Half and full cell researches of ternary MoS2/graphene/CNT aerogel compostie for enhanced lithium storage performances

Guanghui Yuan1a*, Rui Cao2b, Ye Chen1c, Xinyu Ge1d, Qiong Xu2e, Zhaozhe Wang3f

1Department of Chemistry and Chemical Engineering, Ankang Research Centre of New Nano-materials Science and Technology, Ankang University, Shaanxi Ankang 725000, China;
2Shaanxi Key Laboratory of Catalysis, School of Chemical & Environment Science, Shaanxi University of Technology, Hanzhong, Shaanxi 723001, China;
3Shaanxi Huaqin Power Technology Company Limited, Shaanxi Huayin Technology Company Limited, The National and Local Joint Engineering Research Center for Deep Processing of Vanadium Products, Shaanxi Ankang 725000, China

Abstract—Without using any templates, a ternary MoS2/graphene/carbon nanotubes (MoS2/GN/CNT) aerogel compostie is prepared by convenient hydrothermal synthesis method. The free-standing MoS2/GN/CNT aerogel can be cut directly as binder free electrodes in lithium-ion batteries. The MoS2/GN/CNT electrodes can hold as high as 695 and 579 mAh g⁻¹ discharge capacities after 200 cycles at 200 mA g⁻¹ in MoS2/GN/CNT//Li half cells and MoS2/GN/CNT//LiCoO2 full-cells, respectively. The strengthened electrochemical properties are owed by the thin GN/CNT layers and their jagged and wrinkled surfaces, which can enhance the composite conductivity and shorten the Li⁺ diffusion distance, as well as buffer the volume change of electrodes during the charge-discharge cycles.

1. Introduction
Nowadays, the increasing requirements for better energy storge batteries lead to the rapid development of more selective materials with outstanding capacities. Unfortunately, the existing anode materials, like graphite, can only supply the limited 372 mAh g⁻¹ theoretical discharge capacity. MoS2, one of the typical two-dimensional (2D) layered-structure compounds, has brought about widespread attention as electrode materials in lithium-ion batteries (LIBs) [1,2]. As a semiconductor material, MoS2 has low electrical and ionic conductivity. Adding to the huge electrode volume change, the pristine MoS2 electrode only show the inferior electrochemical performance like fast capacity fading, which greatly limited the practical application of MoS2 in LIBs [3,4]. In order to conquer aboved disadvantages, many researches have been focused to package MoS2 into different conductive networks such as carbon matrixes [5,6]. Despite the MoS2-carbon hybrids show promising electrochemical performance, there are many respects to be improved such as the complex synthesis pathways and the improvement space of lithium storage abilities. Most researches concentrate on various compositeMoS2-carbon powders. The binder-free composite and flexible electrodes of LIBs are focused on, aiming to power new applications[7,8]. Herein, a flexible free standing

*chem_yuan@163.com, b729953728@qq.com, c1191468128@qq.com, d2670005691@qq.com, e348184589@qq.com, f435219728@qq.com
MoS$_2$/graphene/carbon nanotubes (MoS$_2$/GN/CNT) aerogel composite is designed through hydrothermal method. Comparing to pristine MoS$_2$ and MoS$_2$/graphene (MoS$_2$/GN), the MoS$_2$/GN/CNT composite exhibits amazing lithium storage properties. Synergetic electrochemical effects of the content, structure and surface of the ternary MoS$_2$/GN/CNT composite is investigated in detail.

2. Methods and Materials

The graphene oxide (GO) sample is prepared through an optimized Hummers' method [9]. Carbon nanotubes (CNT) is ultrasonic treated at 70 °C for 1 hours in a concentrated H$_2$SO$_4$/HNO$_3$ (3:1 in volume) mixture and then washed by distilled (DI) water until neutral. MoS$_2$/GN/CNT composite is synthesized from the hydrothermal method. Typically, 3.420 g (NH$_2$)$_2$CS, 2.723 g Na$_2$MoO$_4$$\cdot$2H$_2$O, 0.240 g sodium dodecyl benzene sulfonate, 200 mg GO, 100 mg as-modified CNT and 20 mL ethanol are successively dissolved into 80 mL deionized water under ultasonic mixing for 2 hours to form a homogeneous solution. The solution is then heated at 220 °C for 20 hours in Teflon autoclaves. After cooled down naturally, the black cylinders in autoclaves are transferred and washed several times by ethanol and DI water. After vacuum freeze-dried for 4 hours, the MoS$_2$/GN/CNT aerogel are finally obtained. As a contrast, MoS$_2$/GN and MoS$_2$ samples are synthesized by similar method.

The samples are tested successively by X-ray diffraction (XRD), electron scanning microscopy (SEM) and X-ray energy dispersive spectrometer (EDS). Contents in the MoS$_2$/GN/CNT aerogel are measured using thermogravimetric analysis (TGA) under air atmosphere.

Electrochemical characterizations are carried out by coin-cells (CR2025) with lithium and commercial LiCoO$_2$ as counter electrodes, respectively. MoS$_2$/GN/CNT and MoS$_2$/GN working electrodes are pressed and cut the aerogels directly into 10 mm disks. Pristine MoS$_2$ working electrodes are prepared by mixing MoS$_2$, acetylene black and polyvinylidene fluoride (75:15:10 in weight) in 1-methyl-2-pyrrolidinone. Separator is the microporous polypropylene film. Electrolyte solution is the mixture of dimethyl carbonate, diethyl carbonate and ethylene carbonate (1:1:1 in volume) with 1.0 M LiPF$_6$ in. All cells are measured by LAND battery tester and CHI-660 workstation.

3. Results and Discussions

3.1. Structure and morphology characterization

Crystal structures of the synthesized samples are firstly characterized by XRD (Fig. 1a). The XRD pattern of GN sample has two peaks at 26.2° and 44.8°, corresponding to (002) and (100) carbon reflections. All patterns of MoS$_2$, MoS$_2$/GN aerogel and MoS$_2$/GN/CNT aerogel perfectly match the hexagonal MoS$_2$ (JCPDS 37-1492). In addition, both MoS$_2$/GN and MoS$_2$/GN/CNT composites display a diffraction peak at 26.2°, reflecting the good dispersion of GN in composites. No detectable peak of GO sample is observed in MoS$_2$/GN and MoS$_2$/GN/CNT XRD patterns, indicating that the initial graphene oxide is fully reduced into graphene during the experiment progress.

Fig. 1 (a)XRD patterns and (b)TGA curves of the prepared samples.
The MoS$_2$ contents in MoS$_2$/GN and MoS$_2$/GN/CNT composites are tested with 10 °C min$^{-1}$ heating rate by TGA curve under air atmosphere. As listed in Fig. 1b, the residue of MoS$_2$ sample is 82.0% after oxidation in air from ambient temperature to 700°C, because of the gradually conversion of MoS$_2$ to MoO$_3$. The residues of MoS$_2$/GN and MoS$_2$/GN/CNT samples are 75.7% and 72.9%, respectively, owed to the oxidation of MoS$_2$ and combustion of GN and CNT into CO$_2$ in air. Based on TGA curves, the contents of MoS$_2$ in MoS$_2$/GN and MoS$_2$/GN/CNT samples are about 92.3% and 88.9%, respectively.

The surface morphologies and inner structures of the pristine MoS$_2$, MoS$_2$/GN and MoS$_2$/GN/CNT composites are measured by SEM and TEM (Fig. 2). The pristine MoS$_2$ particles have rough surfaces and show three dimensional flower-like morphologies (Fig. 2a,2d). Each MoS$_2$ flower-like cluster is 200-300 nm in diameter, made up of many nano-flakes. Each MoS$_2$ nano-flake has layered structure with about 20 nm thickness. MoS$_2$ cluster in MoS$_2$/GN and MoS$_2$/GN/CNT composites still hold the flower-like morphologies as in Fig. 2b and 2c. The MoS$_2$ nano-flakes are wrapped by GN layers to assemble the three dimensional staggered structure in MoS$_2$/GN composite (Fig. 2e). In the MoS$_2$/GN/CNT composite, the MoS$_2$ nano-flakes are embedded closely by the curved GN layers with
irregular wrinkled CNT interspersed in (Fig. 2f). The HRTEM image in Fig. 2g reveals the clearly resolved lattice fringes of MoS\textsubscript{2} particles. Fig. 2h and Fig. 2i exhibit the obvious lattice fringes of MoS\textsubscript{2}, GN and CNT, respectively. The characterization data confirm that the successful synthetic process method.

3.2. Half-cell electrochemical characterizations

To detect the roles of GN and CNT in enhancing electrochemical properties, the MoS\textsubscript{2}/GN/CNT aerogel electrodes are measured at 0.1 mV s\textsuperscript{-1} in 0-3.0 V. Fig. 3a lists the initial CV curves in three cycles. The initial cathodic CV curve exhibits two typical peaks at 0.5 V and 1.8 V, which are ascribed to the formation of solid electrolyte interphase (SEI) layer and the conversion reduction reaction of MoS\textsubscript{2} to Mo metal and Li\textsubscript{2}S, respectively. In the subsequent anodic curve, two major oxidation peaks about 1.5 and 2.3 V are related to the partial oxidation of Mo to form MoS\textsubscript{2} and the oxidation of Li\textsubscript{2}S to S [10,11]. The redox peak potentials and currents in second and third CV scans show the similar shape and good repeatability, suggesting the stable reactive reversibility of the MoS\textsubscript{2}/GN/CNT electrode. Fig. 3b shows the initial three charge and discharge cycles of the MoS\textsubscript{2}/GN/CNT aerogel electrode. The profile has two obvious charge plateaus and one discharge plateau in curves, which are consistent with the tested CV data. At 100 mA g\textsuperscript{-1}, the MoS\textsubscript{2}/GN/CNT electrode cell shows a high initial discharge capacity of 2100 mAh g\textsuperscript{-1}.

Fig. 3 (a) CV cycles, (b) charge–discharge curves, (c) rate performances, (d) cycle abilities, and (e) nyquist plots of the prepared electrodes in lithium-ion half-cells.

Rate performances of these electrodes are shown in Fig. 3c. Reversible discharge capacities of MoS\textsubscript{2}/GN/CNT aerogel electrode are 1286, 1078, 934, 784 and 607 mAh g\textsuperscript{-1} at 100, 200, 500, 1000 and 2000 mA g\textsuperscript{-1}, respectively. Further decrease of the current density to 100 mA g\textsuperscript{-1} mostly recovers the discharge capacity of 1051 mAh g\textsuperscript{-1}. It is obvious that MoS\textsubscript{2}/GN/CNT aerogel electrode has better reversible discharge capacities of 300-600 mAh h g\textsuperscript{-1} than that of MoS\textsubscript{2} and MoS\textsubscript{2}/GN electrode at each current density. The rate properties strengthen is attributed to the multiple additive effects of GN and CNT including enhancing conductivity, dispersing MoS\textsubscript{2} distribution, and absorbing the reaction products. Fig. 3d shows cycle performances of the prepared electrodes at 200 mA g\textsuperscript{-1}, respectively. Obviously, MoS\textsubscript{2}/GN/CNT aerogel electrode exhibits most excellent cycle ability, in which the reversible discharge capacity is as high as 695 mAh g\textsuperscript{-1} after 200 cycles. The MoS\textsubscript{2} and MoS\textsubscript{2}/GN electrodes only deliver the discharge capacities of 174 and 510 mAh g\textsuperscript{-1}, respectively. The superior cycle performances are owed by the favorable inter-connected morphologies and good shuttle effect.
suppression in the MoS$_2$/GN/CNT aerogel electrode. EIS measurements for the three electrodes are tested after first cycle, as listed in Fig. 3e. All Nyquist plots are composed of semicircle curves in high-frequency regions attributing to the charge transfer resistance of the electrodes, and declined line curves of Warburg impedance in low frequency regions relating to the Li$^+$ diffusion resistance [12]. The charge-transfer impedances of MoS$_2$, MoS$_2$/GN and MoS$_2$/GN/CNT electrodes at the electrode/electrolyte interface are about 220, 125 and 90 $\Omega$, respectively, indicating the most convenient charge-transfers of the MoS$_2$/GN/CNT electrode. The EIS results keep up with foregoing suggestions on the lithium storage performances enhancement of the MoS$_2$/GN/CNT aerogel electrode.

3.3. Full-cell electrochemical characterizations

To explore the feasibility in energy storage application, MoS$_2$/GN/CNT aerogel composite and commercial LiCoO$_2$ are used as anode and cathode respectively to assemble MoS$_2$/GN/CNT//LiCoO$_2$ full-cells. Fig. 4a exhibits the initial charge-discharge curves of the MoS$_2$/GN/CNT//LiCoO$_2$ full-cell at 100 mA g$^{-1}$ in 1.0-3.8 V. The charge and discharge curves demonstrate the Li$^+$ transfer between LiCoO$_2$ cathode and MoS$_2$/GN/CNT anode. During the Li$^+$ transfer processes, the reversible redox reactions corresponds to the discharge plateaus at 1.7 and 2.6 V and charge plateau at 2.3 V. According to the active mass of MoS$_2$/GN/CNT anode, the initial charge and discharge capacities of the full-cell are 2348 and 1148 mA h g$^{-1}$, respectively. The high charge capacity of the first cycle indicates the inevitable formation of SEI layer and the irreversible decomposition of electrolyte. The discharge capacities maintain gradually at 1033 and 1013 mA h g$^{-1}$ in the followed several cycles, with the corresponding coulombic efficiencies increase to 84.2% and 91.8%, respectively. Figure 4b demonstrates the corresponding cycle abilities of the MoS$_2$/GN/CNT//LiCoO$_2$ full-cell at current density of 200 mA g$^{-1}$. The discharge capacity stabilises at 579 mA h g$^{-1}$ after 200 cycles. Based on the initial discharge capacity of 914 mA h g$^{-1}$, the capacity retention is 63.3%. The coulombic efficiency holds steady at above 95% after 10 cycles, showing the lithium storage stability of the MoS$_2$/GN/CNT electrode in lithium ion full-cells.

![Fig. 4 (a) Charge–discharge profiles and (b) cycle abilities of MoS$_2$/GN/CNT aerogel electrodes in full-cells.](image)

4. Conclusion

A ternary MoS$_2$/graphene/carbon nanotubes (MoS$_2$/GN/CNT) aerogel has been prepared successfully by a convenient hydrothermal co-assembling method. Being used as electrode, the MoS$_2$/GN/CNT aerogels can be pressed and cut directly into 10 mm disks. The fabricating process is facile without any conductive additives or binders. The MoS$_2$/GN/CNT binder-free electrode deliver reversible discharge capacities of 695 and 579 mA h g$^{-1}$ after 200 cycles at 200 mA g$^{-1}$ in MoS$_2$/GN/CNT//Li half-cell and MoS$_2$/GN/CNT//LiCoO$_2$ full-cell, respectively. The enhanced lithium storage abalities are ascribed to the novel three dimensional flower-like MoS$_2$ morphologies, the thin staggered GN layers and irregular wrinkled CNT interspersion in the ternary aerogel composite, which can enhance
conductivity, absorb the reaction products, and maintain structural stability to improve the cycle ability in lithium-ion half and full batteries.

Acknowledgments
This work was financially supported by the Natural Science Foundation of Shaanxi Province (No. 2021GY-153), the Merit-based Projects Foundation of Department of Human Resources and Social Security of Shaanxi Province for Returned Overseas Personnel (No. 2019RS-37), Industrial Projects Foundation of Ankang Science and Technology Bureau (Nos. AK2020-GY02-2 and AK2020-GY02-3), the Joint Graduate Education Programs of Ankang University (No 2020AYXNZX05), and National Undergraduate Training Program for Innovation and Entrepreneurship (No. S202011397013).

References
[1] Rahul K, Raj KA, Mitra S, Bhargava P (2021) Correction to: Carbon Derived from Sucrose as Anode Material for Lithium-Ion Batteries. J. Electron. Mater., 48: 7593.
[2] Yuan G, Bai J (2016) Orange peels derived activated carbon as sulfur cathode supporter for lithium/sulfur batteries. Adv. Mater. Res., 1120: 493-497.
[3] Liu Y, Fan LZ, Jiao L (2017) Graphene intercalated in graphene-like MoS2: A promising cathode for rechargeable Mg batteries. J. Power Sources, 340: 104-110.
[4] Yuan G, Wang G, Wang H Bai J (2016) Half-cell and full-cell investigations of 3D hierarchical MoS2/graphene composite on anode performance in lithium-ion batteries. J. Alloys Compd., 660: 62-72.
[5] Wang W, Guo S, Zhang P, Liu J, Chen L (2021) Interlayer expanded MoS2/nitrogen-doped carbon hydrangea nanoflowers assembled on nitrogen-doped three-dimensional graphene for high-performance lithium and sodium storage. ACS Appl. Energy Mater. doi: 10.1021/acsaem.1c00609.
[6] Yuan G, Geng M, Zhang P, Li B (2020) Hybrids of LiMn2O4 nanoparticles anchored on carbon nanotubes/graphene sheets as long-cycle-life cathode material for rechargeable hybrid aqueous batteries. J. Solid State Electrochem., 24: 601-607.
[7] Chen L, Liu Y, Deng Z, Jiang H, Li C (2021) Edge-enriched MoS2@C/rGO film as self-standing anodes for high-capacity and long-life lithium-ion batteries. Sci. China Mater., 64: 96-104.
[8] Wang J, Wang G, Wang H (2015) Flexible free-standing Fe2O3/graphene/carbon nanotubes hybrid films as anode materials for high performance lithium-ion batteries." Electrochim. Acta 182: 192-201.
[9] Ren J, Ren R, Lv Y (2018) A flexible 3D graphene@CNT@MoS2 hybrid foam anode for high-performance lithium-ion battery. Chem. Eng. J., 353: 419-424.
[10] Cui C, Wei Z, Xu J, Zhang Y (2018) Three-dimensional carbon frameworks enabling MoS2 as anode for dual ion batteries with superior sodium storage properties. Energy Storage Mater., 15: 22-30.
[11] Yuan G, Cao R, Geng M, Jin H, Li B, Xu Q (2020) Zeolitic imidazolate frameworks-derived activated carbon as electrode material for lithium-sulfur batteries and lithium-ion batteries, J. Electronic Mater., 10: 6156-6164.
[12] Aurbach D (2003) Electrode–solution interactions in Li-ion batteries: a short summary and new insights. J. Power Sources, 119: 497-503.