Supporting Information for:

## Remarkable Ion Transport and Electrochemical Characteristics of Magnesium Fluorinated Alkoxyaluminate-Diglyme Electrolytes for Rechargeable Magnesium Batteries

Toshihiko Mandai\*, Yong Youn, Yoshitaka Tateyama

Center for Green Research on Energy and Environmental Materials, National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan

CORRESPONDING AUTHOR FOOTNOTES

Telephone: +81-29-860-4464, E-mail: MANDAI.Toshihiko@nims.go.jp



Figure S1. <sup>1</sup>H NMR spectra of (a)  $Mg[B(HFIP)_4]_2$  and (b)  $Mg[Al(HFIP)_4]_2$ . The spectrum data of

Mg[B(HFIP)<sub>4</sub>]<sub>2</sub> was transcribed from Ref. 32 of the main text.



Figure S2. SEM image of Cu working electrode after galvanostatic polarization at 1 mA cm<sup>-2</sup> for 1 h

in 0.3 mol dm<sup>-3</sup> Mg[Al(HFIP)<sub>4</sub>]<sub>2</sub>/G2 at 30 °C.



**Figure S3**. Liquid densities of 0.3 mol dm<sup>-3</sup> (a) Mg[B(HFIP)<sub>4</sub>]<sub>2</sub>/Gn and (b) Mg[Al(HFIP)<sub>4</sub>]<sub>2</sub>/Gn (n = 1-4) measured in the temperature range of 20–80 °C. Based on the deviation from the slope made using the density-temperature profiles at the lower temperatures, the appropriate temperature range capable to characterize the transport properties was adopted.



**Figure S4**. Ionic conductivities of (a) Mg[B(HFIP)<sub>4</sub>]<sub>2</sub>/G2 and (b) Mg[Al(HFIP)<sub>4</sub>]<sub>2</sub>/G2 measured in the temperature range of 20–70 °C.



Figure S5. Ionic conductivities of (a)  $Mg[B(HFIP)_4]_2/G3$  and (b)  $Mg[Al(HFIP)_4]_2/G3$  measured in the

temperature range of 20–70 °C.



**Figure S6**. Voltage profiles of galvanostatic polarization in (a) 0.3 mol dm<sup>-3</sup> Mg[B(HFIP)<sub>4</sub>]<sub>2</sub>/Gn and (b) 0.3 mol dm<sup>-3</sup> Mg[Al(HFIP)<sub>4</sub>]<sub>2</sub>/Gn (n = 1-4) recorded on carbon fiber electrodes at 1 mA cm<sup>-2</sup> at 30 °C. Insets display the magnified profiles of the steady state.



Figure S7. Calculated RDF profiles of (left) B and (right) Al surroundings in 0.3 mol dm<sup>-3</sup> Mg[Z(HFIP)<sub>4</sub>]<sub>2</sub>/G3.



Figure S8. (a) Mg 2p, (b) O 1s, and (c) F 1s XPS spectra recorded on the magnesium metal deposited

from 0.3 mol dm<sup>-3</sup> Mg[Z(HFIP)<sub>4</sub>]<sub>2</sub>/G2 (Z = B or Al).



**Figure S9**. CVs of 0.1, 0.3, 0.5 mol dm<sup>-3</sup> Mg[Z(HFIP)<sub>4</sub>]<sub>2</sub>/G2 (Z = B or Al) recorded on Pt electrode at a scan rate of 10 mV s<sup>-1</sup> at 30 °C.



**Figure S10**. SEM images and corresponding EDX mapping of the electrodeposited magnesium obtained from (a) 0.5 mol dm<sup>-3</sup> Mg[B(HFIP)<sub>4</sub>]<sub>2</sub>/G2 and (b) 0.5 mol dm<sup>-3</sup> Mg[Al(HFIP)<sub>4</sub>]<sub>2</sub>/G2. (c) The corresponding voltage profiles of galvanostatic polarization recorded on carbon fiber substrates at 1 mA cm<sup>-2</sup> at 30 °C were also included.



**Figure S11**. (a) Galvanostatic magnesium deposition/dissolution cycling profiles and (b) corresponding Coulombic efficiency in 0.3 and 0.6 mol dm<sup>-3</sup> Mg[B(HFIP)<sub>4</sub>]<sub>2</sub>/G2. The 0.6 mol dm<sup>-3</sup> solution required over 60 times of pre-cycling to complete the conditioning of the electrolyte and/or [electrolyte | anode] interface.