Supporting Information for:

## A Fundamental Study on the [(μ-Cl)<sub>3</sub>Mg<sub>2</sub>(THF)<sub>6</sub>]<sup>+</sup> Dimer Electrolytes for Rechargeable Mg Batteries

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**Synthesis and Materials.** All reactions and manipulations were performed under Ar using a glovebox. Solvents were pre-purged with N<sub>2</sub> and were dried using an activated alumina column and stored with activated 3 Å molecular sieves under Ar. All reagents were used as received. MgCl<sub>2</sub>, AlPh<sub>3</sub>, AlEtCl<sub>2</sub>, AlCl<sub>3</sub>, and TBACl were purchased from Aldrich. 2MgCl<sub>2</sub>-Al Lewis acid electrolytes were prepared according to the published procedure.<sup>[1]</sup>

**NMR Studies.** <sup>27</sup>Al{<sup>1</sup>H} NMR spectra were recorded on a Varian Inova spectrometer (500 MHz for <sup>1</sup>H) at 25 °C. and are referenced to external AlCl<sub>3</sub>/H<sub>2</sub>O. The natural abundance liquid state <sup>25</sup>Mg NMR experiments were carried out using a homemade 15 mm outside diameter large sample volume probe on a Varian-Agilent 900MHz NMR spectrometer at a magnetic field of 21.1 T. The Larmor frequency was 55.1 MHz for <sup>25</sup>Mg. The experiments were conducted at room temperature, i.e., 25 °C. Each of the liquid state 25Mg NMR spectra were acquired using a single pulse sequence with a pulse angle of about 45°, a recycle delay time of 1s, and about 512 to 30000 scans depending on the Mg concentration and the linewidth of the peak. The 25Mg NMR spectra were referenced to 1.0 M MgCl2 (0 ppm).

**Electrochemistry.** All electrochemical experiments were carried out under an atmosphere of Argon. Cyclic voltammetry experiments were performed with a CH Instruments model 660C potentiostat. The working electrodes (1.0 mm PEEK-encased glassy carbon, Cypress Systems EE040; 2.0 mm Pt working electrode, CH Instruments, CHI102) were polished using Al<sub>2</sub>O<sub>3</sub> (BAS CF-1050, dried at 150 °C under vacuum) suspended in methanol, and then rinsed with neat tetrahydrofuran. A glassy carbon rod (Structure Probe, Inc.) was used as the counter electrode. A piece of Mg strip was freshly polished and used as the reference electrode.

The electrolyte conductivity was measured using WP CP650 conductivity meter (OAKTON Instruments).

**Mass Spectrometry.** Mass spectra were acquired on an orthogonal TOF MS instrument (model G1969A, Agilent Technologies, Santa Clara, CA). The standard interface was replaced by a subambient pressure ionization with nanoelectrospray (SPIN)

source interface. The SPIN source consists of a dual ion funnel interface with a chemically etched ESI emitter positioned at the entrance of the high pressure ion funnel inside the first vacuum region of the instrument as described in detail previously.<sup>[2]</sup> Samples were injected by direct infusion using a syringe pump (model no. 22, Harvard Apparatus, Holliston, MA, USA) from a 100  $\mu$ L syringe (Hamilton, Las Vegas, NV, USA) operated at a flow rate of 200 nL/min. Spectra were summed over one minute with a one second TOF acquisition time over a 200-2000 *m/z* range with a 0.1 *m/z* step size in positive ion mode.

**Raman Spectroscopy.** Raman spectroscopic data were collected using a Horiba's LabRAM confocal Raman microscope controlled by LabSpec software. A 532 nm wavelength laser is chosen for excitation. A 10X NA 0.3 microscope objective is used to focus the laser to the sample in a 0.5 mL glass vial containing solution or solid samples. 600 grooves/mm grating and 1800 groove/mm grating are selected for wide spectral window and narrow spectral window respectively. Each spectrum was accumulated for 200 seconds.

Author contributions. T.B.L. conceived and designed this work. T.B.L. and J. L. prepared the manuscript. T.B.L. prepared the electrolytes for all spectroscopic studies and performed <sup>27</sup>Al{<sup>1</sup>H} NMR and electrochemical studies. J.C. and K.Q.T. helped on SPIN MS data collection. D.H.H helped on Raman data collection. X.C.D, J.Z.H and M.Y.H collected <sup>25</sup>Mg NMR data. All authors helped on discussions and revisions of the paper. The authors declare no competing financial interests.



Figure S1. Raman Spectra of solid  $[(\mu-Cl)_3Mg_2(THF)_6]AlPh_3Cl$  (blue trace) and MgCl<sub>2</sub> THF solution (black trace).





Figure S2. Dependence of  ${}^{25}Mg{}^{1}H$  chemical shift (top) and peak width (bottom) of  $[(\mu-Cl)_3Mg_2(THF)_6]AlPh_3Cl$  on the concentration of Cl<sup>-</sup>.



Figure S3. <sup>27</sup>Al NMR spectra of  $[(\mu-Cl)_3Mg_2(THF)_6]AlPh_3Cl$  (0.1 M in THF) recorded before (brown spectrum) and after (blue spectrum) addition of 0.1 M Cl<sup>-</sup> (TBACl, tetrabutylammonium chloride).



Figure S4. SPIN-MS data of  $[(\mu-Cl)_3Mg_2(THF)_6]AlPh_3Cl (2 mM in THF)$  recorded without (a) and with (b) Cl<sup>-</sup> (2 mM, TBACl, tetrabutylammonium chloride)



Figure S5. SPIN-MS data of  $[(\mu$ -Cl)<sub>3</sub>Mg<sub>2</sub>(THF)<sub>6</sub>]AlEtCl<sub>3</sub> (2 mM in THF).



Figure S6. Cyclic Voltammograms of  $[(\mu-Cl)_3Mg_2(THF)_6]AlPh_3Cl (0.1 M)$  in the presence of various concentrations of TBACl as indicated (0.01, 0.03, 0.05, 0.07, and 0.09 M)

Figure S7. The plots of Mg cycling charges (red and blue traces) and solution conductivity (green) versus Cl<sup>-</sup> concentrations.



Scheme S1. A proposed mechanism of Mg<sup>2+</sup> and Cl<sup>-</sup> transports between Mg anode and a cathode.

## **References**:

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