

Electronic Supplementary Information

Highly Alcohol-based Magnesium Electrolytes for Rechargeable Magnesium Batteries

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Experimental. Anhydrous *n*-butanol, *tert*-butanol, and trimethylsilanol were obtained from Aldrich and were used as received. 2.0 M THF solutions of ethylmagnesium chloride and butylmagnesium chloride were also obtained from Aldrich. All reactions were carried out in an Ar-filled glovebox with both oxygen and moisture level below 0.5ppm.

Syntheses. All the ROMgCl salts were synthesized under the same condition. For example, 296 mg of anhydrous *n*-butanol was slowly added to 2 mL of 2.0 M THF solution of ethylmagnesium chloride in an Ar-filled glove box. The reaction is extremely exothermic and releases a large amount of gas (ethane). After the reaction is finished and cooled, appropriate amount of solid AlCl₃ was added to the solution under stirring.

X-Ray Crystallography. Single-crystal X-ray data were collected at 173 K on a Bruker SMART APEX CCD diffractometer with fine-focus Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$), operated at 50 kV and 30 mA. The structure was solved using the direct methods and was refined on F2 using the SHELXTL 6.12 software package (Bruker AXS, Inc., Madison, WI, 1997). Absorption

corrections were applied using SADABS. Hydrogen atoms were placed in idealized positions and refined using a riding model.

Electrochemistry. Cyclic voltammograms (CVs) of three-electrode cells were taken at room temperature using the electrochemical instrument of CHI604B Electrochemical Workstation. The working electrode was Pt disk and magnesium ribbon served as counter and reference electrodes. All of the electrodes were polished with a corundum suspension and rinsed with dry acetone before use.

Ionic conductivity was measured by impedance spectroscopy, and an aqueous solution of 0.1 M KCl was used as a reference to calibrate the house-made ionic conductivity cells.

Electrochemical magnesium deposition and dissolution on polished Cu pieces were examined with standard 2032 coin cells. Polished magnesium disk was used as counter electrode and glass filter as separator. The cells were assembled in a glove box containing less than 1 ppm water and O₂. During this experiment, a constant deposition current density of 0.1 mA cm⁻² was passed through the cell for 1 h, and then the same dissolution current density was applied until cut-off voltage of 0.5 V vs. Mg.

Mo₆S₈ was prepared by the molten salt method.¹ Electrochemical experiments were carried out using coin cells. The electrodes were prepared by apply a mixture of as-synthesized Mo₆S₈, acetylene black and PTFE (weight-ratio: 80:10:10) onto a stainless steel mesh. The loading of active material is between 3.0 and 5.0 mg. The batteries were assembled as 2032-type coin cells inside an argon-filled glovebox by using the Mo₆S₈ as the cathode electrode, magnesium metal as the anode electrode, glass fiber membrane (Whatman, GF/D) as the separator. Galvanostatic discharge-charge experiments were tested in the voltage range of 0.2-2.0 V on an Arbin battery test system at different temperatures.

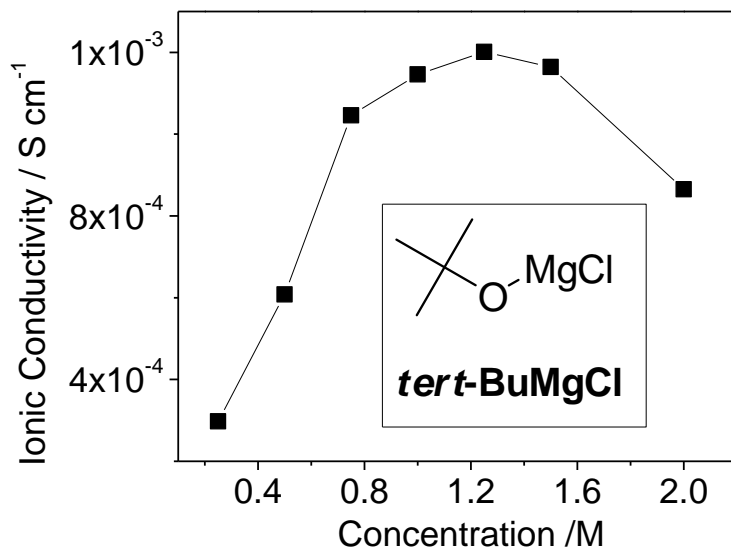


Fig. S1. The ionic conductivity of the THF solution of *tert*-BuOMgCl was measured as a function of concentration.

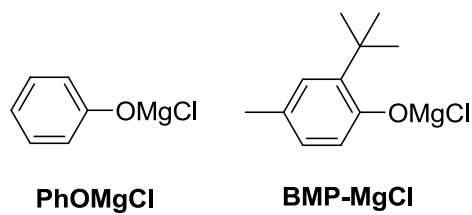


Fig. S2. The chemical structure of the oxygen-containing phenol-based magnesium electrolytes: PhOMgCl and BMP-MgCl.

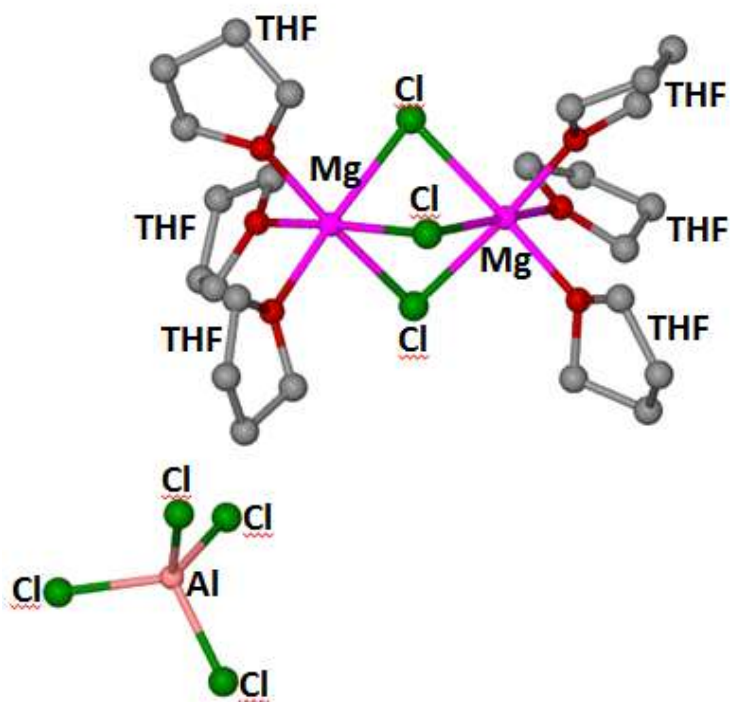


Fig. S3. Structure of the single crystal, grown out of the THF solution of $(\text{BMC-MgCl})_2/\text{AlCl}_3$. Hydrogen atoms, THF of the crystallization are omitted for clarity. The low crystal quality did not allow for a satisfactory refinement. However, the identity and structural connectivity of the ions could be determined unambiguously, and revealed this structure.

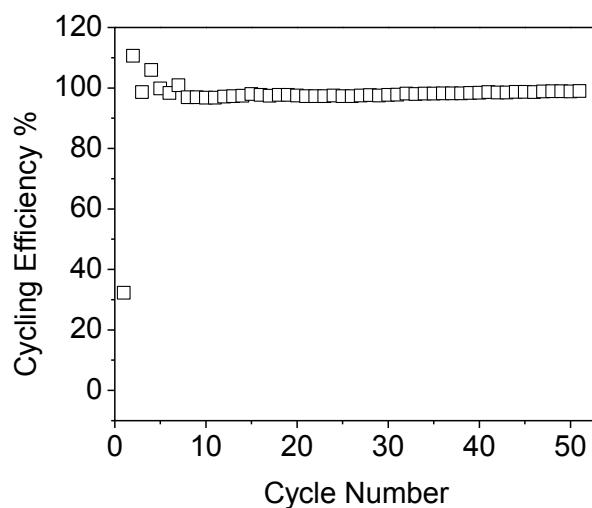


Fig. S4. The cycling efficiencies of Mg deposition and dissolution on Cu in the 1.0 M $(\text{Me}_3\text{SiOMgCl})_6\text{-AlCl}_3/\text{THF}$ electrolyte.

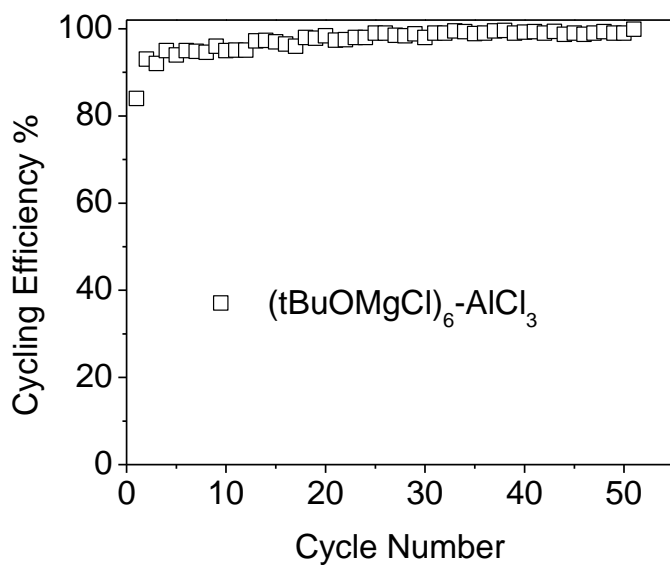


Fig. S5. The cycling efficiencies of Mg deposition and dissolution on Cu in the 1.0 M (*tert*-BuOMgCl)₆-AlCl₃/THF electrolyte.

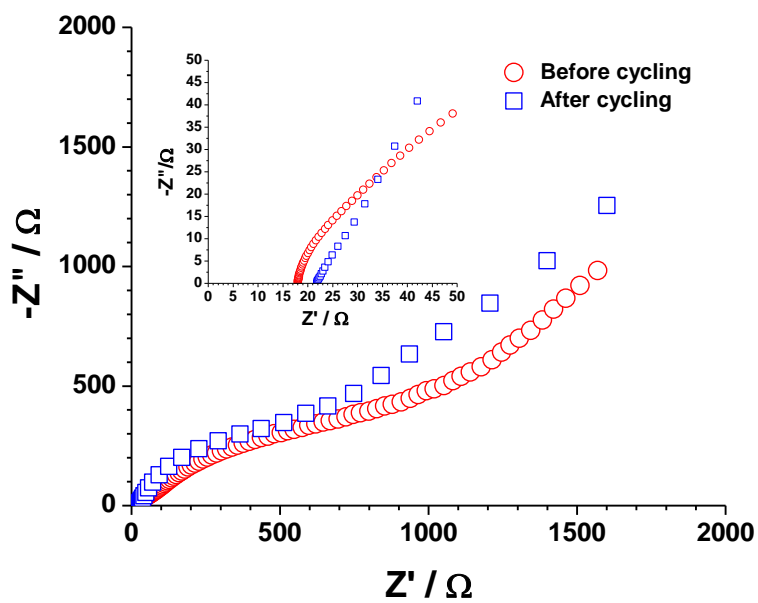


Fig. S6. Impedance of Mg-Mo₆S₈ cell before and after cycling in 1.0 M (*tert*-BuOMgCl)₆-AlCl₃/THF electrolyte under a current rate of 0.1 C in at 20 °C.

References

1. E. Lancry, E. Levi, A. Mitelman, S. Malovany and D. Aurbach, *J. Solid State Chem.*, 2006, **179**, 1879-1882.