

Electronic Supplementary Information

Toward high-performance rechargeable magnesium batteries with Cu₂Se-CTAB nanoparticles cathode and Mg[B(HFIP)₄]₂/DME electrolyte

Tengteng Zhang, Zihang Gao, Jiguang Zhang, Rui Shi , Yana Liu, Jun Wang
and Yunfeng Zhu*

*College of Materials Science and Engineering, Nanjing Tech University, 30 South Puzhu Road, Nanjing
211816, P. R. China. E-mail: zhangjiguang@njtech.edu.cn;*

Experimental Section

Synthesis of Cu₂Se-CTAB Nanoparticles

0.145 g of Cu(NO₃)₂·3H₂O and an appropriate amount (0.05 g, 0.1 g, 0.15 g, 0.2 g) of CTAB in 55 mL of deionized water, followed by ultrasonic stirring for 20 minutes. After complete dissolution, add 0.0519 g of Na₂SeO₃, stir for 20 minutes to form a blue-green suspension. Then, add 5 mL of N₂H₄·H₂O dropwise and stir for 20 minutes. The resulting brown solution is transferred to a 100 mL polytetrafluoroethylene reaction autoclave liner and reacted at 180°C for 24 hours. After the reaction is complete, centrifuge to collect the product and wash alternately with alcohol and deionized water six times. Then, vacuum dry at 60°C for 12 hours to obtain the solid product, Cu₂Se-CTAB nanoparticles, which are black powder. For comparison, Cu₂Se nanoparticles were also prepared using the same process without adding CTAB.

Preparation of Electrolyte

The entire preparation process of the APC electrolyte is completed within an argon glove box. First, take 0.6667 g of anhydrous AlCl_3 powder and place it in a brown screw-cap vial. Then, add 7.5 mL of anhydrous THF to the powder slowly, and stir for 12 hours. After that, add 5 mL of phenylmagnesium chloride solution (2 M in THF) to the above solution, and stir for another 12 hours. This will yield the required 0.4 M AlCl_3 -PhMgCl/THF electrolyte, which is the APC electrolyte.

The preparation of the electrolyte $\text{Mg}[\text{B}(\text{HFIP})_4]_2/\text{DME}$ involves the following steps: First, under an argon atmosphere at 0 °C, 2.13 mL of hexafluoroisopropanol is added to 10 mL of dibutylmagnesium heptane solution within 10 minutes to obtain the solid product $\text{Mg}(\text{HFIP})_2$. Then, 20 mL of ethylene glycol dimethyl ether (DME) is slowly added to the mixture, and it is stirred for 30 minutes at 25°C. Subsequently, 24.4 mL of borane tetrahydrofuran complex is added dropwise over 30 minutes, followed by the slow addition of 7.07 mL of hexafluoroisopropanol over 1 hour, and the mixture is stirred for 24 hours at 25°C. After that, the mixture is vacuum dried at 60°C to obtain approximately 14.9~15.6 g of white microcrystalline powder, which is the solid product $\text{Mg}[\text{B}(\text{HFIP})_4]_2 \cdot \text{DME}$. Next, 4.956 g of $\text{Mg}[\text{B}(\text{HFIP})_4]_2 \cdot \text{DME}$ is placed in a brown vial, and 10 mL of DME is added dropwise and stirred for 24 hours to obtain the 0.3 M $\text{Mg}[\text{B}(\text{HFIP})_4]_2/\text{DME}$ electrolyte.

Electrochemical and Material Characterizations

The cathode is prepared by grinding 0.07 g of active material (Cu_2Se -CTAB), 0.02 g of carbon black (Super P), and 0.01 g of polyvinylidene fluoride (PVDF) uniformly

and transferring the mixture to a 5 mL small beaker. Then, 0.5 mL of NMP is added dropwise and stirred for 4 hours to form a uniform black slurry. The slurry is coated onto the current collector carbon foil using a 200 μm doctor blade and dried in a vacuum oven at 60°C for 12 hours. The dried material is cut into circular electrodes with a diameter of 12 mm. The loading amount of the active material is calculated by weighing and is found to be 1.5~2.0 mg cm^{-2} . The test cell is a CR2032 coin cell, assembled within an argon glove box. The separator used is a Whatman GF/D glass fiber membrane with a diameter of 18 mm. The anode is a piece of metal magnesium foil cut to 11 \times 11 mm in size with a thickness of 0.3 mm, which is polished and chamfered with sandpaper to remove the surface oxide layer. Galvanostatic charge-discharge (GCD) tests and rate performance tests are conducted using a Neware battery testing system, with the test environment temperature controlled at 25°C and the test range set at 0.1~2.0 V vs. Mg/Mg²⁺. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) tests are performed using a Shanghai Chenhua CHI760E electrochemical workstation, with the test ranges set at 0.1~2.0 V vs. Mg/Mg²⁺ and 0.01~105 Hz, respectively.

Material Characterizations

The phases of the samples were investigated by X-ray diffraction (XRD) with Cu K α (40 kV and 35 mA) using an ARL X'TRA diffractometer. The micromorphology was revealed by field emission scanning electron microscopy (SEM, Hitachi, S4800) and X-ray photoelectron spectroscopy (XPS, Thermo, ESCALAB 250 XI) measurement was carried out to analyze the valence state of selected elements and

surface composition of the samples.

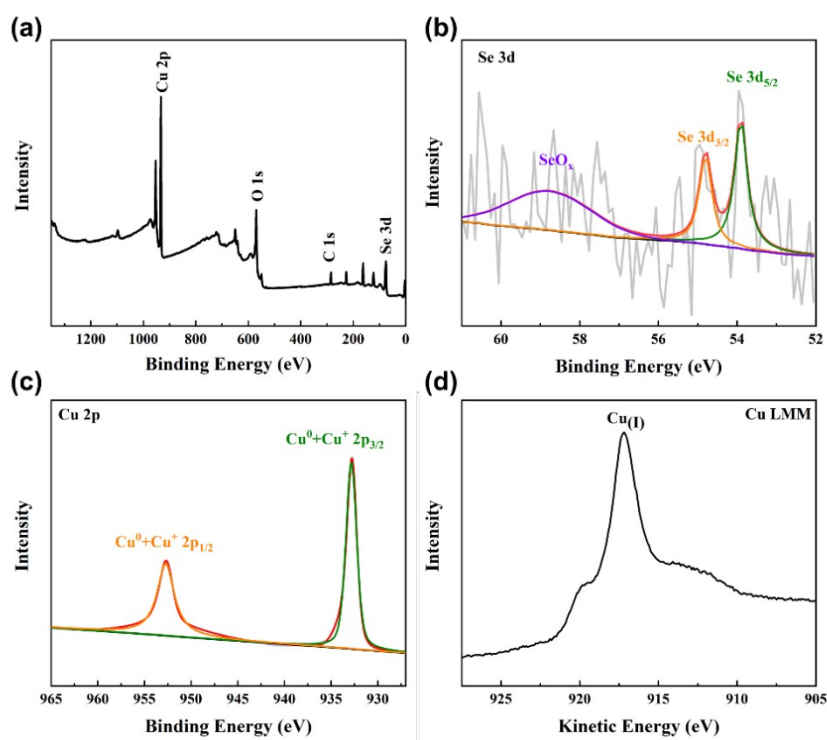


Fig. S1. XPS spectra of (a) full survey, (b) Cu 2p, (c) Se 3d and (d) Cu LMM for Cu₂Se-100CTAB.

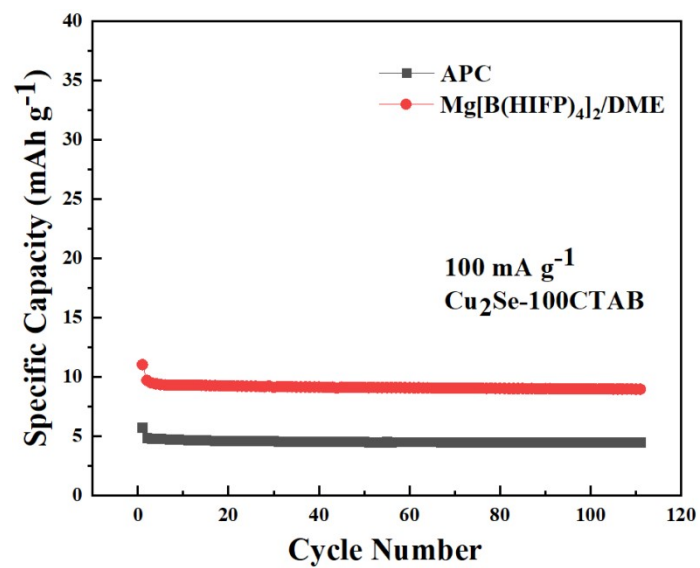


Fig. S2. Short cycling performance of CTAB at 100 mA g⁻¹ in APC electrolyte and 0.3 M Mg[B(HFIP)₄]₂/DME electrolyte.

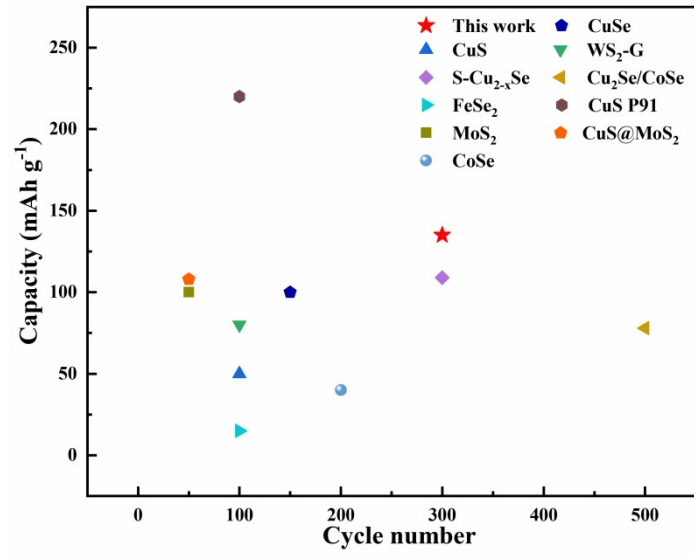


Fig. S3. cycling performance of Cu₂Se-CTAB and other cathode materials at 100 mA g⁻¹ for magnesium-based batteries in the literature^[1-8].

Table S1. cycling performance of Cu₂Se-CTAB and other cathode materials at different current density for magnesium-based batteries in the literature.

Materials	electrolytes	Rate (mA g ⁻¹)	Cycle number	Capacity (mAh g ⁻¹)	Ref
CuSe	APC	100	150	100	[1]
CuS	APC	100	100	50	[2]
WS ₂ -G	APC	100	100	75	[3]
S-Cu _{2-x} Se	(HMDS) ₂ Mg-AlCl ₃	100	300	109	[4]
MoS ₂	APC-LiCl	100	50	100	[5]
CuS@MoS ₂	APC-LiCl	100	50	107	[5]
CoSe	APC-LiCl	50	50	114	[6]
Cu ₂ Se/CoSe	APC-LiCl	100	500	78	[6]
FeSe ₂	APC-LiCl	100	100	20	[7]
CuS P91	Mg[B(HFIP) ₄] ₂ /DME	100	100	220	[8]
MgV ₂ O ₄	APC	200	300	111.7	[9]
VSe ₂	(HMDS) ₂ Mg-AlCl ₃	50	30	100	[10]
Cu₂Se- CTAB	Mg[B(HFIP)₄]₂/DME	100	300	134	This work

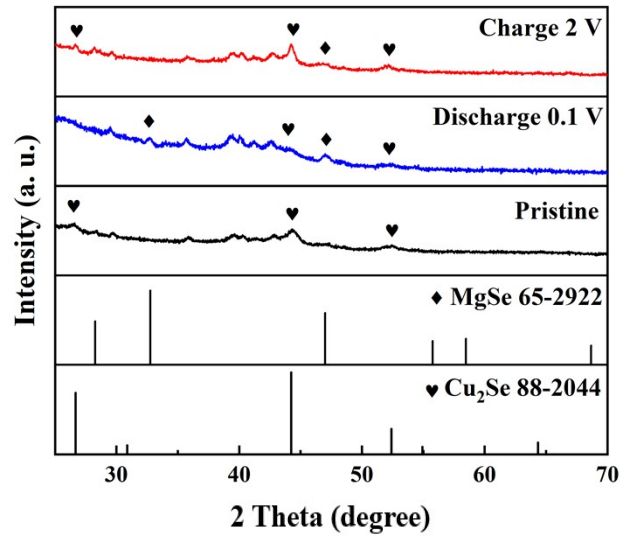


Fig. S4 Ex-situ XRD patterns of the Cu₂Se-100CTAB at various charge/discharge states.

References

1. S. Yang, F. Q. Ji, Z. T. Wang, Y. Q. Zhu, K. K. Hu, Y. P. Ouyang, R. J. Wang, X. L. Ma and C. B. Cao, *Electrochim. Acta*, 2019, **324**.134864.
2. Q. Zhang, Y. B. Hu, J. Wang and F. S. Pan, *J. Magnes. Alloy*, 2023, **11**, 192-200.
3. M. Latha, S. Biswas and J. V. Rani, *Ionics*, 2020, **26**, 3395-3404.
4. D. Chen, Y. J. Zhang, X. Li, J. W. Shen, Z. X. Chen, S. A. Cao, T. Li and F. Xu, *Chem. Eng. J.*, 2020, **384**.123235.
5. J. X. Wang, X. Wang, J. D. Yang, X. Y. Dong, X. Chen, Y. Zhang, W. Zeng, J. Y. Xu, J. F. Wang, G. S. Huang and F. S. Pan, *J. Electrochem. Soc.*, 2022, **169**.073502.
6. Z. H. Gao, R. Shi, Y. P. Zhao, J. G. Zhang, J. C. Liu, Y. F. Zhu, Y. N. Liu, J. Wang and L. Q. Li, *Electrochim. Acta*, 2023, **469**.143298.
7. C. H. Zhang, L. R. Zhang, N. W. Li and X. Q. Zhang, *Energies*, 2020, **13**.4375.
8. X. Q. He, R. Q. Cheng, X. Y. Sun, F. Z. Sun, Y. Fu, Y. T. Li, P. Li, Z. Li, H. Xu, R. M. Laine and J. X. Zou, *Adv. Funct. Mater.*, 2024,2413893.
9. Q. Ding, T. L. Han, T. Zhou, X. R. Lin and J. Y. Liu, *Chem. Eur. J.*, 2024, **30**.e202302978.
10. D. G. Tao and F. Xu, *Mater. Lett.*, 2021, **300**.130221.