Supporting Information for

High-efficient Electrodeposition of Magnesium alloy-based Anodes for Ultra-stable Rechargeable Magnesium-ion Batteries

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Experimental Section

Preparation of magnesium electrode.

The disks of Mg metal were polished with sandpaper, cleaned with ethanol, and then stored in an Ar-filled glove box (H₂O, $O_2 < 0.1$ ppm) after drying at 80 °C for 6 h under vacuum conditions.

Synthesis of Mg-Sn@Mg and Mg-Bi@Mg alloys.

Mg-Sn@Mg alloys: Anhydrous magnesium sulfate (MgSO₄, Aladdin, 99.99%), 0.06M tin (II) sulfate (SnSO₄, Aladdin, AR), and sodium citrate dihydrate (C₆H₅Na₃O₇•2H₂O, AR, Aladdin, 99%) were dissolved into the deionized water (DI water) with continuous stirring for 0.5 h until a homogeneous and transparent solution was obtained as the plating solution. A two-electrode electrochemical cell was utilized to electrodeposit Mg-Sn alloy on Mg foil (Mg-Sn@Mg anode) at 6 V for 30~240s with platinum mesh as the counter electrode.

Mg-Bi@Mg alloys: Anhydrous magnesium sulfate (MgSO₄, Aladdin, 99.99%), 0.06 M bismuth(III) nitrate pentahydrate (Bi(NO₃)₂·5H₂O, Aladdin, 99.0%), and sodium citrate dihydrate (C₆H₅Na₃O₇•2H₂O, AR, Aladdin, 99%) were dissolved into the deionized water (DI water) with continuous stirring for 2 h until a homogeneous and transparent solution was obtained as the plating solution. A two-electrode electrochemical cell was utilized to electrodeposit Mg-Bi alloy on Mg foil (Mg-Bi@Mg anode) at 15 V for 5~10 min with platinum mesh as the counter electrode.

Electrolyte preparations

The electrolyte with 0.4 M (PhMgCl)₂-AlCl₃ in tetrahydrofuran (THF) (called APCelectrolyte) was obtained by dissolving the predetermined amount of PhMgCl·THF and AlCl₃ in THF under stirring for at least 24h.

Materials Characterizations

X-ray diffraction (XRD) measurements were performed with an X'Pert³ MRD e diffractometer (Cu Kα radiation). Scanning electron microscopy (SEM) and energydispersive spectrometry (EDS) experiments were carried out with a field emission scanning electron microscope (Hitachi S-4800). X-ray photoelectron spectroscopy (XPS) analysis was performed with a PerkinElmer PHI 550 spectrometer with Al Ka (1486.6 eV) as the X-ray source. The contact angles were measured by a KRüSS GmbH Instrument (DSA25S, Germany) using the ADVANCE software under a sessile drop model at 25 °C. The in situ optical images were obtained on an optical microscope (YM730TR, Suzhou Yuescope, China) at 4.0 mA cm⁻².

Electrochemical Characterizations

The CR2032 coin-type cells were fabricated for electrochemical assessment. The mixture of Mo_6S_8 , polyvinylidene difluoride (PVDF), and super P (8:1:1) was dissolved in N-methyl-2-pyrrolidone (NMP) to create a slurry. This slurry was subsequently coated onto the carbon paper.

All electrochemical measurements were tested using a CHI760E electrochemical workstation (Chenghua Instrument Co. Ltd. Shanghai, China) or a Land CT3002A battery tester (Wuhan, China) at 30 °C. All cells were assembled within an Ar-filled glove box (Vigor, < 0.1 ppm of water and oxygen). Glass microfiber separators were used for all electrochemical assessments. Charge/discharge tests were performed at 25 °C and 0.2 C (1 C = 128 mA g⁻¹) for two cycles and then at 1C and 10 C in the range of 0.2~1.95 V using a Land battery tester (Land, Wuhan) to examine the cycling stability of the electrode materials. The cells were also tested at rates of 0.1 C, 0.2 C, 0.5 C, 1 C, 2 C and 5 C then at a rate of 0.1 C to analyze the rate capability. In addition, cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed using a CHI760E electrochemical analyzer. CV curves for different scan rates (0.1~1.0mV s⁻¹) were recorded at 0.2~1.95 V. The EIS tests were performed from 100k to 0.01 Hz with a potential amplitude of 5 mV. EIS measurements for different samples of symmetric cells at the 1st, 20th, and 100th cycles were tested on an electrochemical workstation. The in-situ optical visualization observation images were obtained on an optical microscope (YM730TR, Suzhou Yuescope, China).



Fig. S1. Cross-sectional SEM image of the Mg-Sn@Mg anode.



Fig. S2. Cross-sectional SEM image of the Mg-Bi@Mg anode.



Fig. S3. XRD pattern of the as-prepared Mg-Cu@Mg sample.



Fig. S4. SEM image of the as-prepared Mg-Cu@Mg.



Fig. S5. Full survey XPS spectrum of the Mg-Sn@Mg.



Fig. S6. Full survey XPS spectrum of the as-prepared Mg-Bi@Mg.



Fig. S7. (a) Full survey XPS spectrum of Mg foil. (b) High-resolution Mg 1s spectrum of Mg foil.



Fig. S8. Cyclic Voltammetry of the APC electrolyte in a three-electrode set-up. Scan rate: 100 mV/s, voltage: -0.6V~4.0V. Working electrode: Pt, Reference electrode: Mg foil, Counter electrode: Mg foil.



Fig. S9. (a) Cycling performance and (b) the corresponding voltage hysteresis of symmetric cells with bare Mg and Mg-Cu@Mg electrodes at 0.1 mA cm⁻² and 0.1 mAh cm⁻².



Fig. S10. Contact angles of APC electrolyte on bare Mg and Mg-Cu@Mg.



Fig. S11. Relationship between nucleation overpotential and current density at different current densities corresponding to Fig. 3f, g and h.



Fig. S12. SEM image of Mg-Sn@Mg after 200 cycles.



Fig. S13. SEM image of Mg-Bi@Mg after 200 cycles.



Fig. S14. XRD patterns of the Mg-Sn@Mg anode after magnesiation and 10 cycles.



Fig. S15. XRD patterns of the Mg-Bi@Mg anode after magnesiation and 10 cycles.



Fig. S16. The initial CV curves for Mo_6S_8 // bare Mg, Mo_6S_8 //Mg-Sn@Mg, and Mg-Bi@Mg full cells.



Fig. S17. CV curves of (a) $Mo_6S_8//Mg$ -Cu@Mg full cell at different scan rates from 0.1 to 1.0 mV s⁻¹ in the voltage range of 0.2–1.95V and (b) the square root of scan rate (v^{0.5}) of bare Mg and Mg-Cu@Mg.



Fig. S18. The Nyquist plots of full cells based on bare Mg, Mg-Sn@Mg and Mg-Bi@Mg anodes.



Fig. S19. Charge–discharge profiles for a Mo₆S₈//Mg-Sn@Mg cell at 0.1, 0.2, 0.5, 1, 2, and 5 C, respectively.



Fig. S20. Charge–discharge profiles for a Mo₆S₈//Mg-Bi@Mg cell at 0.1, 0.2, 0.5, 1, 2, and 5 C, respectively.



Fig. S21. Charge–discharge profiles for a Mo₆S₈//bare Mg cell at 0.1, 0.2, 0.5, 1, 2, and 5 C, respectively.



Fig. S22. Cycling performance of the Mo₆S₈//bare Mg and Mo₆S₈//Mg-Cu@Mg full cells at 1 C.



Fig. S23. Cycling performance of Mo_6S_8 //bare Mg, Mo_6S_8 //Mg-Sn @Mg and Mo_6S_8 //Mg-Bi@Mg full cells at 0.5 C

Resistance	Bare Mg	Mg-Sn@Mg	Mg-Bi@Mg
$R_{\rm s}(\Omega)$	22.55	22.78	16.22
$R_{ct}(\Omega)$	85067	26000	40686

Table S1. The values of ohmic resistance (R_s) and charge transfer resistance (R_{ct}) for Mg//Mg symmetric cells.

Table S2. The values of ohmic resistance (R_s) and charge transfer resistance (R_{ct}) for Mg//Mg symmetric cells after different cycles.

Cycle	$R_{ m s}(\Omega)$	$R_{ct}(\Omega)$
Initial	22.55	85067
After 20 cycles	20.97	60077
After 100 cycles	23.95	189780

Table S3. The values of ohmic resistance (R_s) and charge transfer resistance (R_{ct}) for Mg-Sn @Mg//Mg-Sn @Mg symmetric cells after different cycles.

Cycle	$R_{ m s}(\Omega)$	$R_{ct}(\Omega)$
Initial	16.57	16171
After 20 cycles	17.17	1696
After 100 cycles	45.78	4559

Table S4. The values of ohmic resistance (R_s) and charge transfer resistance (R_{ct}) for Mg-Bi@Mg//Mg-Bi@Mg symmetric cells after different cycles.

Cycle	$R_{ m s}(\Omega)$	$R_{ct}(\Omega)$
Initial	37.2	58125
After 20 cycles	56.08	2782
After 100 cycles	43.51	2184

Calculated	Ma S //hora Ma	Mo ₆ S ₈ // Mg-	Mo ₆ S ₈ // Mg-
parameters	MO_6S_8 // bare Mg	Sn@Mg	Bi@Mg
D_{Mg}^{2+} at A (cm ² s ⁻¹)	3.20×10-9	4.53×10-9	5.51×10-9
D_{Mg}^{2+} at C (cm ² s ⁻¹)	2.75×10-9	4.20×10-9	4.72×10-9

Table S5. A summary of Mg²⁺ diffusion coefficients (D_{Mg}^{2+}) of Mo₆S₈//bare Mg, Mo₆S₈//Mg-Sn @Mg and Mo₆S₈//Mg-Bi@Mg full cells.

Table S6. The values of ohmic resistance (R_s) and charge transfer resistance (R_{ct}) for $Mo_6S_8//Mo_6S_8//Mg$ -Sn @Mg and $Mo_6S_8//Mg$ -Bi@Mg full cells.

Full cells	$R_{\rm s}(\Omega)$	$R_{ct}(\Omega)$
Bare Mg	8.873	4000
Mg-Sn@Mg	8.872	4029
Mg-Bi@Mg	25.46	4688