

A PVP incorporated MoS₂ as Mg ion host with enhanced capacity and durability

Canlong Wu,^b Guangyu Zhao,^{*a} Shan Gong,^b Naiqing Zhang^{*a} and Kening Sun^a

a. Academy of Fundamental and Interdisciplinary Sciences, Harbin Institute of Technology, Harbin, 150001, China *Email: zhaogy810525@gmail.com (G. Zhao), znqmw@163.com (N. Zhang).

b. School of Chemistry and Chemical Engineering, Harbin Institute of Technology, Harbin, 150001, China.

Experimental

1 Material Synthesis and Characterizations

Synthesis of MoS₂ microspheres and MoS₂-PVP nanospheres: MoS₂ microspheres and are synthesized by hydrothermal method. In a typical synthesis^{1, 2}, 0.62 g sodium molybdate dihydrate (Na₂MoO₄•2H₂O) and 1.14g thiourea (CH₄N₂S) were added into 60 mL deionized (DI) water, and the mixed solution was transferred into a 100 mL Teflon-line autoclave after 30 min of magnetic stirring. To prepare MoS₂ microspheres with different interlayer distance, the hydrothermal reactions were maintained at 180 and 200 °C for 24 h. To synthesize MoS₂-PVP nanospheres^{3, 4}, 0.6 g polyvinylpyrrolidone (PVP) was added into 60 mL DI water and was stirred for 1h to make it dissolved. Then 0.62 g Na₂MoO₄•2H₂O and 1.14 g CH₄N₂S were added into the above solution, and the mixture was transferred into a 100 mL Teflon-line autoclave after 1h of magnetic stirring. The hydrothermal reaction was maintained at 180 and 200 °C for 24 h, and the reaction system was cooled down to room temperature naturally. The obtained products were collected by centrifugation, washed with distilled water and ethanol, and dried at 60 °C under vacuum. MoS₂ microspheres and MoS₂-PVP nanospheres prepared at 200 °C are marked as M1 and M2, while MoS₂ microspheres and MoS₂-PVP nanospheres prepared at 180 °C are marked as M3 and M4.

Characterizations of products: Scanning electron microscope (SEM) images and energy dispersive spectra (EDS) of products were obtained using a Hitachi Su-8100. A

PANalytical X'pert PRO X-ray diffractometer with Cu K α radiation ($\lambda=1.5418 \text{ \AA}$) was employed to obtain X-ray diffraction (XRD) patterns. Transmission electron microscope (TEM) images and selected area electro diffraction (SAED) patterns were obtained on a JEOL-2100. The surface area of the materials was analyzed by the Brunauer-Emmett-Teller (BET) method with a Micromeritics Accelerated Surface Area and Porosimetry System (ASAP) 2020. The gas used was N₂ with a liquefaction temperature of $-195.87 \text{ }^\circ\text{C}$, and the gas desorption time was 6 h. The total pore volume and pore size distribution were evaluated by the Barrett-Joyner-Halenda (BJH) model.

2 Battery Fabrication and Electrochemical Characterizations

The cathodes were prepared from a mixture of 80 wt.-% O-MoS₂ or PVP-MoS₂ powder, 10 wt.-% acetylene black, and 10 wt.-% polyvinylidene difluoride (PVDF) binder. The mixture was added to N-methyl-2-pyrrolidinone (NMP) solvent to form a homogeneous slurry, which was then spread into stainless steel (SS) foams. This slurry-foam was dried in a vacuum oven at $80 \text{ }^\circ\text{C}$ for 12 h, and pressed at 10 MPa for 5 min to give a cathode with an area of 1 cm^2 and thickness of 0.1 cm. The RMBs were assembled into 2032-type coin cells with MoS₂ cathodes, Mg metal anodes and microporous membrane (Celgard 2400) as separator. An APC electrolyte was used in fabricating the RMBs and prepared in a glove box filled with high purity argon gas. 0.25 M aluminium chloride (AlCl₃) in anhydrous tetrahydrofuran (THF) solution was slowly added dropwise to 2 M phenyl magnesium chloride (MgPhCl) solution in THF under vigorous stirring to form the APC electrolyte of 0.25 M concentration. The galvanostatic charge/discharge tests of RMBs were carried out in a BTS-2000 Neware Battery Testing System and a PARSTAT 2273 electrochemical workstation.

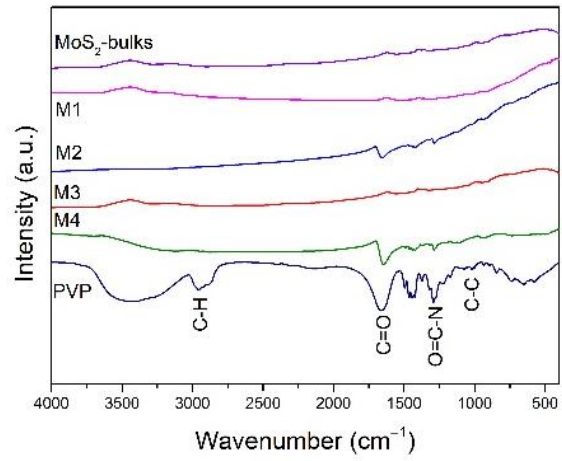


Fig. S1 FTIR spectra of MoS₂-bulks, M1, M2, M3, M4 and PVP.

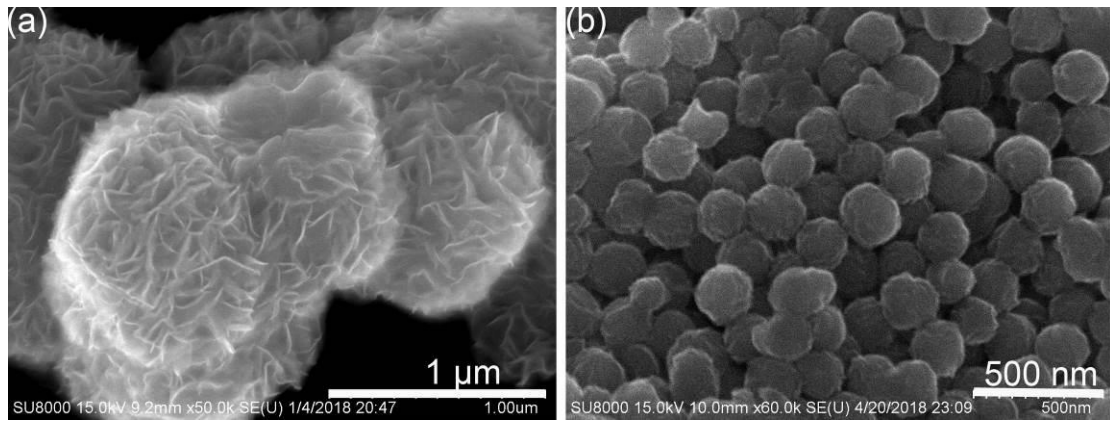


Fig. S2 SEM images of (a) M1 and (b) M2.

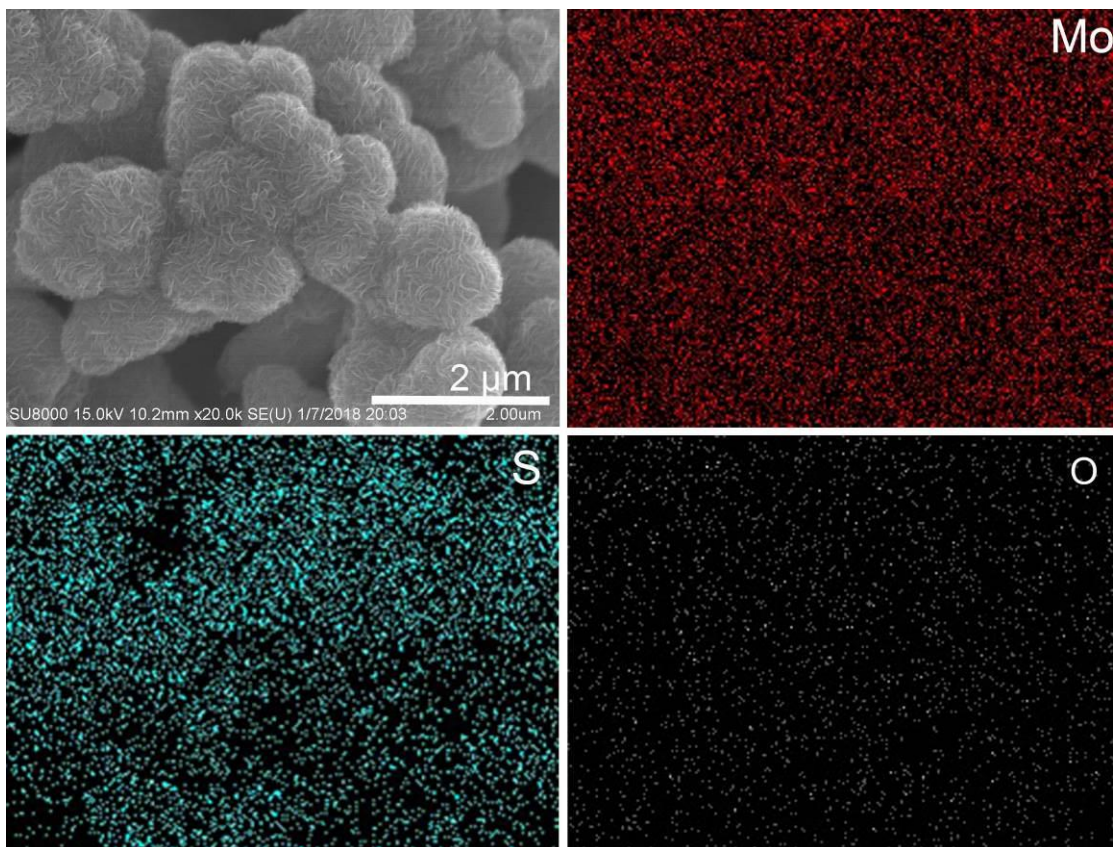


Fig.S3 EDS mapping images of M3.

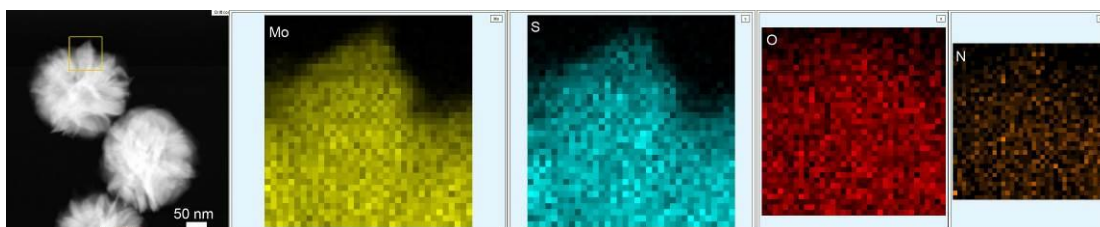


Fig.S4 EDS mapping images of M4.

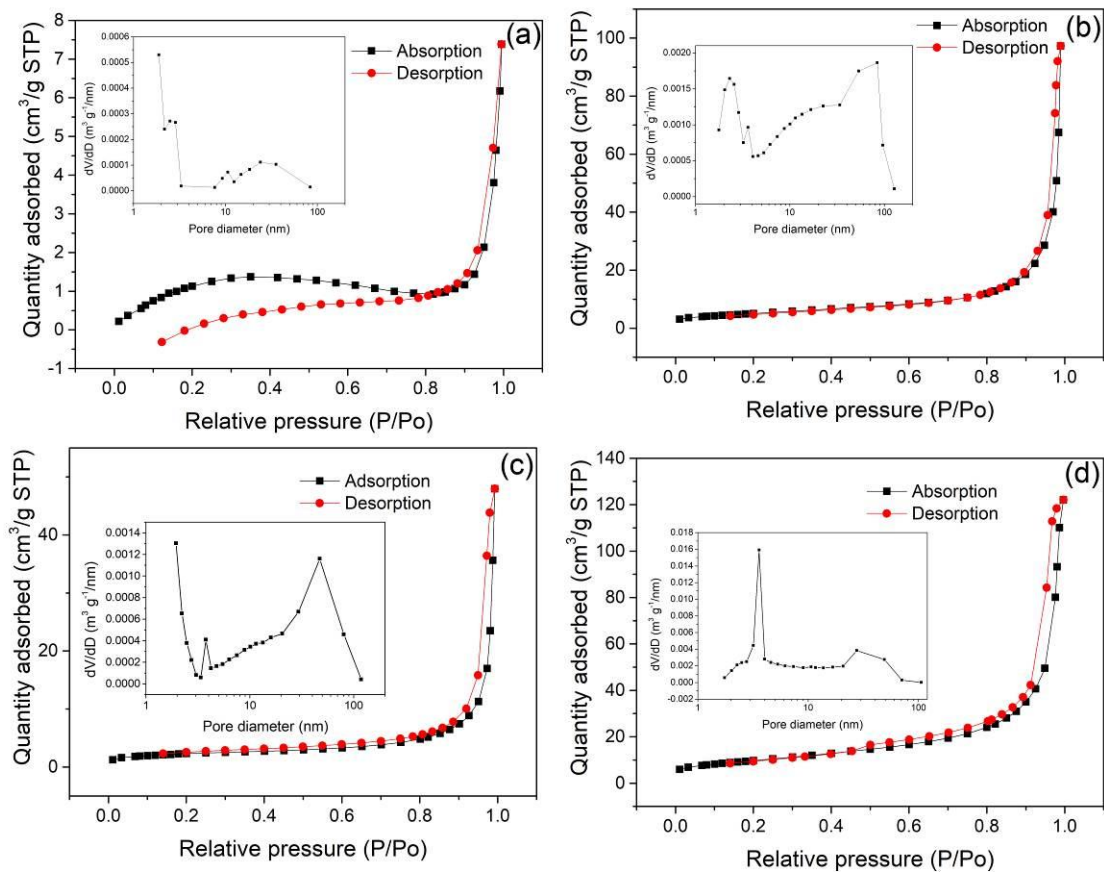


Fig. S5 Nitrogen adsorption/ desorption curves of (a) M1, (b) M2, (c) M3 and (d) M4 (insets are the Pore distribution curves).

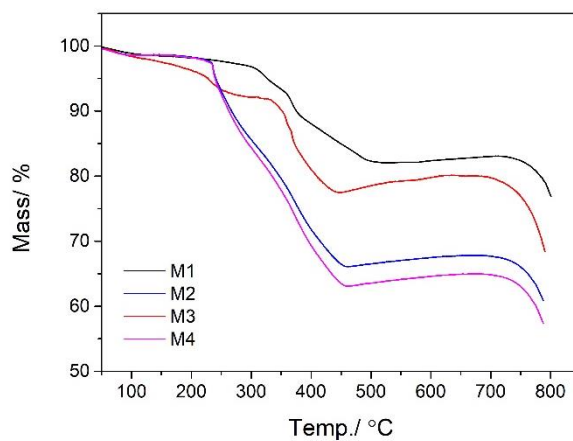


Fig. S6 TGA analysis results of M1, M2, M3 and M4.

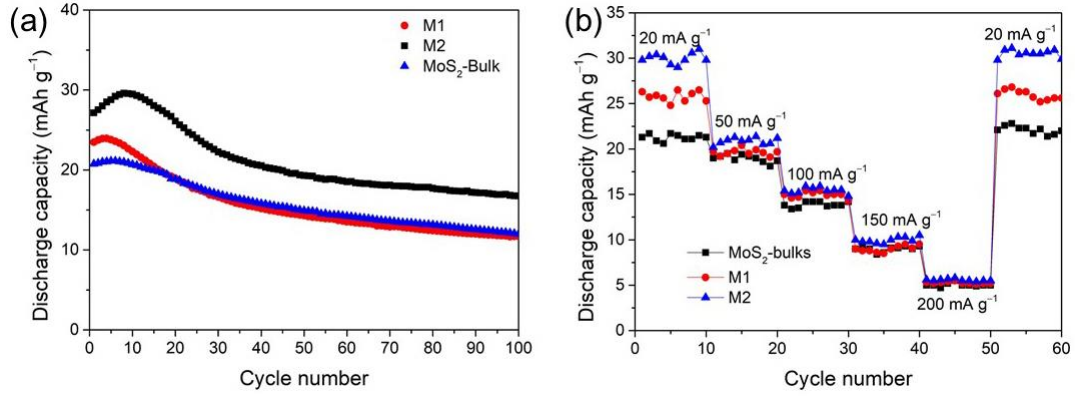


Fig. S7 (a) Cycle performance of M1, M2 and MoS₂-bulks in the current density of 20 mA g⁻¹, (b) Rate performance of M1, M2 and MoS₂-bulks.

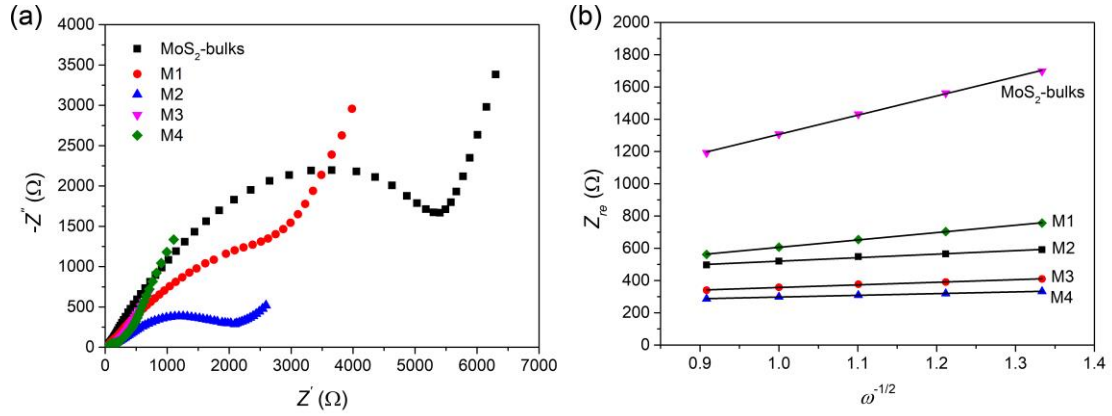


Fig. S8 (a) Electrochemical impedance spectroscopy analysis of MoS₂-bulks, M1, M2, M3 and M4; (b) the relationship between Z_{re} and $\omega^{-1/2}$ in the low-frequency region

The diffusion coefficients of Mg²⁺ in host lattice can be calculated according to the following equation:

$$D = \frac{R^2 T^2}{2n^4 F^4 A^2 \sigma^2 C^2} \quad (1)$$

where n is the number of electrons per-molecule during the Mg²⁺ interacting, A is the surface area of the cathode, D is the diffusion coefficient of Mg²⁺, R is the gas constant, T is the absolute temperature, F is the Faraday constant, C is the concentration of Mg²⁺, and σ is the Warburg factor which has a relationship with Z_{re} :

$$Z_{re} = R_D + R_L + \sigma \omega^{-1/2} \quad (2)$$

Fig. S8b shows the relationship between Z_{re} and the square root of frequency ($\omega^{-1/2}$) in the low-frequency region. The ratio of the diffusion coefficients of Mg^{2+} in the five samples is 5: 13: 15: 42: 51.

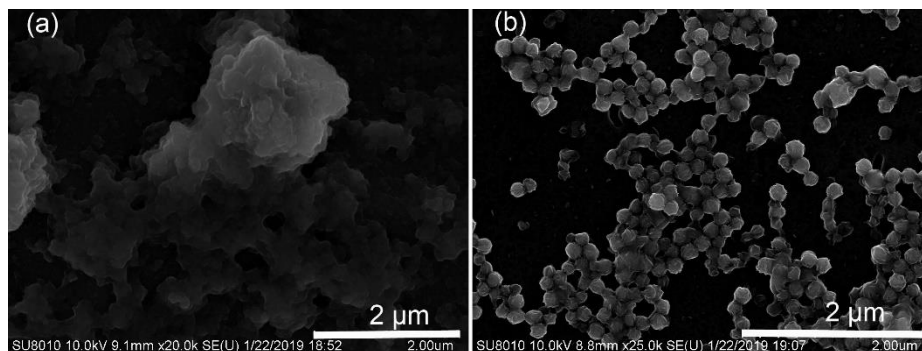


Fig. S9 SEM images of (a) M3 and (b) M4 after cycling tests.

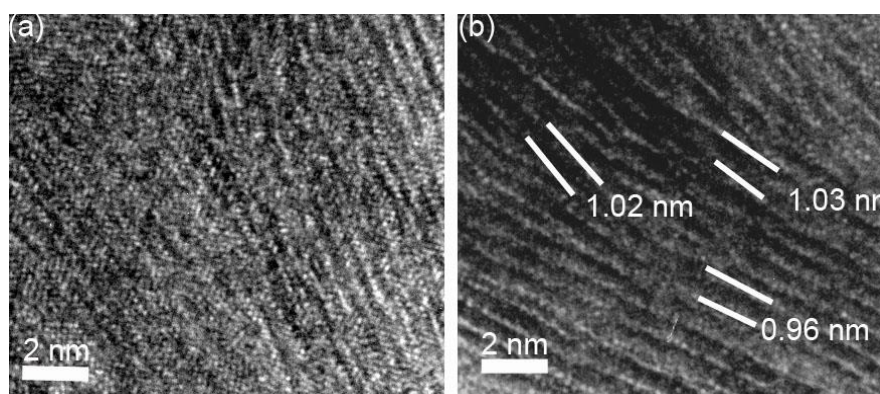


Fig. S10 TEM images of (a) M3 and (b) M4 after cycling tests.

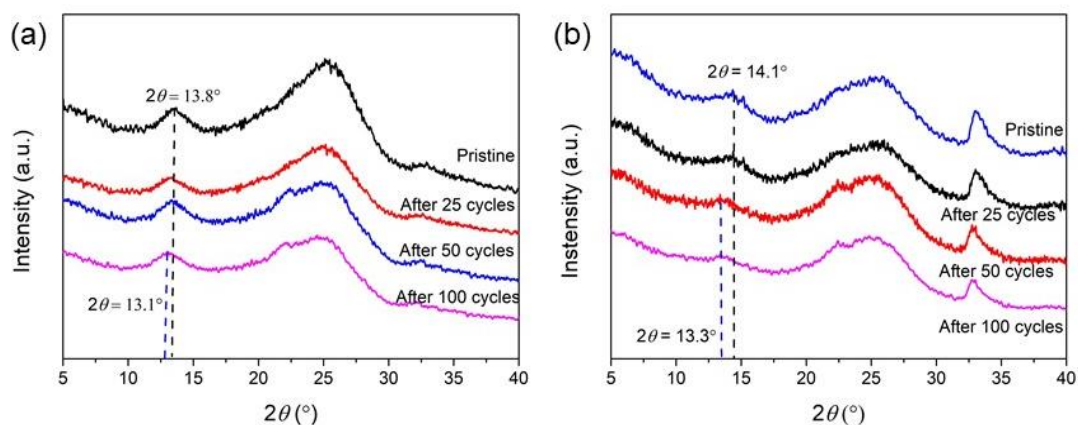


Fig. S11 (a) Ex-XRD patterns of pristine M1 and M1 after 100 cycles, (b) Ex-XRD patterns of pristine M2 and M2 after 100 cycles.

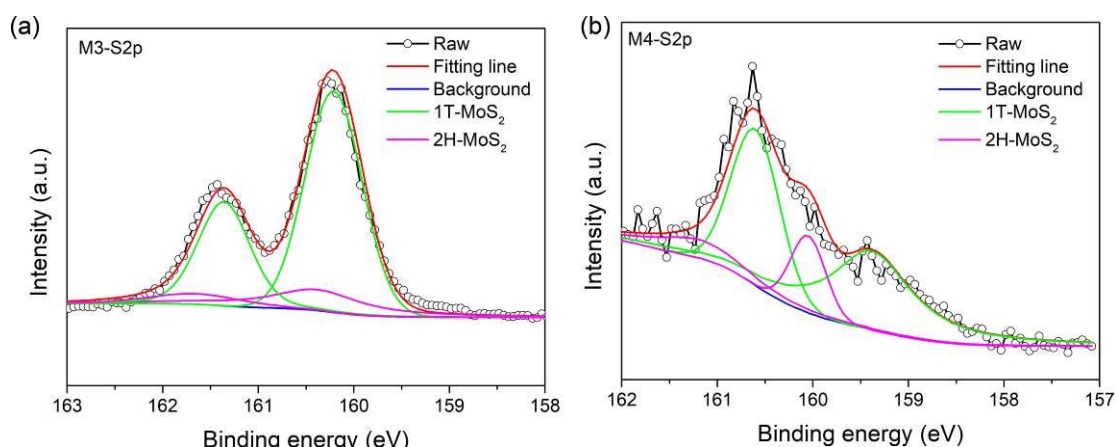


Fig. S12 S2p XPS spectra of M3 and M4.

Table.1 summary of electrochemical performances of MoS₂ when used as Mg-ion hosts in the reported works.

MoS ₂ Cathodes	Initial capacity (mAh g ⁻¹)	Cycle number	Capacity after cycling test (mAh g ⁻¹)	Current density for cycle (mA g ⁻¹)	References
MoS ₂ -PEO	75	30	75	5	5
Graphene-like MoS ₂	115.9	50	82.5	20	6
MoS ₂ /rGO	100	50	80	20	7
MoS ₂ /C	213	50	84.3	50	8
MoS ₂ /graphen	75	200	75	25	9
MoS ₂ /graphene	105	120	87.6	20	10
PVP-MoS ₂	143.2	100	128.9	20	Our study

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