Edge-enriched MoS₂ for kinetics-enhanced potassium storage

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ABSTRACT

Potassium-ion batteries (PIBs) hold great promise as alternatives to lithium ion batteries in post-lithium age, while face challenges of slow reaction kinetics induced by the inherent characteristics of large-size K⁺. We herein show that creating sufficient exposed edges in MoS₂ via constructing ordered mesoporous architecture greatly favors for improved kinetics as well as increased reactive sites for K storage. The engineered MoS₂ with edge-enriched planes (EE-MoS₂) is featured by three-dimensional bicontinuous frameworks with ordered mesopores of ~ 5.0 nm surrounded by thin wall of ~ 9.0 nm. Importantly, EE-MoS₂ permits exposure of enormous edge planes at pore walls, renders its intrinsic layer spacing more accessible for K⁺ and accelerates conversion kinetics, thus realizing enhanced capacity and high rate capability. Impressively, EE-MoS₂ displays a high reversible charge capacity of 506 mAh·g⁻¹ at 0.05 A·g⁻¹, superior cycling capacities of 321 mAh·g⁻¹ at 1.0 A·g⁻¹ after 200 cycles and a capacity of 250 mAh·g⁻¹ at 2.0 A·g⁻¹, outperforming edge-deficient MoS₂ with nonporous bulk structure. This work enlightens the nanoarchitecture design with abundant edges for improving electrochemical properties and provides a paradigm for exploring high-performance PIBs.

KEYWORDS

molybdenum disulfide, enriched edges, potassium-ion batteries, kinetics

1 Introduction

As one of the most promising substitutes for commercial lithium-ion batteries (LIBs), potassium-ion batteries (PIBs) have captured increasing attention owing to natural abundance of potassium in contrast to lithium (17,000 vs. 20 ppm in the earth crust) [1]. Additionally, an intrinsic merit lies in that the redox potential of K⁺/K (−2.93 V vs. standard hydrogen electrode, E°) is quite close to that of Li⁺/Li (−3.04 V vs. E°), endowing PIBs with a high working voltage and energy density analogue to LIBs [2–5]. Nonetheless, the large radius of K⁺ (1.38 Å), approximately twice as that of Li⁺ (0.76 Å), undoubtedly retards “rocking chair” chemistry kinetics and induces acute volume expansion of electrode [6–9], which renders the promising PIBs into a dilemma. Hence, resolving the above-mentioned problems is crucial but challenging for the further development of PIBs.

Recent years have witnessed the enormous endeavors devoted to exploring high-performance anodes for PIBs. Given the low cost and easy availability, carbon materials have been investigated, however, their theoretical specific capacity (278 mAh·g⁻¹) remains unsatisfactory according to the formation of one-stage KC₈ in graphite structure via the intercalation chemistry [10–12]. In contrast, materials involved in the conversion or alloying chemistry for K⁺ storage are anticipated to provide much higher capacity, such as transition metal dichalcogenides (TMDs) [13, 14] and phosphides (TMPs) [15, 16]. TMDs have been receiving extensive attention owing to their potential advantages of layered structures with large interlayer spacing, which is favorable for ions diffusion and conversion kinetics [17]. However, a vast

number of layers with compact stacking by van der Waals interactions undoubtedly pose limitations to the efficient utilization of TMDs in micrometer size, especially at high rate operations for electrochemical energy storage. To make full utilization of interlayer space in TMDs, exposing more sites/edges is a promising way, including (1) constructing TMDs nanostructures like hollow tubes [18], microspheres [19] and yolk-shell structure [12] and (2) further expanding the interlayer spacing via intercalation technology, such as increasing the interspace of MoS₂ from 0.64 to 0.92 and 1.085 nm [20, 21]. However, large gaps still exist between the achieved results and their theoretical capacity (e.g., 670 mAh·g⁻¹ for MoS₂). For instance, MoS₂@CT with enlarged layer spacing of 1.085 nm exhibited a capacity of only 232 mAh·g⁻¹ at 1.0 A·g⁻¹ [20]. Even with addition of conductive carbon, the performance is still limited to a capacity of 131 mAh·g⁻¹ at 2.0 A·g⁻¹ for MoS₂/N-doped-C [18]. Evidently, the above structure designs are still incapable of accomplishing the maximum utilization of laminar MoS₂ on account of inferior ion diffusion and limited active sites. Recently, the concept of edge engineering has been demonstrated to play a great role in boosting electrochemical activities, such as constraining Li dendrites [22], improving performance of aluminum batteries [23], Na/Li batteries [24] and Li-S batteries [25]. It could thus be envisioned while not yet explored that designing structures with highly exposed edges could resolve the sluggish kinetics and limited capacity caused by large-size K⁺, considering that plenty of edge planes could offer more easy access of K⁺ to promote ions diffusion and increase reactive sites in MoS₂. Therefore, elaborate engineering of MoS₂ with more exposed edge planes is highly

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promising to further facilitate the utilization of two-dimensional layered structure for boosting K storage capability.

Herein, we propose a strategy of constructing three-dimensional (3D) bicontinuous MoS₂ skeletons at mesoscale to expose enriched edges (EE-MoS₂) by template-assisted approach, which was found helpful to address the challenge of sluggish kinetics and limited active sites. Mesoscale MoS₂ skeletons with thickness about 9.0 nm, corresponding to ~ 15 layers theoretically, enable more edge planes such as (002) plane to expose as compared with edge-deficient MoS₂ (ED-MoS₂). Combined with regular mesopores of ~ 5 nm surrounded by mesoscale skeleton, these exposed edges planes at mesopore walls would provide great potential in enhancing kinetics and K⁺ storage capacity. As expected, the electrochemical performances reveal that the as-prepared EE-MoS₂ maintains a high stable capacity of 321 mAh·g⁻¹ that is twice as high as 145 mAh·g⁻¹ of ED-MoS₂ at 1.0 A·g⁻¹ after 200 cycles. The prominent capacity of 245 mAh·g⁻¹ (the 25th cycle for rate test) at higher rate of 2.0 A·g⁻¹ has also been achieved for EE-MoS₂, representing one of the best performances for TMDs-based materials for PIBs anode. Our finding suggests that fabricating edge-enriched planes may open a new avenue to obtain advanced electrochemical energy storage materials.

2 Results and discussion

Conceptually, by confining the MoS₂ skeleton at mesoscale, the number of stacked layers within skeleton will decrease considerably exposing more edge planes at the mesopore walls, thus enhancing kinetics by promoted K⁺ diffusion and offering more accessible active sites for conversion reaction, as illustrated in Fig. 1. In contrast, bulk and nonporous ED-MoS₂ in micrometers exhibit large extended sheets without mesoscale skeleton, indicative of limited edge planes/sites for facilitating K storage. According to this concept, we constructed EE-MoS₂ by hard template-assisted approach. The starting Mo compound, phosphomolybdic acid hydrate (H₃PO₄·12MoO₃, PMA), was exerted a smooth conversion into EE-MoS₂ via an initial impregnation into KIT-6, followed by calcination, sulfidation and the final template removal (Fig. S1 in the Electronic Supplementary Material (ESM)). As schematically depicted in Fig. 2(a), EE-MoS₂ has a 3D bicontinuous interconnected porous structure and the mesoscale skeleton is composed of the inherent laminar structure stacked by van der Waals interaction, thus exposing more edge planes at the mesopore walls, as shown in side view and top view. Scanning electron microscopy (SEM) image reveals the porous structure of EE-MoS₂, while ED-MoS₂ exists in the bulk particles (Fig. S2 in the ESM). The regular interlinked skeletons and periodic mesopores can be confirmed by transmission electron microscopy (TEM) image, in which stripe-like structures with space groups *P6mm* and *Ia3d* are present [26] (Fig. 2(b)), illustrating the porous ordered nano-architecture of EE-MoS₂. In a magnified TEM image (Fig. 2(c)), the thickness of interconnected skeletons (mainly composed of (002) plane) was measured to be about 9.0 nm, corresponding

Figure 1 The illustration of charge/discharge process of EE-MoS₂ and ED-MoS₂.

Figure 2 (a) Structural illustration. (b)–(d) TEM and HRTEM images. (e)–(g) HAADF image and its corresponding EDS mappings of Mo and S. (h) XRD pattern. (i) N₂ adsorption/desorption isotherms. (j) Pore size distribution of EE-MoS₂.

to only ~ 15 layers. The reduction of layers cuts down ions migration distance and exposes more edges, facilitating conversion kinetics and increasing reactive sites. And the size of mesopores surrounded by these skeletons was measured to be ~ 5.0 nm. In a high-resolution TEM (HRTEM) image (Fig. 2(d)), the crystalline lattices with spacings of 2.61 and 6.20 Å are indexed as (100) and (002) planes of MoS₂, respectively [27, 28]. As is observed from high-angle annular dark-field (HAADF) image and energy dispersive spectra (EDS) mappings, only Mo and S are uniformly distributed, demonstrating the phase purity with complete removal of the template (Figs. 2(e)–2(g)). The phase characteristics was furthermore evaluated by X-ray diffraction (XRD) pattern, which shows the main Bragg peaks at 14.4°, 32.7°, 39.5° and 58.3° (Fig. 2(h)), attributed to respective (002), (100), (103) and (110) planes of the hexagonal MoS₂ with the space group *P6₃/mmc* (194) (JPCDS No. 37-1492) [27, 29]. For the pore properties of EE-MoS₂, the sample bears a H1-type hysteresis loop ranging from 0.45 to 0.90 (*P/P*₀ value) assigned to the type IV isotherms via N₂ adsorption/desorption test (Fig. 2(i)), further corroborating the mesoporous characteristics of EE-MoS₂ [30]. The mesoporous feature endows EE-MoS₂ with a large Brunauer–Emmett–Teller (BET) surface area of 124 m²·g⁻¹ and average pore size is centered at ~ 4.8 nm (Table S1 in the ESM and Fig. 2(j)), consistent with the TEM result. To our best knowledge, EE-MoS₂ owns the highest BET surface area among the reported pure MoS₂. To exhibit the overwhelming superiority of EE-MoS₂ in K storage, ED-MoS₂ was also synthesized via the direct decomposition and subsequent sulfidation of PMA without template (Fig. S3 in the ESM), which exists in bulk form with nonporous structure and extended sheets in micrometer size range.

Cyclic voltammetry (CV) test was conducted to unravel K storage behaviors (Fig. S4 in the ESM). Two observable peaks at ~ 0.78 and ~ 0.45 V, in the first potassiation process, can be attributed to the irreversible reaction of solid electrolyte interphase (SEI) layer and the conversion from MoS₂ to Mo and K₂S [31]. During the depotassiation scan, the oxidation peak located at ~ 1.74 V corresponds to the transformation of reduced products back into MoS₂ [32]. The well overlapped CV

profiles of 2nd and 3rd cycles verify the prominent electrochemical reversibility.

Figure 3(a) describes the galvanostatic charge/discharge profiles of 3rd cycle at 0.1 A·g⁻¹ for MoS₂. EE-MoS₂ possesses a lower polarization voltage (e.g., 1.04 V) than ED-MoS₂ (e.g., 1.65 V), indicating that the plentiful edge planes decrease the polarization. Rate performance is an important index for evaluating reaction kinetics of electrode materials. As to EE-MoS₂, the average capacities of 484, 409, 393 and 342 mAh·g⁻¹ at stepwise current densities from 0.1 to 1.0 A·g⁻¹ were obtained, respectively (Fig. 3(b) and Fig. S5(a) in the ESM). Strikingly, the average capacity of 250 mAh·g⁻¹ is still achieved at a higher current density of 2.0 A·g⁻¹. And the capacity recovers completely when the current density switches back to 0.1 A·g⁻¹, even higher than its original level (e.g., 620 mAh·g⁻¹). In contrast, ED-MoS₂ displays lower capacities than EE-MoS₂ at various rates (Fig. 3(b) and Fig. S5(b) in the ESM). Figure 3(c) depicts the superior rate performance of EE-MoS₂ over previously reported TMDs and the other anode materials (Table S2 in the ESM). The rate performance of EE-MoS₂ exceeds the majority of TMDs, including MoS₂ [18, 20, 21, 31, 32], MoSe₂ [17, 33, 34], VSe₂ [35], NiS₂ [36], and even those composited with conductive carbons. Considering that the rate capability is governed by both electronic and ionic conductivity, the superior rate capability of EE-MoS₂ without compositing with carbon further highlights the importance of edge engineering for boosting K⁺ transport/diffusion. As for the cycling stability, the variations of discharge capacity of EE-MoS₂ and ED-MoS₂ are described in Fig. 3(d). Different from ED-MoS₂ with solid bulk particles, EE-MoS₂ undergoes a capacity increase in the first 100 cycles probably due to the activation process with electrolyte penetration into the interior of porous EE-MoS₂. The first-cycle discharge and charge capacities of 713 and 506 mAh·g⁻¹ were obtained at 0.05 A·g⁻¹, respectively, corresponding to an initial Coulombic efficiency (ICE) of 71.0% for EE-MoS₂ (Fig. S6(a) in the ESM). However, under the same conditions, ED-MoS₂ reveals a discharge capacity of 603 mAh·g⁻¹ with lower ICE of 55.3% (Fig. S6(b) in the ESM). Generally, increasing the surface

area will give rise to the irreversible electrolyte decomposition and thus a reduced ICE [37]. In our case, although EE-MoS₂ exhibits 31-time higher surface area than ED-MoS₂, its ICE is still much higher than that of edge-deficient one, manifesting the edges actually could mitigate the undesirable side reactions with more K⁺ participating in reversible storage. After the initial two cycles at 0.05 A·g⁻¹, the cells were further cycled at 1.0 A·g⁻¹, and a high and stable capacity of 321 mAh·g⁻¹ is retained after 200 cycles with Coulombic efficiency over 99% during the whole cycling, demonstrating the stability of such edge-enriched structures for reversible K storage. The capacity is 2.2 times as high as that of ED-MoS₂ with 145 mAh·g⁻¹ under the same conditions (Fig. S6(c) in the ESM). The prominent cycling stability and high capacity are also confirmed by well-overlapped charge/discharge curves of EE-MoS₂ at different cycles at 1.0 A·g⁻¹ (Fig. 3(e)). Such an enhancement on electrochemical performance could be originated from the prominent conversion activity promoted by the increased edge planes. As is depicted in Fig. 3(f) and Fig. S7 in the ESM, all the electrochemical impedance spectroscopy (EIS) plots are comprised of a deformed semicircle in high-medium frequency domain and an oblique line in low frequency region for both anodes [17]. The equivalent circuit models for EIS spectra are described in the inset. In fresh batteries, EE-MoS₂ possesses charge transfer resistance (R_{ct}) of ~ 6,700 Ohm, clearly lower than that (e.g., ~ 9,000 Ohm) of ED-MoS₂ (Fig. S7 in the ESM). More importantly, R_{ct} decreases to ~ 2,533 Ohm after 40th cycles for the edge-enriched one, whereas R_{ct} of the edge-deficient counterpart decreases to only ~ 4,093 Ohm (Table S3 in the ESM). And the R_{ct} value of EE-MoS₂ is also lower than that of some reported works (Table S4 in the ESM). These comparisons fully reveal that EE-MoS₂ has superior (de)potassiation kinetics over ED-MoS₂.

To figure out the boost of K storage capability in EE-MoS₂, galvanostatic intermittent titration technique (GITT) inspections were carried out to assess the thermodynamics and kinetics (Figs. 4(a) and 4(b), and Fig. S8 in the ESM). As is shown in Figs. 4(a) and 4(b), EE-MoS₂ displays a lower V_{gap} in contrast with

Figure 3 (a) The third galvanostatic charge/discharge profiles at 0.1 A·g⁻¹. (b) Rate performance and (d) long cycling test of EE-MoS₂ and ED-MoS₂ at 1.0 A·g⁻¹ (the initial two cycles were tested at 0.05 A·g⁻¹). (c) Comparison of the rate performance of EE-MoS₂ with other TMDs-based anode materials for PIBs reported previously. (e) Galvanostatic charge/discharge profiles of EE-MoS₂. (f) EIS of EE-MoS₂ and ED-MoS₂ after 40th cycles (inset: equivalent circuit simulation).

Figure 4 (a) and (b) GITT profiles for EE-MoS₂ and ED-MoS₂, respectively. (c) Ion diffusion coefficients calculated by GITT in charge/discharge processes. (d) CV curves at varying sweep rates. (e) The linear logarithm relationship between peak current and scan rates (inset: a summary of b values) of EE-MoS₂. (f) and (g) Capacitive and diffusion-dominated fractions at a scan rate of 0.3 mV·s⁻¹ for EE-MoS₂ and ED-MoS₂, respectively. (h) Diffusion-dominated contribution at various sweep rates of EE-MoS₂ and ED-MoS₂.

ED-MoS₂ within the equilibrium voltage hysteresis, indicative of a higher energy conversion efficiency and a lower polarization for EE-MoS₂ [38]. Moreover, the edge-enriched sample has lower reaction internal resistances than the edge-deficient one in both charge/discharge processes (Fig. S9 in the ESM), suggesting the faster reaction kinetics over that of ED-MoS₂ [39]. In addition, K⁺ diffusion coefficients ($\sim 10^{-11}$ cm²·s⁻¹) of EE-MoS₂ are higher than that ($\sim 10^{-13}$ cm²·s⁻¹) of the ED-MoS₂ counterpart (Fig. 4(c)). It is inferred that this remarkable promotion in diffusion coefficient stems from edge-enriched planes with easy access for K⁺. To further verify this point, rate-scan CV was carried out to calculate the diffusion-dominated contribution to capacity (Fig. 4(d) and Fig. S10(a) in the ESM). The *b* values of peaks A and C are 0.78 and 0.94 (calculated according to Eq. S(1) in the ESM) for EE-MoS₂ (Fig. 4(e)), respectively, suggesting the simultaneous presence of diffusion-dominated and capacitive contributions to capacity [40–42]. Whereas the *b* values of peaks A and C are 0.91 (diffusion-dominated and capacitive contributions) and 1.13 (only capacitive contribution) for ED-MoS₂ (Fig. S10(b) in the ESM), respectively. For EE-MoS₂, the diffusion-dominated fraction occupies 35.0% of its total capacity at 0.3 mV·s⁻¹, while the corresponding ratio for ED-MoS₂ is 25.7% (Figs. 4(f) and 4(g), calculated according to Eq. S(2) in the ESM). Further diffusion-dominated proportions at various rates were revealed in Fig. 4(h), and Figs. S11 and S12 in the ESM. Although they both display decreasing diffusion fractions with incremental scan rates, EE-MoS₂ exhibits higher diffusion-dominated portions in contrast to ED-MoS₂. This disparity is especially obvious at 0.9 mV·s⁻¹ and ED-MoS₂ lags by 19.3% behind EE-MoS₂. The promoted diffusion-dominated contribution is attributed to the facile electrolyte diffusion and through ordered mesostructure and easy access for K⁺ diffusion generated by thin skeletons with exposed edges. It is undeniable that the enormous edges with ordered mesostructure and high surface area improve diffusion-dominated contribution.

To further gain an insightful understanding, we conducted the theoretical calculations based on density functional theory (DFT) approach. As mentioned above, mesostructures endow EE-MoS₂ with sufficient exposed edges and large interior surface area in comparison with ED-MoS₂. Hence, we simplify EE-MoS₂ and ED-MoS₂ as monolayer and double-layer MoS₂ models, respectively (Fig. 5(a)). The adsorbed sites for K in MoS₂ are usually classified into two types: octahedral (O_h) and

tetrahedral (T_h) sites [36, 43]. For both ED-MoS₂ and EE-MoS₂, T_h adsorption energies of -1.72 and -2.31 eV are higher than those of O_h sites (e.g., -1.94 and -2.54 eV), respectively (Fig. 5(b)), meaning that T_h sites are unstable configuration and finally would transform into O_h types. Meanwhile, the adsorption energies of O_h and T_h sites in EE-MoS₂ are both lower than those of ED-MoS₂, implying the more favorable conversion reaction in EE-MoS₂. And the ions diffusion capability was further evaluated via diffusion energy barriers calculation. The realization of K⁺ migration demands the continuous O_h-T_h-O_h transformation. As for ED-MoS₂, the energy barrier is 0.29 eV, while EE-MoS₂ needs a lower activation energy of 0.19 eV to complete the transformation (Fig. 5(c)), which implies a faster K⁺ transfer in EE-MoS₂ consistent with GITT and rate-scan CV results. Such rapid K⁺ transfer and smooth conversion reaction are closely associated with much more edges in EE-MoS₂.

Ex-situ HRTEM was applied to investigate the possible (de)potassiation mechanism of MoS₂. Potassiated MoS₂ still exists in form of laminated structure with the expanding lattice fringe of (002) plane from 6.20 to 6.65 and 6.85 Å upon discharging to 0.78 V, indicative of the K⁺ insertion in MoS₂ (Fig. 6(a)). At the final discharge state (0.01 V), the layered structure disappears and Mo⁰ and K₂S emerge as evidenced by *d*(110) = 1.98 Å and *d*(220) = 2.81 Å, respectively, representing the occurrence of conversion reaction (Fig. 6(b)). Then when charged to 1.74 V, the laminar structure reappears with lattice spacing of 7.28 Å belonging to (002) plane, suggesting the incomplete extraction of K⁺ (Fig. 6(d)). At fully charged state (3.00 V), MoS₂ recovers its laminar crystalline structure with lattice fringe of 6.76 Å, illustrating the electrochemical reversibility of (de)potassiation (Fig. 6(e)). In *ex-situ* X-ray photoelectron spectroscopy (XPS) (Figs. 6(c) and 6(f)), despite the presence of Mo⁵⁺ and Mo⁴⁺ in the sample, Mo⁰ species is present at 0.01 V, consistent with *ex-situ* HRTEM results. At fully charged state (3.00 V), most of Mo species exist in Mo⁶⁺, Mo⁵⁺ and Mo⁴⁺ with little of Mo⁰, meaning the approximately complete removal of K⁺. In *in-situ* Raman spectra, peaks E_{2g} and A_{1g} vibrations located at ~ 380 and 410 cm⁻¹ are attributed to the in-plane and out-of-plane Mo-S phonon

Figure 5 (a) K adsorption models. (b) K adsorption energies. (c) Energy profiles along the diffusion path on the edge and in the bulk for MoS₂.

Figure 6 *Ex-situ* HRTEM images at varying charge/discharge state. (a) 0.78 V, (b) 0.01 V, (d) 1.74 V, (e) 3.00 V; *ex-situ* XPS spectra at (c) 0.01 V and (f) 3.00 V. (g) *In-situ* Raman spectra of EE-MoS₂ during cycling.

modes in MoS₂, respectively (Fig. 6(g)) [21, 31, 44]. With continuous discharging to 0.01 V, peaks E_{2g} and A_{1g} gradually fade and they reemerge in charge process, further corroborating the (de)potassiation mechanism of K storage in MoS₂.

3 Conclusions

In summary, we demonstrated the rational design of EE-MoS₂ for high capacity and fast K storage. The bicontinuous mesoscale skeletons with mesopores enable sufficient edge planes exposed at pore walls, thus rendering its intrinsic layer spacing readily accessed by K⁺ with enhanced diffusion-dominated process and accelerated conversion reaction, as verified in detail by GITT, rate-scan CV investigations and theoretical calculations. Consequently, EE-MoS₂ exhibits high capacity, remarkable rate performance and superior cycle stability, far exceeding its counterpart edge-deficient bulk MoS₂ and the majority of reported TMDs. The engineering and utilization of edge-enriched active sites in compact stacked laminar-structured materials could be valuable for various TMDs families in electrochemical energy storage in future.

4 Experimental

4.1 Materials synthesis

Typically, 2.0 g SiO₂ template (KIT-6, synthesized according to Ref. [30]) was added into ethanolic solution of phosphomolybdic acid (H₃PO₄·12MoO₃, PMA; 1.48 g PMA dissolved into 3 mL ethanol) and stirred for 1 h at room temperature. Subsequently, the obtained mixture was dried at room temperature overnight. Afterwards, the resulted sample was calcined at 450 °C for 5 h to crystallize MoO₃ and then sulfurized in a center of tubular furnace at 600 °C for 3 h with thiourea as a sulfur source laid at upstream in N₂ flow. Finally, EE-MoS₂ was achieved by etching the SiO₂ template with 4% HF aqueous solution overnight. For comparison, ED-MoS₂ was prepared via the direct decomposition of PMA and subsequent sulfidation under the same conditions as EE-MoS₂.

4.2 Characterization

The sample phase composition was determined by powder XRD on a Bruker D8 ADVANCE diffractometer (Cu K α radiation, 0.15406 nm). N₂ adsorption/desorption measurements were conducted on a Micromeritics ASAP 2020. The specific surface area and pore size distribution curve were obtained according to the BET theory and the Barret-Joyner-Halenda (BJH) method using the absorption data. And the average pore size was calculated by BJH adsorption (4V/A) approach. TEM investigation was carried on a JEOL JEM-2100F. XPS data were collected on a Kratos (Shimadzu, Axis Suprato) spectrometer to characterize the surface chemistry state. *In-situ* Raman spectra data were collected on a Renishaw Invia RM200 (London, UK) combined with CV test at a scan rate of 1 mV·s⁻¹ on a CHI 660E electrochemical workstation (Shanghai Chenhua, China).

4.3 Electrochemical measurements

The half-cell electrochemical tests were conducted in 2032-type coin cells with metal K plate as the counter electrode and with 1 M potassium bis(fluorosulfonyl)amide (KFSI) in ethyl methyl carbonate (EMC) as electrolyte. The active material, Super P, carboxymethyl cellulose (CMC) and styrene-butadiene rubber (SBR) as binder in a weight ratio of 7:2:1 (CMC:SBR = 8:2) in deionized water was mixed into slurry and coated on copper foil. The coated foil was dried in a vacuum oven at 80 °C

for 8 h and then cut into round electrode in diameter of 10 mm. The total loading amount of each electrode is ~ 1.2 mg·cm⁻². The cells were assembled in an Ar-filled glovebox with oxygen and moisture concentrations kept below 0.1 ppm. Land CT 2001A battery testing system (Land, China) was employed to conduct galvanostatic discharge/charge tests ranging from 0.01 to 3.00 V versus K/K⁺ at room temperature. A CHI 660E electrochemical workstation (Shanghai Chenhua, China) was used to carry out CV and EIS measurements within a frequency range of 100 kHz–0.01 Hz. A current pulse of 50 mA·g⁻¹ for 1 h followed by relaxation for 4 h was exerted to complete GITT analysis.

4.4 Computational calculation methods

The theoretical calculations were employed to depict K⁺ migration in MoS₂ based on DFT. Vienna *ab-initio* simulation package (VASP) was employed to conduct all calculations with given pseudopotential according to the projector-augmented wave (PAW) and the Perdew-Burke-Ernzerhof (PBE) method. Moreover, the cut-off energy was set to 400 eV and the Brillouin zone was described with a 4×4×2 Γ -centered k-mesh for 3×3×1 supercell. The optimizations of all structures were terminated until the self-consistent force less than 10⁻³ eV·Å⁻¹ and the energy between two consecutive steps less than 10⁻⁶ eV. And the barrier energy of K⁺ migration was calculated utilizing the climbing nudged elastic band (CI-NEB) method. In our calculation, the adsorption energy was calculated from the equation: $E_{\text{ads}} = E_{\text{total}} - E_{\text{MoS}_2} - E_{\text{K}}$, where E_{total} is the total energy of MoS₂ with K atom absorbed structure, E_{MoS_2} and E_{K} is the total energy of MoS₂ structure and K⁺, respectively.

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