambda_{\mathrm{Li}^+} = t_{+,\mathrm{LiFSA}}\Lambda_{\mathrm{LiFSA}} = t_{+,\mathrm{LiFSA}}\left(\Lambda_{\mathrm{LiFSA}}^\infty - S_{\mathrm{LiFSA}}\sqrt{c_{\mathrm{Li}^+}}\right), \tag{1}$$

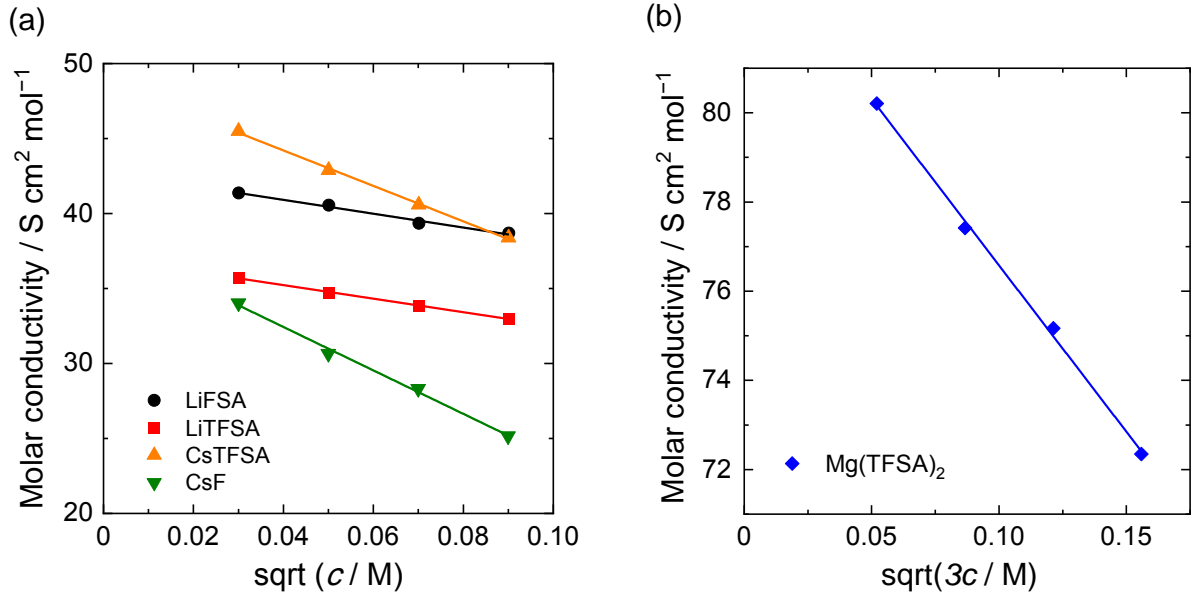**Figure S1.** The concentration dependence of the molar conductivity of (a) LiFSA, LiTFSA, CsTFSA, CsF, and (b) Mg(TFSA)$_2$ solutions.

Table S1. The molar conductivity of infinite dilution, Λ_I^∞, and concentration parameter, S_I, obtained from the slope and the intercept of concentration dependence of the molar conductivities.

	Λ_I^∞/S cm^2 mol^{-1}	S_I/S cm^2 mol^{-1} M$^{-1/2}$
LiFSA	42.8 ± 0.2	46 ± 4
LiTFSA	37.03 ± 0.09	45 ± 1
CsTFSA	48.9 ± 0.2	118 ± 3
CsF	38.2 ± 0.4	144 ± 7
Mg(TFSA)$_2$	84.0 ± 0.2	75 ± 2

$$\lambda_{FSA^-} = (1 - t_{+,LiFSA})\Lambda_{LiFSA} = (1 - t_{+,LiFSA})(\Lambda_{LiFSA}^\infty - S_{LiFSA}\sqrt{c_{FSA^-}}). \tag{2}$$

λ_i values of the other ions were obtained in order with the above λ_{Li^+} and λ_{FSA^-};

$$\lambda_{TFSA^-} = \Lambda_{LiTFSA} - \lambda_{Li^+}$$
$$= (\Lambda_{LiTFSA}^\infty - S_{LiTFSA}\sqrt{c_{TFSA^-}}) - t_{+,LiFSA}(\Lambda_{LiFSA}^\infty - S_{LiFSA}\sqrt{c_{TFSA^-}}). \tag{3}$$

$$\lambda_{Cs^+} = \Lambda_{CsTFSA} - \lambda_{TFSA^-}$$
$$= \left[\Lambda_{CsTFSA}^\infty - S_{CsTFSA}\sqrt{c_{Cs^+}}\right] \tag{4}$$
$$-\left[(\Lambda_{LiTFSA}^\infty - S_{LiTFSA}\sqrt{c_{Cs^+}}) - t_{+,LiFSA}(\Lambda_{LiFSA}^\infty - S_{LiFSA}\sqrt{c_{Cs^+}})\right].$$

$$\lambda_{F^-} = \Lambda_{CsF} - \lambda_{Cs^+}$$
$$= \left[\Lambda_{CsF}^\infty - S_{CsF}\sqrt{c_{F^-}}\right] \tag{5}$$
$$-\left\{\left[\Lambda_{CsTFSA}^\infty - S_{CsTFSA}\sqrt{c_{F^-}}\right]\right.$$
$$\left.- \left[(\Lambda_{LiTFSA}^\infty - S_{LiTFSA}\sqrt{c_{F^-}}) - t_{+,LiFSA}(\Lambda_{LiFSA}^\infty - S_{LiFSA}\sqrt{c_{F^-}})\right]\right\}$$

$$\lambda_{\text{Mg}^{2+}} = \Lambda_{\text{Mg(TFSA)}_2} - 2\lambda_{\text{TFSA}^-}$$

$$= \left[\Lambda_{\text{Mg(TFSA)}_2}^{\infty} - S_{\text{Mg(TFSA)}_2}\sqrt{3c_{\text{Mg}^{2+}}} \right] \tag{6}$$

$$- 2\left[\left(\Lambda_{\text{LiTFSA}}^{\infty} - S_{\text{LiTFSA}}\sqrt{c_{\text{Mg}^{2+}}} \right) - t_{+,\text{LiFSA}} \left(\Lambda_{\text{LiFSA}}^{\infty} - S_{\text{LiFSA}}\sqrt{c_{\text{Mg}^{2+}}} \right) \right].$$

2 Equilibrium concentration

2.1 Li$^+$/F$^-$ hybrid electrolyte solution

2.1.1 Precipitation equilibrium model without the triple ion formation

For the precipitation equilibrium model, the equilibrium constant to be considered is:

$$K_1 = n_{\text{Li}^+} n_{\text{F}^-}. \tag{7}$$

The mass balance of the titration solution is represented by:

$$n_{\text{Li,t}} = n_{\text{Li}^+} + n_{\text{LiF}}, \tag{8}$$

for Li, and

$$n_{\text{F,t}} = n_{\text{F}^-} + n_{\text{LiF}}, \tag{9}$$

72   for F, where n_{LiF} is the amount of LiF precipitate. The total amounts are related to the concentration

73   and volute of the analyte, $c_{0,\mathrm{Li}}, c_{0,\mathrm{F,hybrid}}$ and V_{hybrid}, and those of the titrant, $c_{0,\mathrm{CsF}}$ and V_{CsF}.

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$$n_{\mathrm{Li^+}} + n_{\mathrm{LiF}} = c_{0,\mathrm{Li}}V_{\mathrm{hybrid}}\left(= n_{\mathrm{Li,t}}\right), \tag{10}$$

$$n_{\mathrm{F^-}} + n_{\mathrm{LiF}} = c_{0,\mathrm{CsF}}V_{\mathrm{CsF}} + c_{0,\mathrm{F,hybrid}}V_{\mathrm{hybrid}}\left(= n_{\mathrm{F,t}}\right). \tag{11}$$

By considering Eqs. (7), (10), and (11), we can get:

$$n_{\mathrm{F^-}} = \frac{K_1}{n_{\mathrm{Li^+}}}, \tag{12}$$

$$n_{\mathrm{Li,t}} - n_{\mathrm{F,t}} = n_{\mathrm{Li^+}} - n_{\mathrm{F^-}} = n_{\mathrm{Li^+}}\left(1 - \frac{K_1}{n_{\mathrm{Li^+}}}\right)$$

$$(n_{\mathrm{Li^+}})^2 - \left(n_{\mathrm{Li,t}} - n_{\mathrm{F,t}}\right)n_{\mathrm{Li^+}} - K_1 = 0 \tag{13}$$

$$n_{\mathrm{Li^+}} = \frac{\left(n_{\mathrm{Li,t}} - n_{\mathrm{F,t}}\right) + \sqrt{\left(n_{\mathrm{Li,t}} - n_{\mathrm{F,t}}\right)^2 + 4K_1}}{2}.$$

$$n_{\mathrm{LiF}} = n_{\mathrm{Li,t}} - n_{\mathrm{Li^+}}. \tag{14}$$

Consequently, we can evaluate c_i ($i = \mathrm{Li^+, F^-, FSA^-,}$ and $\mathrm{Cs^+}$) at any arbitrary titration points.

$$c_{\mathrm{Li^+}} = \frac{n_{\mathrm{Li^+}}}{V_{\mathrm{t,Li/F}}}, \tag{15}$$

$$c_{F^-} = \frac{n_{F^-}}{V_{t,Li/F}},$$

$$c_{FSA^-} = \frac{n_{Li,t}}{V_{t,Li/F}},$$

$$c_{Cs^+} = \frac{n_{F,t}}{V_{t,Li/F}}.$$

2.1.2 Model with both of the precipitation and the triple ion formation equilibria

In the model of both of the precipitation and the triple ion formation equilibria, the equilibrium constants to be considered are Eq. (7).

$$K_2 = \frac{n_{Li_2F^+}}{(n_{Li^+})^2 n_{F^-}}, \tag{16}$$

and

$$K_2 = \frac{n_{LiF_2^-}}{n_{Li^+}(n_{F^-})^2}. \tag{17}$$

The mass balance of the titration solution is given by:

$$n_{Li,t} = n_{Li^+} + n_{LiF} + 2n_{Li_2F^+} + n_{LiF_2^-}, \tag{18}$$

for Li, and

$$n_{F,t} = n_{F^-} + n_{LiF} + n_{Li_2F^+} + 2n_{LiF_2^-}, \tag{19}$$

for F, where $n_{Li_2F^+}$ and $n_{LiF_2^-}$ are the amounts of Li_2F^+ and LiF_2^- triple ions, respectively. The mass

balance concept gives:

$$n_{Li^+} + n_{LiF} + 2n_{Li_2F^+} + n_{LiF_2^-} = c_{0,Li}V_{hybrid}(= n_{Li,t}), \tag{20}$$

$$n_{F^-} + n_{LiF} + n_{Li_2F^+} + 2n_{LiF_2^-} = c_{0,CsF}V_{CsF} + c_{0,F,hybrid}V_{hybrid}(= n_{F,t}). \tag{21}$$

From Eqs. (7), (16), and (17),

$$n_{Li_2F^+} = K_1K_2n_{Li^+}, \tag{22}$$

$$n_{LiF_2^-} = \frac{K_1{}^2K_2}{n_{Li^+}}. \tag{23}$$

Substituting $n_{Li_2F^+}$ and $n_{LiF_2^-}$ into Eqs. (20) and (21),

$$n_{Li,t} - n_{F,t} = n_{Li^+} - n_{F^-} + n_{Li_2F^+} - n_{LiF_2^-} = \left(n_{Li^+} - \frac{K_1}{n_{Li^+}}\right)(1 + K_1K_2)$$

$$(1 + K_1K_2)(n_{Li^+})^2 - (n_{Li,t} - n_{F,t})n_{Li^+} - K_1(1 + K_1K_2) = 0 \tag{24}$$

$$n_{\text{Li}^+} = \frac{\left(n_{\text{Li,t}} - n_{\text{F,t}}\right) + \sqrt{\left(n_{\text{Li,t}} - n_{\text{F,t}}\right)^2 + 4K_1(1 + K_1K_2)^2}}{2(1 + K_1K_2)}.$$

The amounts n_{F^-}, $n_{\text{Li}_2\text{F}^+}$, and $n_{\text{LiF}_2^-}$ can be obtained from Eqs. (12), (22) and (23), respectively,

while n_{LiF} is given from Eq. (20) as follows.

$$n_{\text{LiF}} = n_{\text{Li,t}} - \left(n_{\text{Li}^+} + 2n_{\text{Li}_2\text{F}^+} + n_{\text{LiF}_2^-}\right). \tag{25}$$

Consequently, we can evaluate c_i ($i = \text{Li}^+, \text{F}^-, \text{Li}_2\text{F}^+, \text{LiF}_2^-, \text{FSA}^-,$ and Cs^+) at any arbitrary

titration points.

$$\begin{aligned}
c_{\text{Li}^+} &= \frac{n_{\text{Li}^+}}{V_{\text{t,Li/F}}}, \\
c_{\text{F}^-} &= \frac{n_{\text{F}^-}}{V_{\text{t,Li/F}}}, \\
c_{\text{Li}_2\text{F}^+} &= \frac{n_{\text{Li}_2\text{F}^+}}{V_{\text{t,Li/F}}}, \\
c_{\text{LiF}_2^-} &= \frac{n_{\text{LiF}_2^-}}{V_{\text{t,Li/F}}}, \\
c_{\text{FSA}^-} &= \frac{n_{\text{Li,t}}}{V_{\text{t,Li/F}}}, \\
c_{\text{Cs}^+} &= \frac{n_{\text{F,t}}}{V_{\text{t,Li/F}}}.
\end{aligned} \tag{26}$$

Limited case of no precipitation

Even in this model, the precipitation would not occur when $n_{\text{F,t}}/n_{\text{Li,t}}$ is very small or very

large. Therefore, the case in which only triple ions are formed without precipitation is also discussed here. In this case, only K_2 must be considered by ignoring K_1. The mass balance of the titration solution is given by:

$$n_{\text{Li,t}} = n_{\text{Li}^+} + 2n_{\text{Li}_2\text{F}^+} + n_{\text{LiF}_2^-}, \tag{27}$$

for Li, and

$$n_{\text{F,t}} = n_{\text{F}^-} + n_{\text{Li}_2\text{F}^+} + 2n_{\text{LiF}_2^-}, \tag{28}$$

for F. The mass balance concept gives:

$$n_{\text{Li}^+} + 2n_{\text{Li}_2\text{F}^+} + n_{\text{LiF}_2^-} = c_{0,\text{Li}}V_{\text{hybrid}}\left(= n_{\text{Li,t}}\right), \tag{29}$$

$$n_{\text{F}^-} + n_{\text{Li}_2\text{F}^+} + 2n_{\text{LiF}_2^-} = c_{0,\text{CsF}}V_{\text{CsF}} + c_{0,\text{F,hybrid}}V_{\text{hybrid}}\left(= n_{\text{F,t}}\right). \tag{30}$$

From Eqs. (16) and (17),

$$n_{\text{Li}_2\text{F}^+} = K_2(n_{\text{Li}^+})^2 n_{\text{F}^-}, \tag{31}$$

$$n_{\text{LiF}_2^-} = K_2 n_{\text{Li}^+}(n_{\text{F}^-})^2. \tag{32}$$

Substituting these amounts of the ions into Eqs. (29) and (30),

$$n_{\text{Li},t} = n_{\text{Li}^+} + K_2 n_{\text{Li}^+} n_{\text{F}^-}(2n_{\text{Li}^+} + n_{\text{F}^-}), \tag{33}$$

$$n_{\text{F},t} = n_{\text{F}^-} + K_2 n_{\text{Li}^+} n_{\text{F}^-}(n_{\text{Li}^+} + 2n_{\text{F}^-}). \tag{34}$$

Unfortunately, it is not easy to solve Eqs. (33) and (34), but we may reasonably ignore the triple ion

formation when $n_{\text{F},t}/n_{\text{Li},t}$ was very small or large.

Limited case A) Assumption of $n_{\text{LiF}_2^-} \approx 0$ at $n_{\text{F},t} \ll n_{\text{Li},t}$

In this case, the mass balance of the solution is rewritten by:

$$n_{\text{Li},t} = n_{\text{Li}^+} + 2n_{\text{Li}_2\text{F}^+}, \tag{35}$$

for Li, and

$$n_{\text{F},t} = n_{\text{F}^-} + n_{\text{Li}_2\text{F}^+}, \tag{36}$$

for F. These equations are further rewritten as follows:

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$$n_{\text{Li}^+} + 2n_{\text{Li}_2\text{F}^+} = c_{0,\text{Li}}V_{\text{hybrid}}(= n_{\text{Li,t}}), \tag{37}$$

$$n_{\text{F}^-} + n_{\text{Li}_2\text{F}^+} = c_{0,\text{CsF}}V_{\text{CsF}} + c_{0,\text{F,hybrid}}V_{\text{hybrid}}(= n_{\text{F,t}}). \tag{38}$$

Substitutting Eq. (31) into Eq. (37),

$$n_{\text{Li,t}} = n_{\text{Li}^+} + 2K_2(n_{\text{Li}^+})^2 n_{\text{F}^-},$$

$$n_{\text{F}^-} = \frac{n_{\text{Li,t}} - n_{\text{Li}^+}}{2K_2(n_{\text{Li}^+})^2}. \tag{39}$$

Substituting Eq. (39) and Eq. (31) into Eq. (38),

$$n_{\text{F,t}} = n_{\text{F}^-} + K_2(n_{\text{Li}^+})^2 n_{\text{F}^-}$$

$$n_{\text{F,t}} = \frac{n_{\text{Li,t}} - n_{\text{Li}^+}}{2K_2(n_{\text{Li}^+})^2} + \frac{n_{\text{Li,t}} - n_{\text{Li}^+}}{2} \tag{40}$$

$$K_2(n_{\text{Li}^+})^3 + K_2\big(2n_{\text{F,t}} - n_{\text{Li,t}}\big)(n_{\text{Li}^+})^2 + n_{\text{Li}^+} - n_{\text{Li,t}} = 0.$$

The analytical solution of this cubic equation for n_{Li^+} can be obtained by Cardano's method. Then, n_{F^-} and $n_{\text{Li}_2\text{F}^+}$ can be calculated from Eqs. (39) and (31), respectively. Consequently, we can evaluate c_i (i = $\text{Li}^+, \text{F}^-, \text{Li}_2\text{F}^+, \text{LiF}_2^-, \text{FSA}^-$, and Cs^+) at any arbitrary titration points.

$$c_{\text{Li}^+} = \frac{n_{\text{Li}^+}}{V_{\text{t,Li/F}}},$$

$$c_{\text{F}^-} = \frac{n_{\text{F}^-}}{V_{\text{t,Li/F}}},$$

$$c_{\text{Li}_2\text{F}^+} = \frac{n_{\text{Li}_2\text{F}^+}}{V_{\text{t,Li/F}}},$$

$$c_{\text{LiF}_2^-} = 0, \qquad\qquad\qquad (41)$$

$$c_{\text{FSA}^-} = \frac{n_{\text{Li,t}}}{V_{\text{t,Li/F}}},$$

$$c_{\text{Cs}^+} = \frac{n_{\text{F,t}}}{V_{\text{t,Li/F}}}.$$

Limited case B) Assumption of $n_{\text{Li}_2\text{F}^+} \approx 0$ at $n_{\text{Li,t}} \ll n_{\text{F,t}}$

In this case, the mass balance of the titration solution is rewritten by:

$$n_{\text{Li,t}} = n_{\text{Li}^+} + n_{\text{LiF}_2^-}, \qquad\qquad (42)$$

for Li, and

$$n_{\text{F,t}} = n_{\text{F}^-} + 2n_{\text{LiF}_2^-}, \qquad\qquad (43)$$

for F. Further rewritten gives:

$$n_{\text{Li}^+} + n_{\text{LiF}_2^-} = c_{0,\text{Li}} V_{\text{hybrid}} \left(= n_{\text{Li,t}} \right), \qquad\qquad (44)$$

$$n_{F^-} + 2n_{LiF_2^-} = c_{0,CsF}V_{CsF} + c_{0,F,hybrid}V_{hybrid}(= n_{F,t}). \tag{45}$$

Substituting Eq. (32) into Eq. (45),

$$n_{F,t} = n_{F^-} + 2K_2 n_{Li^+}(n_{F^-})^2,$$

$$n_{Li^+} = \frac{n_{F,t} - n_{F^-}}{2K_2(n_{F^-})^2}. \tag{46}$$

Substituting Eq. (46) and Eq. (32) into Eq. (44),

$$n_{Li,t} = n_{Li^+} + K_2 n_{Li^+}(n_{F^-})^2,$$

$$n_{Li,t} = \frac{n_{F,t} - n_{F^-}}{2K_2(n_{F^-})^2} + \frac{n_{F,t} - n_{F^-}}{2}, \tag{47}$$

$$K_2(n_{F^-})^3 + K_2(2n_{Li,t} - n_{F,t})(n_{F^-})^2 + n_{F^-} - n_{F,t} = 0.$$

The analytical solution of Eq. (47) for n_{F^-} can be obtained by Cardano's method. n_{Li^+} and $n_{LiF_2^-}$ can be given from Eqs. (46) and (32), respectively. Consequently, we can evaluate c_i (i = $Li^+, F^-, Li_2F^+, LiF_2^-, FSA^-,$ and Cs^+) at any arbitrary titration points.

$$c_{Li^+} = \frac{n_{Li^+}}{V_{t,Li/F}},$$

$$c_{F^-} = \frac{n_{F^-}}{V_{t,Li/F}}, \tag{48}$$

$$c_{\mathrm{Li_2F^+}} = 0,$$

$$c_{\mathrm{LiF_2^-}} = \frac{n_{\mathrm{LiF_2^-}}}{V_{\mathrm{t,Li/F}}},$$

$$c_{\mathrm{FSA^-}} = \frac{n_{\mathrm{Li,t}}}{V_{\mathrm{t,Li/F}}},$$

$$c_{\mathrm{Cs^+}} = \frac{n_{\mathrm{F,t}}}{V_{\mathrm{t,Li/F}}}.$$

Table S2. The results of conductivity titration of the diluted $\mathrm{Li^+/F^-}$ hybrid electrolyte solution with the CsF solution.

$n_{\mathrm{F,t}}/n_{\mathrm{Li,t}}$	conductivity κ /mS cm^{-1}
0.017	0.307
0.050	0.307
0.10	0.311
0.25	0.313
0.50	0.320
0.75	0.327
1.0	0.335
1.5	0.378
2.0	0.422
2.5	0.460
3.0	0.489
4.0	0.531

Table S3. The initial experimental condition of conductivity titration of the diluted $\mathrm{Li^+/F^-}$ hybrid electrolyte solution with the CsF solution.

$c_{\mathrm{0,Li}}$ / mM	$c_{\mathrm{0,F,hybrid}}$ /mM	V_{hybrid} /mL	$c_{\mathrm{0,CsF}}$ /mM
7.5	0.125	1.7	50

2.2 Mg^{2+}/F^- hybrid electrolyte solution

2.2.1 Precipitation equilibrium model without the ion association

For the precipitation equilibrium model, the equilibrium constant to be considered is:

$$K_3 = n_{Mg^{2+}}(n_{F^-})^2. \tag{49}$$

The mass balance of the titration solution is given by:

$$n_{Mg,t} = n_{Mg^{2+}} + n_{MgF_2}, \tag{50}$$

for Mg, and

$$n_{F,t} = n_{F^-} + 2n_{MgF_2}, \tag{51}$$

for F, where n_{MgF_2} is the amount of MgF_2 precipitate. The mass balance concept yields:

$$n_{Mg^{2+}} + n_{MgF_2} = c_{0,Mg(TFSA)_2} V_{Mg(TFSA)_2} (= n_{Mg,t}), \tag{52}$$

$$n_{F^-} + 2n_{MgF_2} = c_{0,CsF} V_{CsF} (= n_{F,t}). \tag{53}$$

where $c_{0,\mathrm{Mg(TFSA)_2}}$ and $V_{\mathrm{Mg(TFSA)_2}}$ is the concentration and the initial volume of the analyte,

respectively. From Eqs. (49), (52), and (53),

$$n_{\mathrm{Mg}^{2+}} = \frac{K_3}{(n_{\mathrm{F}^-})^2}, \tag{54}$$

$$2n_{\mathrm{Mg,t}} - n_{\mathrm{F,t}} = 2\frac{K_3}{(n_{\mathrm{F}^-})^2} - n_{\mathrm{F}^-}$$

$$(n_{\mathrm{F}^-})^3 - (2n_{\mathrm{Mg,t}} - n_{\mathrm{F,t}})(n_{\mathrm{F}^-})^2 - 2K_3 = 0. \tag{55}$$

Thus, we can obtain n_{F^-}. $n_{\mathrm{Mg}^{2+}}$ is given by Eq. (54), while $n_{\mathrm{MgF_2}}$ is given by:

$$n_{\mathrm{MgF_2}} = n_{\mathrm{Mg,t}} - n_{\mathrm{Mg}^{2+}}. \tag{56}$$

Consequently,

$$c_{\mathrm{Mg}^{2+}} = \frac{n_{\mathrm{Mg}^{2+}}}{V_{\mathrm{t,Mg/F}}},$$

$$c_{\mathrm{F}^-} = \frac{n_{\mathrm{F}^-}}{V_{\mathrm{t,Mg/F}}},$$

$$c_{\mathrm{TFSA}^-} = \frac{2n_{\mathrm{Mg,t}}}{V_{\mathrm{t,Mg/F}}}, \tag{57}$$

$$c_{\mathrm{Cs}^+} = \frac{n_{\mathrm{F,t}}}{V_{\mathrm{t,Mg/F}}}.$$

2.2.2 Model with both of the precipitation and the ion association equilibria

In the model of both precipitation and association equilibria, the equilibrium constants to be considered are Eq. (49) and

$$K_4 = \frac{n_{MgF^+}}{n_{Mg^{2+}} n_{F^-}}.$$ (58)

The mass balance is given by:

$$n_{Mg,t} = n_{Mg^{2+}} + n_{MgF_2} + n_{MgF^+},$$ (59)

for Mg, and

$$n_{F,t} = n_{F^-} + 2n_{MgF_2} + n_{MgF^+},$$ (60)

for F, where n_{MgF^+} is the amount of MgF^+. Equations (59) and (60) are rewritten as follows:

$$n_{Mg^{2+}} + n_{MgF_2} + n_{MgF^+} = c_{0,Mg(TFSA)_2} V_{Mg(TFSA)_2} (= n_{Mg,t}),$$ (61)

$$n_{F^-} + 2n_{MgF_2} + n_{MgF^+} = c_{0,CsF} V_{CsF} (= n_{F,t}).$$ (62)

Equations (49) and (58) are also rewritten as follows:

$$n_{Mg^{2+}} = \frac{K_3}{(n_{F^-})^2},$$

(63)

$$n_{MgF^+} = \frac{K_3 K_4}{n_{F^-}}.$$

(64)

Substitution of Eqs. (63) and (64) into Eqs. (61) and (62) yields:

$$2n_{Mg,t} - n_{F,t} = 2n_{Mg^{2+}} - n_{F^-} + n_{MgF^+} = \frac{2K_3}{(n_{F^-})^2} - n_{F^-} + \frac{K_3 K_4}{n_{F^-}}$$

$$(n_{F^-})^3 + (2n_{Mg,t} - n_{F,t})(n_{F^-})^2 - K_3 K_4 n_{F^-} - 2K_3 = 0.$$

(65)

Thus, we can obtain n_{F^-}, and then $n_{Mg^{2+}}$ and n_{MgF^+} are given by Eqs. (63) and (64), respectively, while n_{MgF_2} can be obtained from Eq. (61) as follows:

$$n_{MgF_2} = n_{Mg,t} - (n_{Mg^{2+}} + n_{MgF^+}).$$

(66)

Consequently,

$$c_{Mg^{2+}} = \frac{n_{Mg^{2+}}}{V_{t,Mg/F}},$$

$$c_{F^-} = \frac{n_{F^-}}{V_{t,Mg/F}},$$

(67)

$$c_{\text{MgF}^+} = \frac{n_{\text{MgF}^+}}{V_{\text{t,Mg/F}}},$$

$$c_{\text{TFSA}^-} = \frac{2n_{\text{Mg,t}}}{V_{\text{t,Mg/F}}},$$

$$c_{\text{Cs}^+} = \frac{n_{\text{F,t}}}{V_{\text{t,Mg/F}}}.$$

Limited case of no precipitation

We can say that the precipitation would not occur at $n_{\text{F,t}}/n_{\text{Mg,t}} \ll 1$. Therefore, the case in which only the associated ion is formed without the precipitation is discussed here using only K_4 (without K_3). The mass balance is written as follows:

$$n_{\text{Mg,t}} = n_{\text{Mg}^{2+}} + n_{\text{MgF}^+}, \tag{68}$$

for Mg, and

$$n_{\text{F,t}} = n_{\text{F}^-} + n_{\text{MgF}^+}, \tag{69}$$

for F. Equations (68) and (69) are rewritten as:

$$n_{\text{Mg}^{2+}} + n_{\text{MgF}^+} = c_{0,\text{Mg(TFSA)}_2} V_{\text{Mg(TFSA)}_2} (= n_{\text{Mg,t}}), \tag{70}$$

$$n_{\text{F}^-} + n_{\text{MgF}^+} = c_{0,\text{CsF}} V_{\text{CsF}} (= n_{\text{F,t}}). \tag{71}$$

From Eq. (58),

$$n_{MgF^+} = K_4 n_{Mg^{2+}} n_{F^-}. \tag{72}$$

Substituting Eq. (72) into Eq. (70),

$$n_{Mg,t} = n_{Mg^{2+}} + K_4 n_{Mg^{2+}} n_{F^-}$$

$$n_{Mg^{2+}} = \frac{n_{Mg,t}}{1 + K_4 n_{F^-}}. \tag{73}$$

Substituting Eqs. (72) and (73) into Eq. (71),

$$n_{F,t} = n_{F^-} + K_4 n_{Mg^{2+}} n_{F^-} = n_{F^-} + \frac{n_{Mg,t} K_4 n_{F^-}}{1 + K_4 n_{F^-}}$$

$$K_4 (n_{F^-})^2 + \left[1 + K_4 \left(n_{Mg,t} - n_{F,t}\right)\right] n_{F^-} - n_{F,t} = 0 \tag{74}$$

$$n_{F^-} = \frac{-\left[1 + K_4 \left(n_{Mg,t} - n_{F,t}\right)\right] + \sqrt{\left[1 + K_4 \left(n_{Mg,t} - n_{F,t}\right)\right]^2 + 4 K_4 n_{F,t}}}{2 K_4}.$$

$n_{Mg^{2+}}$ and n_{MgF^+} can be calculated from Eqs. (73) and (72), respectively. Consequently,

$$c_{Mg^{2+}} = \frac{n_{Mg^{2+}}}{V_{t,Mg/F}},$$

$$c_{F^-} = \frac{n_{F^-}}{V_{t,Mg/F}},$$

$$c_{MgF^+} = \frac{n_{MgF^+}}{V_{t,Mg/F}}, \quad (75)$$

$$c_{TFSA^-} = \frac{2n_{Mg,t}}{V_{t,Mg/F}},$$

$$c_{Cs^+} = \frac{n_{F,t}}{V_{t,Mg/F}}.$$

Tables S4. The results of conductivity titration of the Mg(TFSA)$_2$ electrolyte solution with the CsF solution.

$n_{F,t}/n_{Mg,t}$	conductivity κ /mS cm^{-1}
0.0	0.365
0.25	0.367
0.50	0.367
0.76	0.369
1.0	0.369
1.5	0.367
2.0	0.373
2.5	0.388
3.0	0.413

Table S5. The initial experimental condition of conductivity titration of the diluted Mg(TFSA)$_2$ electrolyte solution with the CsF solution.

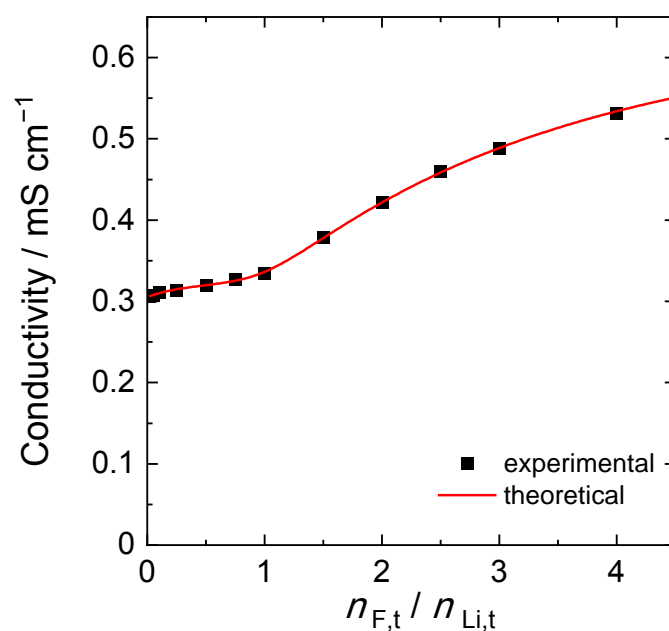| $c_{0,Mg(TFSA)_2}$ / mM	$V_{Mg(TFSA)_2}$ /mL	$c_{0,CsF}$ /mM
4.0	1.7	50

Figure S2. Conductivity titration results for the diluted Li^+/F^- hybrid electrolyte (square dots). The refined results are obtained on the model by assuming both of the the precipitation and the triple ion equilibria occur and given by the solid red line. The fitting parameters are: $K_{SP,LiF}$ =$(8.1 \pm 0.8) \times 10^{-7}$, $K_T = (8 \pm 1) \times 10^5$, $\lambda_T^\infty = 18.7 \pm 0.8$ S cm² mol⁻¹, and $S_T = 60 \pm 10$ S cm² mol⁻¹ M⁻¹/². The lines were calculated with the center values of the refined parameters.
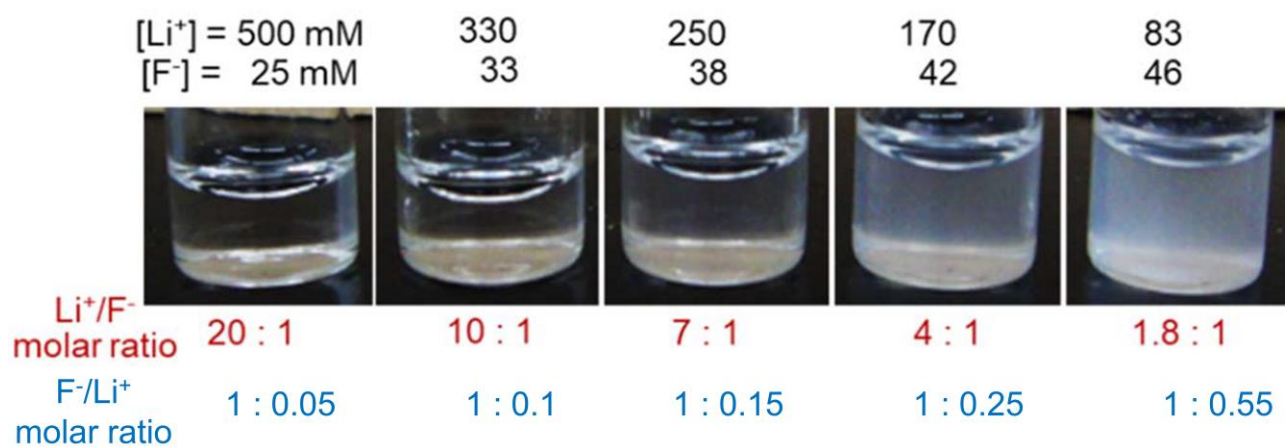
Figure S3. Series of photo-images of the solutions and suspensions prepared by the mixing 50 mM CsF/GBL with 1 M LiFSA/GBL at various ratios. Reprinted with permission from Kawasaki et al.[1]

REFERENCES

1. M. Kawasaki, K. Morigaki, G. Kano, R. Takekawa, J. Kawamura, Y. Yokoyama, K. Kano, T. Abe, and Z. Ogumi, *J. Electrochem. Soc.*, **169**, 110508 (2022).