

A novel rechargeable battery with magnesium anode, titanium dioxide cathode, and magnesium borohydride/tetraglyme electrolyte

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Supporting Information

Preparation of electrolyte

The preparation was conducted in an argon-filled glove box (Mbraun, Unilab, Germany) with H₂O and O₂ below 2 ppm. 0.5 mol L⁻¹ Mg(BH₄)₂/LiBH₄/TG ([LiBH₄]=1.5 mol L⁻¹) electrolyte was prepared by dissolving the predetermined amount of Mg(BH₄)₂ (Sigma-Aldrich, 95%) and LiBH₄ (J&K Scientific, 95%) in tetraglyme (TG) (from Aladdin, and further dried using a 3 Å molecular sieve) under stirring at 90°C for at least 8 hours.

Material Characterization

XRD measurements were performed on a Rigaku diffractometer D/MAX-2200/PC equipped with Cu K α radiation ($\lambda = 0.15418$ nm). TiO₂ powder was characterized using scanning electron microscopy (SEM) on a JEOL field-emission microscope (JSM-7401F) and transmission electron microscopy (TEM) on a JEOL high-resolution electron microscope (JEM-2010). Brunauer-Emmett-Teller (BET) surface area was measured on an ASAP 2010 M+C surface area analyzer. The *ex situ* Raman spectra were collected at room temperature with a DXR Raman microscope (Thermo Scientific), using a HeNe laser with a wavelength of 532 nm as the excitation source. Intercalated Mg and Li analysis for the discharge electrodes was performed by energy-dispersive X-ray spectroscopy (EDS) on a JEOL field-emission microscope (JSM-7401F) and inductively coupled plasma spectroscopy (ICP) on an iCAP6300 instrument (Thermo). Before the measurement, the electrodes, after being discharged and charged to different potentials at 0.2 C, were washed in an argon-filled glove box (Mbraun, Unilab, Germany) with THF to remove organic matter, and then transferred out of the box and kept without exposure to air before measurements.

Electrochemical Measurements

Electrode slurry was prepared by mixing 80 wt.% active material, 10 wt.% super-P carbon powder (Timcal) and 10 wt.% poly(vinylidene fluoride) (PVDF) dissolved in N-methyl-2-pyrrolidinone. The electrodes were formed by coating the slurry onto stainless steel foil current collectors, drying at 80 °C for 1 hour, pressing at 2 MPa, and drying again at 80 °C for at least 12 hours under vacuum. The electrode, with a diameter of $\Phi 12$ mm, contains 0.5-0.7 mg active material, and the typical thickness of the active layer is 100 μm . Electrochemical behavior was examined via CR2016 coin cells with a magnesium counter electrode, an Entek PE membrane separator and 0.5 mol L⁻¹ Mg(BH₄)₂/LiBH₄/TG ([LiBH₄] = 1.5 mol L⁻¹) electrolyte. The cells were assembled in an argon-filled glove box. Cyclic voltammetry measurements were performed on a CHI650C Electrochemical Workstation (Shanghai, China). Galvanostatic discharge-charge measurements were conducted at ambient temperature on a Land battery measurement system (Wuhan, China) with the cut-off voltages of 0.5/1.7 V vs. Mg.

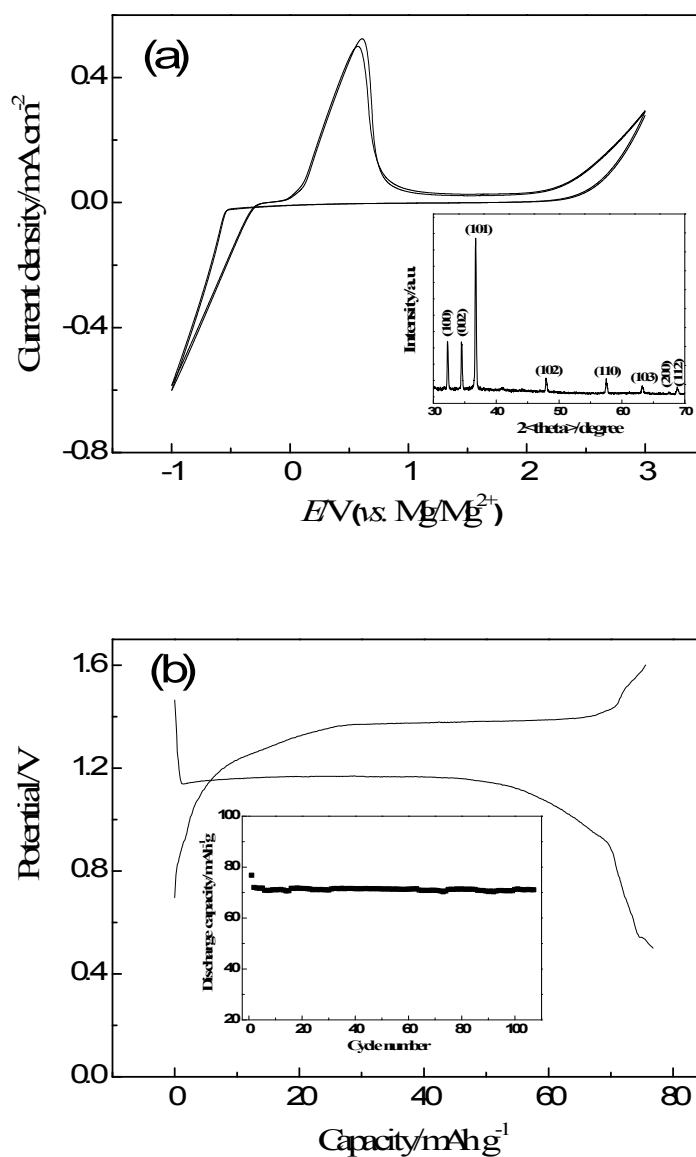


Fig. S1

Fig. S1. (a) CVs of the electrochemical Mg deposition and dissolution on non-inert stainless steel (SS) disk electrode from the electrolyte of $0.5 \text{ mol L}^{-1} \text{ Mg}(\text{BH}_4)_2/\text{LiBH}_4/\text{TG}$ ($[\text{LiBH}_4]=1.5 \text{ mol L}^{-1}$) at 50 mV s^{-1} , magnesium ribbon as counter and reference electrodes. The anodic stability of the electrolyte solution on SS electrode is up to 2.4 V. The inset of (a) shows the XRD pattern of the resulting deposit from the solution. The main diffraction peaks can be attributed to metallic Mg (JCPDS file 35-0821), indicating that deposition of pure metal Mg was obtained from the solution. (b) The initial discharge-charge curve at 0.05 C of Mg/Mo₆S₈ coin-cell with $0.5 \text{ mol L}^{-1} \text{ Mg}(\text{BH}_4)_2/\text{LiBH}_4/\text{TG}$ ($[\text{LiBH}_4]=1.5 \text{ mol L}^{-1}$) electrolyte, inset is the cycling stability. Excellent cycling performance indicates good compatibility of the electrolyte with the Mg intercalation cathode material.

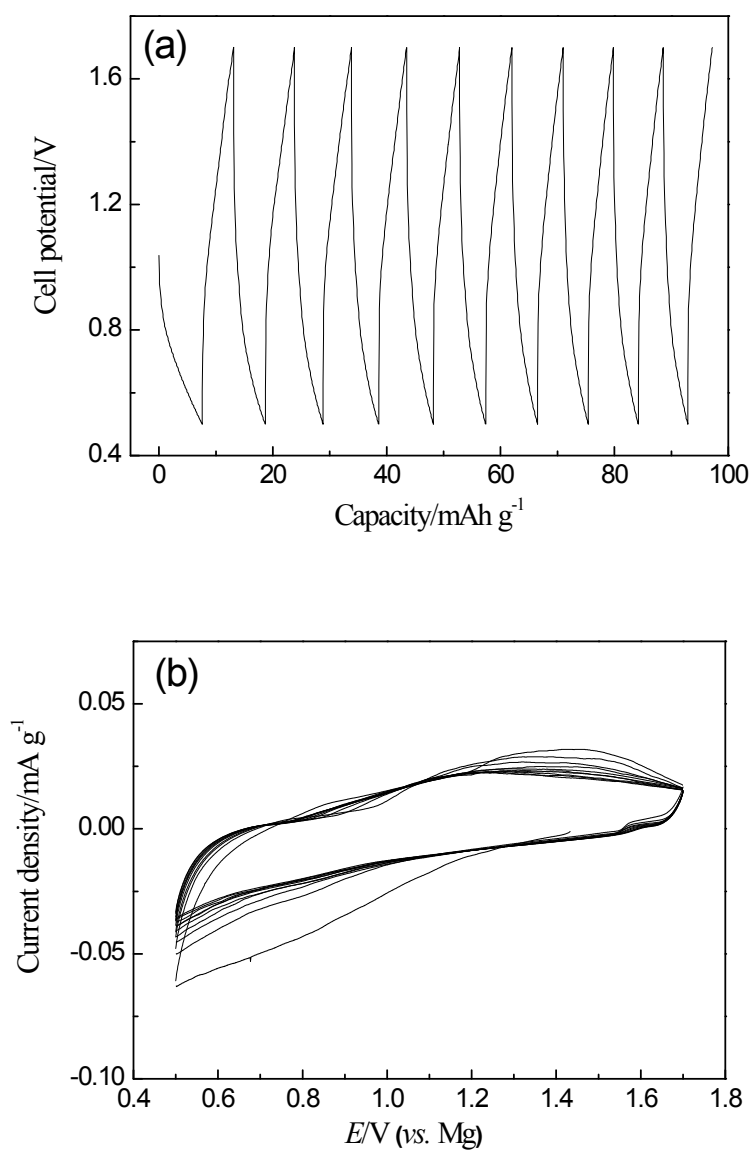


Figure S2

Fig. S2. (a) The galvanostatic discharge/charge curves of a commercial anatase TiO₂/Mg coin cell with 0.4 mol L⁻¹ (PhMgCl)₂-AlCl₃/THF electrolyte at a rate of 0.2 C. (b) The cyclic voltammograms of the cell at 0.5 mV s⁻¹. TiO₂ exhibits poor electrochemical performance in 0.4 mol L⁻¹ (PhMgCl)₂-AlCl₃ electrolyte.

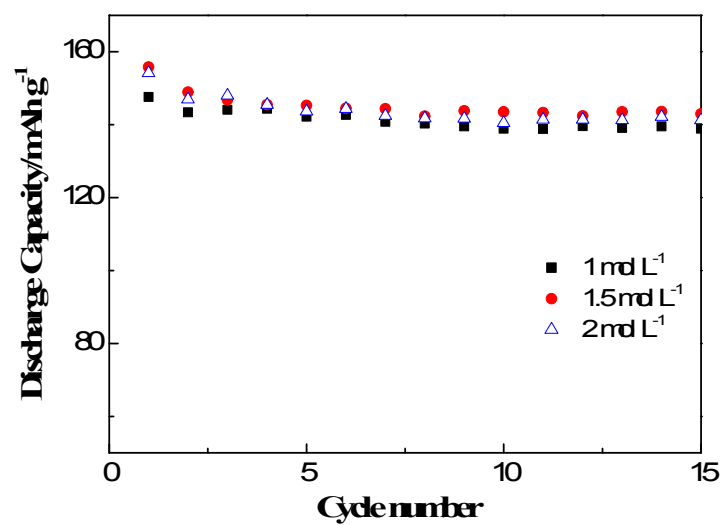


Figure S3

Fig. S3. The cycling performance for the commercial anatase TiO₂/Mg coin cells with Mg(BH₄)₂/LiBH₄/TG electrolytes of different LiBH₄ concentrations (1, 1.5 and 2 mol L⁻¹) at 0.2C. The cell with 1.5 mol L⁻¹ LiBH₄ concentration shows slight higher discharge capacities and better retention.

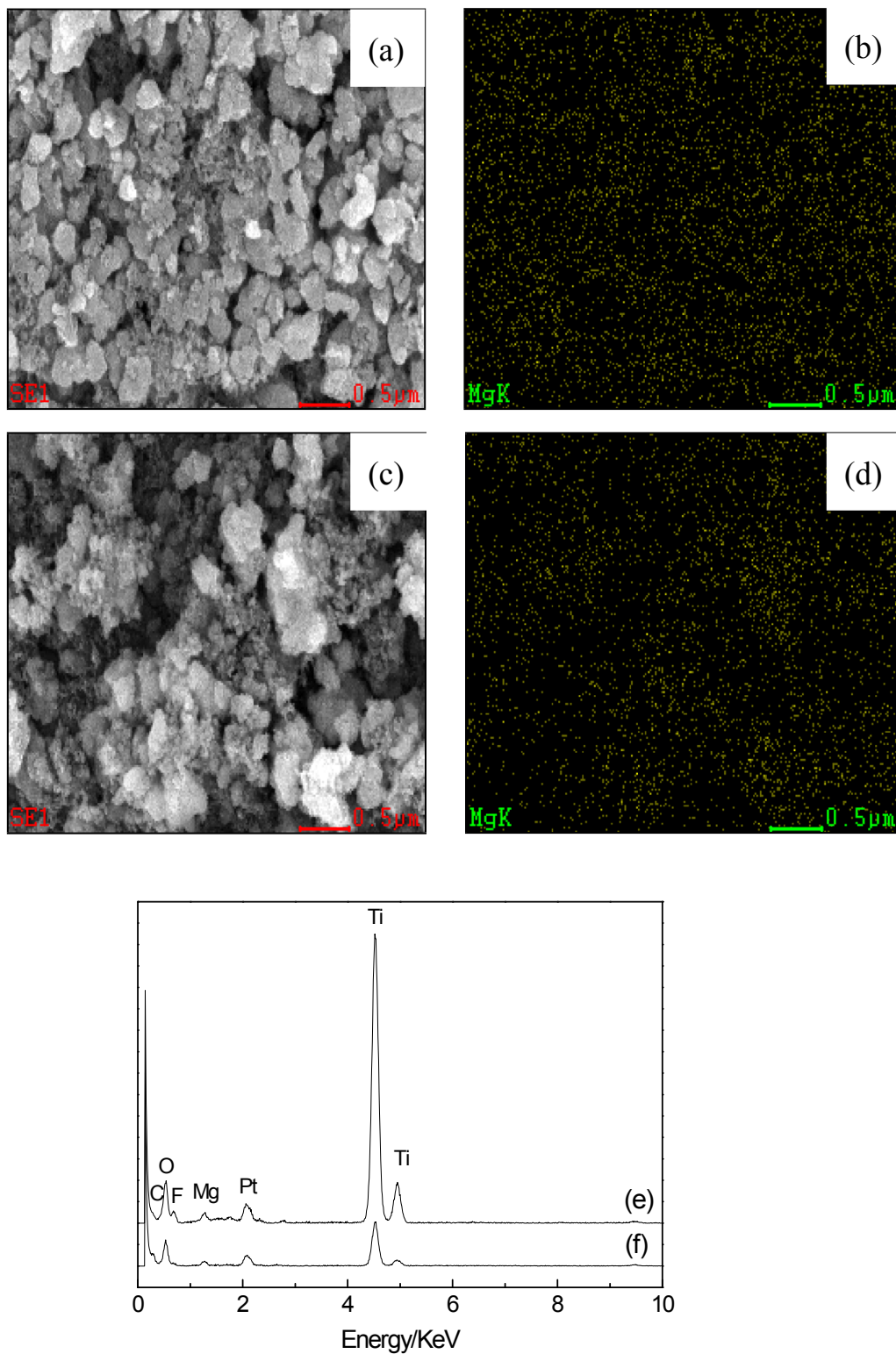


Figure S4

Fig.S4. SEM images and Mg mapping, as well as energy-dispersive X-ray spectroscopy (EDS) analysis recorded for the discharge electrodes (sputtered by Pt) from the points B (a, b, e) and D (c, d, f) indicated in Fig. 3a.