Electronic supplementary information for

Structural modification by adding Li cations into Mg/Cs-TFSA molten salt facilitating Mg electrodeposition

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The first peak observed at around 1.4 Å in Fig. S1 is assigned to N-S, S-O, S-C, and C-F bonds in the TFSA anion.[1] The second peak at around 2.1 Å is also assigned to O-O and F-F correlations. The third peak at around 2.7 Å is also assigned to N-O, N-C, S-F, and O-C correlations. Intriguingly, although the contribution of the intra-molecular atom-atom correlations is minor regardless of the composition, a clear difference was observed at these distances between atoms.

The shortest bond is the C-F correlation, as shown in Fig. S2(d). The peaks observed at around the first neighbor length within 2.0 Å are assigned to N-S, S-O, S-C, and C-F bonds. Each bond is independent of the composition dependence. The other $g_{ij}(r)$ beyond the first neighbor covalent bond on the TFSA anion are shown in Fig. S3. It is confirmed that the S-S correlation clearly changed with the ratio of *cis*- and *trans*-conformers in the TFSA anion.

We calculated the average coordination numbers up to 4.0 Å, as summarized in Table S1. The integral maximum distance of 4.0 Å was determined as the distance of the clear structural change from the experimental $g(r)$ in Fig. S1. These coordination numbers are not equal to the numbers of ionic bonds. The average coordination number of the anion around the cation, $N_{\text{Cation-N}}$, shows the composition dependence. Regarding $N_{\text{Cs-N}}$, only $Cs_{1.0}[TFSA]_{1.0}$ gives a small coordination number, which is consistent with $g_{\text{Cs-N}}(r)$, as shown in Fig. 3 (c). The $N_{\text{Mg-N}}$ in $Mg_{0.1}Cs_{0.9}[TFSA]_{1.1}$ is twice as large as $N_{\text{Cs-N}}$, which corresponds to the differences in the charge and size between the Mg^{2+} and Cs^+ ions. However, this relationship is not retained in $Li_{0.1}Mg_{0.1}Cs_{0.8}[TFSA]_{1.1}$.

The $N_{\text{cation-cation}}$ are shown in the four lines from the bottom in Table S1. The $N_{\text{Cs-Cs}}$ decreases with adding Li^+ or/and Mg^{2+} contents. The fractions of $N_{\text{Cs-Li}}$, $N_{\text{Cs-Mg}}$, and $N_{\text{Mg-Li}}$ are almost constant in these compositions.
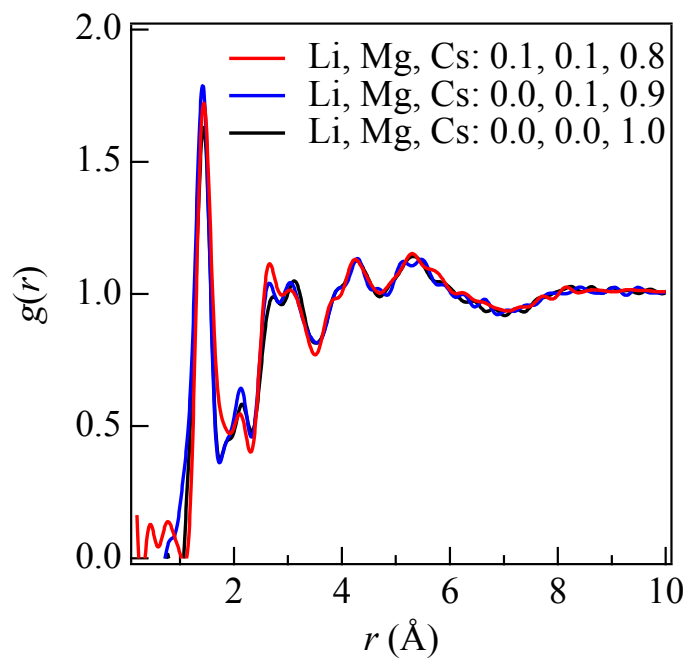
Figures

Fig. S1 Pair distribution functions $g(r)$ for alkali TFSA molten salts at 438 K. Line colours correspond to those in Figure 1.
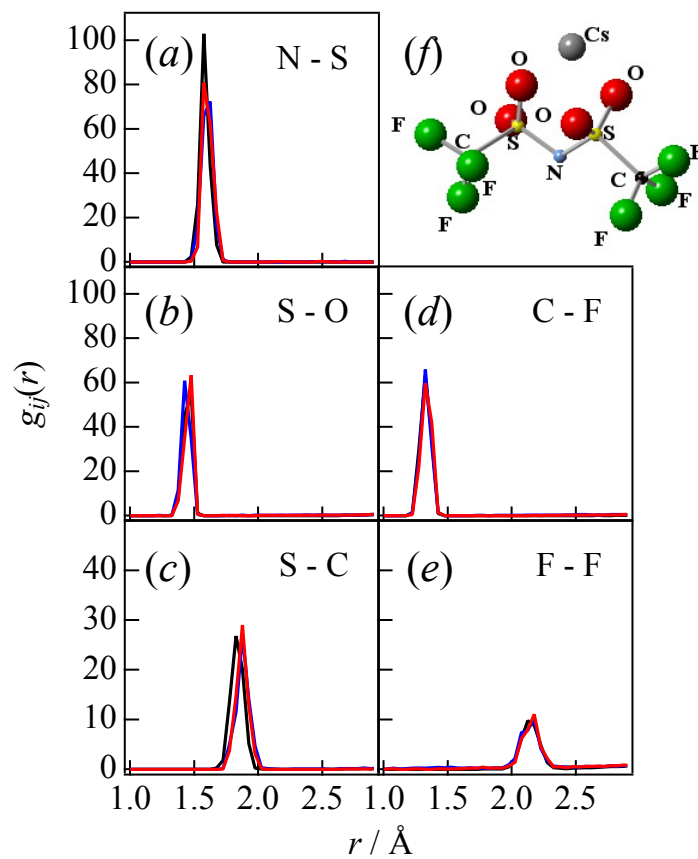
Fig. S2 Partial pair distribution functions $g_{ij}(r)$ for alkali TFSA molten salts at $r < 2.3$ Å obtained by the RMC-MM simulation (a-e). A TFSA anion model (f) in the RMC-MM. Line colours correspond to those in Figure 1.
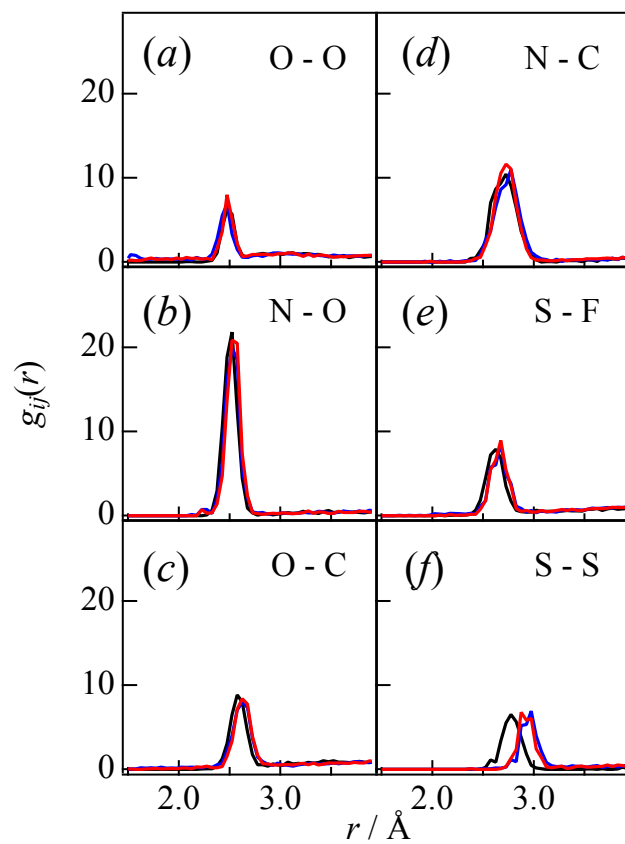
Fig. S3 Partial pair correlation functions $g_{ij}(r)$ for alkali TFSA molten salts at around $r = 2.7$ Å obtained by RMC-MM simulation (a-f). Line colours correspond to those in Figure 1.
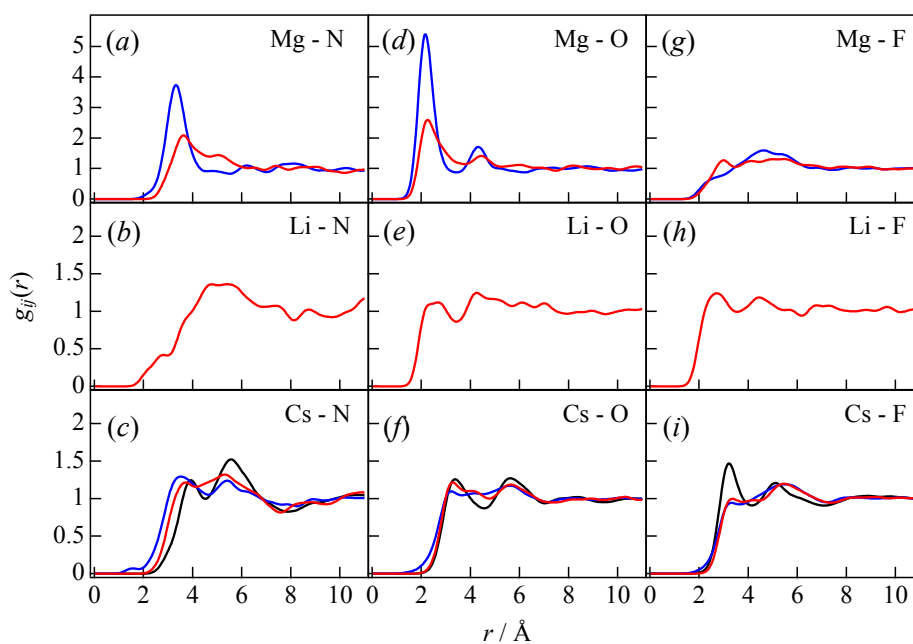
Fig. S4 Pair distribution functions, $g(r)$, for Mg-N (a), Li–N (b), Cs–N (c), Mg-O (d), Li–O (e), Cs–O (f), Mg-F (g), Li–F (h), and Cs–F (i) derived using the RMC-MM models for alkali TFSA molten salts. Line colours correspond to those in Figure 1.
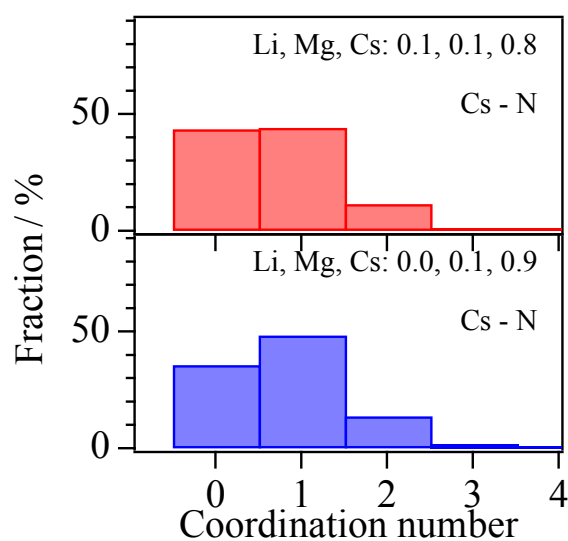

Fig. S5 Coordination number statistics for alkali TFSA molten salts obtained using the RMC-MM model. Normalized fractions of Cs – N coordination numbers within 4.0 Å.
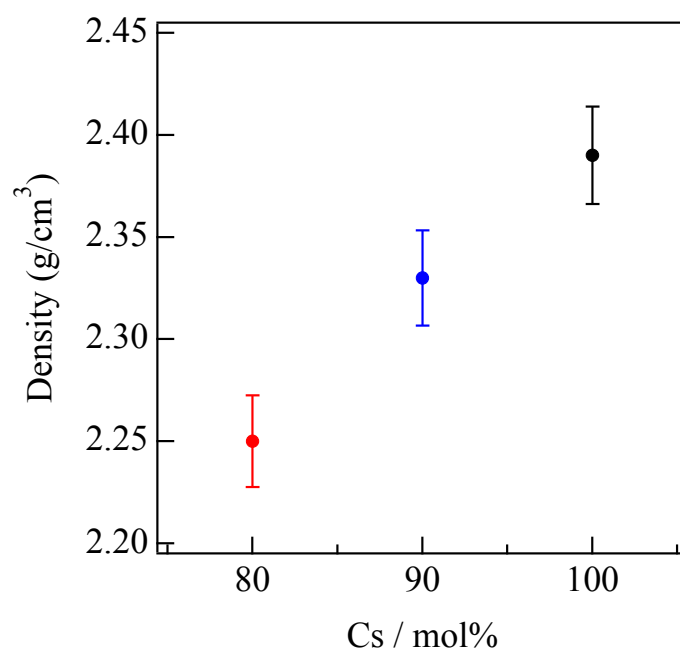
Fig. S6 Density of alkali TFSA molten salts at 438 K measured using a graduated cylinder. Circle colours correspond to those in Figure 1.

Table S1. Average coordination numbers in alkali TFSA molten salts at $r < 4.0$ Å obtained using the RMC-MM models. N_{i-j}: partial coordination number of j atoms around i atoms (N_{j-i} in parentheses).

Li, Mg, Cs	0.0, 0.0, 1.0	0.0, 0.1, 0.9	0.1, 0.1, 0.8
N_{Cs-N}	0.55	0.82	0.70
	(0.53)	(0.67)	(0.51)
N_{Li-N}	-	-	0.50
			(0.05)
N_{Mg-N}	-	1.56	1.10
		(0.14)	(0.10)
N_{Cs-Cs}	0.53	0.21	0.18
N_{Cs-Li}	-	-	0.11
			(0.84)
N_{Cs-Mg}	-	0.05	0.05
		(0.46)	(0.36)
N_{Mg-Li}	-	-	0.08
			(0.08)
N_{N-N}	0.13	0.10	0.11

Reference

1. Bodo, E.; Gontrani, L.; Caminiti, R.; Plechkova, N. V.; Seddon, K. R. and Triolo, A., Structural Properties of 1-Alkyl-3-methylimidazolium Bis{(trifluoromethyl)sulfonyl}amide Ionic Liquids: X-ray Diffraction Data and Molecular Dynamics Simulations, *J. Phys. Chem. B,* 2010**, 114**, 16398-16407.