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Intercalation Na-Ion Storage in Two-Dimensional $\text{MoS}_{2-x}\text{Se}_x$ and Capacity Enhancement by Selenium Substitution

Abstract

Two-dimensional (2D) layered transition-metal dichalcogenides has been regarded as highly promising electrode materials for fast-rate Li-ion and Na-ion batteries. Monolayer or multilayer MoS_2 nanoflakes have been employed for metal ion batteries but the material suffers from poor cyclic stability due to damage of the layered structure in a decomposition reaction. Herein, we synthesize ultrathin $\text{MoS}_{2-x}\text{Se}_x$ nanoflakes quasi-vertically aligned on the graphene-like carbon foam (the obtained material is referred to as $\text{MoS}_{2-x}\text{Se}_x/\text{GF}$) and investigate the Na-ion storage property using in-situ Raman spectroscopy and ex-situ XRD measurements. We show that by choosing appropriate potential range, it is possible to maintain the 2D layered structure and thus significantly improve the capacity retention due to the intercalation mechanism. As a freestanding electrode, the $\text{MoS}_{2-x}\text{Se}_x/\text{GF}$ demonstrates high-rate reversible Na-ion storage, where both the capacity and rate-performance are enhanced by the selenium substitution. This study sheds new light on better understanding of the metal ion storage mechanism of 2D transition metal chalcogenides that are being widely investigated.

Keywords: 2D materials; Na-ion battery; transition-metal dichalcogenides; in-situ Raman; charge storage mechanism.

Introduction

In the pursuit of the large-scale energy storage systems, sodium-based energy storage devices, such as sodium-ion batteries (SIBs), sodium-sulfur batteries and sodium ion capacitors, have drawn enormous attention recently. SIBs have been investigated as promising alternative to lithium-ion batteries (LIBs) due to lower cost of sodium salt and similar processing technology as LIBs. In comparison with the ionic diameter of lithium ion (0.67 Å), the larger sodium ion (1.06 Å) leads to inferior electrochemical performance, resulting from its sluggish ion transport kinetics in the crystal structure. Furthermore, the large ionic diameter also results in severe structural distortion of the active material accompanied by phase changes or structural pulverization.¹⁻² Current research efforts are being devoted to development of new electrode materials and surface engineering to improve the rate and cycle performance.

2D layered transition metal dichalcogenides (TMDs) have been intensively investigated as anode materials in LIBs and SIBs.³⁻⁶ Among them, MoS₂ has been leveraged as the anode material in SIBs, because of its high theoretical capacity (~670 mAh g⁻¹, based on 4 mol of Na⁺ insertion) and small lattice expansion during sodiation and desodiation processes.⁷⁻⁸ However, the cycling performance of MoS₂ anode material in SIBs has been poor, for which an accepted reason is the irreversible decomposition reaction during the first discharge to a low potential region. It has been proposed that the sodiation mechanism of MoS₂ proceeds in two stages,^{5, 9} and the corresponding reaction can be written as:

In the high potential range, sodium ions first intercalate into the lattice (Eq. 1), followed by decomposition reaction in the low potential range (Eq. 2). During the first sodiation process, MoS₂ decomposes to metallic Mo, which is regarded as the main cause to poor cycle performance. Maier and coworkers prepared the single-layered ultrasmall MoS₂ nanoplates embedded in thin carbon nanowires, which showed a remarkable discharge capacity of 623 mAh g⁻¹ at 1 A g⁻¹.¹⁰ However, the capacity dropped to 56 % only after 100 cycles. Choi et al. enhanced the cycle performance with nearly no capacity loss for 100 cycles by adopting the liquid-phase exfoliated MoS₂ nanosheet and adjusting the potential range to 0.4-2.6 V.¹¹ Unfortunately, it was sacrificed with capacity (around 110 mAh g⁻¹ at 0.8 A g⁻¹). Therefore,

maintaining a good cycle performance without sacrificing capacity is highly meaningful but so far remains a challenge. In this work, we made big progress towards this goal by introducing selenium into MoS₂ crystal structure to expand the layer spacing (atomic size of selenium is ~1.2 Å and ~1.05 Å for sulfur), and choosing a proper potential range. The increased lattice spacing can facilitate the intercalation of sodium ions into the layers, which can enhance the electrochemical kinetics and rate performance.

Ex-situ X-ray diffraction (XRD) measurements have been conducted to unveil the sodiation mechanism of MoS₂.^{9, 12} Wang et al. investigated the process with ex-situ XRD at three stages.¹² The diffraction peak of Na₂S emerged when the electrode was fully discharged to 0.005 V, and still existed when the electrode was fully re-charged to 2.5 V. In contrast, the peak of MoS₂ fully disappeared and could not recover. Similarly, Dou et al. have also studied the process with ex-situ XRD and observed the same phenomenon when the electrode was discharged to 0.01 V and re-charged to 2.5 V.⁹ These data implies irreversible reaction in the first cycle. Nevertheless, the ex-situ XRD measurements cannot provide accurate information once the 2D nanomaterial becomes amorphous or oxidized during exposure to air ambient. *Herein*, we employed both ex-situ XRD and in-situ Raman measurements to track the sodiation and desodiation processes of our MoS_{2-x}Se_x nanosheet electrode. As Raman peaks are very sensitive to composition and phase change, it is especially a useful investigative tool for 2D materials.

To implement the ideas mentioned above, we judiciously designed the electrode by growing MoS_{2-x}Se_x alloy with an ultrathin nanoflake structure on 3D graphene foam backbone. The obtained MoS_{2-x}Se_x/GF material is directly used as freestanding anode for SIBs. We have observed **significantly** higher capacity and rate performance due to selenium substitution induced lattice expansion and pseudocapacitive effect. Furthermore, we also provide strong evidence by in-situ Raman measurement to the intercalation mechanism in a properly selected potential range. Our study provides better understanding and manipulation of the metal ion storage in layered TMD materials.

Characterization of MoS₂ and MoS_{2-x}Se_x nanoflakes

The pristine graphene foam framework was characterized by SEM with low and high resolution

in Figure S1. The MoS₂ has a porous and frizzy nanoflake structure (Figure 1a), which can enlarge the electrode surface area and enable efficient ion transport. After the selenium substitution with a suitable concentration, the obtained MoS_{2-x}Se_x/GF maintains the uniform nanoflake morphology (Figure 1b and S2). The phase and composition are identified with X-ray diffraction (XRD) and Raman spectroscopy measurement. The XRD patterns of both MoS₂/GF and MoS_{2-x}Se_x/GF depicted in Figure 1c show the obvious characteristic peaks, which indicates their good crystallinity. In comparison with MoS₂, the corresponding XRD peaks of MoS_{2-x}Se_x shift to lower degree. This reveals that the selenium substitution has enlarged the lattice spacing. For example, the (002) peak of the MoS₂ at 14.55° shifts to 13.6° after the selenization, corresponding to lattice spacing from 6.08 to 6.51 Å due to the larger diameter of selenium atom than sulfur. Larger lattice spacings are favorable in facilitating the intercalation and deintercalation of sodium ions between the interlayers.¹³⁻¹⁴ The Raman spectrum of MoS₂/GF (black curve in Figure 1d) shows two characteristic peaks located at 403 and 377 cm⁻¹, corresponding to the A_{1g} (out of plane) and E_{2g}¹ (in plane) modes of MoS₂.¹⁵⁻¹⁶ For the MoS_{2-x}Se_x/GF sample (red curve), additional Raman peaks due to Mo-Se vibrations appear after the selenization, and meanwhile the peak intensities of Mo-S vibration modes decrease. The peak located at 287 cm⁻¹ attributes to the E_{2g}¹ vibration mode of Mo-Se.¹⁷⁻¹⁹ The two peaks at 237.7 and 250.6 cm⁻¹ come from the splitting of MoSe₂-like A_{1g} mode, which results from the different coordination configuration of Se and S around Mo.²⁰⁻²¹

The structures of MoS₂/GF and MoS_{2-x}Se_x/GF were further examined by high-resolution transmission electron microscopy (HRTEM) (Figure 2a-f). Indeed both samples have similar thin flake structure with a thickness of ~7 nm. The lattice spacings of MoS₂, as identified in Figure 2c, are 0.22, 0.26 and 0.61 nm, corresponding to the (103), (101) and (002) crystal planes. The corresponding lattice spacings of MoS_{2-x}Se_x are 0.24, 0.28 and 0.68 nm (Figure 2f). The expansion of lattice spacings due to selenium substitution is good accordance with the XRD result. X-ray photoelectron spectroscopy (XPS) measurement was used to investigate the surface chemical composition difference on the two samples (Figure S3 and S4a). The two obvious peaks located at 229.3 and 232.4 eV (Figure 2g) corresponds to Mo 3d_{5/2} and Mo 3d_{3/2} in the MoS_{2-x}Se_x/GF sample, which are very similar with the spectrum in the MoS₂/GF except for small energy shift around 0.5 eV (Figure S4b).¹⁴ Selenium element was detected only in

the $\text{MoS}_{2-x}\text{Se}_x/\text{GF}$ sample: The peaks at 161.1 and 166.8 eV come from the Se $3p_{3/2}$ and $3p_{1/2}$ (Figure 2h), and the peaks at 54.8 and 55.6 eV come from Se $3d_{5/2}$ and Se $3d_{3/2}$ (Figure 2i). And the Se composition ratio in the $\text{MoS}_{2-x}\text{Se}_x/\text{GF}$ sample was determined to be $x=0.9$ based on the XPS intensity ratios. Furthermore, energy dispersive X-ray spectroscopy (EDX) mapping analysis of $\text{MoS}_{2-x}\text{Se}_x/\text{GF}$ (in Figure S5a) also confirms the existence of Mo, S and Se elements and their homogeneous distribution. The S:Se ratio estimated from EDX spectrum is about 14:0.86 in the $\text{MoS}_{2-x}\text{Se}_x$ (Figure S5b).

Electrochemical property in Na-ion storage

The freestanding MoS_2/GF and $\text{MoS}_{2-x}\text{Se}_x/\text{GF}$ were directly used as electrodes to investigate the electrochemical measurements in SIBs. Their typical cyclic voltammetry (CV) curves for initial three cycles in a potential range from 0.5 to 3.0 V (vs. Na^+/Na) with a scan rate of 0.2 mV s^{-1} are illustrated in Figure S6a and b. They have obvious irreversible capacities in the low voltage range (mainly 0.8-0.5 V) during the first cathodic processes, which result from the formation of solid electrolyte interface (SEI) on the surface of electrode materials, but their reversibility has been enhanced from further cycles. The CV curves of both MoS_2/GF and $\text{MoS}_{2-x}\text{Se}_x/\text{GF}$ (Figure 3a) show multiple redox peaks superimposed with capacitive currents. Especially the quasi-rectangular CV curves within the potential range from 0.5 to 2.4 V indicate the good capacitive-like electrochemical property.^{8, 12} Compared to the MoS_2/GF electrode, the $\text{MoS}_{2-x}\text{Se}_x/\text{GF}$ exhibits a 3.2 times higher capacity (calculated from CV curves). Their galvanostatic discharge-charge profiles (Figure 3b) reveal the quasi-linear behavior, which is also indicative to capacitive-model dominating mechanism. In terms of the electrochemical impedance spectroscopy (EIS), as depicted in Figure 3c, the electrochemical reaction impedance in electrode and ion diffusion impedance in electrolyte can be determined by the semicircle in high frequency region and the straight line in low frequency region, respectively. Based on the simulation equivalent circuit (Inset in Figure 3c), the simulated values of Ohmic resistance (R_s) and charge-transfer resistance (R_p) for the $\text{MoS}_{2-x}\text{Se}_x/\text{GF}$ electrode are about 4.2 and 420Ω , respectively, which are lower than those of the MoS_2/GF electrode (5.2 and 585Ω). It demonstrates the selenium substitution can improve the electrode conductivity.

The MoS_2/GF electrode displays higher first-cycle coulombic efficiency of 60 % than that

of MoS_{2-x}Se_x/GF electrode with 55 % (Figure 3d). After SEI stabilization, in the next 500 cycles, both of them show nearly 100% coulombic efficiency. The third discharge capacities of the two electrodes are 208 and 178 mAh g⁻¹, respectively. Note that the capacities were calculated based on active materials only without adding the mass of graphene foam since our main purpose is to discuss the intrinsic electrochemical property of the material rather than performance of a full battery cell. The specific capacity of GF beyond 0.5 V is about 0.5 mAh g⁻¹ at the current density of 0.2 A g⁻¹ (see Figure S7). Their capacity retentions are at about 77 % after 500 cycles. This significant improvement in capacity retention originates from a properly selected potential range. To compare, we also measured the cycling stability of our MoS_{2-x}Se_x/GF electrode in the potential range of 0.01-3.0 V vs. Na⁺/Na (see Figure S8a), which exhibits a much poorer cycle performance of about 60 % after 300 cycles. This electrochemical instability is correlated to the change of microscale morphology. The MoS_{2-x}Se_x/GF sample tested within the potential range of 0.01-3.0 V after 300 cycles shows severe agglomeration (see SEM images in Figure S8b). In contrast, when cycled in the potential range of 0.5-3.0 V, both MoS₂/GF and MoS_{2-x}Se_x/GF electrodes still exhibit the nanoflake structure after 500 cycles with only slight agglomeration on the surface (see Figure S9a and b). In addition, both MoS_{2-x}Se_x/GF and MoS₂/GF electrodes show good rate performance, but the former has some enhancement (data presented in Figure 3e). The better rate performance results from the expanded lattice spacing after the selenium substitution. After cycling at various current from 0.2 to 5 A/g and then back to 0.2 A/g, both electrodes can recover the initial capacities and maintain in the next 50 cycles. The above results demonstrate that adjustment of potential range is an effective approach to improve electrochemical performance.

Pseudocapacitance enhancement

The better rate performance of MoS_{2-x}Se_x/GF draws our attention to understand the kinetics origin. The analyses of redox capacitive contribution of the two electrodes have been adopted to investigate their electrochemical kinetics. The capacitive effect of the electrode at different redox peaks can be qualitatively analyzed from CV curves according to the equation between measured current (*i*) and scan rate (*v*): $i = av^b$, where *a* and *b* are parameters.³ When the *b* value approaches to 1, the electrode kinetics is controlled by capacitive processes; while the *b* is close

to 0.5, the electrode kinetics is diffusion limited (including diffusion on surface, subsurface and bulk lattice). Details of the results for both electrodes are presented in Figure S10 and S11. Their CV shapes have been well preserved with increasing scan rate from 0.2 to 1.0 mV s⁻¹. The linear dependence ($b \approx 1$) of the current on the sweep rate is determined for both electrodes (Figure S10b and S11b). The MoS_{2-x}Se_x/GF electrode shows generally higher b values than those of the MoS₂/GF electrode, which suggests the enhanced capacitive process after the selenium substitution.

While the total capacity of nanostructured material generally comes from both diffusion-limited and capacitive currents, we can empirically quantify the contributions of the two processes by conducting the standard CV fitting. To do this, we separate the current response (i) into capacitive-derived and diffusion-derived current at a fixed potential (v).³ According to the relationship of $i(V) = k_1v + k_2v^{1/2}$, where k_1v is the capacitive part, $k_2v^{1/2}$ is the diffusion-controlled part, v is the scan rate, and k_1 and k_2 are constants. For example, at scan rate of 0.4 mV s⁻¹, the fitting analysis generates the capacitive fraction within the entire potential range of 0.5 – 3 V (shaded regions in Figure S10c and S11c), which are calculated to be 63.8 % and 68.4 % in MoS₂/GF and MoS_{2-x}Se_x/GF electrodes, respectively. Following this route, capacitive contribution ratios at other different scan rates are determined and presented in Figure S10d and S11d. One can see that, as the scan rate increases, the fraction of capacitive contribution enlarges, which is reasonable since the bulk diffusion vs capacitive (surface-dominated diffusion) processes depends on the scan rate. By comparing the contribution fractions between the MoS_{2-x}Se_x/GF and MoS₂/GF electrodes (see data in Figure 3f), we can see that former exhibits higher capacitive contribution than the latter at all scan rates. Recalling the above-mentioned rate performance result, we may conclude that the capacitive contribution plays an important role in improving the capacity retention at different discharge currents. And the selenium substitution has enhanced the pseudocapacitance effect by enhancing the lattice spacings.

On the intercalation mechanism

In-situ Raman measurement is an effective characterization to investigate the composition and crystal structure change during sodiation and desodiation processes. For comparison, we

conducted the in-situ Raman measurement of the $\text{MoS}_{2-x}\text{Se}_x/\text{GF}$ electrode during the first sodiation and desodiation processes in two discharge/charge potential ranges: 0.5-3.0 V (Figure 4) and 0.01-3.0 V (Figure S12). Therein, the Raman spectrum at open circuit voltage (OCV) of 2.4 V shows the fingerprint peaks of MoS_2 and MoSe_2 in the range of 200-500 cm^{-1} . The Raman peaks at 237.8 and 253.3 cm^{-1} come from the peak splitting of MoSe_2 A_{1g} vibration mode, and the peak at 287 cm^{-1} corresponds to the MoSe_2 E_{2g}^1 vibration mode. The peaks located at 377.1 and 405.4 cm^{-1} are attributed to in-plane E_{2g}^1 and out-of-plane A_{1g} modes of MoS_2 , respectively. Discharging the cell down to 0.8 V results in continuous attenuation of the Mo-Se and Mo-S peaks (Figure S12a), which is due to the increase of intercalated sodium ions. When the discharge potential further goes to 0.6 V, the characteristic Raman peaks become invisible and there is also no emergence of any new peak, suggesting the disappearance of $\text{MoS}_{2-x}\text{Se}_x$ 2D structure. And there is no emergence of new peak even when the cell was deep discharged to 0.01 V. Afterwards, the cell was charged from 0.01 V onwards until back to 3.0 V (Figure S12b). Surprisingly, the Mo-Se and Mo-S Raman peaks never reappear. This implies that the pristine 2D structure in $\text{MoS}_{2-x}\text{Se}_x$ has been destroyed after the first discharge to 0.01 V. This is also confirmed by ex-situ XRD measurement (Figure S12c). Compared to the initial XRD curve, the characteristic peaks of $\text{MoS}_{2-x}\text{Se}_x/\text{GF}$ disappear when the electrode is discharged to 0.01 V and re-charge to 3.0 V. The above results jointly confirm that the irreversible loss of the layered structure of $\text{MoS}_{2-x}\text{Se}_x$ in the first sodiation (discharge) process to 0.01 V.

In contrast, it is found that the 2D structure is reversible in the potential range of 0.5-3.0 V. As shown in Figure 4, when first discharged to 0.7 V. The characteristic Raman peaks of Mo-S and Mo-Se become very weak and even unresolvable (Figure 4a). However, in the subsequent charge process (Figure 4b), the fingerprint peaks reappear beyond 0.9 V and grow in intensity with further increase in potential. We also conducted ex-situ XRD measurement at three stages to double confirm the crystal structure (see data in Figure 4c). The new peak at 7.3° emerges when the electrode was discharged to 0.5 V, which results from the expansion of lattice spacing (1.22 nm) after the intercalation of sodium ions. All the characteristic peaks of $\text{MoS}_{2-x}\text{Se}_x/\text{GF}$ reappear when the cell is charged back to 3.0 V, implying that the crystal structure is preserved during the full sodiation and desodiation cycle, and that the Na-ion

storage occurs via intercalation into the layers rather than the commonly-discussed “decomposition” reaction (Figure 4d).

Based on the in-situ Raman and ex-situ XRD results, we can see that whether or not the 2D layered crystal structure of $\text{MoS}_{2-x}\text{Se}_x$ (and also MoS_2 and MoSe_2) depends on the discharge potential range. When discharged to below 0.5 V, the 2D structure will be destroyed because of decomposition reaction. However, it can be well preserved if the discharge voltage is maintained just above 0.5 V. Therefore, the adjustment of potential range is key to maintaining the 2D structure in $\text{MoS}_{2-x}\text{Se}_x$ and therefore enhancing the cycle performance (note that most previous reported MoS_2 or MoSe_2 2D electrodes suffer from severe instability). In addition, the selenium substitution enlarges the lattice spacing of the layered structure and improves the conductivity, which accounts for the enhanced rate performance.

In summary, thin $\text{MoS}_{2-x}\text{Se}_x$ nanoflakes grown quasi-vertically on 3D GF have been employed as freestanding and flexible electrode for Na ion storage. The $\text{MoS}_{2-x}\text{Se}_x/\text{GF}$ electrode with a Se concentration ($x=0.9$) exhibits enhanced rate performance with a higher reversible capacity and capacity retention compared to pure nanoflake MoS_2/GF electrodes. Quantitative analysis reveals that the improved pseudocapacitive contribution, derived from enlarged interlayer spacing by selenium substitution, is the origin of good rate performance. The in-situ Raman together with ex-situ XRD measurements further reveals that the 2D structure in $\text{MoS}_{2-x}\text{Se}_x$ can be preserved due to Na-ion intercalation process in the potential range above 0.5 V. Discharge below 0.5 V leads to damage of the 2D structure and aggregation. The insight of this experiment may be extended to other layered 2D materials in fast-rate metal ion storage.

Experiment

Material Synthesis. $\text{MoS}_{2-x}\text{Se}_x$ nanoflake/3D graphene foam ($\text{MoS}_{2-x}\text{Se}_x/\text{GF}$) was prepared with a hydrothermal reaction and a selenization process. A 0.06 g amount of sodium molybdate ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$) and 0.12 g of thiourea were dissolved with 30 mL of distilled water at ambient temperature. After the complete dissolution, the mixture was transferred into a Teflon-lined stainless steel autoclave. A piece of graphene foam substrate ($\sim 1 \text{ mg cm}^{-2}$, synthesized by the CVD method) was soaked inside the solution, then the autoclave was kept in an electric oven at 220°C for 12 hours. After cooling to room temperature, the sample was washed with distilled water and ethanol with three times. The obtained sample was dried under vacuum at 70°C for 12 h to achieve the 3D graphene foam supported MoS_2 nanoflake. Then MoS_2/GF was obtained after a calcination in Ar atmosphere for

2 h, and $\text{MoS}_{2-x}\text{Se}_x/\text{GF}$ was synthesized with a calcination at 700°C for 2h in a mixed Ar-H_2 (2% H_2) atmosphere with addition of selenium powder (0.3 g) placed at the upstream side of the furnace.

Characterization and Electrochemical measurement. The morphologies of the samples were characterized by field-emission scanning electron microscopy (FESEM, JEOL, Model JSM-7600F). The crystalline structures were determined by X-ray diffraction (XRD, Bruker D-8 Avance). Raman spectroscopy were measured with a WITec-CRM200 confocal microscopy Raman system with a 532-nm excitation source. The high-resolution transmission electron microscopic (HRTEM) analysis was performed with a JEOL (Model JEM-2100F). The X-ray diffraction spectroscopy (XPS) analysis was conducted using a Thermal Scientific Theta Probe system XPS with a monochromatic $\text{Al K}\alpha$ (486.7 eV) X-ray source.

Electrochemical performances were carried out using CR2032 coin-type cells, which was assembled with sodium foil served as both reference and counter electrodes and active material as working electrode under room temperature. The working electrode was the as-prepared freestanding graphene foam supported MoS_2 and $\text{MoS}_{2-x}\text{Se}_x$ nanoflakes. The mass loadings of MoS_2 on GF and $\text{MoS}_{2-x}\text{Se}_x$ on GF are about 1.08 and 1.95 mg cm^{-1} for electrochemical measurements. 1 M NaPF_6 in ethylene carbonate (EC)–diethyl carbonate (DEC)–fluoroethylene carbonate (FEC) (1:1:0.05 in volume) and a glass fiber were used as the electrolyte and separator, respectively. The cells were assembled in an Ar-filled glove box (Mbraun, Unilab, Germany) with both moisture and oxygen content below 0.1 ppm. The cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were performed via an electrochemical workstation (CHI 760D, Chenhua, Shanghai). Galvanostatic charge-discharge tests were carried out by Neware battery testers.

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Figure 1. FESEM images of (a) MoS_2/GF and (b) $\text{MoS}_{2-x}\text{Se}_x/\text{GF}$. (c) XRD spectra and (d) Raman spectra of MoS_2/GF and $\text{MoS}_{2-x}\text{Se}_x/\text{GF}$.

Figure 2. TEM and HRTEM images of (a-c) MoS_2/GF and (d-f) $\text{MoS}_{2-x}\text{Se}_x/\text{GF}$. XPS spectra of $\text{MoS}_{2-x}\text{Se}_x/\text{GF}$: (g) Mo 3d and S 2s, (h) S 2p and Se 3p and (i) Se 3d.

Figure 3. Electrochemical properties of MoS_2/GF and $\text{MoS}_{2-x}\text{Se}_x/\text{GF}$ for SIB in the voltage range of 0.5–3.0 V vs. Na^+/Na . (a) Third-cycle CV comparison with a scan rate of 0.4 mV s^{-1} , (b) third galvanostatic discharge-charge profiles at a current density of 0.2 A g^{-1} and (c) Nyquist plots at 3.0 V after ten cycles (the resistance is simulated using the same equivalent circuit inseted in the figure). (d) Cycling stability at 0.2 A g^{-1} , (e) rate capability with different current densities and (f) normalized ratios about diffusion and capacitive current contribution.

Figure 4. In-situ Raman spectra of the $\text{MoS}_{2-x}\text{Se}_x/\text{GF}$ electrode at different cut-off potentials during (a) discharge and (b) charge processes (0.5-3.0 V). (c) Ex-situ XRD spectra indicating the recovery of 2D structure after one cycle. (d) First sodiation/desodiation processes at different stages. Similar data for MoS_2/GF electrode is shown in Supplementary Information.

Supporting information for

Intercalation Na-Ion Storage in Two-Dimensional $\text{MoS}_{2-x}\text{Se}_x$ and Capacity Enhancement by Selenium Substitution

Figure S1. SEM images of graphene foam in low (a) and high (b) resolution.

Figure S2. The image of $\text{MoS}_{2-x}\text{Se}_x/\text{GF}$ in low magnification.

Figure S3. XPS spectra survey of $\text{MoS}_{2-x}\text{Se}_x/\text{GF}$.

Figure S4. XPS spectra of MoS_2/GF : (a) survey, (b) Mo 3d and (c) S 2p.

Figure S5. (a) Element mapping images of Mo, S and Se. (b) EDX spectrum of $\text{MoS}_{2-x}\text{Se}_x/\text{GF}$ electrode.

Figure S6. CV curves with a scan rate of 0.2 mV s^{-1} of (a) MoS₂/GF and (b) MoS_{2-x}Se_x/GF electrodes and their first three discharge and charge profiles at a current density of 0.2 A g^{-1} in (c) and (d).

Figure S7. Cycle stability of graphene foam at 0.2 A g^{-1} within the potential range of 0.5-3.0 V.

Figure S8 (a) Cycling stability of $\text{MoS}_{2-x}\text{Se}_x$ at 0.2 A g^{-1} for 300 cycles within the potential range of 0.01-3.0 V vs. Na^+/Na . (b) Morphology of $\text{MoS}_{2-x}\text{Se}_x/\text{GF}$ electrode after 300 cycles at 0.2 A g^{-1} with low and high (insert) resolution.

Figure S9. Morphologies of (a) MoS_2/GF and (b) $\text{MoS}_{2-x}\text{Se}_x/\text{GF}$ electrodes after 500 cycles at 0.2 A g^{-1} with low and high (insert) resolution.

Figure S10. Quantitative analysis of sodium storage behavior of MoS_{2-x}Se_x/GF electrode. (a) CV curves at different scan rates. (b) Relationship between logarithm redox peak current and logarithm scan rate. (c) Diffusion current contribution (blue area) and capacitive current contribution (red area) at 0.4 mV s⁻¹. (d) Normalized current contribution ratios of diffusion and capacitive parts at different scan rates.

Figure S11. Quantitative analysis of sodium storage behavior of MoS₂/GF electrode. (a) CV curves at different scan rates. (b) Relationship between logarithm redox peak current and logarithm scan rate. (c) Diffusion current contribution (blue area) and capacitive current contribution (red area) at 0.4 mV s⁻¹. (d) Normalized current contribution ratios of diffusion and capacitive parts at different scan rates.

Figure S12. In-situ Raman spectra of the MoS₂/GF electrode at different cut-off voltages during (a) discharge and (b) charge processes (0.01V-3.0 V) (c) Ex-situ XRD patterns of MoS₂/GF electrode at different stages.