



Electrochemical lithium storage performance of three-dimensional foam-like biocarbon/MoS₂ composites

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Abstract: Molybdenum disulfide (MoS₂) was loaded on biocarbon using waste camellia dregs (CDs) as the carbon source, which was further coated with dopamine hydrochloride to construct biocarbon/MoS₂ electrode composites. The electrochemical lithium storage performance of the composites with different MoS₂ contents was investigated. SEM results demonstrated that the composite had a three-dimensional foam-like structure with MoS₂ as the interlayer. XRD and HRTEM tests revealed that MoS₂ interlayer spacing in the composite was expanded. XPS analysis showed that new Mo—N bonds were formed in the active material. The electrochemical tests showed that the composite with a MoS₂ content of 63% had a high initial specific capacity of 1434 mA·h/g at a current density of 100 mA/g. After a long cycle at a high current, it also showed good cycling stability and the capacity retention was nearly 100%. In addition, it had good lithium ion deintercalation ability in the electrochemical kinetics test.

Key words: electrochemical lithium storage performance; lithium-ion batteries; camellia dregs; MoS₂; composites; pseudocapacity; anode

1 Introduction

Advances in energy storage technology are critical to the current and future sustainable and renewable energy supply and demand. As one of the most advanced electrochemical energy storage devices, lithium-ion batteries (LIBs) have been widely used in portable electronic devices such as computer and smartphones and electronic vehicle [1–3]. To date, graphite-based anode material for LIBs suffers from a relatively low theoretical value of specific capacity of 372 mA·h/g [4], which limits the electrochemical performance of rechargeable LIBs.

MoS₂, as one of the most attractive 2D transition-metal disulfides, has been intensively studied in the renewable energy related fields due to its unique layered structure and fascinating

properties [5,6]. It has a graphene-like lamellar structure, in which the inter-lamellar space between stacked atom layers (S—Mo—S) is regulated by weak van der Waals forces and its internal structure is more receptive to Li⁺ ions [7]. When MoS₂-based composite is used as anode material for LIBs, it can reach a theoretical capacity up to 670 mA·h/g [8]. However, the electrochemical properties of pure MoS₂-based materials are often critically impeded by their poor electrical conductivity, which is detrimental to the utilization and capacity retention of the active electrode materials [9].

Driven by the trend toward environmental protection, low cost, and renewable energy, biomass materials as the renewable natural resources are expected to flourish as the promising material scaffolds [10]. The special structures and rich surface properties of biomass materials will be highly beneficial to electrochemical reactions [11],

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which can deliver more active sites, high surface area, hierarchical porosity, high electronic conductivity, and abundant functional groups. These merits are favorable for the transport and diffusion of ions, thereby improving the charge storage capacity [12]. Inspired by the merits of MoS_2 and biomass-derived carbon materials, herein, we introduced camellia dregs (CDs) to rationally design and synthesize CDs/ MoS_2 anode materials with unique structure and high conductivity. The effects of MoS_2 content on the microstructures and electrochemical properties were also evaluated.

2 Experimental

2.1 Materials synthesis

2.1.1 Synthesis of CDs/ MoS_2 -I composite

CDs/ MoS_2 composites were synthesized by hydrothermal and heat treatments. The synthesis process is as follows: 0.3 g of Na_2MoO_4 and 0.5 g of *L*-cysteine were dissolved in 70 mL of deionized water and stirred for 30 min to form a yellow solution. Then, 0.5 g of CDs powder crushed by a planetary miller was dispersed into the yellow solution and stirred continuously at room temperature for about 30 min. After that, the solution was transferred into a 100 mL Teflon-lined stainless steel autoclave, sealed and kept at 200 °C for 24 h. After cooling to room temperature, the product was collected by filtration and washed with deionized water. After being dried at 80 °C for 12 h, the as-obtained products (0.3 g) were added to 0.5% dopamine hydrochloride solution and vigorously stirred for 30 min. The mixture was then transferred into a 100 mL Teflon-lined stainless steel autoclave, and kept at 80 °C for another 24 h. The final precipitate was collected by centrifugation and dried at 80 °C for 12 h. Finally, the powder was annealed at 600 °C for 2 h in a tubular furnace at a heating rate of 2 °C/min under Ar atmosphere. The CDs/ MoS_2 -II and CDs/ MoS_2 -III composites were synthesized by the same process, excepting for the change of the amount of CDs powder.

2.1.2 Synthesis of MoS_2

Na_2MoO_4 and *L*-cysteine were dispersed in deionized water and transferred into Teflon-lined stainless steel autoclave. After keeping at 200 °C for 24 h, the product was washed and dried and then annealed at 600 °C for 2 h in a tubular furnace.

2.1.3 Synthesis of CDs

CDs were prepared using the same procedure as that for MoS_2 .

2.2 Material characterization

The crystalline phases of samples were identified by powder X-ray diffractometry (XRD, Bruker D8 Advance with Cu K_α radiation, Japan). Raman measurement and thermogravimetric analysis (TGA) were performed using a laser Raman spectrometer (Renishaw Invia-reflex) and a thermogravimetric analyzer (Netzsch STA 409PC system), respectively. The nitrogen adsorption-desorption behaviors and pore size distributions were analyzed using a Micromeritics TriStar II 3fle analyzer. The surface properties of the sample were measured by X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, Thermo Fisher Scientific, America). The morphology of the synthesized CDs/ MoS_2 composites was observed by scanning electron microscopy (SEM, S-4800, Hitachi, Japan). The microstructure of the composites was further characterized by using transmission electron microscopy (TEM, FEI-F20, America).

2.3 Electrochemical measurements

The anode electrodes were fabricated by mixing active materials, super carbon black and polymer binder (polyvinylidene fluoride (PVDF)) at a mass ratio of 7:2:1. Then, the mixture was dissolved in *N*-methyl pyrrolidinone (NMP) and magnetically stirred for 24 h. Subsequently, the obtained slurries were coated on Cu foils followed by vacuum drying at 60 °C for 6 h. The copper foils were punched into a wafer and dried again. CR2032-type coin cells were assembled for tests, with lithium foil as the counter and reference electrodes and the electrolyte was ethylene carbonate and ethyl methyl carbonate with a volume ratio of 1:1. The electrochemical measurements were performed on a Land CT2001A system (Wuhan, China) at room temperature. The mass loading of active materials was about 0.89 mg/cm^2 . The current density and capacity were calculated based on the CDs/ MoS_2 composites. Cyclic voltammetry (CV) measurements were carried out on a CHI660e electrochemical workstation (Shanghai, China) in a voltage range of 0.01–3.0 V. The electrochemical impedance spectroscopy (EIS) was recorded in the frequency range from 100 kHz to 0.01 Hz.

3 Results and discussion

The synthetic route of the CDs/MoS₂ composites is illustrated in Fig. 1, and the detailed steps of the synthesis are described in the Section 2.

The morphology and structure of the as-prepared materials were investigated by SEM, TEM, and HRTEM measurements. Figures 2(a) and (b) show SEM images of the CDs/MoS₂-I composite. Interestingly, CDs/MoS₂ exhibits 3D foam-like structure with MoS₂ nanoflowers as the interlayer. This foam-like structure can provide very short Li-ion diffusion path length and afford large available active sites. The TEM and HRTEM images reveal that the curved MoS₂ nanosheets are wrapped by a thin carbon layer (Figs. 2(c)) and (d)). Additionally, the interlayer spacing (d) between adjacent MoS₂ monolayer for CDs/MoS₂-I sample is 0.96 nm, which is larger than that of pure MoS₂ (0.62 nm) [13]. The enlargement of MoS₂ layer spacing in the composite is due to the incorporation of carbon layer originated from CDs, which may cause volume expansion and reduce stacking and agglomeration of MoS₂. The elemental distributions

throughout the CDs/MoS₂-I composite by EDS mapping are shown in Figs. 2(e₁–e₅). It is observed that C, S, Mo, and N elements are distributed uniformly on the composite surface.

In order to detect the phase of the products, powder X-ray diffraction (XRD) analysis was conducted. The detailed XRD patterns of CDs, MoS₂ and CDs/MoS₂ composites are shown in Fig. 3. It is clearly visible that no extra peaks are observed on the CDs except for the broad peak ($2\theta=22.6^\circ$), suggesting that the substrate is amorphous carbon. For pure MoS₂, the diffraction peaks at 2θ around 14.3° , 32.7° , 39.5° and 58.3° can be indexed to the (002), (100), (103) and (110) crystal planes of 2H-MoS₂ (JCPDS No. 37-1492), respectively. Accordingly, the (002) plane of MoS₂ has a d -spacing of 6.2 Å. For CDs/MoS₂ composites, the broad (002) peak of the CDs is not observed, implying a highly dispersed state of carbon in the composites, which can promote the electron transfer. Meanwhile, the peak intensity at 2θ of 14.3° becomes weak and two new peaks appear at 2θ of 8.8° and 17.5° . A similar phenomenon appeared in previous report [14]. A lower angle in the CDs/MoS₂ corresponds to a large interlayer spacing

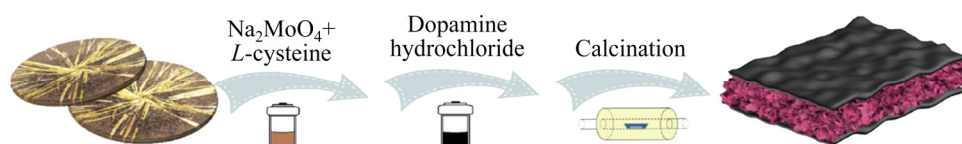


Fig. 1 Schematic illustration of synthesis of CDs/MoS₂ composites

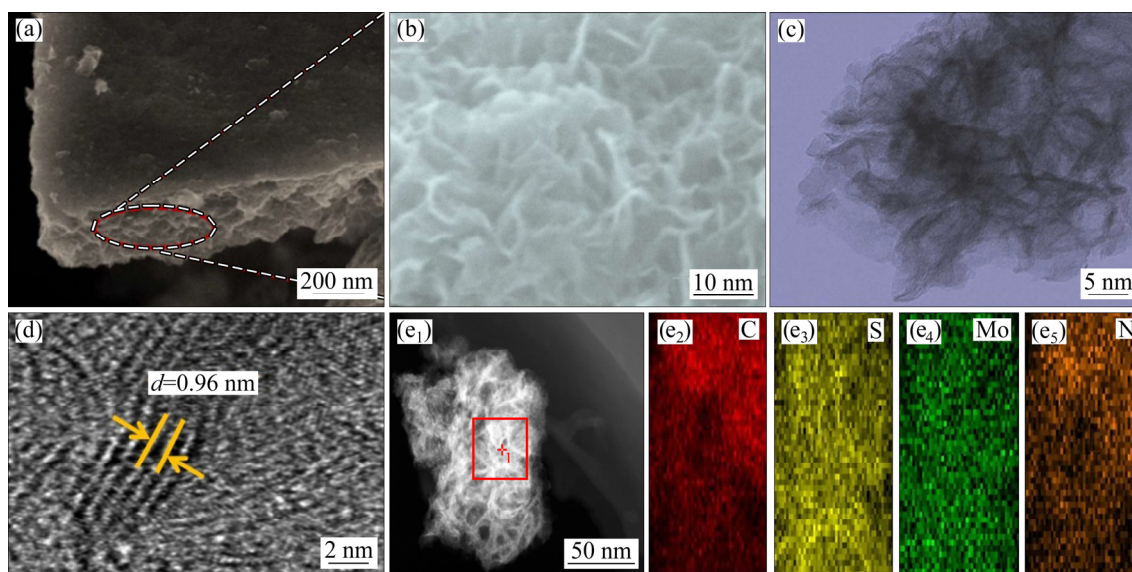


Fig. 2 SEM (a, b), TEM (c), HRTEM (d) images and EDS elemental mappings (e₁–e₅) of C, S, Mo and N of CDs/MoS₂-I composite

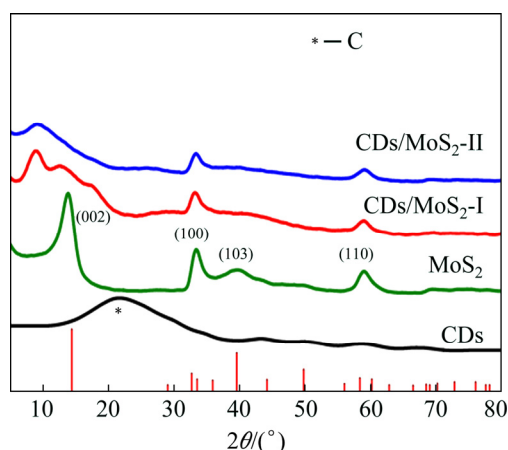


Fig. 3 XRD patterns of CDs, MoS₂ and CDs/MoS₂ composites

(from 0.62 to 0.98 nm), which could be ascribed to the presence of oxygen inherited from biomass precursor in MoS₂ [15]. The interlayer spacing is in agreement with the crystal lattice fringes from HRTEM (Fig. 2(d)). Notably, the expansion of the *d*-spacing (9.8 Å) can accelerate the kinetic process of Li⁺ intercalation/deintercalation and reduce the volume change during this process.

To further investigate the structural characteristics of CDs, pure MoS₂ and CDs/MoS₂ composites, the Raman spectra of the samples were measured from 300 to 2000 cm⁻¹ (Fig. 4). CDs and CDs/MoS₂ composites have identical peaks between 1200 and 1800 cm⁻¹. The two main peaks at 1362 and 1589 cm⁻¹ are typical D and G bands of carbon materials, respectively. The intensity ratio of the D band and G band (*I_D*/*I_G*) can be used to reflect the graphitization degree in carbon materials. The *I_D*/*I_G* ratios in CDs/MoS₂-I, CDs/MoS₂-II and CDs/MoS₂-III composites are 0.92, 0.90, and 0.88, respectively, which are higher than that of CDs (0.79). This indicates that the formation of MoS₂ layers on CDs can promote the disorder of carbon structure in the composite materials. CDs/MoS₂ composites show two peaks similar to the pure MoS₂ at around 379 and 402 cm⁻¹ in the low wavenumber region, which can be assigned to *E*_{2g}¹ and *A*_{1g} modes of 2H-MoS₂, respectively [15]. The vibrational peak for *E*_{2g}¹ is related to the planer vibration, whereas the *A*_{1g} peak indicates the lattice expansion along the *c*-axis vibration along the out-of-plane direction of the sulfides [16].

The thermogravimetric analysis (TGA) was utilized to estimate the mass fraction of MoS₂ in the

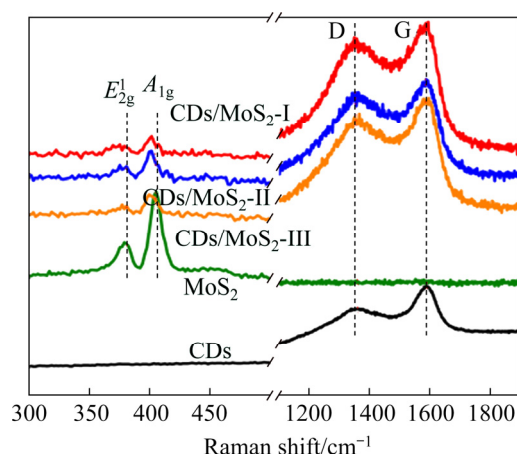


Fig. 4 Raman spectra of CDs, MoS₂ and CDs/MoS₂ composites

CDs/MoS₂ composites. In the case of CDs/MoS₂ composites, the mass loss is attributed to the conversion of MoS₂ to MoO₃ and combustion of carbon in air. According to the TGA results, the mass fractions of MoS₂ in the CDs/MoS₂-I, CDs/MoS₂-II and CDs/MoS₂-III composites are determined to be 63%, 51% and 53%, respectively (Fig. 5).

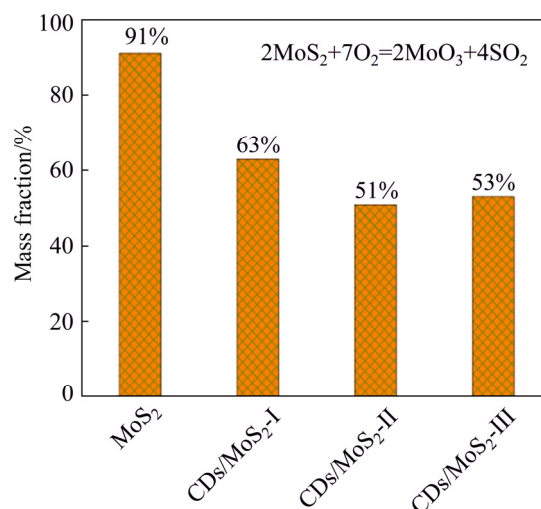


Fig. 5 Mass fractions of MoS₂ in CDs/MoS₂ composites

XPS measurements were further performed to investigate the valence states of elements by determining the corresponding binding energies. Figure 6 shows the high-resolution XPS spectra of Mo 3d and N 1s. In Fig. 6(a), the binding energies of Mo 3d_{3/2} and Mo 3d_{5/2} are observed at 232.9 and 229.7 eV, respectively, corresponding to Mo⁴⁺ in the 2H-MoS₂ [17]. Additionally, two small peaks at 226.9 and 236.2 eV could be assigned to S 2s and Mo⁶⁺ species, respectively. The existence of Mo⁶⁺

may be due to the insertion of oxygen into MoS₂ to form MoO₃. Figure 6(b) displays the XPS spectrum of N 1s. The peak can be deconvoluted into four sub-peaks at 398.8 eV (pyridinic—N), 400.6 eV (pyrrolic—N), 401.9 eV (graphitic—N), and 395.6 eV (Mo—N bonds). The peak located at 395.6 eV can be ascribed to Mo—N bonds [18,19]. The formation of Mo—N bonds can induce the defects of adjacent C atoms and provide a number of active sites. Meanwhile, various chemical states of N have also positive effect on offering high electrical conductivity and active sites, which is conducive to enhance the electrochemical performance of LIBs [20].

The CDs/MoS₂ composites were used as LIBs anode materials. Cyclic voltammetry (CV) curves of CDs/MoS₂-I electrode were tested to evaluate the Li-ion reaction behavior. Figure 7(a) records the first, third, fourth and fifth cycles in the voltage range of 3–0.01 V at a scan rate of 0.2 mV/s. In the first discharge process, the broad shoulder starting from 1.25 to 0.5 V is observed, which corresponds to the formation of Li_xMoS₂ caused by the intercalation of Li⁺ into the interlayer spacing

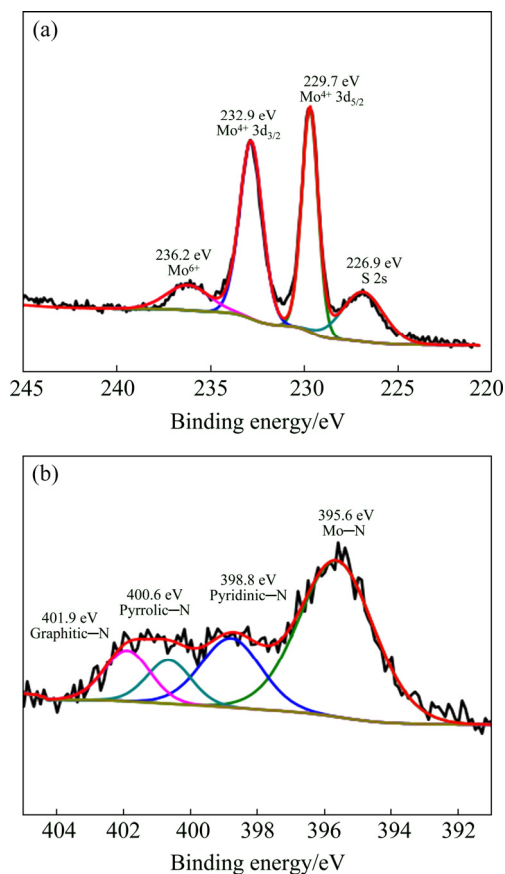


Fig. 6 XPS spectra of Mo 3d (a) and N 1s (b) of CDs/MoS₂-I composite

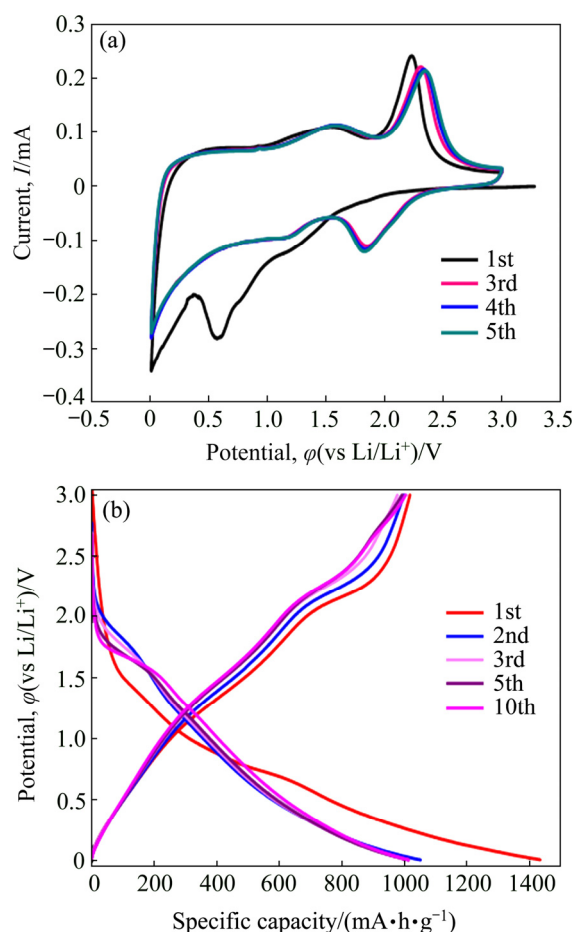
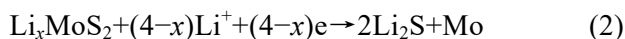
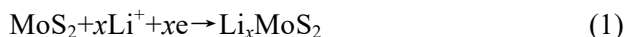
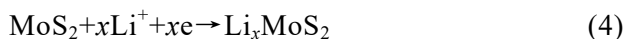


Fig. 7 Electrochemical performance of CDs/MoS₂-I composite: (a) CV curves at scan rate of 0.2 mV/s; (b) Galvanostatic discharge-charge profiles at 100 mA/g

between the Mo—S layer [21]. The peak at around 0.5 V originates from the decomposition of Li_xMoS₂ to metallic Mo and lithium sulfides, as well as the concomitant generation of solid electrolyte interface (SEI) film [22]. The reactions involved in the above process can be summarized as Eqs. (1) and (2):



In the subsequent discharge cycles, the voltage profiles become different from those of the first discharge. Two obvious reduction peaks at 1.8 and 1.1 V clearly emerge, which can be ascribed to a multi-step Li⁺ insertion mechanism [23]. In the anodic scan, the weak oxidation peak at 1.7 V and the dominant peak at 2.3 V correspond to the possible partial oxidation of Mo into MoS₂ and the oxidation of Li₂S into sulfur [24,25]. The reactions can be expressed in the following equations:



Additionally, it is worth mentioning that the CV curves after the first cycle nearly overlap with each other, suggesting the excellent cycling stability. The charge/discharge curves of the CDs/MoS₂-I electrode at 100 mA/g are shown in Fig. 7(b). Two pairs of plateaus can be observed at 2.3/1.8 and 1.7/1.1 V, respectively. As exhibited in Fig. 7(b), CDs/MoS₂-I delivers the initial discharge and charge specific capacities of 1434 and 1018 mA·h/g, respectively. The initial coulombic efficiency (CE) is 71% and the irreversible capacity is mainly ascribed to the formation of SEI film and electrolyte decomposition [26]. The CE then reaches nearly 100% from the second cycle, confirming the excellent reversibility of lithium ion insertion/extraction reactions in the CDs/MoS₂-I electrode.

We also studied the Li⁺ diffusion kinetics by analyzing the CV curves of CDs/MoS₂-I composite at various scan rates [27]. The CV curves at various scan rates (0.2–1 mV/s) display that the intensities of current peaks gradually increase with the increase of scan rate (Fig. 8(a)). In general, the current response (*I*) against scan rate (*v*) is dominated by Eqs. (5) and (6):

$$I = av^b \quad (5)$$

$$\lg I = \lg a + b \lg v \quad (6)$$

where *a* is a constant, *b* is determined by the relationship between the $\lg I$ and $\lg v$ [28–30]. Generally, a *b* value approaching 0.5 implies a diffusion-controlled battery-type behavior, while a *b* value of 1.0 indicates a capacitive behavior dominating the charge storage process. Figure 8(b) presents the *b* values at different oxidation and reduction states and the calculated *b* values for cathodic and anodic peaks are 0.844 and 0.726,

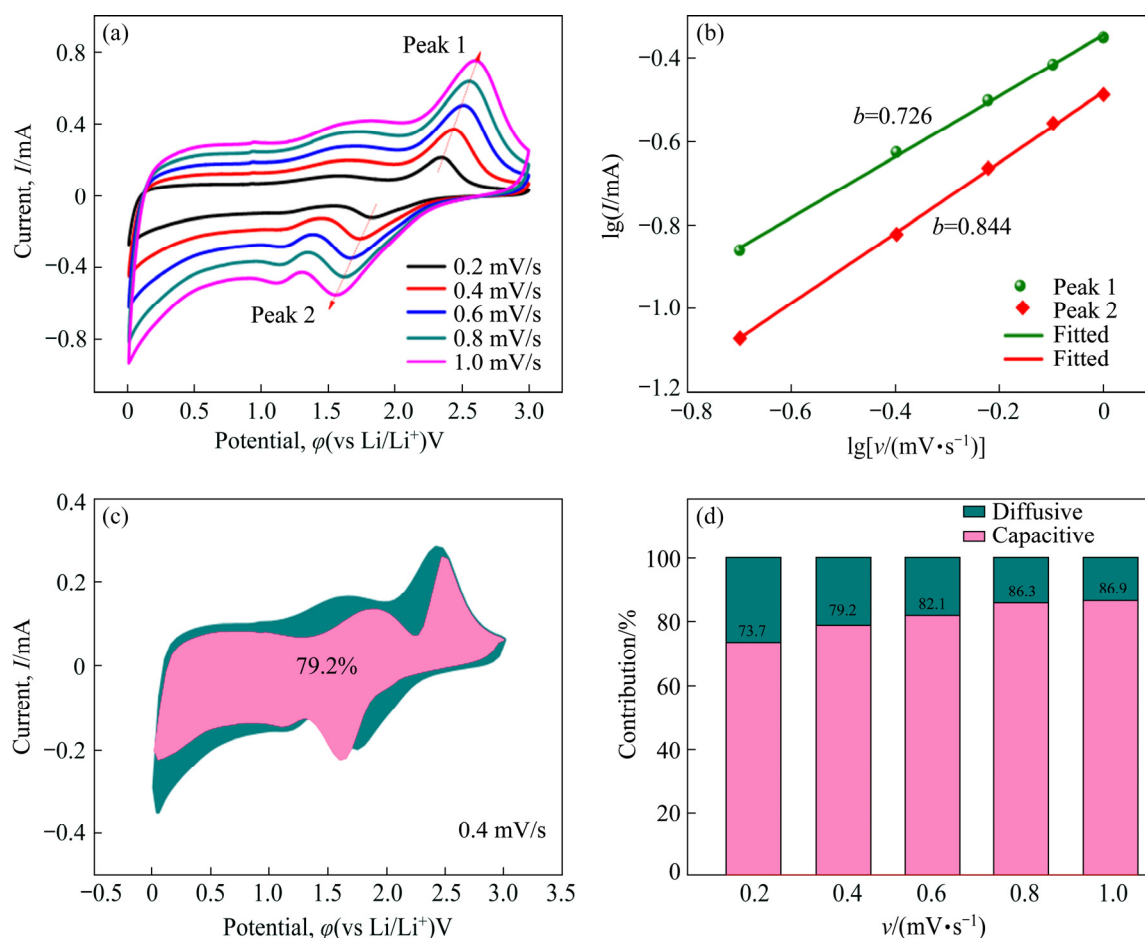


Fig. 8 CV profiles of CDs/MoS₂-I at various scan rates (a), determination of *b* values by plots of $\lg I$ versus $\lg v$ (b), capacitive contribution at scan rate of 0.4 mV/s (c) and contributions of capacitive and diffusion-controlled capacities at various scan rates (d)

respectively. This suggests that the dominant charge storage mechanism in the CDs/MoS₂-I electrode is capacitive-controlled behavior, corresponding to a fast Li-ion intercalation/deintercalation process [31]. The measured current response (I) at a fixed potential (φ) can be quantitatively separated into a diffusion ($k_2v^{1/2}$) and a capacitive contribution (k_1v), which can be expressed by Eqs. (7) and (8) [32,33]:

$$I(\varphi) = k_1v + k_2v^{1/2} \quad (7)$$

$$I(\varphi)/v^{1/2} = k_1v^{1/2} + k_2 \quad (8)$$

Figure 8(c) shows the capacitive contribution in the CDs/MoS₂-I electrode, which reaches 79.2% at a scan rate of 0.4 mV/s. The capacitive contribution gradually increases to 86.9% with the increasing sweep rate, as shown in Fig. 8(d). Such capacitive behavior is highly beneficial to the long-term cycling stability and high rate capacity.

Figure 9(a) shows the electrochemical cycling performance of all the samples. Evidently, the capacities of CDs/MoS₂ composites are much higher than those of MoS₂ and the CDs-derived carbon. It can be considered that the bare MoS₂ and the CDs are perfectly combined to form the CDs/MoS₂ composites, where a synergetic effect between MoS₂ and CDs allows an excellent performance of CDs/MoS₂ composites. Especially, the discharge capacity of CDs/MoS₂-I electrode can be maintained at around 1064 mA·h/g at 100 mA/g after 100 cycles, demonstrating a stable cycling performance. In contrast, the specific capacities of bare MoS₂ and the CDs are only 101 and 334 mA·h/g, respectively. The rate performance of CDs, MoS₂ and CDs/MoS₂ composite electrodes was further studied (Fig. 9(b)). The CDs delivers lower capacities of 334, 262, 213, 169 and 145 mA·h/g at 100, 200, 500, 1000 and 2000 mA/g, respectively. Pure MoS₂ electrode delivers a specific capacity of 750 mA·h/g (from the 5th cycle) at 100 mA/g, but its specific capacities decay rapidly with the increase of current densities. Notably, CDs/MoS₂ composites show superior rate capability. Especially, CDs/MoS₂-I electrode delivers average discharge capacities of 845, 712, 602, 494 and 357 mA·h/g at 100, 200, 500, 1000 and 2000 mA/g, respectively. After returning to low current rate of 100 mA/g, the capacity of CDs/MoS₂-I electrode can be recovered to 779 mA·h/g.

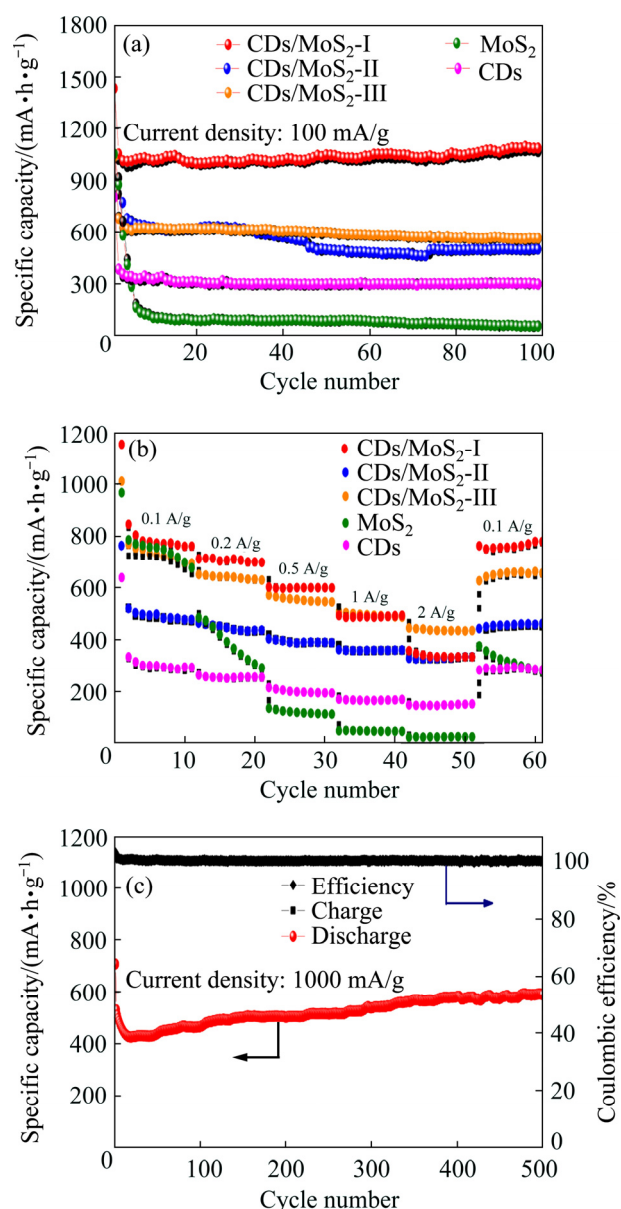


Fig. 9 Cycling stability of CDs, MoS₂ and CDs/MoS₂ composites at 100 mA/g (a), rate performance (b) and cycling stability at 1000 mA/g and coulombic efficiency (c) of CDs/MoS₂-I composite

From Fig. 9(c), we can see that CDs/MoS₂-I is robust enough to achieve a long cycle life at a high current density of 1000 mA/g, with a reversible capacity of ~600 mA·h/g after 500 cycles. Most strikingly, the CE is well maintained at nearly 100% throughout the cycles after the initial fluctuations, indicating a good reversibility.

EIS analysis was carried out to gain a better understanding of the electrochemical performance. Figure 10 exhibits the Nyquist plots, which consist of a semicircle in the high frequency region and a line in the relatively low frequency region. The

diameter of the semicircle denotes the SEI film resistance (R_{SEI}) and charge-transfer resistance (R_{ct}) at the interface, and an oblique straight line represents the Warburg impedance (Z_w) and R_s is the internal resistance [34]. The equivalent circuit was inset of Fig. 10. The R_{ct} of the CDs/MoS₂-I electrode (31 Ω) is much lower than that of the CDs (50 Ω), MoS₂ (113 Ω), CDs/MoS₂-II (46 Ω) and CDs/MoS₂-III (45 Ω), revealing the lowest charge transfer resistance, which is favorable for enhancing the capacity and cycling stability.

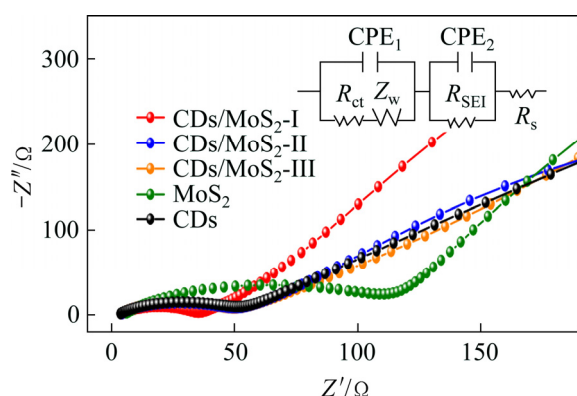


Fig. 10 Nyquist plots and equivalent circuit (inset) used for EIS analysis of all electrodes obtained after 20 cycles at 100 mA/g

The superior electrochemical performance of the CDs/MoS₂-I anode is attributed to its unique structure. Specifically, the three-dimensional foam-like structure with expanded layer spacing allows the electrolyte to enter the interior of the electrode and expose the edges of the layer for the convenient insertion of Li⁺. As illustrated in Fig. 11, when Li⁺ enters into MoS₂ monolayer, the electrode will undergo redox reaction. The expanded interlayer of MoS₂ can provide short Li-ion diffusion path length and accommodate the volume expansion. Furthermore, CDs as the carbon sources contain small amount of nitrogen source. When they are hydrothermally hybridized with MoS₂, Mo—N bond will be formed. The introduction of polydopamine can not only increase the amount of Mo—N bond, but also stabilize the structure of the composite. The presence of the Mo—N bond can cause the defects to produce more active sites. The synergistic effect of these multiple advantages renders the CDs/MoS₂-I anode with excellent electrochemical lithium-ion storage performance.

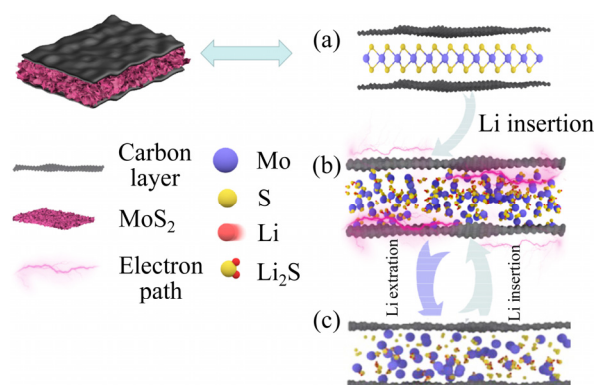


Fig. 11 Schematic illustration of fast charge storage of CDs/MoS₂ composites

4 Conclusions

(1) 3D foam-like CDs/MoS₂ composites were successfully synthesized by simple hydrothermal and carbonization.

(2) XRD results at a low 2θ value revealed that the interlayer spacing of MoS₂ increased, which can reduce the stacking and agglomeration of MoS₂. XPS evidenced nitrogen doping into the composite material to form a new Mo—N bond, which resulted in more active sites and increased the electrochemical activity.

(3) Compared with pure MoS₂ or CDs-derived carbon, the as-prepared CDs/MoS₂-I composite exhibited a high specific capacity of 1064 mA·h/g at 100 mA/g after 100 cycles and a good reversibility.

Acknowledgments

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三维泡沫状结构生物质碳/MoS₂ 复合材料的 电化学储锂性能

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摘 要:以废弃油茶籽粕作为碳源,将 MoS₂ 负载于生物质碳上,再涂覆聚多巴胺盐酸盐构建复合型生物质碳/MoS₂ 电极材料。研究不同 MoS₂ 含量复合电极材料的电化学储锂性能。SEM 观察结果表明,该复合材料具有以 MoS₂ 作为夹层的三维泡沫状结构。XRD 和 HRTEM 测试结果表明 MoS₂ 的层间距增大。XPS 分析结果显示,活性材料中已形成 Mo—N 键。电化学性能测试结果表明,MoS₂ 含量为 63% 的活性材料在 100 mA/g 电流密度下具有较高的初始比容量(1434 mA·h/g)。在大电流、长循环条件下此电极材料呈良好的循环稳定性,其容量保持率接近 100%,在电化学动力学过程中具有较好的锂离子脱嵌能力。

关键词: 电化学储锂性能; 锂离子电池; 油茶籽粕; 二硫化钼; 复合材料; 赝电容; 负极

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