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3D MoS₂ foam integrated with carbon paper as binder-free anode for high performance sodium-ion batteries

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1 Introduction

ABSTRACT

Molybdenum sulfide (MoS₂) with well-designed porous structure has the potential to be great electrode materials in sodium-ion batteries due to its high theoretical capacity and abundant resource, however, hindered by its intrinsic low conductivity and stability. Herein, MoS₂ with 3D macroporous foam structure and high conductivity was obtained through SiO₂ templates and integrated with carbon paper (3D F-MoS₂/CP). It has showed superior specific capacity (225 mA h g⁻¹, 0.4–3 V) and cycling stability (1000 cycles) at high rate (2000 mA g⁻¹), with a low decay rate (0.033% per cycle) in sodium-ion batteries. The excellent electrochemical performance may originate from its unique integrated structure: 3D MoS₂ macropores providing high surface area and abundant transfer channels while carbon paper enhancing the conductivity of MoS₂ and avoiding unnecessary side reactions brought by binder addition. © 2021 Science Press and Dalian Institute of Chemical Physics, Chinese Academy of Sciences. Published by ELSEVIER B.V. and Science Press. All rights reserved.

Substantial attention has been given to electrochemical energy storage (EES) [1,2] due to energy crisis and environmental pollution. Great progress has been made with commercially available lithium-ion batteries (LIBs) as a successful representation. However, the shortage, high cost and uneven distribution of lithium resources hinder its large-scale application in EES [3]. Sodiumion batteries (SIBs) have become promising alternatives to LIBs due to the abundant sodium resources, suitable redox potential and similar charge store mechanism [4–7]. However, compared to Li⁺, the larger diameter of Na⁺ makes the insertion/extraction processes more difficult and results in larger volumetric variation of electrode materials, leading to poor capacity and cycling stability [8,9]. Therefore, a reasonable design of host electrode materials is the key to improve the electrochemical performance of sodiumion batteries.

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Electrode materials with different compositions and structures have been developed for SIBs, such as carbon-based materials, titanium-based materials, organic compounds and transition metal sulfides from 1D to 3D [4], and excellent progresses have been achieved. Among them, molybdenum disulfide (MoS₂), a typical 2D layered material, has received intensively attention due to its high theoretical capacity (670 mA h g^{-1}) and ordered interlayer structure (0.62 nm) that is suitable for Na⁺ (r = 1.02 Å) insertion/extraction [10,11]. However, there are few inherent defects hinder the performance of MoS₂. Firstly, its low conductivity impedes fast Na⁺ storage. Secondly, the large volume change during charge/discharge processes results in continuous pulverization of the host materials. Finally, the layered MoS₂ has high surface energy and tends to restack during cycling, which will result in capacity decay [12–14]. Moreover, the use of binder in the traditional electrode manufacturing process will further reduce the material conductivity and impede its performance. In order to tackle these defects, various strategies have been proposed such as expanding the MoS₂ interlayer from 0.62 to 1 nm [15–19], manufacturing MoS₂ porous structure from microporous to macroporous [14,20-22], building materials with different dimensions from 1D to 3D [15,17,20,23–27], constructing composites with various carbon materials including MoS₂/C, MoS₂/Graphene and MoS₂/rGO, etc.

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[28–32]. Each method has showed its unique strength, and the combination of different strategies tends to yield better performance. However, how to incorporate multiple methods' advantages and manipulate them working synergistically to exhibit high performance is still a big challenge.

In this presentation, a flexible electrode with 3D foam MoS₂ built on carbon paper (3D F-MoS₂/CP) was successfully fabricated, as a combination of different methods with the advantages of high conductivity and binder free (inherited from carbon paper), macroporous nanostructure and 3D MoS₂ framework (created by SiO₂ templates, ~100 nm). High conductivity facilitates the electrons transfer, binder-free avoids the side reactions caused by binder addition, while macroporous 3D framework of MoS₂ benefits the exposure of active sites, the penetration of electrolytes and Na⁺ diffusion [21]. The 3D F-MoS₂/CP can be synthesized in large-scale (up to 20×20 cm²), cut into different shapes and sizes (Fig. S1, Supporting Information) and used as binder-free electrode without further treatment. The binder-free 3D F-MoS₂/CP electrode showed excellent high rate performance (225 mA h g^{-1} at 2000 mA g^{-1}) in sodium-ion batteries, with superior stability (1000 cycles, at 2000 mA g^{-1}) and high Coulombic efficiency (>99.8%), which may mainly benefit from its distinctly integrated structure.

2 Experimental

2.1 Materials synthesis

2.1.1 Sample preparation of 3D F-MoS₂/CP

Firstly, 0.1 g sodium molybdate dihydrate (Beijing InnoChem Co., Ltd 99%) and 0.5 g thiourea (Sinopharm Chemical Reagent Co., Ltd 99%) were dissolved in deionized water, then 3.2 g SiO₂ nanospheres (30 wt% in ethylene glycol, ~100 nm, Alfa Aesar) were added into the solution while ultrasounding until a homogeneous dispersion was formed. After that, the dispersion was sprayed on the cleaned carbon paper followed with drying process. The obtained sample was further annealed at 500 °C for 2 h (heating rate of 10 °C min⁻¹) under argon atmosphere. Finally, the 3D F-MoS₂/CP was gained by HF treatment (Sinopharm Chemical Reagent Co., Ltd 40%) under room temperature for several hours followed with washing and drying processes.

2.1.2 Sample preparation of 2D MoS₂/CP

For comparison, the 2D MoS_2/CP sample was prepared by the same experimental procedures but without the addition of SiO_2 nanospheres.

2.1.3 Sample preparation of 3D foam MoS₂

0.1 g sodium molybdate dihydrate and 0.5 g thiourea were dissolved in deionized water, then 3.2 g SiO₂ nanospheres were added

into the solution under ultrasounding till a homogeneous dispersion was formed. After removing the solvent, the obtained solid power was annealed at 500 °C for 2 h (heating rate of 10 °C min⁻¹) under argon atmosphere. The final product was obtained by HF (aq) treatment under room temperature for several hours followed with washing and drying processes.

2.2 Materials characterization

Scanning electron microscopy (SEM) was conducted on FEI Quanta 200F. High resolution transmission microscope (HRTEM) was carried out on FEI TECNAI G2 F30. High resolution Scanning electron microscopy (HRSEM) was carried out on HITACHI S5500. Thermogravimetric analysis (TGA) was performed on PE Diamond TG/DTA. BET was carried out on KANGTA Quadrasorb evo. X-ray diffraction (XRD) was carried out on Rigaku D/Max 2500/PC. Raman spectroscopy was performed on a LabRAM HR 800 Raman spectrometer. XPS was carried out on KRATOS Axis Ultra ^{DLD}. The vacuum degree in the analysis room was 9.8 \times 10⁻¹⁰ Torr, and the excitation source was Al Ka ray (HV = 1486.6 eV).

2.3 Electrochemical measurements

Electrochemical experiments were performed using CR2032 coin cells. The as-obtained 3D F-MoS₂/CP and 2D MoS₂/CP materials were cut into a circle of 10 mm in diameter and directly used as free-standing electrodes. The 3D foam MoS₂ electrode was made by mixing the active material, acetylene black, and polyvinylidene fluoride binder at a weight ratio of 7:2:1, and then pasted onto a Cu foil current collector and dried in a vacuum oven at 60 °C. Metallic Na pieces were used as counter electrodes and reference electrodes. A glass fiber mem-brane (Whatman/F) was used as separator. The solution of 1 M NaClO₄ in a 1:1 vol mixture of ethylene carbonate/diethyl carbonate (EC/DEC) with 5 wt% fluoroethylene carbonate (FEC) as the electrolyte. The galvanostatic discharge/ charge measurements were performed in the voltage range of 0.4-3 V (vs. Na/Na⁺) on a NEWARE battery testing system. In the full cell test, the mass ratio of 3D F-MoS₂/CP anode and Na₃V₂(- PO_4)₃/C cathode is 1:4.2. The voltage window was 0.4–3 V, the electrolyte and separator were the same as in the half cell. Cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and linear sweep voltammetry (LSV) tests were performed on an electrochemical workstation (Gamry). CV was measured in a voltage range of 0.4-3 V at room temperature. EIS of the electrodes were measured, applying a 5 mV amplitude signal in the frequency of 0.01 Hz-100 kHz. LSV tests were performed at a scanning rate of 0.05 V /s in a voltage range of 0-0.4 V.



Scheme 1. The synthesis route illustration of binder-free 3D F-MoS₂/CP electrode and digital photo of large-scale produced 3D F-MoS₂/CP electrode.



Fig. 1. Morphology and nanostructure characterizations of 3D F-MoS₂/CP binder-free electrode. (a, b) SEM images. (c, d) HRSEM images. (e, f) HRTEM images.

3 Results and discussion

Scheme 1 shows the synthesis process of binder-free 3D F- MoS_2/CP electrode, using commercial CP as substrate and SiO₂ nanospheres as templates. CP was cleaned before use (see Experimental Section 2.1 for details). The X-ray diffraction (XRD) pattern of the cleaned commercial CP only shows peaks of carbon without other impurities (Fig. S2, Supporting Information). After loaded with MoS₂ precursors, simple calcination and HF etching processes were used to obtain 3D F- MoS_2/CP electrode. 2D MoS_2/CP and 3D foam MoS_2 were synthesized as contrasts through similar method without SiO₂ template and CP substrate, respectively (see Experimental Section 2.1 for details). More importantly, the binder-free 3D F- MoS_2/CP electrode prepared through this method shows excellent flexibility and can be obtained in large-scale (up to 20×20 cm², Scheme 1) in a short time (7 h).

The commercial CP is constructed by carbon fibers with a clean and smooth surface, as shown in Fig. S3. After coated by 3D MoS₂ foam, the SEM images (Fig. 1a and b) of 3D F-MoS₂/CP clearly show the rough surface of carbon fibers coated with lots of attachments. The high resolution scanning electron microscopy (HRSEM) images (Fig. 1c and d) further demonstrate the foam structure of 3D F-MoS₂/CP with abundant macropores (~100 nm), which will benefit the electrolytes transfer and Na⁺ diffusion. Furthermore, the foam framework and the fine layered nanostructure of MoS₂ were further confirmed by high resolution transmission electron microscopy (HRTEM).

As shown in Fig. 1e-f, the 3D F-MoS₂/CP exhibits macroporous structure fabricated by layered MoS₂ nanosheets with a typical layer distance of 0.62 nm. The HRSEM images of 3D foam MoS₂ and 2D MoS₂/CP are placed in Supporting Information (Fig. S4 and S5). With SiO₂ nanospheres as templates, the 3D foam MoS₂ also presents a macroporous structure (Fig. S4) with high surface area (134.4 m²/g, Fig. S6). The surface area is calculated by per gram, thus 3D F-MoS₂/CP showed lower surface area (18.3 m²/g, Fig. S6) than 3D foam MoS₂ due to the low loading amount of MoS₂ (8.6 wt%). The 2D MoS₂/CP is formed by small MoS₂ blocks that are uniformly and densely attached to the carbon fibers (Fig. S5), thus giving the lowest surface area (2.6 m²/g, Fig. S6).

Compared with 2D MoS₂/CP, the 3D macroporous structure shows higher surface area and exposes more active sites, which will facilitate the sodiation/desodiation processes [21].

Fig. 2a shows the X-ray diffraction (XRD) pattern of 3D F-MoS₂/ CP. Compared with standard PDF cards, hexagonal 2H-MoS₂ was obtained. Furthermore, the Raman spectrum of 3D F-MoS₂/CP (Fig. 2b) also displays the fingerprint peaks of 2H-MoS₂, with the peak at 385 cm⁻¹ is in-plane E_{2g}^1 mode while at 408 cm⁻¹ is outof-plane A_{1g} mode [33]. Besides, in the range of 1200–1800 cm⁻¹, the peaks at 1355 cm⁻¹ and 1581 cm⁻¹ are clearly seen, which are ascribed to the D (disordered) band and G (graphite) band of carbon paper. To further determine the loading amount of 3D foam MoS₂ on carbon paper, thermogravimetric analysis (TGA) was performed (Fig. S7). The weight loss of pure MoS₂ is mainly owing to the oxidation of MoS₂ to MoO₃ in air [31,34], the loading ratio is ~ 8.6 wt%. Through the same method, the MoS₂ loading amount of 2D MoS₂/ CP is 10.7 wt% (Fig. S8), comparable to the 3D F-MoS₂/CP sample.

X-ray photoelectron spectroscopy (XPS) was utilized to further confirm the chemical configuration and the surface electronic states of MoS₂ in these samples (Fig. 2c-f and Fig. S9-S10). As shown in Fig. 2c, the S 2p, Mo 3d, C 1s, Mo 3p and O 1s spectra of 3D F-MoS₂/CP are displayed without other impurities. Three peaks centered at 226.39, 229.1 and 232.25 eV have been observed in the high-resolution XPS spectra of Mo 3d, which are attributed to S 2s, Mo $3d_{5/2}$ and Mo $3d_{3/2}$, respectively (Fig. 2d). Meanwhile, the peak at 235.38 eV is assigned to $Mo^{6+} 3d_{3/2}$, which is formed by surface oxidation of Mo^{4+} in air [14]. In the S 2p spectrum of 3D F-MoS₂/CP, two peaks are observed at 161.7 and 162.9 eV, assigning to S $2p_{3/2}$ and S $2p_{1/2}$ [35], respectively (Fig. 2e). Fig. 2f exhibits three peaks at 284.6, 285.5 and 289.19 eV, which correspond to C–C, C–O, and C=O, respectively [14,35–37]. Both 3D foam MoS₂ and 2D MoS₂/CP XPS spectra show similar peaks, confirming the same chemical configuration with 3D F-MoS₂/CP, as shown in Fig. S9 and S10.

The electrochemical performance of the binder-free 3D F-MoS₂/ CP electrode as anode for sodium-ion batteries is shown in Fig. 3. The initial five cyclic voltammetry (CV) curves of 3D F-MoS₂/CP electrode with a scan rate of 0.2 mV s⁻¹ under the voltage window of 0.4–3 V (vs. Na/Na⁺) are shown in Fig. 3a. In the first discharge



Fig. 2. Structure and composition characterizations of 3D F-MoS₂/CP. (a) XRD pattern of the 3D F-MoS₂/CP (measured without CP). (b) Raman spectrum of the 3D F-MoS₂/CP. (c) XPS survey spectrum of 3D F-MoS₂/CP and high-resolution XPS spectra of Mo 3*d* (d), S 2*p* (e), C 1*s* (f).

process, a reduction peak occurs at 0.68 V, which is associated with Na⁺ intercalation into MoS₂ and the formation of Solid-Electrolyte-Interface (SEI) film [20–21,38]. In the first charge process, a broad oxidation peak can be discovered in the range of 1.2–2.0 V, which corresponds to the deintercalation of the Na_xMoS₂ to MoS₂ and Na metal [14]. Moreover, the oxidation and reduction peaks nearly coincide from the third cycle on, indicating the 3D F-MoS₂/CP electrode has outstanding reversibility and cycling stability during the Na⁺ insertion and extraction processes.

The galvanostatic charge/discharge curves of 3D F-MoS₂/CP at current density of 2000 mA g⁻¹ under voltage range of 0.4–3.0 V (*vs.* Na/Na⁺) are shown in Fig. 3b. In the initial discharge curve, a voltage plateau at 0.75 V was observed but disappears in the subsequent cycles, which agrees with the CV result. At 2000 mA g⁻¹, the initial discharge capacity is 1080 mA h g⁻¹, which may originate from the high theoretical capacity of MoS₂, high conductivity and binder-free nature of CP. For the initial capacity attenuation, there are several possible reasons: (i) The decomposition of electrolyte and the formation of SEI film; (ii) The specific surface area affects the amount of the formed SEI film. The larger the specific surface area, the lower the initial Coulombic efficiency; (iii) Other unknown side reactions between the electrode and the electrolyte; (iv) The inherent slow Na⁺ diffusion kinetics and ion mobility [39,40]. From 30th to 100th cycle, the charge and discharge profiles are almost overlapped, suggesting that the electrode materials have stable structure during the sodiation/desodiation processes, which is beneficial for long-term cycling.

To evaluate the cycling stability and rate performance of 3D F-MoS₂/CP, the assembled sodium-ion batteries were tested for 100 cycles and under various charge/discharge rates, using 3D foam MoS₂, 2D MoS₂/CP and CP as contrasts under the same conditions. The results are shown in Fig. 3c and d. CP has an initial discharge capacity of 1.22 mA h g^{-1} , but decreases to 0.05 mA h g^{-1} rapidly. Thus, the CP itself doesn't contribute much to the electrochemical performance of these electrodes. Both 3D F-MoS₂/CP and 3D foam MoS₂ show better results than 2D MoS₂/CP, indicating the superiority of 3D macroporous structure over the utilization of CP. The 3D F-MoS₂/CP binder-free electrode shows obviously the best performance, due to the advantages union of 3D macroporous MoS₂ nanostructure and CP. At a current density of 200 mA g⁻¹, after 100 cycles, the 3D F-MoS₂/CP shows the highest capacity of 325 mA h g^{-1} . The 3D F-MoS₂/CP also shows high rate performance as shown in Fig. 3d. When cycled at various current densities of 50, 100, 300, 500, 1000 and 2000 mA g^{-1} , the 3D F-MoS₂/CP electrode



Fig. 3. Electrochemical performance of different samples. (a) CV curves of the 3D F-MoS₂/CP (the first five cycles scanning at 0.2 mV s⁻¹ in voltage range of 0.4–3 V). (b) Galvanostatic discharge/charge voltage curves of the 3D F-MoS₂/CP at a current density of 2000 mA g⁻¹. (c) Cycling performance of the 3D F-MoS₂/CP in comparison to 3D foam MoS₂, 2D MoS₂/CP and CP at a current density of 2000 mA g⁻¹ (the first two cycles are activated at a current density of 50 mA g⁻¹). (d) Rate performance of the 3D F-MoS₂/CP in comparison to 3D F-MoS₂/CP in comparison to 3D foam MoS₂, 2D MoS₂/CP and CP. (e) Long-term cycling property and Coulombic efficiency of the 3D F-MoS₂/CP at a current density of 2000 mA g⁻¹.

delivers the discharge capacities of 490, 438, 377, 329, 274 and 225 mA h g⁻¹, respectively, which are superior to those of 3D foam MoS_2 (161, 146, 130, 120, 108 and 98 mA h g⁻¹), 2D MoS_2/CP (139, 129, 111, 101, 88 and 70 mA h g⁻¹) and CP (1.36, 0.75, 0.49, 0.41, 0.28 and 0.27 mA h g⁻¹) electrodes. When the current density returns to 50 mA g⁻¹, the capacity recovery of 3D F-MoS₂/CP is 423 mA h g⁻¹. After repeated circulation of large current, the capacity retention rate of 3D F-MoS₂/CP is 86.3%, which further confirmed its good cycling stability. Furthermore, the long-term cycling stability of 3D F-MoS₂/CP was tested as shown in Fig. 3e. The 3D F-MoS₂/CP can be cycled at 2000 mA g⁻¹ for 1000 cycles, with an extremely low decay rate (0.033% per cycle) and a high Coulombic efficiency of 99.8%, the capacity retention after 1000 cycles is 67.4%, showing excellent cycling stability (Table S1, Supporting Information).

In addition, the area capacities of the free-standing electrodes were tested. As shown in Fig. S11. At 120 μ A cm⁻², the 3D F-MoS₂/CP showed high area capacity and excellent cycling stability. After 100 cycles, the capacity is 192 μ A h cm⁻², while the 2D MoS₂/CP and CP are 126 and 1 μ A h cm⁻², respectively. Moreover, the effects of MoS₂ loading mass on electrochemical performance were tested. The results are shown in Fig. S12. When the MoS₂ load (7.4 wt%) is close to 3D F-MoS₂/CP (8.6 wt%), the long-term cycling and rate performance of both samples are similar. When MoS₂ load



Fig. 4. Morphology and nanostructure characterizations of 3D F-MoS₂/CP binderfree electrode after 1000 long-term cycles under the current density of 2000 mA g^{-1} . (a, b) Digital photos. (c) HRSEM image. (d) HRTEM image.

goes higher (49 wt% and 75 wt%, Supporting Information, S12 d-i), the performance becomes poorer, which is mostly caused by the low usage efficiency that originated from the low conductivity and high loading amount of MoS₂.

To further explore the practical application potential of 3D F- MoS_2/CP in sodium-ion batteries, we assembled the full cells with commercial $Na_3V_2(PO_4)_3/C$ as the cathode and 3D F- MoS_2/CP as the anode. The cycling performance of the half cell $Na_3V_2(PO_4)_3/C$ is shown in Fig. S13a. At a voltage window of 2.3–4 V and a current density of 50 mA g⁻¹, the first charge capacity is 61.75 mA h g⁻¹. After 100 cycles, the charging capacity is 54.2 mA h g⁻¹, and the Coulombic efficiency is 99.4%. Under the same current density, the full battery performance was tested. The charge and discharge capacity are 729 mA h g⁻¹ (Fig. S13b) and 52 mA h g⁻¹ in the initial cycle and can remain at 46 mA h g⁻¹ and 20 mA h g⁻¹ after 100 cycles (0.4–3 V, Fig. S13c). All in all, 3D F-MoS₂/CP shows good cycling stability.

To disclose more information about the possible reason of 3D F- MoS_2/CP 's high performance, the 3D F- MoS_2/CP binder-free electrode was recycled after 1000 cycles at 2000 mA g⁻¹. The recycled electrode remains intact after long-term cycling (Fig. 4a and b),

indicating the strong durability of this binder-free electrode which is due to the use of CP. Furthermore, the morphology and nanostructure of the recycled 3D F-MoS₂/CP were characterized by HRSEM and HRTEM. As shown by the HRSEM image (Fig. 4c), although part of the MoS₂ foam framework collapses, the macroporous nanostructure of MoS₂ and CP are maintained well. Meanwhile, the HRTEM image (Fig. 4d) reveals that the layered structure of MoS₂ is kept well after cycling. However, the interlayer spacing of MoS₂ is increased (up to 0.7 nm) compared to pristine MoS₂ (0.62 nm), which may be caused by the long-term intercalation/deintercalation processes of sodium ions. The enlarged interlayer spacing will reduce the mass transfer resistance, thus it is beneficial for the long-term cycling ability.

The electrochemical impedance spectroscopy (EIS), Na⁺ diffusion behavior and charge storage behavior of 3D F-MoS₂/CP were investigated, as shown in Fig. 5. The electrochemical impedance spectroscopy (EIS) was measured before charging/discharging. Fig. 5a displays the EIS profiles of 3D F-MoS₂/CP, 3D foam MoS₂ and 2D MoS₂/CP. The high-medium frequency (the semicircular) is composed of charge-transfer impedance (R_{ct}), and the low frequency sloping line represents the Warburg impedance (Z_w) [41].



Fig. 5. (a) EIS Nyquist plots of 3D F-MoS₂/CP, 3D foam MoS₂ and 2D MoS₂/CP. (b) The relationship between Z' and $\omega^{-1/2}$ for 3D F-MoS₂/CP, 3D foam MoS₂ and 2D MoS₂/CP, respectively. (c) CV curves of 3D F-MoS₂/CP binder-free electrode with different scan rates. (d) Log (i) – log (v) plots at different cathodic/anodic peaks. (e) The capacitive contribution (shaded region) of 3D F-MoS₂/CP binder-free electrode at a scan rate of 1.0 mV s⁻¹. (f) The contributions of the capacitive and diffusion controlled storage at different scan rates.

As can be seen from the Nyquist plots, the 3D F-MoS₂/CP electrode has the lowest charge transfer resistance compared with 3D foam MoS₂ and 2D MoS₂/CP. The diffusion behavior of Na⁺ can further be understood by the Na⁺ diffusion coefficient. The equations [42,43] are $D = R^2 T^2 / 2n^4 F^4 \sigma_w^2 A^2 C^2$, $Z' = R + \sigma_w \omega^{-1/2}$. D is the diffusion coefficient of Na^+ , R is the gas constant, T is the absolute temperature, A is the surface area of the electrode, n is the number of the electrons per molecule attending the electronic transfer reaction, *F* is the Faraday constant, *C* is the concentration of Na⁺, σ_w is the slope of the line $Z \sim \omega^{-1/2}$. As shown in Fig. 5b, the slopes σ_w of 3D F-MoS₂/CP, 3D foam MoS₂ and 2D MoS₂/CP are 296.21, 483.58 and 360.25 respectively. According to the above equations, the Na⁺ diffusion coefficient of 3D F-MoS₂/CP electrode is 1.5 and 2.7 times higher than 2D MoS₂/CP and 3D foam MoS₂ respectively. In addition, the Linear Sweep Voltammetry (LSV) tests (Fig. S14) were used to measure the resistance of the binder-free electrodes. As shown in Fig. S14, CP shows the lowest resistance (3.4 Ω). The 3D F-MoS₂/CP (4.0 Ω) showed lower resistance than 2D MoS₂/CP (4.2Ω) , which may be due to the higher contacted area of 3D foam structure with CP. According to the research literature [44], MoS₂ is a semiconductor with low electrical conductivity. Therefore, CP substrate helps to increase the conductivity of MoS₂. The above results demonstrate that the combination of CP and 3D MoS₂ macroporous foam structure increases the conductivity of MoS₂ and provides rapid reaction kinetics of Na⁺, dovetailing well with its excellent cycling and rate performance.

In order to further explore the charge storage behavior of 3D F- MoS_2/CP , the CV curves at different scan rates from 0.4-1.0 mV s⁻¹ were recorded. As shown in Fig. 5c, the outlines of CV curves at different scan rates are almost unchanged and the peak current increases with the scanning rates. According to the relationship between peak current and scanning rate $(i = av^b)$ [45], the log (i) $-\log(v)$ plots were made (Fig. 5d). *i* is measured current, *a* is adjustable parameters, and b is the slope of the plot of $\log(i) vs \log(v)$, 0.883 and 0.718, respectively. b = 0.5 represents diffusioncontrolled intercalation process while b = 1 suggests a surfaceinduced capacitive process. As for 3D F-MoS₂/CP, b value is between 0.5-1 and closer to 1, indicating that charge storage has both intercalation contribution and capacitive contribution, with the latter in dominant position. The ratio of capacitive contribution in total stored charge can be further determined by the equation $i = k_1 v + k_2 v^{1/2}$ [45]. $k_1 v$ and $k_2 v^{1/2}$ correspond to capacitive effects and the intercalation process respectively. As shown in Fig. 5e and f, 3D F-MoS₂/CP electrode displays a capacitive contribution of 66% at 1 mV s⁻¹, as a result of increased capacitive effects (pseudocapacitance and double layer charging) [45] provided by the high surface area of 3D F-MoS₂/CP. The capacitive contribution is in favour of long cycle life which is coincidence with the excellent stability (1000 cycles at 2000 mA g^{-1}) of 3D F-MoS₂/CP.

The above results suggested that the high performance of 3D F- MoS_2/CP is originated from the synergetic effect of 3D macroporous MoS_2 nanostructure and the adoption of CP, with 3D foam construction providing rich specific surface area and active sites, holding volumetric change, facilitating the electrolytes and Na⁺ transfer during charge and discharge processes, with CP increasing the conductivity of MoS_2 and avoiding unnecessary side reactions caused by binder addition [13,46]. All these advantages hinder the capacity decay during long-term cycling, especially under large current density (2000 mA g⁻¹).

4 Conclusion

In summary, the binder-free 3D F-MoS₂/CP electrode with excellent Na⁺ storage properties was prepared by simple calcination and etching method. It can be synthesized in large-scale (up to $20 \times 20 \text{ cm}^2$) and be used directly as binder-free electrode in sodium-ion batteries. The CP improves the conductivity of MoS₂ and avoids side reactions without binder, while the 3D macroporous foam structure provides high surface area, exposes abundant active sites, tolerates volumetric change and facilitates the Na⁺ diffusion kinetics during intercalation/deintercalation processes. Consequently, the 3D F-MoS₂/CP binder-free electrode delivers a high discharge capacity (1080 mA h g⁻¹ at 2000 mA g⁻¹), rate performance and cycling stability, and can be cycled at 2000 mA g⁻¹ for 1000 cycles with an extremely low decay rate (0.033% per cycle) in sodium-ion batteries. This work may shed light on the advantages of strategies' union, and can inspire the development of more advanced electrode materials for the application of high performance sodium-ion batteries.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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