Electronic Supplementary Information

A novel electrolyte system without Grignard reagent for rechargeable magnisium battery

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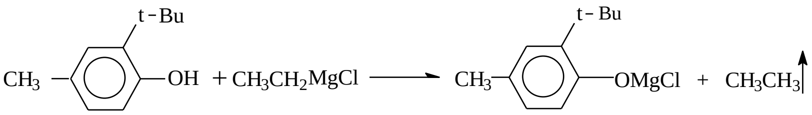
Experimental details:

Preparation of ROMgCl-$AlCl_3$/THF solutions

The synthetic work was conducted under strict inert gas conditions in an argon-filled glove box (M. Braun, Germany) containing less than 2 ppm water and O_2. All the ROMgCl salts were synthesized under the same condition. First, 2-tert-butyl-4-methyl-phenol (2 mmol, 0.3285 g) was added into THF solvent (1 mL) under vigorous stirring. Then, a predetermined quantity of 2 M EtMgCl/THF solution (2 mmol, 1 mL) was added dropwise to the above solution at a molar ratio of 1:1. The reaction was exothermic and released myriad of tiny bubbles of ethane (equation 1). The resulting mixture was stirred for 8 hours at room temperature and 1 M yellow solution of 2-tert-butyl-4-methyl-phenolate magnesium chloride (BMPMC)/THF was obtained. Nuclear Magnetic Resonance (NMR) spectrum of the solution was measured with a Bruker Avance-Ⅲ-400 spectrometer. Chemical shifts were reported in ppm and ^1H, ^{13}C spectra were referenced to tetrahydrofuran（THF）（d_8）solvent signals: ^1H NMR (d_8-THF, 400 MHz): δ 1.31 (9H, methyl protons), 2.01 (3H, methyl protons), 6.09, 6.46–6.47, 6.30 (3H, aromatic protons); ^{13}C NMR (d_8-THF, 100 MHz): δ 24.01-24.62(methyl carbons), 29.569 (methyl carbons), 119.01, 120.14, 126.72, 126.14, 136.02, 163.31 (aromatic carbons).



(1)

$AlCl_3$ (0.1334 g) was added into THF solvent (2 mL) under vigorous stirring. Then, this solution was mixed with the 1 M solution of BMPMC/THF. The resulting solution was stirred for 5 hours at room temperature and 0.5 M solution of $(BMPMC)_2$-$AlCl_3$/THF was obtained. Different Lewis acid-base ratios were examined in order to obtain an optimal composition.

Synthesis and characterization of Mo_6S_8

Synthesis route of Mo_6S_8 followed the literature (see text: reference 18). Its X-ray diffraction (XRD) pattern taken by a Rigaku X-ray diffractometer D/MAX-2200/PC equipped with Cu Ka radiation at the rate of 6.0 °/min is in accordance with the reported result.

Electrochemical Measurements

Specific conductivity of the electrolyte solutions was measured using a FE30 conductivity meter and the inLab 710 conductivity measuring cell (Mettler Toledo, Switzerland). Cyclic voltammograms (CVs) of three-electrode cells were taken at room temperature using the electrochemical instrument of CHI660C Electrochemical Workstation (Shanghai, China). 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. Electrochemical magnesium deposition and dissolution on polished nickel pieces were examined with standard 2016 coin-type cells. Magnesium strip was used as counter electrode and Entek PE membrane as separator. The cells were assembled in a glove box containing less than 1 ppm water and O_2. 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 0.8 V vs. Mg. Before XRD analysis of Mg deposit, the sample was washed in the glove box with drying THF solvent to remove soluble residue and then transferred out of the box and kept without exposure to the atmosphere. The Mo_6S_8 electrode was prepared by casting and pressing a 8:1:1 weight-ratio mixture of Mo_6S_8, super-P carbon powder and polyvinylidene fluoride(PVDF) binder dissolved in N-methyl-2-pyrrolidinone(NMP) onto Cu current collector followed by drying in vacuum at 120 ^{o}C. Standard 2016 coin cells were fabricated using thin Mg disc anode, Entek PE separator, 0.5 M $(BMPMC)_2$-$AlCl_3$/THF electrolyte and Mo_6S_8 cathode. The charge-discharge tests of the coin cells were carried out on a land battery measurement system (Wuhan, China) with the cutoff voltage of 1.7/0.5 V vs. Mg RE.

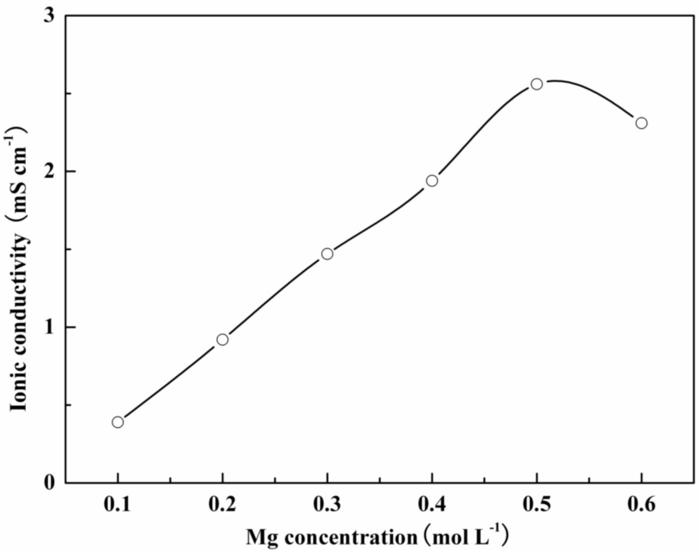


Fig. S1 The ion conductivities of $(BMPMC)_2$-$AlCl_3$/THF solutions containing different concentration of Mg salts (calculated based on Mg content) at room temperature.

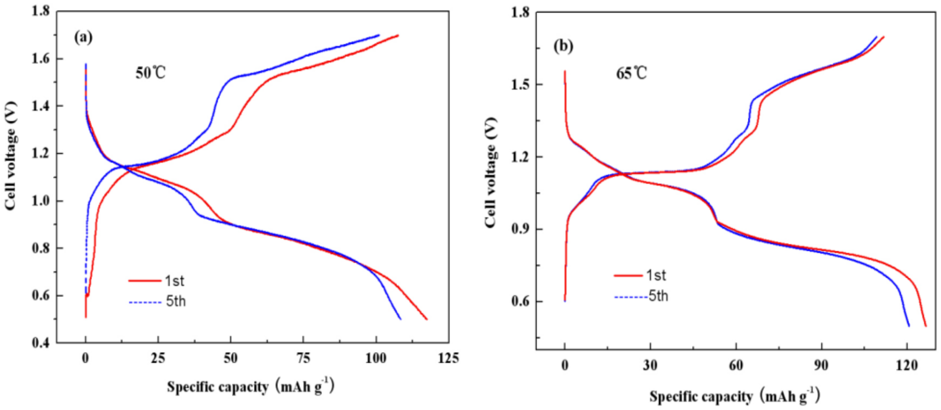


Fig. S2 Cycling behavior of rechargeable Mg/Mo_6S_8 coin-cell using 0.5 M $(BMPMC)_2$-$AlCl_3$/THF electrolyte solution at current rate of 0.05 C and elevated temperatures: (a) 50℃, (b) 65℃