

Supporting information

Reversible Sodium Storage *via* Conversion Reaction of a MoS₂-C Composite

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Experimental

Material synthesis

Synthesis of exfoliated MoS₂/C composite: Firstly, exfoliated MoS₂ (E-MoS₂) was prepared from pristine MoS₂ (P-MoS₂) via a modified exfoliation method in a previous report.²¹ Exfoliated MoS₂/C composite (E-MoS₂/C) was fabricated by the hydrothermal method in the second step. Specifically, 0.27 g glucose was dissolved in 20 mL deionized water, then mixed with 40 mL E-MoS₂ dispersion (4.2 mg mL⁻¹). The obtained mixture was loaded into a Teflon-lined autoclave, which was then sealed and maintained at 150 °C for 5 h, and then allowed to cool down to room temperature naturally. After centrifugation, the black product was then washed three times each with deionized water and absolute ethanol, and dried under vacuum at 80 °C overnight. The E-MoS₂/C was finally obtained after annealing treatment at 450 °C for 2 h and then at 800 °C for 2 h in a mixed 5 % H₂/Ar atmosphere.

Structural characterization

The morphologies of the samples were investigated by field-emission scanning

electron microscopy (FESEM; JEOL JSM-7500FA) and transmission electron microscopy (TEM, JEOL 2011, 200 keV). The XRD patterns were collected by powder X-ray diffraction (XRD; GBC MMA diffractometer) with Cu K α radiation at a scan rate of 1° min⁻¹. Thermogravimetric analysis (TGA) was performed in air with a SETARAM Thermogravimetric Analyzer (France). Ex-situ XPS and XRD were taken on the electrodes at different charging or discharging states. The ex-situ XRD samples were prepared by peeling the electrode materials off the Cu current collector, and using Kapton tape to seal onto XRD holder inside of a glove box. This process can avoid the disturbance of strong Cu peaks and the oxidation of electrode material. The X-ray photoelectron spectra (XPS) experiment was carried out using Al K α radiation and fixed analyser transmission mode. The pass energy was 60 eV for the survey spectra and 20 eV for specific elements. The XPS samples were stored in argon box before test.

Electrochemical measurements

The electrochemical measurements were conducted by assembling coin-type half cells in an argon-filled glove box. The slurry was prepared by fully mixing 80 wt % active materials (P-MoS₂, E-MoS₂, and E-MoS₂/C), 10 wt % carbon black, and 10 wt % polyvinylidene difluoride (PVdF) by planetary mixer (KK-250S). Then, the obtained slurry was pasted on a copper film using a doctor blade with a thickness of 100 μ m, which was followed by drying in a vacuum oven overnight at 80 °C. The working electrode was prepared by punching the electrode film into discs 0.97 cm in diameter. The sodium foil was cut using a surgical blade from sodium bulk stored in mineral oil.

The sodium foil was employed as both reference and counter electrode. The electrodes were separated by a glass fiber separator. Several electrodes with various electrolytes were tested in our work, including P-MoS₂ in 1.0 M NaClO₄ with PC (P-MoS₂ with PC), E-MoS₂ in 1.0 M NaClO₄ with PC (E-MoS₂ with PC), exfoliated MoS₂/C in 1.0 M NaClO₄ with PC (E-MoS₂/C with PC), E-MoS₂/C in 1.0 M NaClO₄ with PC/EC (E-MoS₂/C with PC/EC), and exfoliated MoS₂/C in 1.0 M NaClO₄ with PC/EC + 5 wt % FEC (E-MoS₂/C with PC/EC+FEC). The electrochemical performances were tested on a LAND Battery Tester. Cyclic voltammetry was performed using a Biologic VMP-3 electrochemical workstation.

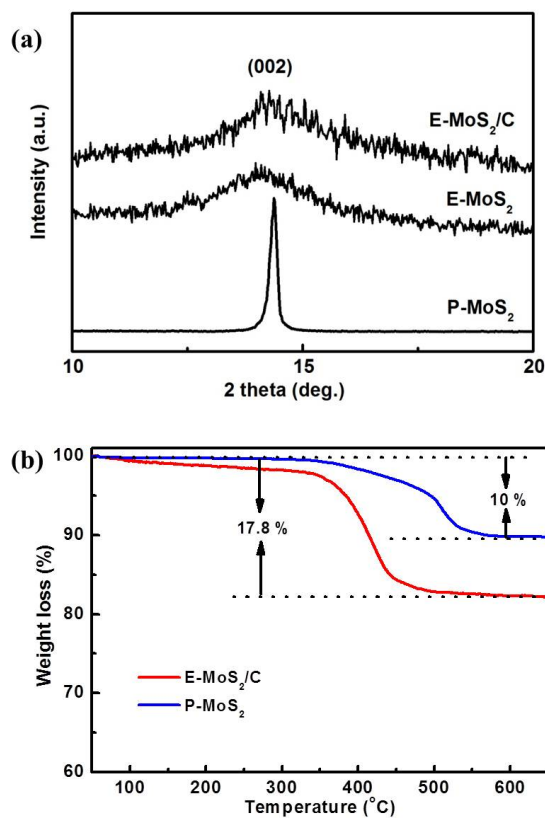


Fig. S1. XRD patterns at range of 10° - 20° P-MoS₂, E-MoS₂, and E-MoS₂/C.

(a) TGA curves of P-MoS₂ and E-MoS₂/C.

The TGA curve of P-MoS₂ is used as a reference, showing a 10 % weight loss after heating to 650 °C in air atmosphere, which indicates that the remaining product after the TGA measurement is pure MoO₃. Based on this fact and assuming that the amorphous carbon is completely decomposed after 650 °C, it is estimated that the MoS₂ content in the composite is approximately 91 wt%, with successful incorporation of about 9 wt% carbon in the E-MoS₂/C.

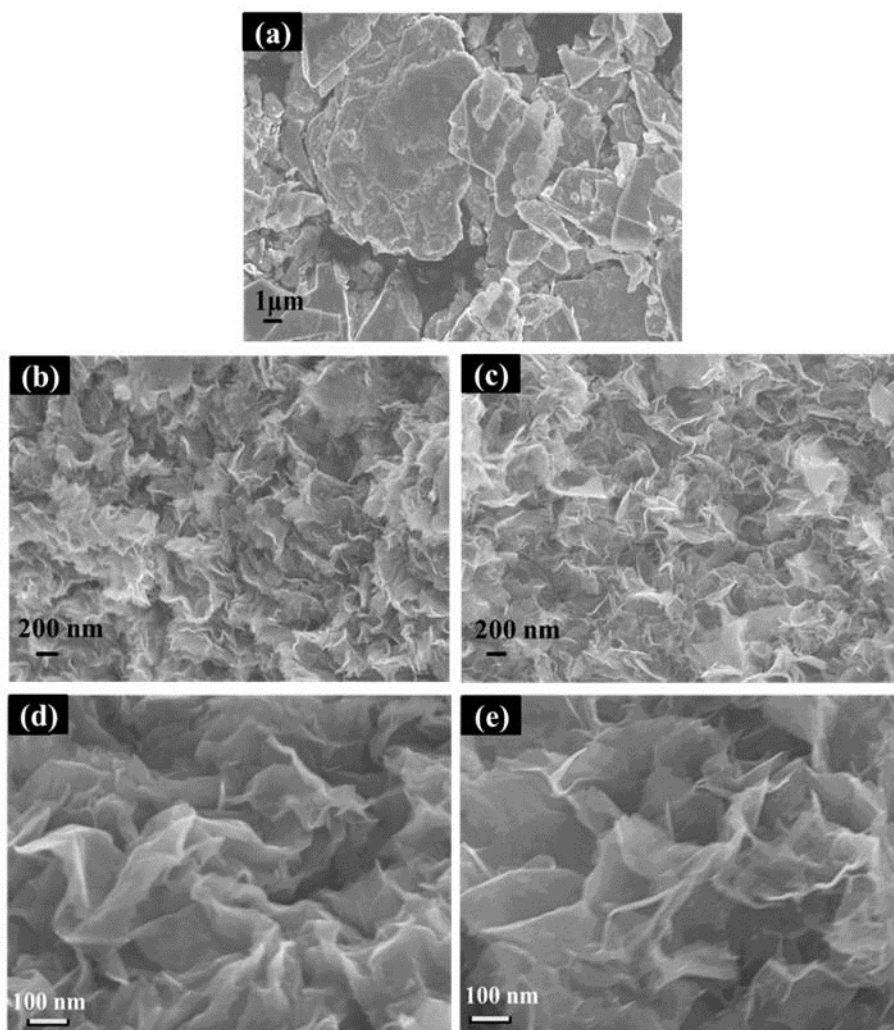
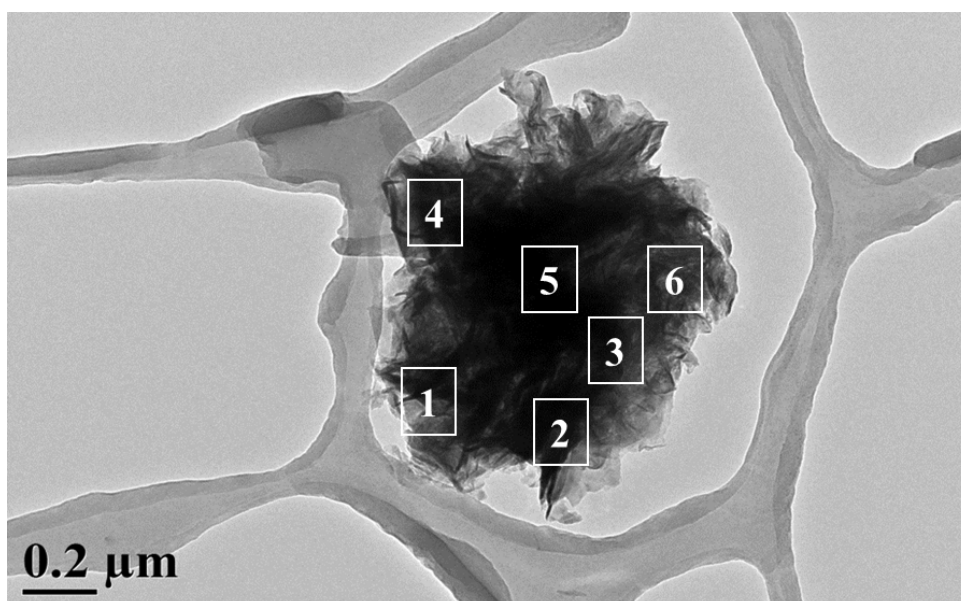


Fig. S2. SEM images of (a) P-MoS₂, (b) E-MoS₂ and (c) E-MoS₂/C at low magnification. SEM images of (d) E-MoS₂ and (e) E-MoS₂/C at high magnification.

Morphological investigations of P-MoS₂, E-MoS₂, and E-MoS₂/C are shown by the SEM images in Fig. S2a-e. Unlike the P-MoS₂ bulk, E-MoS₂ and E-MoS₂/C are in the form of crumpled sheets. This demonstrates the successful exfoliation of the P-MoS₂ into graphene-like nanosheets. Furthermore, it is notable that the nanosheets of E-MoS₂/C are thinner than those of E-MoS₂, indicating that the E-MoS₂/C nanosheets are composed of fewer MoS₂ layers and that the incorporation of carbon restrains the

restacking of the MoS₂ layers. This can be further confirmed by SEM images at higher magnification.



1 Element	Mass%	Atom%	2 Element	Mass%	Atom%
C K	17.42	55.67	C K	15.00	60.39
S K	12.22	14.62	S K	10.08	15.21
Cu K	7.62	4.60	Cu K	5.27	4.01
Mo L *	62.74	25.10	Mo L *	69.66	20.39
3 Element	Mass%	Atom%	4 Element	Mass%	Atom%
C K	19.91	58.83	C K	43.53	81.97
S K	13.73	15.19	S K	8.38	5.91
Cu K	7.63	4.60	Cu K	6.43	2.29
Mo L *	58.72	21.72	Mo L *	41.66	9.82
5 Element	Mass%	Atom%	6 Element	Mass%	Atom%
C K	17.66	55.01	C K	22.40	61.41
S K	15.09	17.60	S K	15.59	16.01
Cu K	5.86	3.45	Cu K	7.42	3.84
Mo L *	61.38	23.93	Mo L *	54.59	18.74

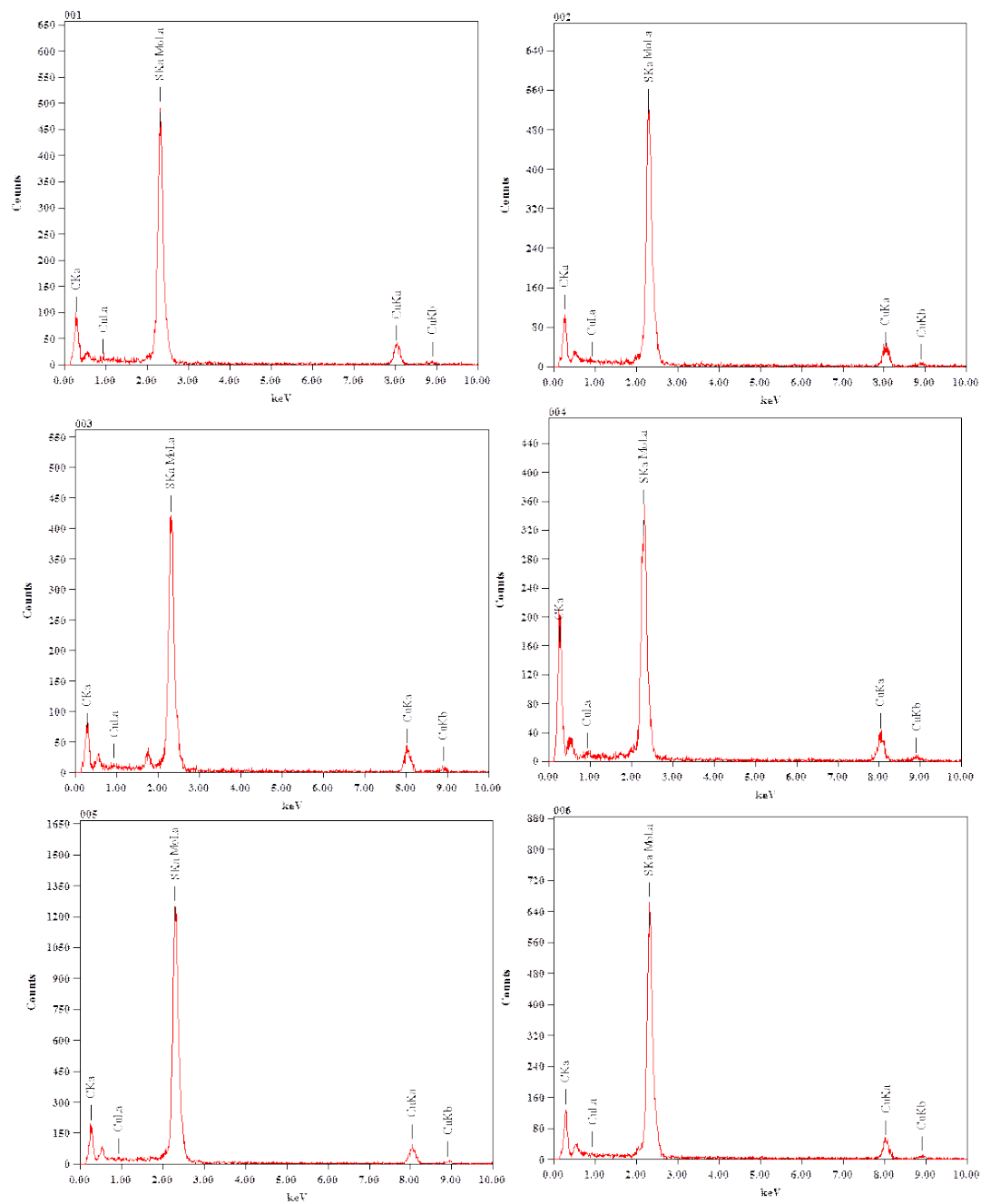


Fig. S3. EDX analysis of E-MoS₂/C flake with six spots.

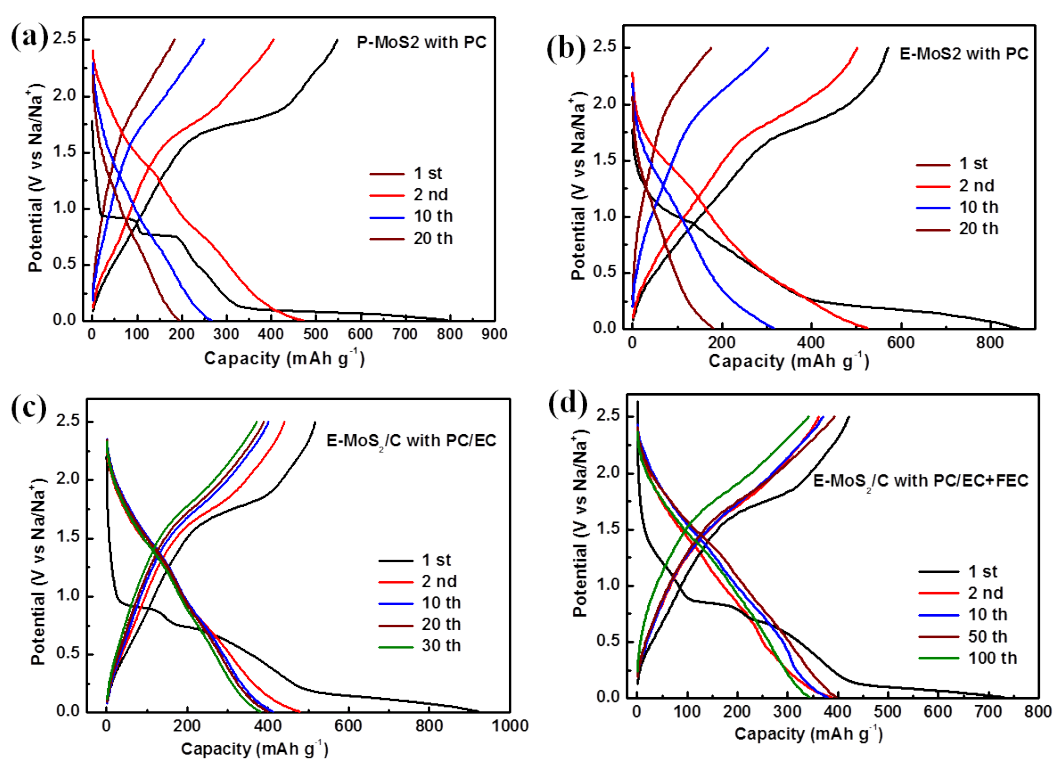


Fig. S4. Charge/discharge profiles of (a) P-MoS₂ with PC, (b) E-MoS₂ with PC, (c) E-MoS₂/C with PC/EC and (d) E-MoS₂/C with PC/EC+FEC. All the electrodes were tested at a current density of 100 mA g⁻¹.

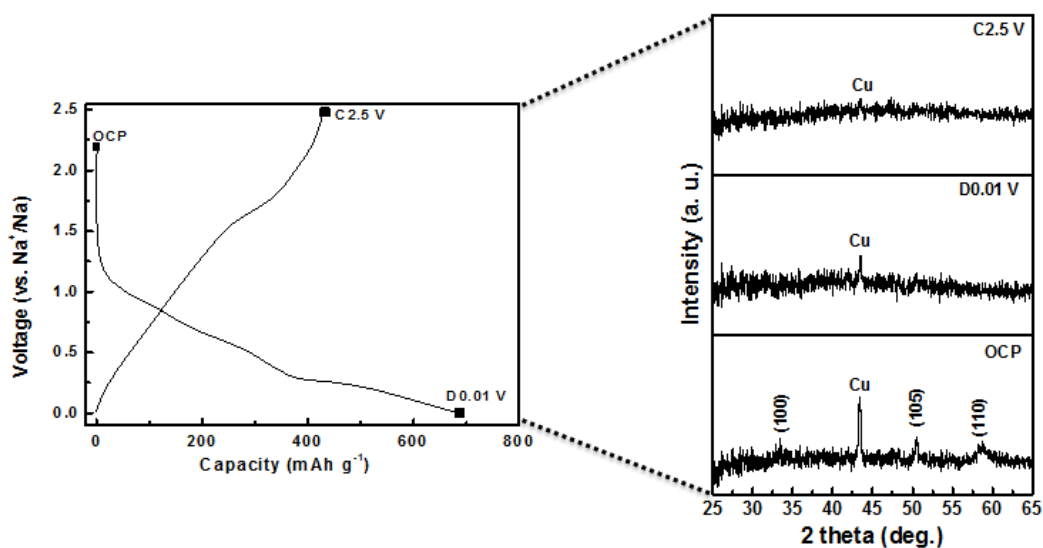


Fig. S5 (a) Initial charge/discharge curves at current rate of 10 mA g⁻¹ and (b) corresponding ex-situ XRD patterns for different states of E-MoS₂/C in 1.0 M NaClO₄ with PC: OCP (open circuit potential), D0.01 V (discharged to 0.01 V) and C2.5 V (charged back to 2.5 V).

The XRD patterns shown in Fig. S5b were subtracted the background of Kapton tape. The fresh electrode coated by Kapton tape can show three typical peaks of E-MoS₂/C, which were indexed to (100), (105), and (110). A small peak located at ~43.5 ° was attributed to the Cu from the current collector. When the electrode was fully discharged to 0.01 V, all of diffraction peaks disappeared and the electrode material showed the amorphous nature. It maintained amorphous when the electrode material was fully charge back to 2.5 V. The results indicate that E-MoS₂/C may undergo a conversion reaction during the charge/discharge process.

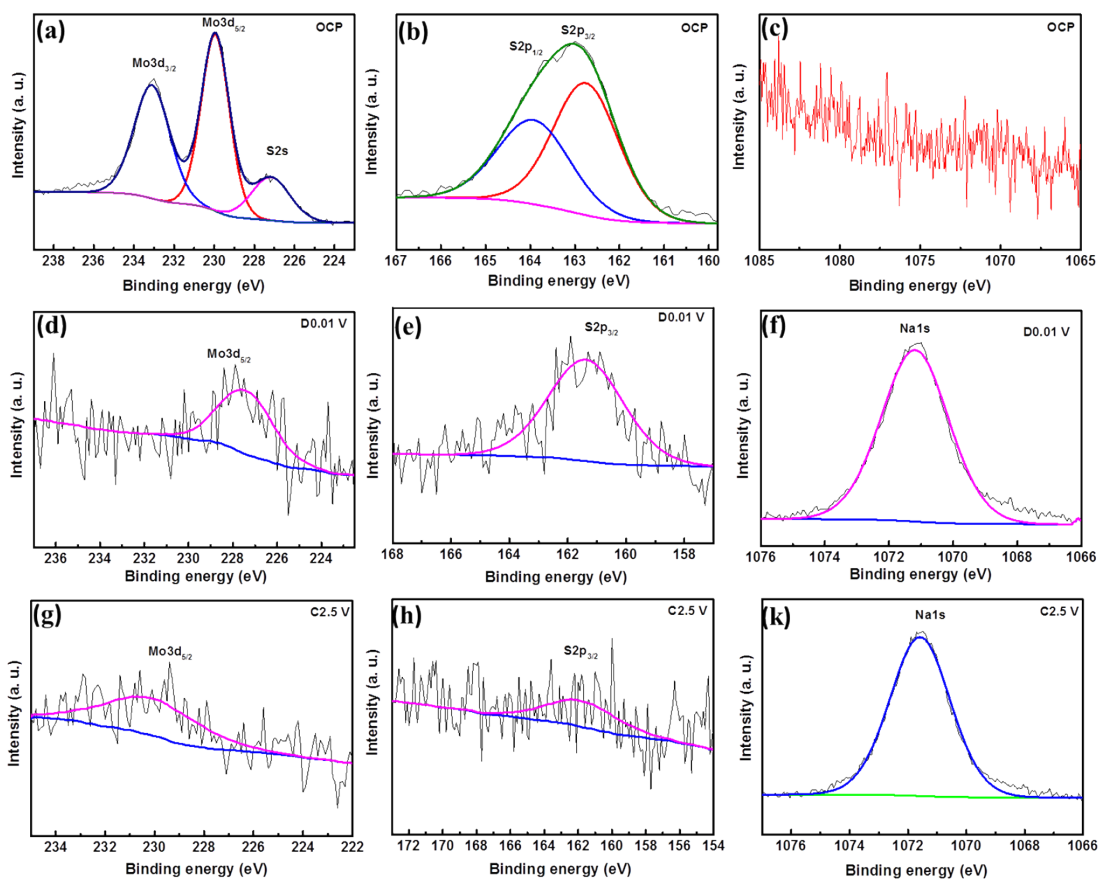


Fig. S6 The XPS spectrum for different states of E-MoS₂/C in 1.0 M NaClO₄ with PC: (a), (d), and (g) Mo 3d spectrum at OCP, D0.01 V, and C2.5 V; (b), (e), and (h) S 2p spectrum at OCP, D0.01 V, and C2.5 V; (c), (f), and (k) Na 1s at OCP, D0.01 V, and C2.5 V.

Further evidence for MoS₂-Na conversion reaction was provided from XPS analysis. For the E-MoS₂/C electrode at OCP state, the Fig. S6a shows the predominant peaks at ca. 229.7 and 232.8 eV, which is ascribed to Mo3d_{5/2} and Mo3d_{3/2} binding energies,

respectively. Correspondingly, the peaks at ca. 162.5 and 163.4 eV can be attributed to $S2p_{3/2}$ and $S2p_{1/2}$ binding energies, respectively. The well-defined spin-coupled Mo and S doublets demonstrate the hexagonal MoS_2 state. No sodium element is observed for the fresh electrode. When the electrode was charged to 0.01 V, the $Mo3d_{5/2}$ peak (Fig. S6a) shifts to ca. 227.5 eV, indicating the reduction of Mo^{4+} to Mo. A distinguished peak at ca. 1071.2 eV in Fig. S6c can be indexed to the Na 1s. The $S2p_{3/2}$ peak shifts to 161.5 eV, which indicates the presence of Na_2S . When it was charged to 2.5 V, the $Mo3d_{5/2}$ peak appears at higher binding energy (~ 230.4 eV), and the S 1s energy binding is ~ 162.1 eV. This indicates the recovery of MoS_2 . The Na 1s peak at ca. 1071.5 eV is probably ascribed to Na_2CO_3 in solid electrolyte interphase (SEI) film. It is noticeable that the intensity of $Mo3d_{5/2}$ and S 1s for MoS_2 is severely lowered, which is likely due to that the formation of thick SEI film on electrode surface. Combining the ex-situ XRD and XPS of E- MoS_2/C electrode, it is reasonable that the E- MoS_2/C underwent a conversion reaction during sodiation/desodiation.

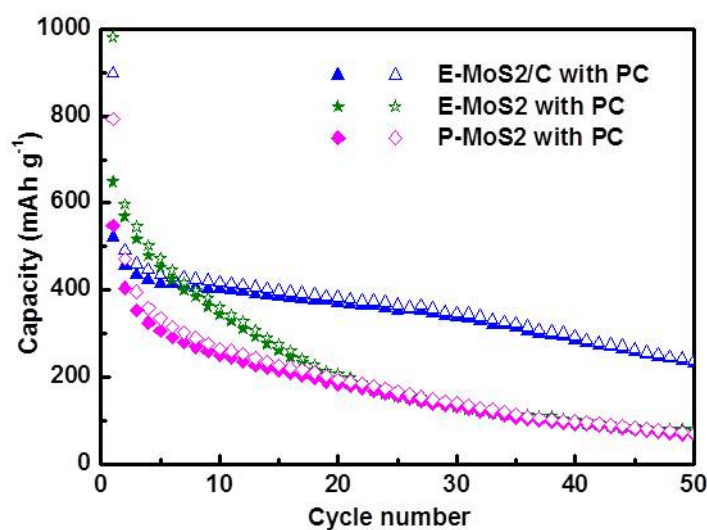


Fig.S7 Cycling performances of E-MoS₂/C in various electrolytes. The applied current density was 100 mA g⁻¹ at 0.01-2.5 V for all electrodes. The solid and open symbols represent charge and discharge capacities, respectively.

Both P-MoS₂ and E-MoS₂ show similar cycling performance after 20 cycles. E-MoS₂ shows higher capacity than P-MoS₂, with average reversible capacity of 366.2 mAh g⁻¹ and 275.3 mAh g⁻¹ in the initial 20 cycles, respectively. This indicates that the E-MoS₂ can accommodate more Na ions due to the d-spacing enlargement effect, while it shows almost the same electrochemical performance as P-MoS₂ for prolonged cycling as a result of its severe restacking. For E-MoS₂/C, the incorporation of carbon can significantly improve the capacity retention.

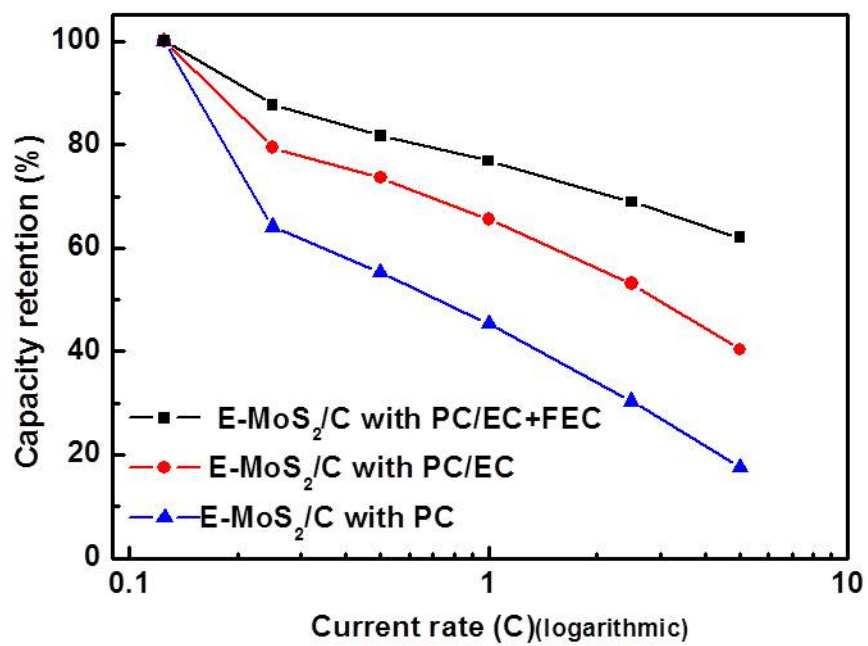


Fig.S8 Capacity retention of E-MoS₂/C in various electrolytes at different current densities.

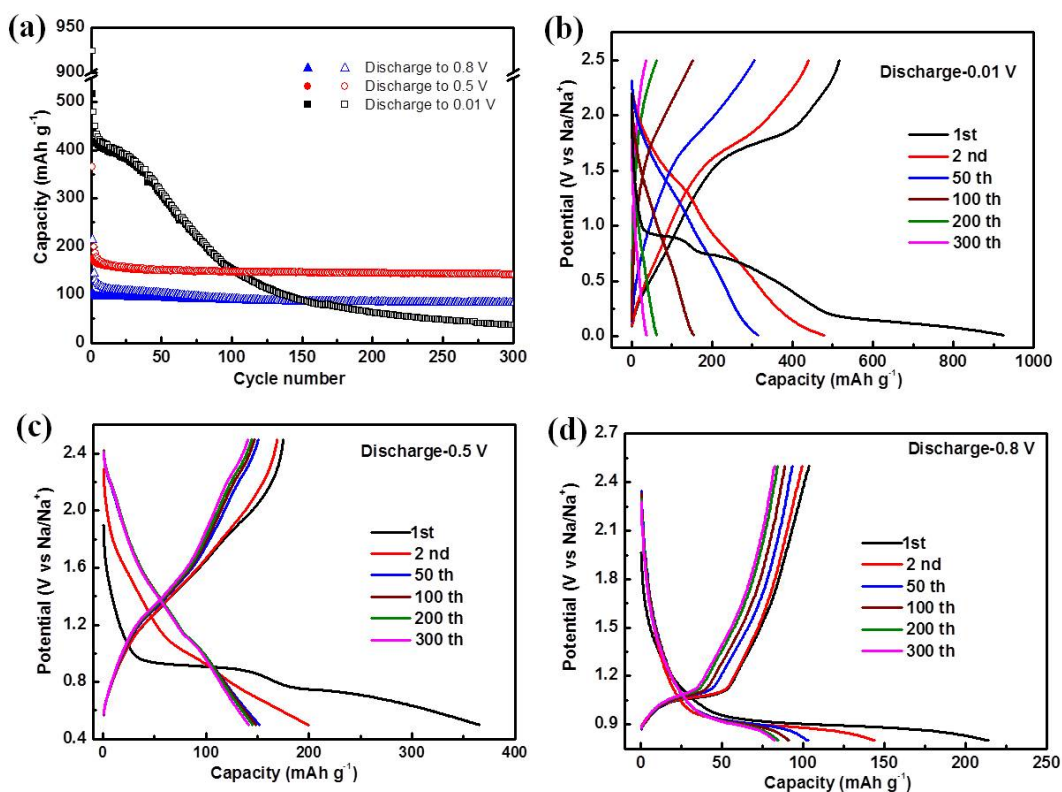


Fig. S9. Cycling performances (a) and charge/discharge profiles (b) of E-MoS₂/C in the voltage ranges from 2.5 V to 0.8 V, 0.5 V, and 0.01 V in 1.0 M NaClO₄ with PC.

It is worth noting that the E-MoS₂/C in 1 M NaClO₄ with PC exhibited distinct cycling performances for different discharge cut-off voltages. In the range of 0.01-2.5 V, the electrode delivers the highest average capacity of 375.5 mAh g⁻¹ for the initial 50 cycles, while it shows serious capacity degradation in successive cycles. When the discharge voltages are cut off at 0.8 V and 0.5 V, even though the capacities decrease to ~83 mAh g⁻¹ and ~140 mAh g⁻¹, respectively, no capacity decay is observed over 300 cycles.

When MoS₂/C composite electrode was tested between 2.5 and 0.8 V (Fig. S9d), the charge/discharge curves show repeatable plateau for 300 cycles, which confirmed

the intercalation/deintercalation process with no change of MoS₂ layer structure. When discharge to 0.5 V, it also showed good cycling stability, which is consistent with the intercalation/deintercalation process with distortion of MoS₂ layer structure. The charge/discharge curves are slope curves instead of obvious plateaus. However, when it was fully discharged to 0.01 V, the distorted MoS₂ was further react with Na ions, which is corresponding to the conversion reaction. This process leads to higher capacity and the conversion reaction process for the following cycles.