

## Supporting Information

# ZnMn Bimetallic Selenide for Rechargeable Aluminum Batteries

*Shimeng Zhao, Yiqun Du, Cheng Xu, Wenyang Zhang, and Jianxin Zhang*<sup>□</sup>

Key Laboratory for Liquid-Solid Structural Evolution and Processing of Materials  
(Ministry of Education), School of Materials Science and Engineering, Shandong  
University, Jinan 250061, PR China.

\*E-mail: [jianxin@sdu.edu.cn](mailto:jianxin@sdu.edu.cn).

## **Experimental Section**

***Synthesis of ZnSe:*** 5 mmol selenium, 5 mmol  $\text{ZnCl}_2$  were dissolved in 80 mL ethanolamine under stirring. The Appropriate amount of hydrazine hydrate is added dropwise to the stirring reagent. The mixture was transferred into a 100 mL stainless-steel autoclave, and it was maintained at 180 °C for 12 h, which was cooled down to room temperature. The powder was obtained by centrifugation and washing several times before drying it under vacuum at 60 °C overnight.

***Synthesis of MnSe:*** 5 mmol selenium, 5 mmol  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  were dissolved in 80 mL ethanolamine under stirring. A certain amount of hydrazine hydrate is added dropwise to the stirring reagent, which was transferred into a 100 mL stainless-steel autoclave, and it was maintained at 180 °C for 12 h. The autoclave was cooled down to room temperature. The product was separated and washed with deionized water and ethanol before drying it under vacuum at 60 °C for 8 h.

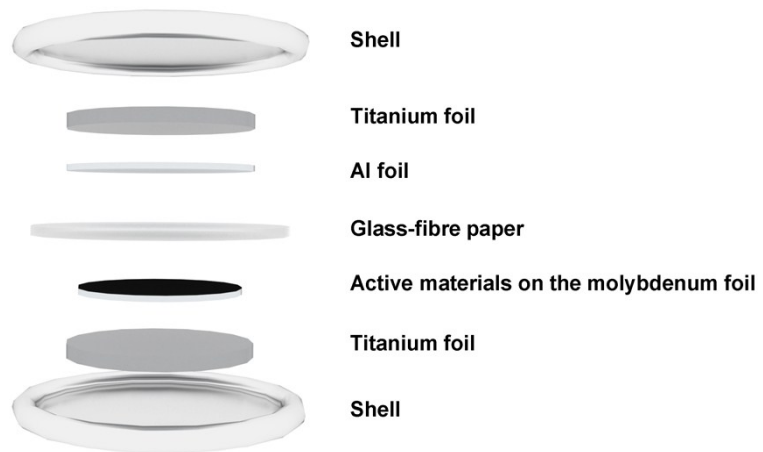
***Synthesis of ZnMn-Se sample:*** 5 mmol selenium, 2.5 mmol  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ , and 2.5 mmol  $\text{ZnCl}_2$  were dissolved in 80 mL ethanolamine under stirring. An Appropriate amount of hydrazine hydrate is added dropwise to the stirring reagent. The mixture was transferred into a 100 mL stainless-steel autoclave, which was kept at 180 °C for 12 h. The autoclave was cooled down to room temperature. The powder was obtained by centrifugation and washing several times before drying it under vacuum at 60 °C overnight.

***Material characterization:*** The morphologies and compositions of ZnSe, MnSe, and ZnMn-Se powders were characterized by field-emission scanning electron microscopy

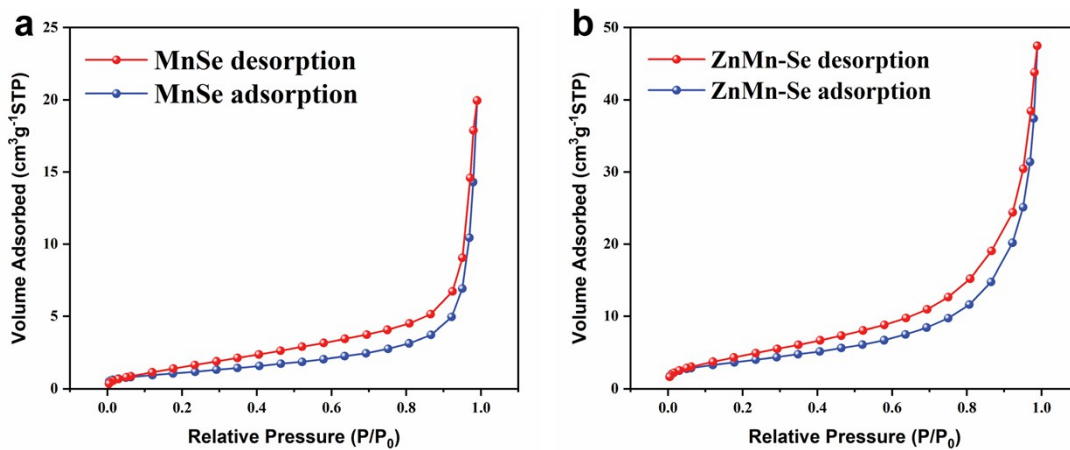
(SEM, JSM-7800F). The X-ray photoelectron spectroscopy was carried out using Thermo ESCALAB 250XI.

For the XPS tests, the cell was fully charged or discharged at  $1 \text{ A g}^{-1}$  between 0.1 and 1.6 V. The electrode slices were taken out from the cell in the argon-atmosphere glove box. Then molybdenum foils with ZnMn-Se were washed with anhydrous methanol to remove the interference of residual electrolyte.

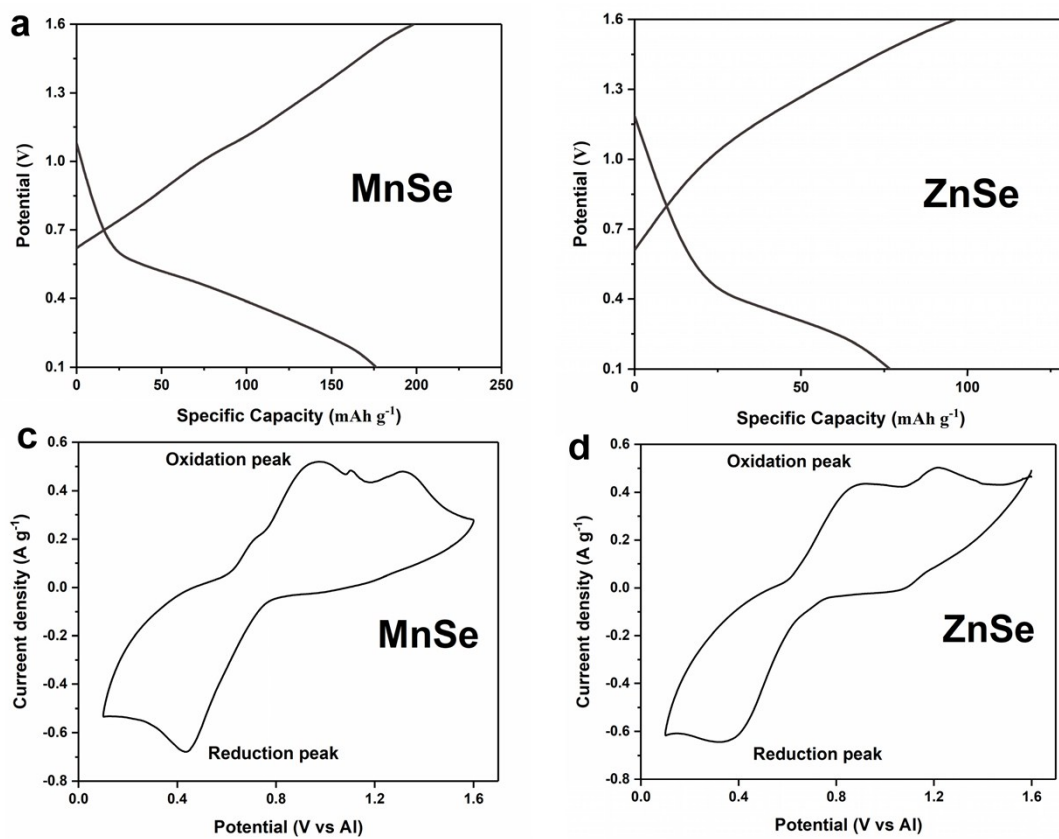
***Electrochemical measurements:*** In order to prepare positive electrode, 80% active materials, 10% PTFE, and 10% acetylene black were mixed in N-methyl pyrrolidone agent under stirring for 12 h to form the slurry. Afterwards, the slurry was pasted to molybdenum foil before drying it at  $60 \text{ }^{\circ}\text{C}$  for 12 h. 2025-coin cells were assembled to explore the electrochemical property. As shown in Fig. S1, aluminum foil acted as the negative electrode, the glass-fibre paper (435 mm thickness, Whatman 934-AH) served as the separator. To avoid corrosion from the  $\text{AlCl}_3/[\text{EMIm}]\text{Cl}$  ionic liquid, titanium foil (0.6 mm thickness) was used as supporters and anticorrosion materials at both the cathode shell and the anode shell.<sup>1</sup> In order to synthesize electrolyte,  $[\text{EMIm}]\text{Cl}$  was dried at  $100 \text{ }^{\circ}\text{C}$  for 10 h to evaporate the water. Then  $\text{AlCl}_3$  has dispersed in the dried  $[\text{EMIm}]\text{Cl}$  with a molar ratio of 1.3:1 in a glove box under stirring for 2 h. The resulting pale-yellow electrolyte can be used before keeping it under room temperature for at least 24 h. The cycling property of RABs was measured on the Land CT2001A system. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) tests were carried out using CHI 660E workstation.



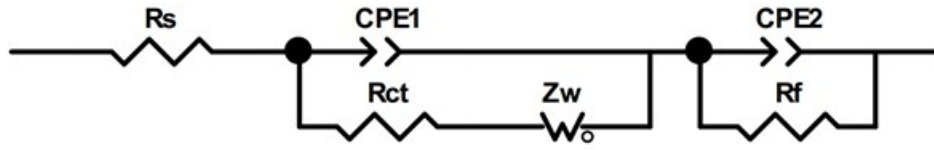
**Fig. S1** The structure of the RABs.



**Fig.S2** The  $\text{N}_2$  adsorption-desorption isotherms for (a) MnSe and (b) ZnMn-Se.



**Fig. S3** The charge/discharge curves of (a) MnSe and (b) ZnSe. The CV curves for (c) MnSe and (d) ZnSe.



**Fig.S4** The fitting model of the EIS spectra.

**Table S1** Comparison of electrochemical properties of ZnMn-Se with other cathodes for RABs.

Cathode materials	Electrolyte	Cycling performance	Ref.
ZnMn-Se	AlCl <sub>3</sub> :[EMIm]Cl=1.3	1 A g <sup>-1</sup> /100 cycle/148 mA h g <sup>-1</sup>	This work
V <sub>2</sub> CT <sub>x</sub> MXene	AlCl <sub>3</sub> :[EMIm]Cl=1.3	1 A g <sup>-1</sup> /100 cycle/76 mA h g <sup>-1</sup>	2
AlV <sub>3</sub> O <sub>9</sub>	AlCl <sub>3</sub> :[EMIm]Cl=1.3	0.1 A g <sup>-1</sup> /150 cycle/196 mA h g <sup>-1</sup>	3
Ni <sub>3</sub> S <sub>2</sub> @Graphene	AlCl <sub>3</sub> :[EMIm]Cl=1.3	0.2 A g <sup>-1</sup> /300 cycle/50 mA h g <sup>-1</sup>	4
Co <sub>3</sub> S <sub>4</sub>	AlCl <sub>3</sub> :[EMIm]Cl=1.3	0.05 A g <sup>-1</sup> /150 cycle/90 mA h g <sup>-1</sup>	5
CuO	AlCl <sub>3</sub> :[EMIm]Cl	0.2 A g <sup>-1</sup> /100 cycle/113 mA h g <sup>-1</sup>	6
TeO <sub>2</sub>	AlCl <sub>3</sub> :[EMIm]Cl=1.3	1 A g <sup>-1</sup> / 54.6 mA h g <sup>-1</sup>	7
SnS <sub>2</sub>	AlCl <sub>3</sub> :[EMIm]Cl=1.3	1 A g <sup>-1</sup> /112 mA h g <sup>-1</sup>	8

## References

1. L. Geng, J. P. Scheifers, C. Fu, J. Zhang, B. P. T. Fokwa and J. Guo, *ACS Applied Materials & Interfaces*, 2017, **9**, 21251-21257.
2. A. VahidMohammadi, A. Hadjikhani, S. Shahbazmohamadi and M. Beidaghi, *Acs Nano*, 2017, **11**, 11135-11144.
3. Z. Li, J. Li and F. Kang, *Electrochimica Acta*, 2019, **298**, 288-296.
4. S. Wang, Z. Yu, J. Tu, J. Wang, D. Tian, Y. Liu and S. Jiao, *Advanced Energy Materials*, 2016, **6**, 1600137.
5. H. Li, H. Yang, Z. Sun, Y. Shi, H.-M. Cheng and F. Li, *Nano Energy*, 2019, **56**, 100-108.
6. X. Zhang, G. Zhang, S. Wang, S. Li and S. Jiao, *Journal of Materials Chemistry A*, 2018, **6**, 3084-3090.
7. J. Tu, M. Wang, Y. Luo and S. Jiao, *ACS Sustainable Chemistry & Engineering*, 2020, **8**, 2416-2422.
8. Y. Hu, B. Luo, D. Ye, X. Zhu, M. Lyu and L. Wang, *Advanced Materials*, 2017, **29**, 1606132.