INORGANIC
CHEMISTRY
FRONTIERS

http://rsc.li/frontiers-inorganic

Journal Name

COMMUNICATION

MoS₂ with intercalation reaction as long-life anode material for Lithium ion batteries

Zhe Hu[a], Qiannan Liu[a], Weiyi Sun[b], Weijie Li[a], Zhanliang Tao*[a,b], Shu-Lei Chou*[a], Jun Chen[b,c], and Shi-Xue Dou[a]

MoS₂ with expanded layers were synthesized and characterized as anode materials for lithium ion batteries in ether-based eletrolyte by cutting off the terminal discharge voltage to 1.0 V to keep MoS₂ away from conversion reaction. The as-prepared MoS₂ achieved 96% of capacity retention even after 1400 cycles and showed good performances in full cell with LiCoO₂ as the counter electrode.

Recently rechargeable batteries have attracted large amount attentions mainly because of their cyclability as sustainable power supply.[1-3] Especially for the rechargeable lithium ion batteries (LIBs), the practical applications mostly facilitate the social development.[4, 5] Among different kinds of electrode materials, MoS₂ has become one of the most popular materials owing to the layered structure like graphite.[6-8] The weak van der Waals force between the adjacent layers is easy to be broken by lithium ion insertion and the fully transition reaction will provide a high specific capacity of 670 mAh·g⁻¹ (four-electron reaction).[9-11] In order to get the optimized electrochemical performances, the reaction mechanism of MoS₂ cycling in 0.1−3.0 V has been wildly discussed.[12, 13] At the first cycle, there is an intercalation process for MoS₂ reacting with Li⁺ to form LiMoS₂, which accompanies the phase change from MoS₂ with trigonal pristine (2H-MoS₂) to trigonal antiprismatic MoS₂(1T-MoS₂).[10] As the interlayer spacing is much larger than graphite, it will introduce less volume change regarding the intercalation process.[14] Then with continuous Li⁺ intercalation, the structure of layered MoS₂ decomposes to Mo metal and Li₂S. This step possesses large volume expansion (~103%) leading to electrode pulverization.[15-17] Because the charge products can never return back to MoS₂ again, the

reaction mechanism of the following cycles is the reversible reaction between Li₂S and S, just the same as Li/S batteries. Here comes the problem that MoS₂ should also come across the difficulties as those in Li/S batteries, such as the severe capacity loss owing to the active materials dissolution, polysulfide shuttling effect, and side reaction between polysulfides and electrolyte.[18-20] So it is urgent to find proper method to solve the problems mentioned above.

The most effective method is the nano-size design together with carbon modification.[21] The nano-size design would provide short ion diffusion path, which will enhance the reaction kinetics.[22] By coating with carbon, the active materials can be protected from the negative effect of the volume expansion and accelerate the surface electron transportation. Qiao and coworkers synthesized mesoporous MoS₂ with expanded interlayer. The as-prepared product showed an initial capacity of 1052 mAh·g⁻¹ and lasted for 100 cycles at 0.1 A·g⁻¹.[18] Although carbon coating leads great improvement on the MoS₂/Li batteries, the cycling performance is still hard to match the need for commercialization, and the broaden voltage region (0.1−3.0 V) still suffers from safety issues like electrolyte decomposition, large volume change (203% after change), and precipitation of lithium metal on the anode surface of LIBs. Thus to further improve the electrochemical performance of MoS₂, there should be more modification beside carbon coating and nano-size design.

According to previous work on MoS₂, FeS₂ and FeSe₂, setting proper cut-off voltage to prevent a conversion type reaction happening is an effective way to improve the cycling life..[23-25] Py et al. has excluded the possibility for lithium/electrolyte co-intercalation.[26] After lithium intercalating there is only 0.14 Å expanded for the MoS₂ interlayer. And the intercalation reaction can confine the charge and discharge platform mainly locating in the voltage range of 1.5−2.0 V. So it is a prominent improvement on the volume and voltage control for intercalation reaction than the conversion type reaction. This inspires us to fabricate the full cell using MoS₂ as anode material mainly because the low volume change and high terminal discharge voltage just like Li₄Ti₅O₁₂, etc.[16, 27] As

a. Institute for Superconducting and Electronic Materials
Australian Institute for Innovative Materials
University of Wollongong, Innovation Campus
Squires Way, North Wollongong NSW 2522 , Australia
b. Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education),
Nankai University, Tianjin, 300071, People's Republic of China.
c. Collaborative Innovation Center of Chemical Science and Engineering, Nankai
University, Tianjin, 300071, People's Republic of China

known, the high-voltage cathode materials (e.g. $LiCoO_2$ and $LiNi_{0.5}Mn_{1.5}O_4$) that always suffer from the risk of electrolyte decomposition when charging over 4.0 V in the practical use. Fig. 1 shows the typical charge and discharge curves of cathode material $LiCoO_2$, and anode materials MoS_2, $Li_4Ti_5O_{12}$, and graphite. Graphite is the most popular commercial anode material owing to its cheap price, relative stable cyclability, and competitive specific capacity. However the charge and discharge curves are almost around 0 V, which probably leads to the deposition of lithium metal on the surface of anode materials and then causes severe safety issues like short circuit. But materials such as MoS_2 and $Li_4Ti_5O_{12}$, which hold much safer voltage region from 1.0−3.0 V (half cell), can not only avoid safety issues like short circuit and large volume change during cycling (full cell) but also lower risk for electrolyte decomposition when served as the counter electrode of high voltage cathode material.[14, 28] Nevertheless, until now there are only a few papers focusing on the MoS_2/Li battery with intercalation reaction.[26, 29-31]

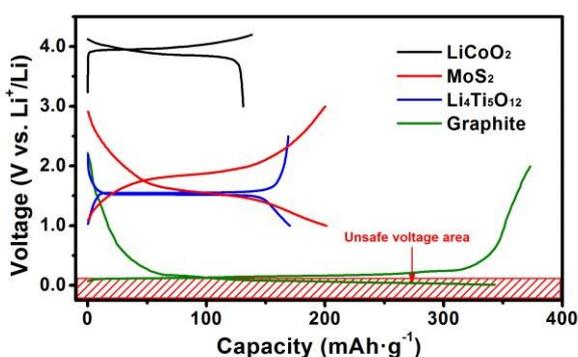**Fig. 1** The typical charge and discharge curves of $LiCoO_2$, MoS_2, $Li_4Ti_5O_{12}$, and graphite.

Herein we have synthesized the MoS_2 with expanded layers (H-MoS_2) through hydrothermal process and freeze-drying method by modifying the experimental method of our previous work.[23] To preserve the layer structure, obtain relative high specific capacity and protect the electrolyte from decomposition, the terminal discharge voltage was set to 1.0 V. The stable charge and discharge platform was ~1.8 V and ~1.6 V, which ensured the possible applications for commercial rechargeable lithium batteries and anode in rechargeable LIBs (full cell with $LiCoO_2$ as the counter electrode).

The H-MoS_2 represents the product procured by hydrothermal treatment, and B-MoS_2 represents the bulk MoS_2 purchased from (Alfa aesar, 10−20 μm). Fig. S1a illustrates the X-ray diffraction (XRD) patterns of H-MoS_2 and B-MoS_2. Results show that the H-MoS_2 shows broadening characteristic peaks, and lower peak intensity. On the contrary, B-MoS_2 holds the sharp and strong XRD peaks. Meanwhile the peak shift of the (002) crystal plane indicates the layers in H-MoS_2 slightly expand. Fig. S1b and S1c depict the high resolution transmission electron microscopy (HRTEM) images of H-MoS_2 and B-MoS_2. The d-spacing calibrated from the crystal fringes is in accordance with the XRD analysis: H-MoS_2 layers (layer

distance of 0.69 nm) arrange disordered and rich-defective, however the B-MoS_2 possesses the neatly restack MoS_2 layers with the d-spacing of 0.62 nm. Through the freeze-drying process, which is also used as the most effective way to fabricate 2D/3D graphene, the ice plays an important role in supporting the morphology.[32] When the ice is evacuated from the powders, the MoS_2 layers with expanded space can preserve. Then the electrochemical performances were tested. Fig. 2a and Fig. S2a exhibit the galvanostatic charge and discharge curves of H-MoS_2 and B-MoS_2 at 0.2 A·g^{-1}. Referring to the initial cycle, the H-MoS_2 has higher discharge platform (~1.5 V) and more specific discharge capacity (260 mAh·g^{-1}) than B-MoS_2 (~1.1 V and 181 mAh·g^{-1}) because of the different d-spacing of (002). Larger layer distance facilitates the kinetics of Li$^+$ intercalation leading to smaller energy barrier and the stable thermodynamics expressing as the stronger capacity for accommodating more Li$^+$.[33, 34] From the cyclic data (Fig. 2b and Fig. S2b),The capacities at 2nd cycle reveal a slight decrease and the detailed values are 195 and 108 mAh·g^{-1} of H-MoS_2 and B-MoS_2, respectively, which should be ascribed to the partial side reaction and the possibility for trace residual Li$^+$ inside the layers. Then the discharge capacity has become a little higher (5−10 mAh·g^{-1}), which is resulted from the activation for the electrode materials.[10] What's more, after 1st cycle the charge and discharge curves changes a bit. As the mechanism of the 1st discharge process is well investigated. It should be the phase conversion from MoS_2(2H) to MoS_2(1T), which is the main reason for the curve changes.[26] Fig. 2b reveals the cyclic performance of the H-MoS_2. After 1st cycle, the specific charge/discharge capacities are around 190 mAh·g^{-1}. And then with gradual activation, the specific capacity keeps stable at 205 mAh·g^{-1} and after 1400 cycles the capacity retention is 96% (compared to the capacity of the second cycle). The coulombic efficiency suffers a low value at 1st cycle (75%) and then gradually increases to near 100% and be stable for 1400 cycles. Fig. 2c shows the rate property of H-MoS_2. The discharge capacities at 0.2, 1, 2, and 3 A·g^{-1} are 200, 115, 70, 50 mAh·g^{-1}, respectively. H-MoS_2 displays high capacity at low current density, and considerable capacity at 1 A·g^{-1}. The H-MoS_2 battery can perform well recover capability for the high current density treatment: the discharge capacity can return back to 200 mAh·g^{-1} at 0.2 A·g^{-1} after treating with 3 A·g^{-1}.

The half cell performance at 0.2 A·g^{-1} in the voltage range of 0.1−3 V was also tested (Fig. S2c and S2d). As expected, the large voltage polarization between the charge and discharge process proves the above analysis that it is not suitable for full cell use. Although the discharge capacity can reach 670 mAh·g^{-1} (4 electrons/ Li$^+$ ions reaction), the large volume change generating from the formation of conversion product Mo and Li$_2$S leads to the capacity fade and worse reaction kinetics, which is proved by the GITT characterization (Fig. S3 and S4). It is clear that after the first discharge process, the H-MoS_2 battery cycling between 0.1−3.0 V shows sluggish ion diffusion (the lithium diffusion coefficient decrease almost 1−2 order of magnitude) leading to the large voltage polarization (Fig. S3b). However the H-MoS_2 battery cycling from 1.0 to

3.0 V possesses a fast lithium migration ($\sim 10^{-9}$ cm$^2\cdot$s^{-1}) ensuring the stable electrochemical performances mentioned above. The ester-based electrolyte (ethylene carbonate and diethyl carbonate) is used to investigate influence of the electrolyte. As shown in Fig. S4, the Li/MoS$_2$ cell also performs well cycling stability. According to the above analysis, it means that the cut-off voltage is the most important reason for achieving long life.
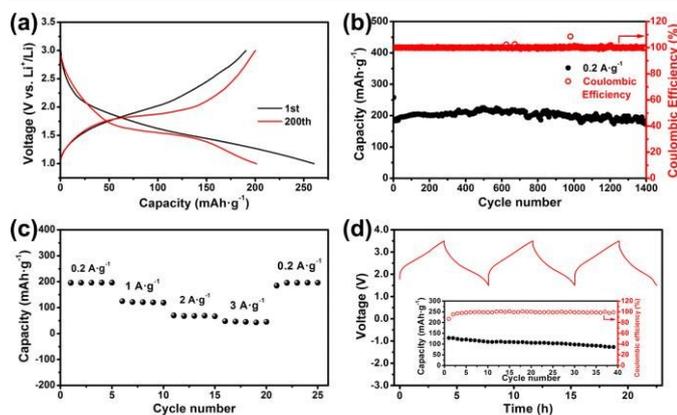

Fig. 2 Electrochemical performances of the as-prepared MoS$_2$ and the full cell assembled by LiCoO$_2$ as cathode and MoS$_2$ as anode. (a) Galvanostatic charge and discharge curves of MoS$_2$ at 1st and 200th cycles at a current density of 0.2 A·g^{-1}. (b) Cyclic performance and (c) rate property of MoS$_2$. (d) Galvanostatic charge and discharge curves of the full cell at the voltage range from 1.5−3.5 V (inset is the cyclic performance).

To further investigate the possibility of using as anode material, we have fabricated the full cell using LiCoO$_2$ as cathode material and H-MoS$_2$ as anode material. The electrochemical performances of the assembled full cell are estimated by the active mass of cathode material and are tested under 0.1C (14 mA·g^{-1}). The galvanostatic charge and discharge curves are shown in Fig. 2d. The average charge platform is ~ 2.80 V and average discharge platform is ~2.35 V. The slope of discharge platform is convenient and accurate for the residual capacity indication. The cyclic data inserted in Fig. 2d shows that the 1st discharge capacity is 120 mAh·g^{-1} with a coulombic efficiency of 82%. Then the coulombic efficiency improves to near 99% along with the capacity loss from 120 to 90.5 mAh·g^{-1}. Gaphite/LiCoO$_2$ full cell is also performed (Fig. S5). The charge and discharge platforms are at 4.0 and 3.6 V, respectively and the discharge capacity is 132 mAh·g^{-1}. After cycling for 30 times, the capacity retention is 91.6%. Thus the performance of MoS$_2$/LiCoO$_2$ battery is comparable with that of commercial type graphite/LiCoO$_2$ battery, and moreover MoS$_2$ possesses higher safety factor because of its high charge and discharge voltage region (Fig. 1). The full cell technology should be improved in further investigations such as to design high tapping density MoS$_2$ with high electrochemical performances. However this result shows the possibility for MoS$_2$ using as anode material for LIBs.

The lectrochemical impedance spectroscopy (EIS) measurement of H-MoS$_2$ at different voltage range was also characterized (Fig. S7). Both EIS data in 1.0−3.0 V and 0.1−3.0 V exhibit one circle at high frequency and a line at low frequency. Comparing the different voltage range, the charge transfer resistance of intercalation reaction is much smaller than that of conversion reaction. Moreover the H-MoS$_2$ shows smaller charge transfer resistance than B-MoS$_2$, resulting from the better nano-design that facilitates the electrochemical reaction kinetics.
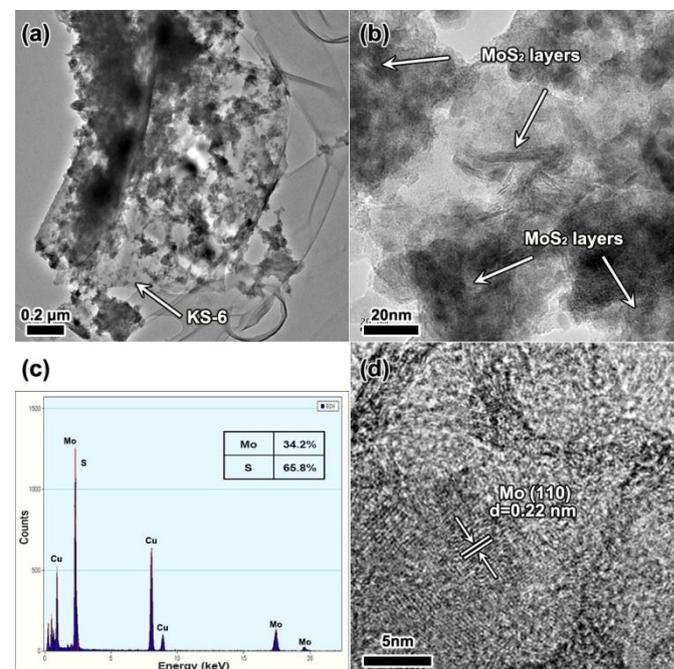
Fig. 3 TEM characterization of the electrode material (half cell) after cycling. (a) The TEM image, (b) HRTEM image, and (c) EDX of MoS$_2$ electrode at 1.0 V after cycling between 1.0 V and 3.0 V for 100 times. (d) HRTEM image of MoS$_2$ electrode at 0.1 V after cycling at 0.1−3.0 V for 10 times.

Fig. 3 shows the further investigations on the electrode material after cycling. The transmission electron microscopy (TEM) and HRTEM images of MoS$_2$ electrode after cycling for 100 times are shown in Fig. 3a and 3b. It is noticed that the graphite (conductive additive, KS-6) is served as the carrier for the MoS$_2$ particles and as the conductive substrate between the collector and MoS$_2$ particles. We also find the MoS$_2$ layers preserved after cycling, which means that the conversion reaction does not happen when the terminal discharge voltage is set to 1.0 V. The energy dispersive X-ray spectroscopy (EDX) measurement is also employed to detect the elemental content of Mo and S. The result shows that the atom ratio of Mo versus S is about 1:2, but still the S has proved to be loss about 2%, which should be ascribed to the systematic error and the partial over-discharge effect. Fig. 3d reveals the electrode material cycling for 10 times in the voltage range of 0.1−3.0 V. Apparently nano-sized Mo particles are detected and found to be a little aggregated, which would cause the separation for the Mo and Li$_2$S leading to a severe capacity loss.[16]

The overall characterization and discussion connect together the proofs of the excellent electrochemical properties of H-MoS$_2$ cycling in 1.0−3.0 V. The expanded layers provide better thermodynamic and kinetics, expressing as the higher discharge voltage and fast ionic conductivity. Eliminating the conversion reaction, the wholly preserved layer-structured MoS$_2$ ensures

ARTICLE

the rechargeable ability for the MoS_2/Li and $LiCoO_2/MoS_2$ batteries. The smaller charge transfer resistance reveals the improved kinetics leading to the smaller voltage polarization.

Conclusions

The as-prepared MoS_2 were synthesized through the hydrothermal process. By cutting off the terminal discharge voltage to 1.0 V in ether-based electrolyte, $H-MoS_2$ exhibits a high discharge capacity of 200 $mAh \cdot g^{-1}$ at 0.2 $A \cdot g^{-1}$ with a stable charge and discharge platform of ~1.8 V and ~1.6 V, respectively. Referring the cyclability, it can cycle for 1400 times with almost no capacity fade. Thus to control the terminal discharge voltage should be an effective way to improve conversion type materials with two key factors that own an intercalation process before the conversion reaction happens and easy-control voltage management. More attentions should focus on the intercalation reaction so that MoS_2 would finally find promising applications as the anode material for rechargeable lithium ion batteries.

Acknowledgement

Notes and references

‡ Footnotes relating to the main text should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

1. B. Dunn, H. Kamath and J.-M. Tarascon, *Science*, 2011, **334**, 928-935.
2. K. Kang, Y. S. Meng, J. Bréger, C. P. Grey and G. Ceder, *Science*, 2006, **311**, 977-980.
3. H. J. Yu, Y. Ren, D. D. Xiao, S. H. Guo, Y. B. Zhu, Y. M. Qian, L. Gu and H. S. Zhou, *Angew. Chem. Int. Ed.*, 2014, **53**, 8963-8969.
4. Y. Sun, J. Zhu, L. Bai, Q. Li, X. Zhang, W. Tong and Y. Xie, *Inorg. Chem. Front.*, 2014, **1**, 58-64.
5. S. Xu, S. Lau and L. A. Archer, *Inorg. Chem. Front.*, 2015, DOI: 10.1039/c1035qi00169b.
6. J. Zhou, J. Qin, X. Zhang, C. Shi, E. Liu, J. Li, N. Zhao and C. He, *ACS nano*, 2015, **9**, 3837-3848.
7. R. Tenne, *Nat. Nanotech.*, 2006, **1**, 103-111.
8. X. Huang, Z. Y. Zeng and H. Zhang, *Chem. Soc. Rev.*, 2013, **42**, 1934-1946.
9. X. Cao, Y. Shi, W. Shi, X. Rui, Q. Yan, J. Kong and H. Zhang, *Small*, 2013, **9**, 3433-3438.
10. H. Hwang, H. Kim and J. Cho, *Nano Lett.*, 2011, **11**, 4826-4830.
11. K. Chang and W. X. Chen, *J. Mater. Chem.*, 2011, **21**, 17175-17184.
12. J. Xiao, X. J. Wang, X. Q. Yang, S. D. Xun, G. Liu, P. K. Koech, J. Liu and J. P. Lemmon, *Adv. Funct. Mater.*, 2011, **21**, 2840-2846.
13. P. Sun, W. Zhang, X. Hu, L. Yuan and Y. Huang, *J. Mater. Chem. A*, 2014, **2**, 3498-3504.
14. Z. Wu, B. Li, Y. Xue, J. Li, Y. Zhang and F. Gao, *J. Mater. Chem. A*, 2015, **3**, 19445-19454.
15. Y. Gong, S. Yang, Z. Liu, L. Ma, R. Vajtai and P. M. Ajayan, *Adv. Mater.*, 2013, **25**, 3979-3984.
16. T. Stephenson, Z. Li, B. Olsen and D. Mitlin, *Energy Environ. Sci.*, 2014, **7**, 209-231.
17. Y. X. Wang, S. L. Chou, D. Wexler, H. K. Liu and S. X. Dou, *Chem. Eur. J.*, 2014, **20**, 9607-9612.
18. H. Liu, D. Su, R. Zhou, B. Sun, G. Wang and S. Z. Qiao, *Adv. Energy Mater.*, 2012, **2**, 970-975.
19. J. Gao, M. A. Lowe, Y. Kiya and H. D. Abruña, *J. Phys. Chem. C*, 2011, **115**, 25132-25137.
20. Y.-X. Yin, S. Xin, Y.-G. Guo and L.-J. Wan, *Angew. Chem. Int. Ed.*, 2013, **52**, 13186-13200.
21. C. B. Zhu, X. K. Mu, P. A. van Aken, Y. Yu and J. Maier, *Angew. Chem. Int. Ed.*, 2014, **53**, 2152-2156.
22. K. Zhang, X. Han, Z. Hu, X. Zhang, Z. Tao and J. Chen, *Chem. Soc. Rev.*, 2014.
23. Z. Hu, L. Wang, K. Zhang, J. Wang, F. Cheng, Z. Tao and J. Chen, *Angew. Chem. Int. Ed.*, 2014, **53**, 12794-12798.
24. Z. Hu, Z. Zhu, F. Cheng, K. Zhang, J. Wang, C. Chen and J. Chen, *Energy Environ. Sci.*, 2015, **8**, 1309-1316.
25. K. Zhang, Z. Hu, X. Liu, Z. Tao and J. Chen, *Adv. Mater.*, 2015, **27**, 3305-3309.
26. M. A. Py and R. R. Haering, *Can. J. Phys.*, 1983, **61**, 76-84.
27. Z. Hu, K. Zhang, Z. Zhu, Z. Tao and J. Chen, *J. Mater. Chem. A*, 2015, **3**, 12898-12904.
28. Z. Zhu, F. Cheng and J. Chen, *J. Mater. Chem. A*, 2013, **1**, 9484-9490.
29. N. Imanishi, K. Kanamura and Z. i. Takehara, *J. Electrochem. Soc.*, 1992, **139**, 2082-2087.
30. C. Julien, S. I. Saikh and G. A. Nazri, *Mater. Sci. Eng. B*, 1992, **15**, 73-77.
31. Y. Miki, D. Nakazato, H. Ikuta, T. Uchida and M. Wakihara, *J. Power Sources*, 1995, **54**, 508-510.
32. L. Qian and H. Zhang, *J. Chem. Technol. Biotechnol.*, 2011, **86**, 172-184.
33. K. Chang, W. Chen, L. Ma, H. Li, H. Li, F. Huang, Z. Xu, Q. Zhang and J.-Y. Lee, *J. Mater. Chem.*, 2011, **21**, 6251-6257.
34. S. Q. Yang, D. X. Li, T. R. Zhang, Z. L. Tao and J. Chen, *J. Phys. Chem. C*, 2011, **116**, 1307-1312.