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A high-performance magnesium/lithium hybrid-ion battery using hollow multi-layered NiS/Co₃S₄/carbon cathode and all-phenyl complex-based electrolyte

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Experimental

1. Preparation of NiS/Co₃S₄/C

1.1 Preparation of hollow NiCo-metal organic frameworks (MOFs) precursor

Typically, 3 g of polyvinyl pyrrolidone (PVP, K30), 1.4 mol of H₃BTC and Ni(NO₃)₂·6H₂O/CoCl₂·6H₂O with a molar mass ratio of 1:1 were dissolved in a mixed solution of deionized water/ethanol/N,N-dimethylformamide (DMF) with a volume of 15 mL each. After stirring vigorously for 1 h, the above clear solution was poured into a 50 mL Teflon-lined autoclave and held at 150 °C for 15 h. After cooling down naturally to room temperature, the resulting lilac precipitate was washed with deionized water and ethanol for several times, and then dried at 80 °C under vacuum.

1.2 Preparation of NiS/Co₃S₄/C spheres

Typically, NiCo-MOFs and sulfur powders with the mass ratio of 1:5 were separately loaded in two ceramic boats. The one containing sulfur powders were placed at the upstream side and another at the center of the tube furnace, which were annealed at 350 °C for 2 h and further incubated at 500 °C for 2 h for the complete sulfurization of NiCo-MOFs and removal of excess sulfur powder, leading to the

formation of hollow NiS/Co₃S₄/C spheres. All reactions take place in a nitrogen atmosphere.

2. Preparation of NiS

In a typical synthesis, 2 mmol L-cysteine and 2 mmol NiCl₂·6H₂O were added to the beaker containing 35 mL ethylene glycol under vigorous stirring for about 2 h at room temperature. Then the mixture was transferred into a Teflon-lined sealed autoclave and maintained at 200 °C for 24 h. After the product was washed with ethanol and water and dried at 60 °C for 10 h.

3. Preparation of Co₃S₄

3.1 Preparation of precursors

In a typical synthesis, 4 mmol CoCl₂·6H₂O and 20 mmol CH₄N₂O were added to the beaker containing 50 mL deionized water. Subsequently, the mix solution was transferred to 100 ml Teflon-lined autoclave and hold at 95 °C for 8 h. The link pink solution was centrifuged and the obtained sediment was thoroughly washed with distilled water and absolute ethanol, and finally dried overnight at 60 °C. The precursor was Co(CO₃)_{0.35}Cl_{0.20}(OH)_{1.10}·1.74H₂O.

3.2 Preparation of Co₃S₄

The precursor (0.072 g) was mixed into 40 mL 1 M thioacetamide solution. Then the mixture was transferred into a Teflon-lined sealed autoclave and maintained at 200 °C for 12 h. After the reaction was completed, the products were washed with ethanol and water several times.

4. Preparation of the electrolytes

0.2667 g of anhydrous aluminum chloride (AlCl₃, 99%, Aladdin) was dissolved into 3 mL of purified tetrahydrofuran (THF, Aladdin) solvent with vigorous stirring for 12 h. Then, 2 mL of 2 M phenyl magnesium chloride in THF was dropped into the solution followed by magnetic stirring vigorously for 12 h. At the last, 0.4 M

anhydrous lithium chloride (LiCl, 99.9%, Aladdin) was dissolved in the above Mg/Li hybrid electrolyte with stirring for 12 h.

5. Characterizations

The morphology and structure were investigated on a field-emissions scanning electron microscope (FESEM, Hitachi Regulus 8100, operated at 5 kV) and transmission electron microscope (TEM, HT-7700). The high-resolution TEM (HRTEM) images were obtained on a JEOL JEM-2010F microscope at an acceleration voltage of 200 kV to get the information on microstructure and crystallinity of the products. X-ray photoelectron spectroscopy (EscalAB 250) was used for characterization. The carbon matrix was characterized by Raman spectroscopy (Renishaw in Via). And the Brunauer Emmett Teller (BET) specific surface area of the sample was measured by a surface area tester (ASAP Micromeritics Tristar 2460).

6. Electrochemical measurements

NiS/Co₃S₄/C (80 wt.%), acetylene black (10 wt.%), and polyvinylidene fluoride binding agent (10 wt.%) with a ratio of 8:1:1 were dispersed in N-methyl-2-pyrrolidone (NMP). Evenly-mixed slurry was coated on a Cu foil and dried under vacuum for 24 h. The rolling pressure was applied on a dried electrode to obtain the corresponding dense electrode and cut the electrodes into discs. The areal mass loading of the active material in the cathodes is about 0.8~1.4 mg cm⁻². The electrodes were put into a coin cell (CR2032) with polished Mg metal as the anode and glass fiber film (Whatman, GF/F) as the separator. An 120 μL Mg-based electrolyte was used in a single coin cell. All cells were assembled in glovebox. The galvanostatic charge-discharge was tested on Neware battery test system. Cyclic voltammetry (CV) curves and electrochemical impedance spectroscopy (EIS) spectra were measured by using an electrochemical workstation (CHI 660E).

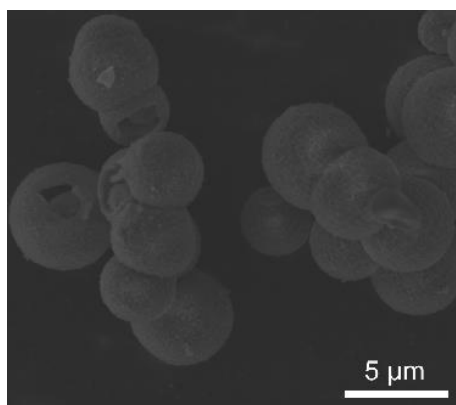


Fig. S1 SEM image of Ni/Co-MOFs precursor.

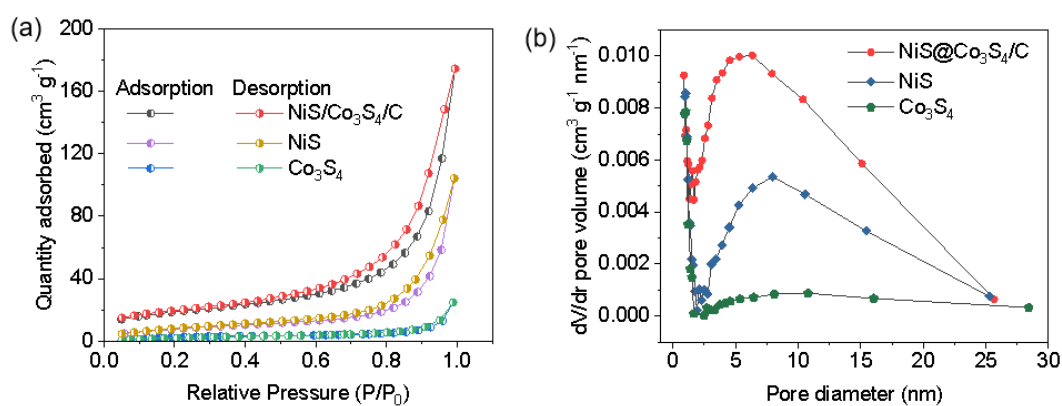


Fig. S2 (a) N_2 adsorption-desorption isotherms and (b) pore-size distribution of $\text{NiS}/\text{Co}_3\text{S}_4/\text{C}$, NiS and Co_3S_4 .

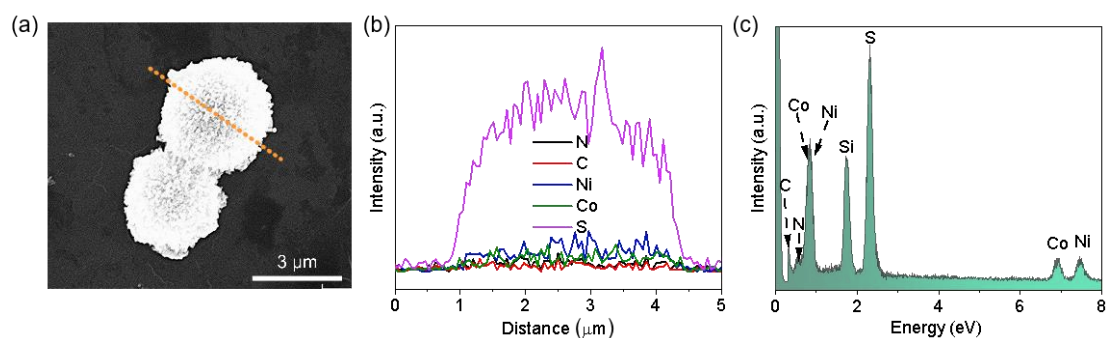


Fig. S3 (a) SEM image, (b) line-scanning curves and (c) EDS spectrum of $\text{NiS}/\text{Co}_3\text{S}_4/\text{C}$.

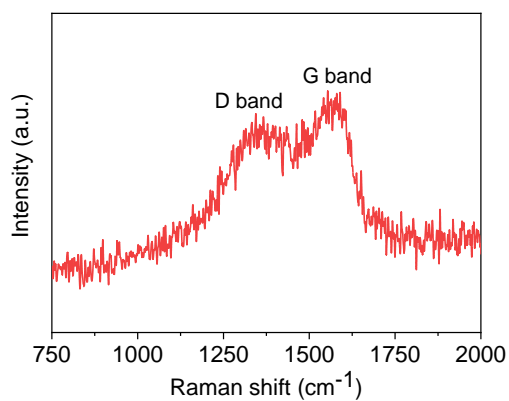


Fig. S4 Raman spectrum of NiS/Co₃S₄/C.

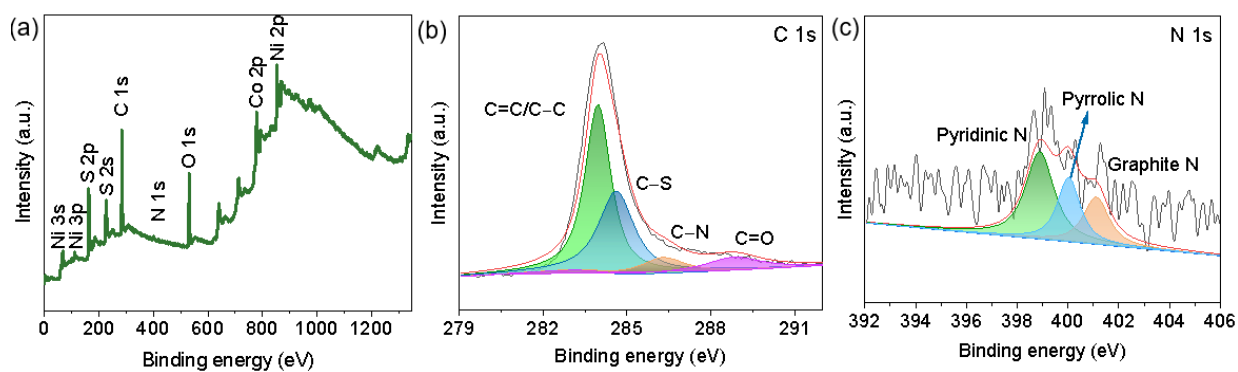


Fig. S5 (a) Survey spectrum of NiS/Co₃S₄/C. XPS spectra of the NiS/Co₃S₄/C: (b) C 1s, (c) N 1s.

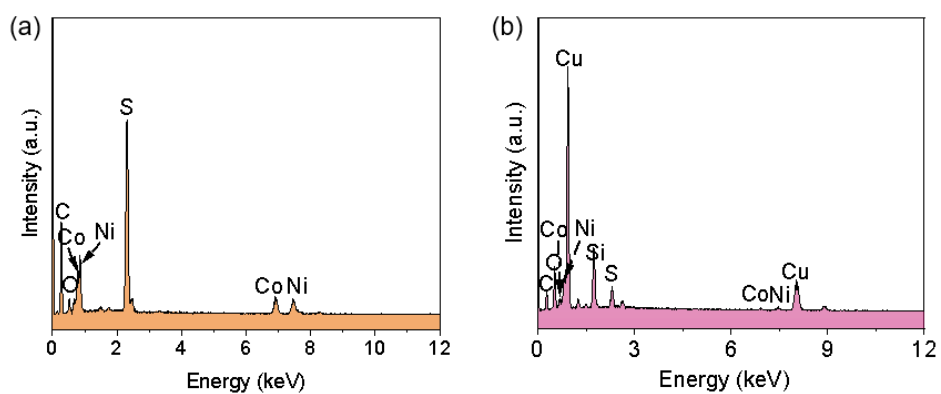


Fig. S6 EDS spectrum of the cathode (a) before and (b) after cycling.

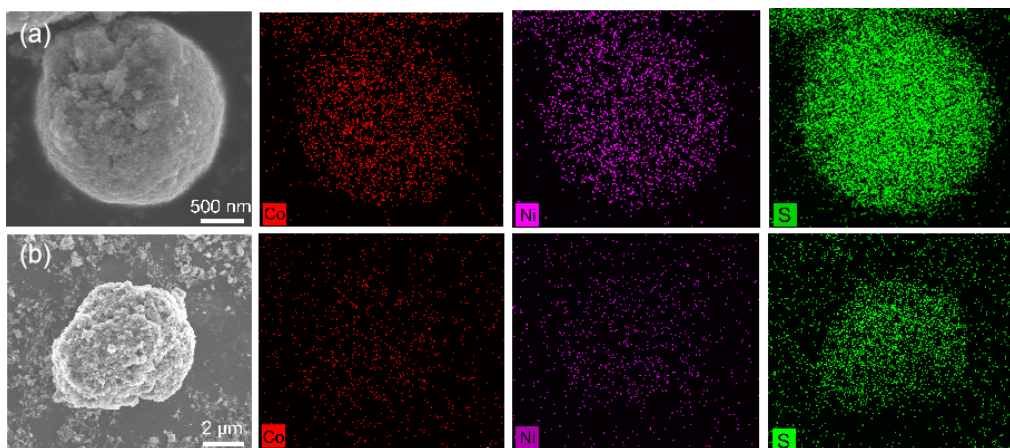


Fig. S7 Mapping images of the cathode materials (a) before and (b) after cycling.

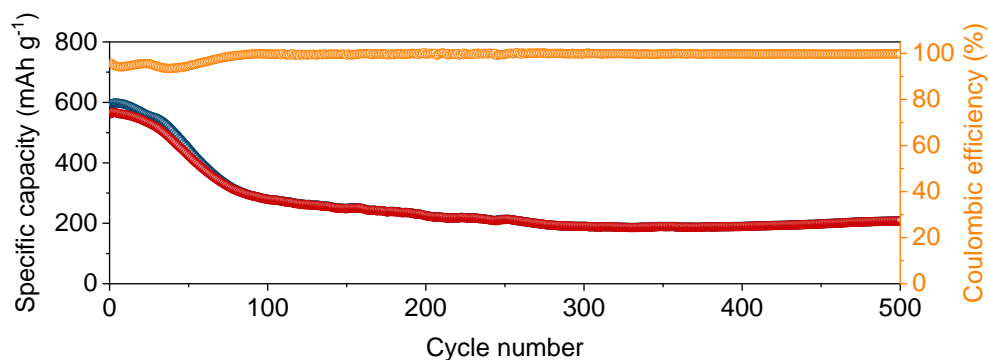


Fig. S8 Cycling performances of NiS/Co₃S₄/C at 0.5 A g⁻¹. A pre-cycling of 5 cycles at 0.2 A g⁻¹ for activation was performed.

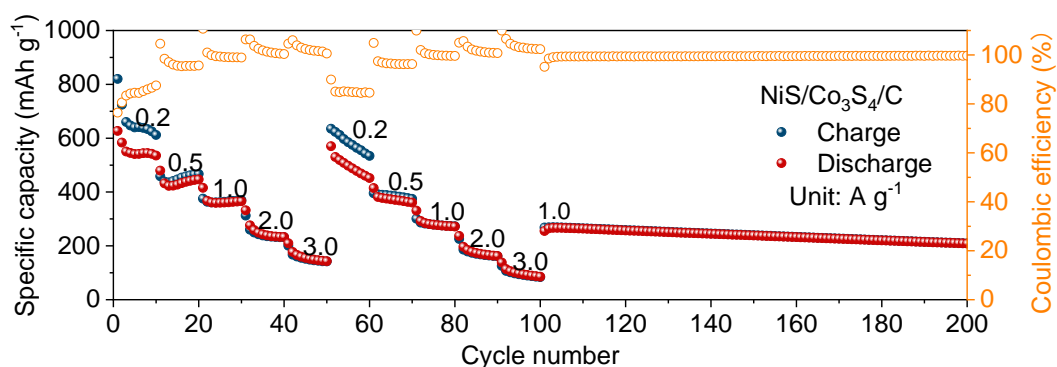


Fig. S9 Rate-performance of NiS/Co₃S₄/C cathode-based MLHB.

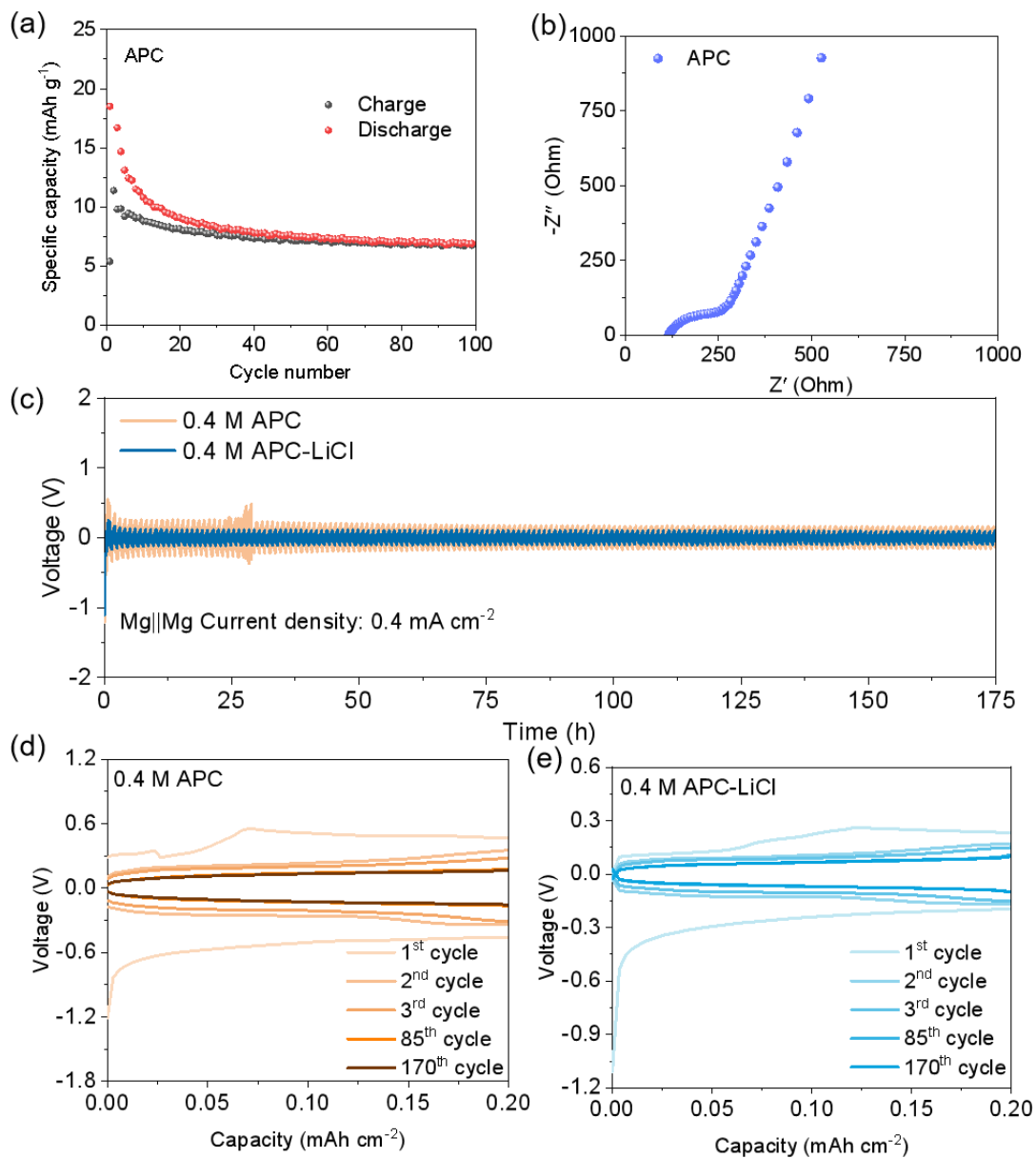


Fig. S10 Electrochemical performances in an 0.4 M APC electrolyte. (a) Cycling performance of NiS/Co₃S₄/C at 0.2 A g⁻¹, (b) EIS spectrum of NiS/Co₃S₄/C after 10 cycles at 0.2 A g⁻¹. (c) Long-term Mg stripping/plating of the Mg|Mg cell using two electrolytes at 0.4 mA cm⁻², and (d) charge and discharge curves with 0.4 M APC and (e) 0.4 M APC-LiCl electrolytes.

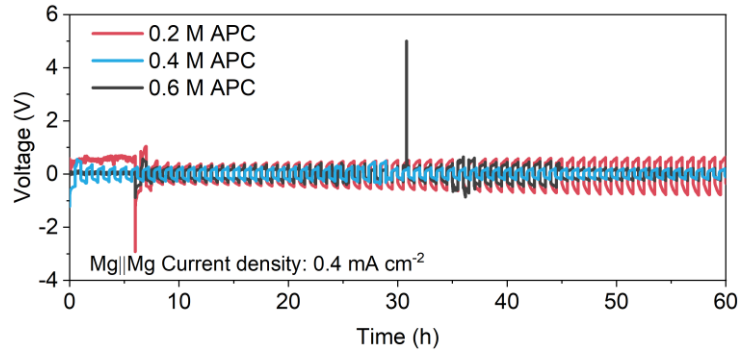


Fig. S11 Mg stripping/plating of the Mg|Mg symmetric cell using different concentrations of APC electrolyte at 0.4 mA cm^{-2} .

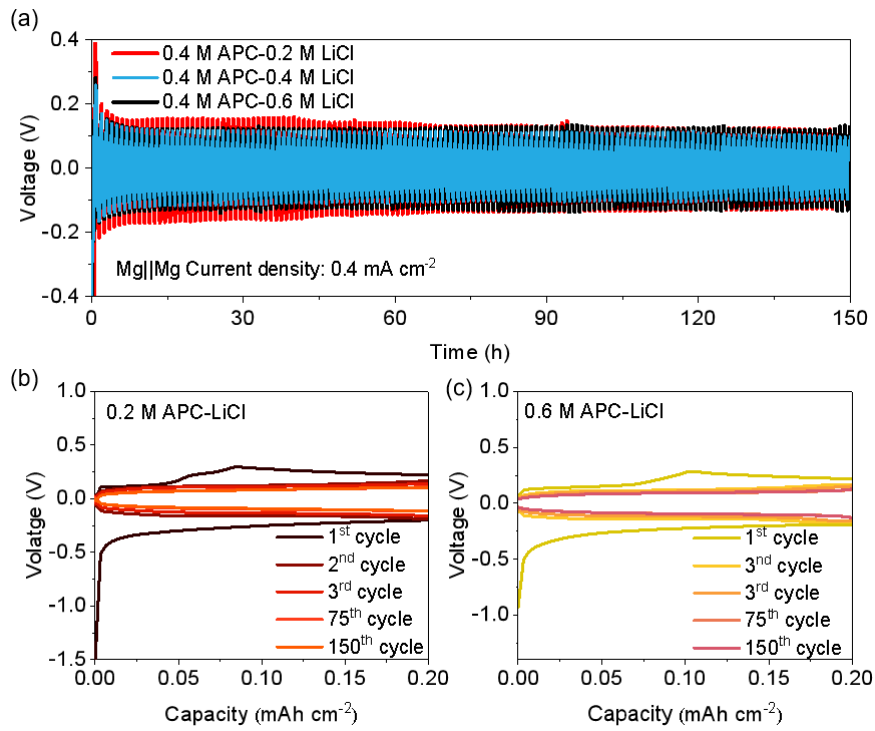


Fig. S12 (a) Mg stripping/plating of the Mg|Mg symmetric cell using different concentrations of LiCl electrolyte at 0.4 mA cm^{-2} , and charge-discharge curves with (b) 0.2 M APC-LiCl and (c) 0.6 M APC-LiCl electrolytes.

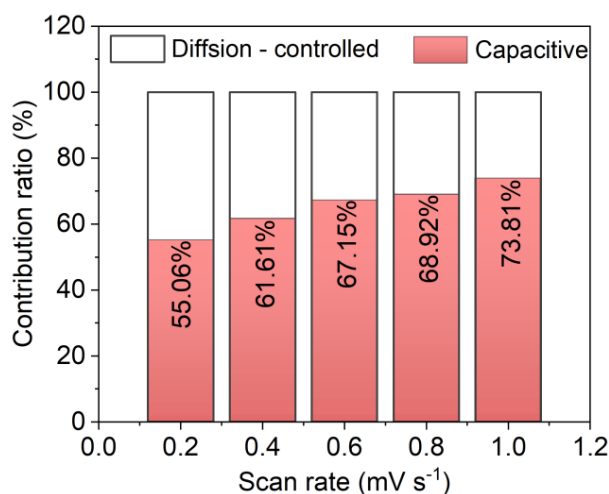


Fig. S13 The contribution of capacitive and diffusion-controlled processes.

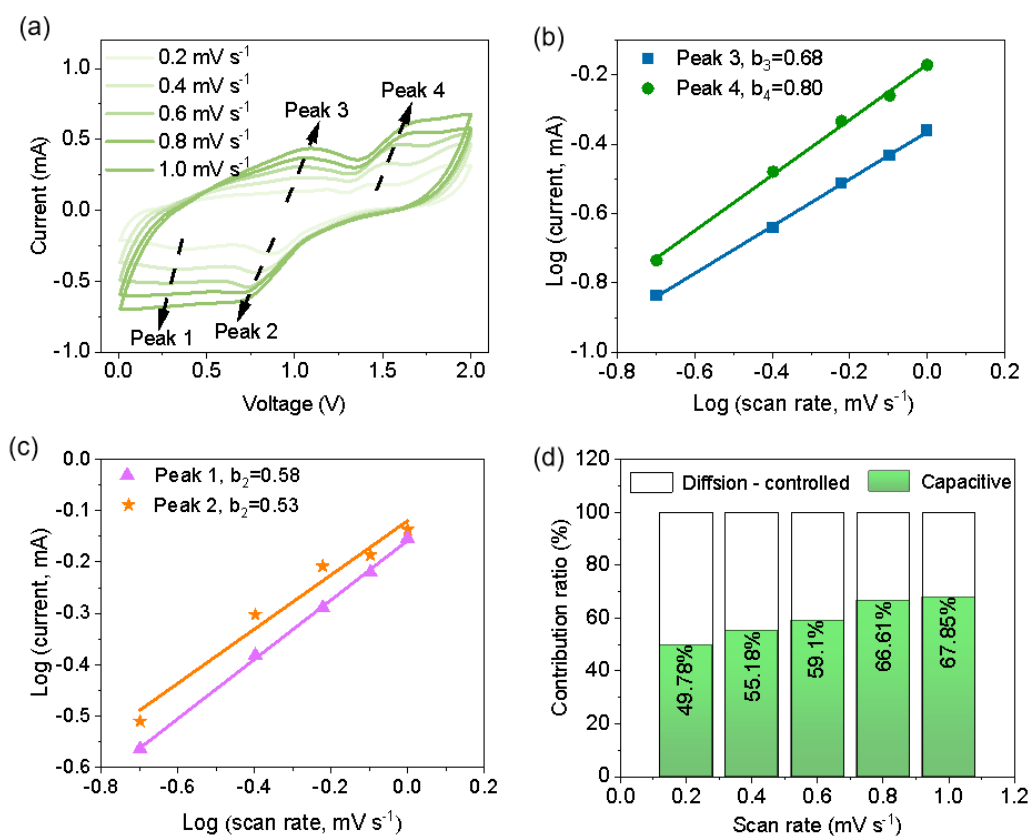


Fig. S14 (a) CV curves of NiS at scanning rates from 0.2 to 1.0 mV s⁻¹. (b, c) The log(*i*) versus log(*v*) plots. (d) The contribution of capacitive and diffusion-controlled processes.

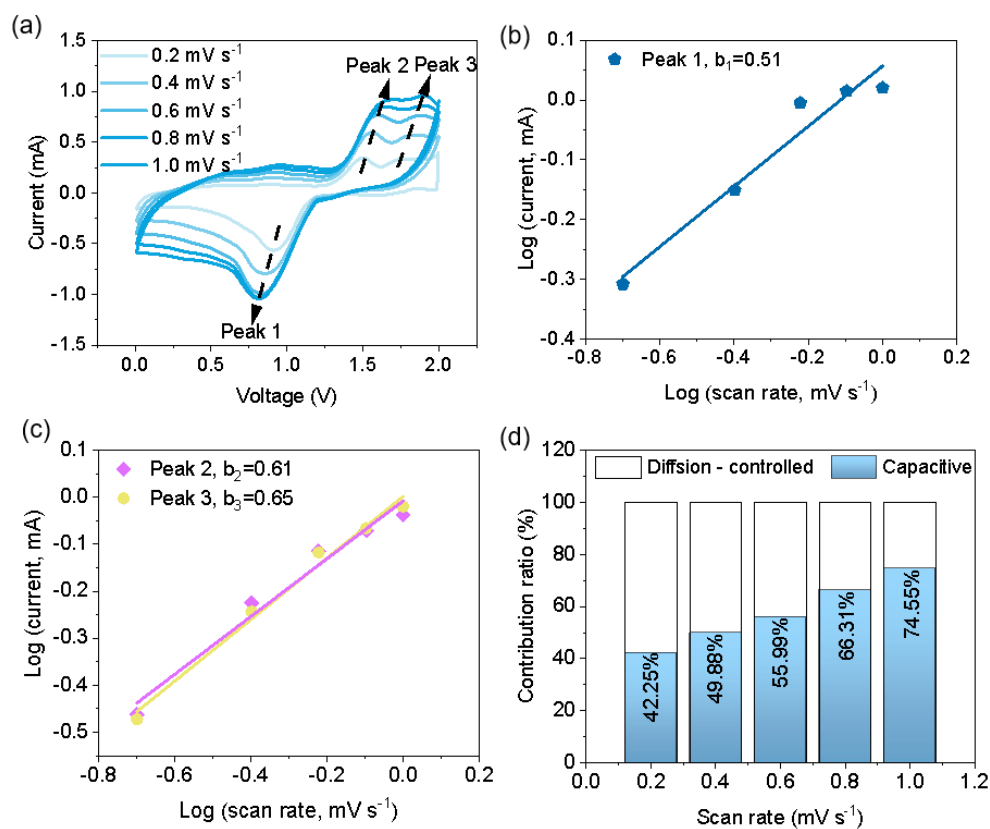


Fig. S15 (a) CV curves of Co_3S_4 at scanning rates from 0.2 to 1.0 mV s^{-1} . (b, c) The $\log(i)$ versus $\log(v)$ plots. (d) The contribution of capacitive and diffusion-controlled processes.

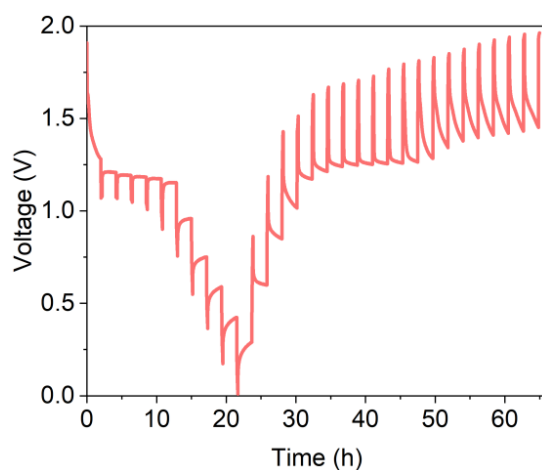


Fig. S16 GITT time-potential distributions of $\text{NiS}/\text{Co}_3\text{S}_4/\text{C}$.

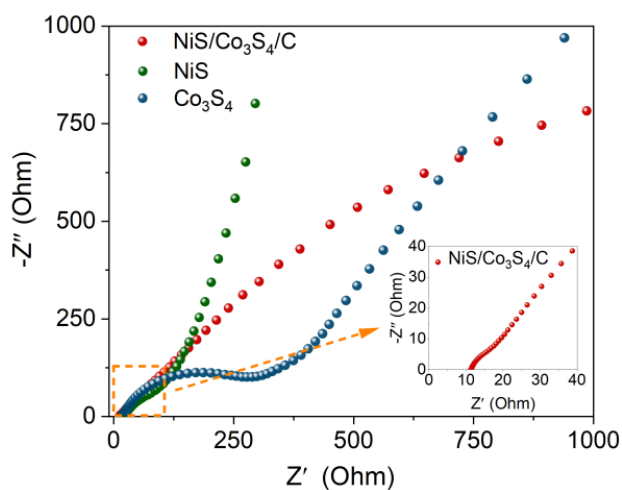


Fig. S17 EIS spectra of NiS/Co₃S₄/C, NiS and Co₃S₄ after 10 cycles at 0.2 A g⁻¹.

Table S1. Comparison on electrochemical performance with various cathodes.

Materials	Current density (A g ⁻¹)	Cycle number	Capacity (mAh g ⁻¹)	Ref.
FeSe ₂	0.015	100	287.0	[1]
MoO ₂	0.05	100	111.0	[2]
Cu ₉ S ₅	0.05	100	300.0	[3]
LiCrTiO ₄ nanowires	0.05	100	128.7	[4]
LiCrTiO ₄ particles	0.05	100	91.6	[4]
MoS ₂	0.05	100	7.5	[5]
MoS ₂ -CuS-EG	0.05	100	172.4	[5]
CuS@MoS ₂	0.1	50	104.7	[6]
A-MoS ₂	0.1	100	128.1	[7]
C-MoS ₂	0.1	100	192.8	[7]
NiS/Co ₃ S ₄ /C	0.2	100	398.1	This work

References

- [1] C. H. Zhang, L. R. Zhang, N. W. Li and X. Q. Zhang, *Energies* 2020, **13**, 4375.
- [2] X. Y. Dong, J. X. Wang, J. D. Yang, X. Wang, J. Y. Xu, X. F. Yang, W. Zeng, G. S. Huang, J. F. Wang and F. S. Pan, *Electrochim. Acta* 2023, **437**, 141498.
- [3] T. Li, A. Q. Qin, H. T. Wang, M. Y. Wu, Y. Y. Zhang, Y. J. Zhang, D. H. Zhang and F. Xu, *Electrochim. Acta* 2018, **263**, 168-175.
- [4] C. X. Zhu, Y. K. Tang, L. Liu, X. H. Li, Y. Gao and Y. N. Li, *ACS Sustainable Chem. Eng.* 2019, **7**, 14539-14544.
- [5] X. J. Hou, H. C. Shi, T. J. Chang, K. M. Hou, L. Feng, G. Q. Suo, X. H. Ye, L. Zhang, Y. L. Yang and W. Wang, *Chem. Eng. J.* 2021, **409**, 128271.
- [6] J. X. Wang, X. Wang, J. D. Yang, X. Y. Dong, X. Chen, Y. Zhang, W. Zeng, J. Y. Xu, J. F. Wang and G. S. Huang, *J. Electrochem. Soc.* 2022, **169**, 073502.
- [7] Z. N. Xiong, G. L. Zhu, H. Wu, G. J. Shi, P. Xu, H. M. Yi, Y. Y. Mao, B. F. Wang and X. B. Yu, *ACS Appl. Energy Mater.* 2022, **5**, 6274-6281.