Supplementary Information

Applying the HSAB Design Principle to the 3.5-V-class All-Solid-State Li-ion Batteries with a Chloride Electrolyte

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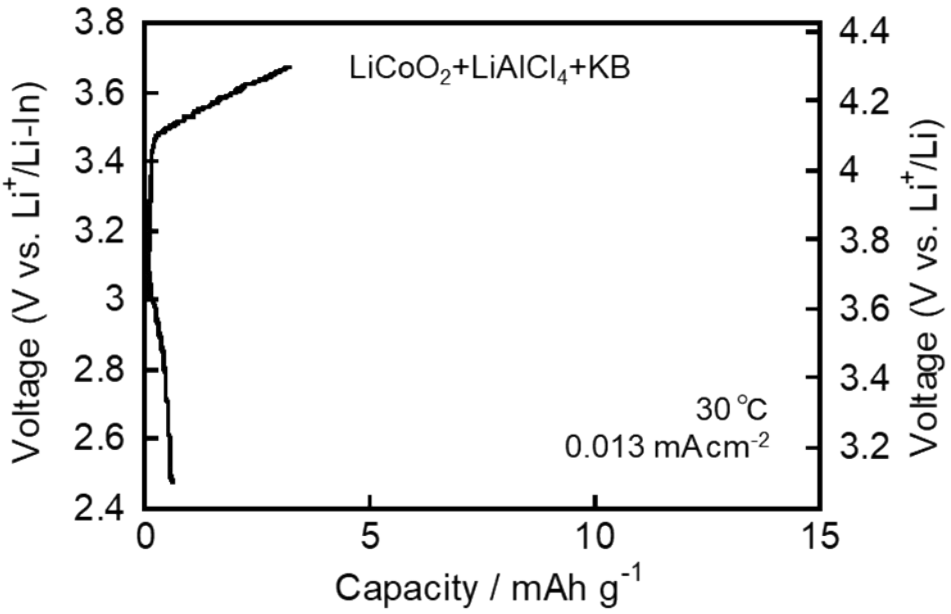

Figure S1. Charge–discharge curve (a) of all-solid-state lithium-ion battery with the mixed electrode containing the $LiCoO_2$ electrode, $LiAlCl_4$ electrolyte, and conductive additive Ketjenblack (KB).

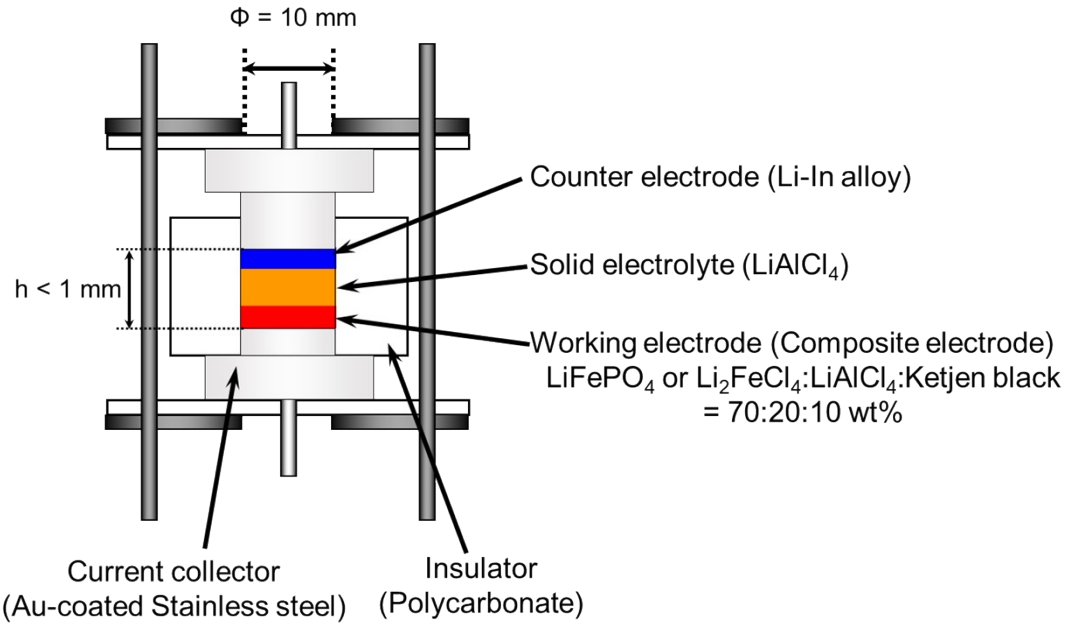

Figure S2. Schematic of the all-solid-state battery used in the evaluation.

Table S1. Reaction equations and the corresponding decomposition energies for Li_2ZrCl_6 and $LiFePO_4$ calculated using the Interface Reactions app implemented in the Materials Project.[1,2]

Molar Fraction	Reaction Equation (normalized to reflect molar fraction)	Decomposition Energy [eV/atom]
0.000	$Li_2ZrCl_6 \rightarrow ZrCl_4 + 2\ LiCl$	0.000
0.750	$0.75\ LiFePO_4 + 0.25\ Li_2ZrCl_6 \rightarrow 0.375\ Fe_2PClO_4 + 0.125\ LiZr_2(PO_4)_3 + 1.125\ LiCl$	**-0.041**
1.000	$LiFePO_4 \rightarrow LiFePO_4$	0.000

Table S2. Reaction equations and the corresponding decomposition energies for Li_3ScCl_6 and $LiFePO_4$ calculated using the Interface Reactions app implemented in the Materials Project.[1,2]

Molar Fraction	Reaction Equation (normalized to reflect molar fraction)	Decomposition Energy [eV/atom]
0.000	$Li_3ScCl_6 \rightarrow ScCl_3 + 3\ LiCl$	-0.012
0.667	$0.667\ LiFePO_4 + 0.333\ Li_3ScCl_6 \rightarrow 0.333\ ScPO_4 + 0.333\ Fe_2PClO_4 + 1.667\ LiCl$	**-0.029**
0.750	$0.75\ LiFePO_4 + 0.25\ Li_3ScCl_6 \rightarrow 0.125\ Li_3Sc_2(PO_4)_3 + 0.375\ Fe_2PClO_4 + 1.125\ LiCl$	-0.026
1.000	$LiFePO_4 \rightarrow LiFePO_4$	0.000

Table S3. Reaction equations and the corresponding decomposition energies for Li_3InCl_6 and $LiFePO_4$ calculated using the Interface Reactions app implemented in the Materials Project.[1,2]

Molar Fraction	Reaction Equation (normalized to reflect molar fraction)	Decomposition Energy [eV/atom]
0.000	$Li_3InCl_6 \rightarrow Li_3InCl_6$	0.000
1.000	$LiFePO_4 \rightarrow LiFePO_4$	0.000

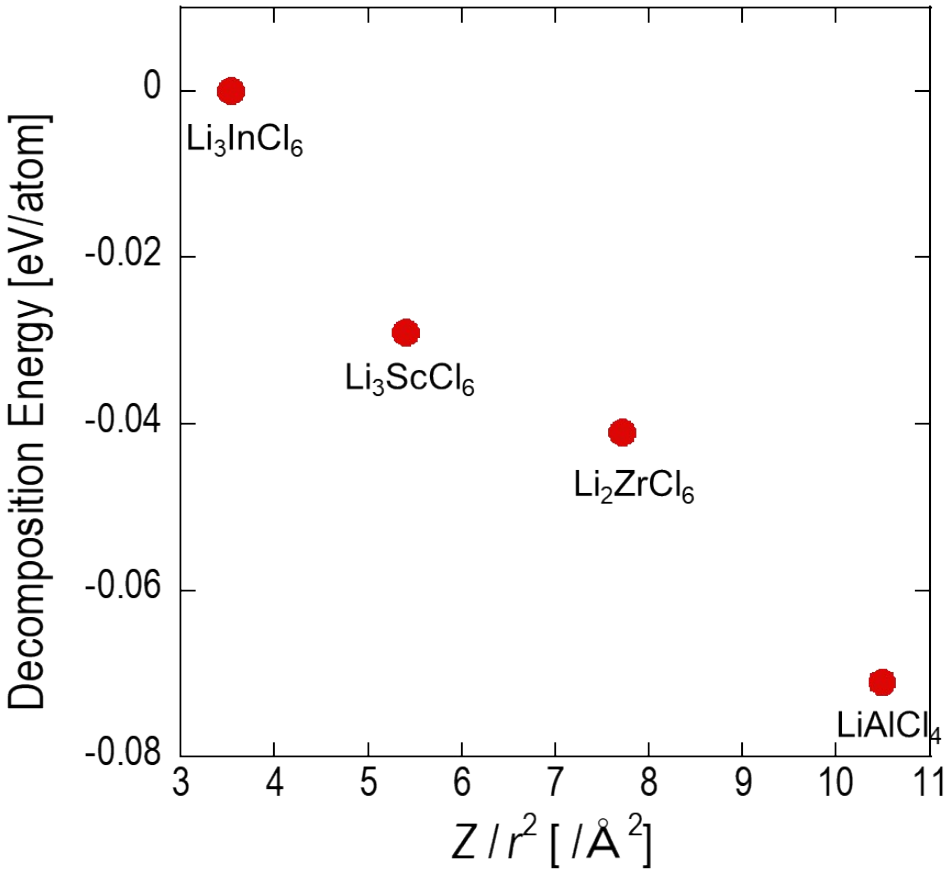

Figure S3. Relationship between the calculated energies of the decomposition reaction of the chloride materials ($LiAlCl_4$, Li_2ZrCl_6,[3] Li_3ScCl_6,[4] and Li_3InCl_6[5]) with $LiFePO_4$ and the charge density index (Z/r^2) of the cations (Al^{3+}, Zr^{4+}, Sc^{3+}, In^{3+}). Z is the formal charge of the cation, and r is the ionic radius of the Shannon (6-coordination).[6]

References

1 W. D. Richards, L. J. Miara, Y. Wang, J. C. Kim and G. Ceder, *Chem. Mater.*, 2016, **28**, 266–273.

2 A. Jain, S. P. Ong, G. Hautier, W. Chen, W. D. Richards, S. Dacek, S. Cholia, D. Gunter, D. Skinner, G. Ceder and K. A. Persson, *APL Mater.*, 2013, 1, 011002.

3 H. Kwak, D. Han, J. Lyoo, J. Park, S. Hoo Jung, Y. Han, G. Kwon, H. Kim, S.-T. Hong, K.-W. Nam, Y. Seok Jung, H. Kwak, J. Park, S. H. Jung, Y. Han, Y. S. Jung, H. Kim, D. Han, K. Nam, J. Lyoo, S. Hong and G. Kwon, *Adv. Energy Mater.*, 2021, **11**, 2003190.

4 L. Zhou, T. T. Zuo, C. Y. Kwok, S. Y. Kim, A. Assoud, Q. Zhang, J. Janek and L. F. Nazar, *Nat. Energy*, 2022, **7**, 83–93.

5 X. Li, J. Liang, J. Luo, M. Norouzi Banis, C. Wang, W. Li, S. Deng, C. Yu, F. Zhao, Y. Hu, T. K. Sham, L. Zhang, S. Zhao, S. Lu, H. Huang, R. Li, K. R. Adair and X. Sun, *Energy Environ. Sci.*, 2019, **12**, 2665–2671.

6 R. D. Shannon, *Acta Crystallogr. Sect. A*, 1976, **32**, 751–767.