University of Wollongong

Research Online

Australian Institute for Innovative Materials -
Papers

Australian Institute for Innovative Materials

1-1-2016

MoS₂ with an intercalation reaction as a long-life anode material for lithium ion batteries

Zhe Hu

University of Wollongong, zh865@uowmail.edu.au

Qiannan Liu

University of Wollongong, ql953@uowmail.edu.au

Weiyi Sun

Nankai University

Weijie Li

University of Wollongong, wl347@uowmail.edu.au

Zhanliang Tao

University of Wollongong, ztao@uow.edu.au

See next page for additional authors

Follow this and additional works at: <https://ro.uow.edu.au/aiimpapers>

Part of the [Engineering Commons](#), and the [Physical Sciences and Mathematics Commons](#)

Research Online is the open access institutional repository for the University of Wollongong. For further information contact the UOW Library: research-pubs@uow.edu.au

MoS₂ with an intercalation reaction as a long-life anode material for lithium ion batteries

Abstract

MoS₂ with expanded layers was synthesized and characterized as an anode material for lithium ion batteries in an ether-based electrolyte by cutting off the terminal discharge voltage at 1.0 V to prevent a MoS₂ conversion reaction. The as-prepared MoS₂ achieved 96% capacity retention even after 1400 cycles and showed good performance in a full cell with LiCoO₂ as the counter electrode.

Keywords

long, life, anode, material, reaction, lithium, mos₂, ion, batteries, intercalation

Disciplines

Engineering | Physical Sciences and Mathematics

Publication Details

Hu, Z., Liu, Q., Sun, W., Li, W., Tao, Z., Chou, S., Chen, J. & Dou, S. (2016). MoS₂ with an intercalation reaction as a long-life anode material for lithium ion batteries. *Inorganic Chemistry Frontiers*, 3 (4), 532-535.

Authors

Zhe Hu, Qiannan Liu, Weiyi Sun, Weijie Li, Zhanliang Tao, Shulei Chou, Jun Chen, and S X. Dou

INORGANIC CHEMISTRY

FRONTIERS

RESEARCH ARTICLE

Cite this: *Inorg. Chem. Front.*, 2016, **3**, 532

MoS₂ with an intercalation reaction as a long-life anode material for lithium ion batteries†

Zhe Hu,^a Qiannan Liu,^a Weiye Sun,^b Weijie Li,^a Zhanliang Tao,^{*a,b} Shu-Lei Chou,^{*a} Jun Chen^{b,c} and Shi-Xue Dou^a

Received 4th November 2015,
Accepted 5th January 2016

DOI: 10.1039/c5qi00237k

rs.c.li/frontiers-inorganic

MoS₂ with expanded layers was synthesized and characterized as an anode material for lithium ion batteries in an ether-based electrolyte by cutting off the terminal discharge voltage at 1.0 V to prevent a MoS₂ conversion reaction. The as-prepared MoS₂ achieved 96% capacity retention even after 1400 cycles and showed good performance in a full cell with LiCoO₂ as the counter electrode.

Recently rechargeable batteries have attracted a large amount of attention, mainly because of their cyclability, as a sustainable power supply.^{1–3} Especially for rechargeable lithium ion batteries (LIBs), practical applications mostly facilitate social development.^{4,5} Among different kinds of electrode materials, MoS₂ has become one of the most popular materials owing to its layered graphite-like structure.^{6–8} The weak van der Waals force between adjacent layers is easy to break by lithium ion insertion and a full conversion reaction provides a high specific capacity of 670 mA h g^{−1} (four-electron reaction).^{9–11} In order to achieve optimized electrochemical performances, the reaction mechanism of MoS₂ cycling at 0.1–3.0 V has been widely discussed.^{12,13} In the first cycle, there is an intercalation process of MoS₂ reacting with Li⁺ to form LiMoS₂, which accompanies a phase change from trigonal prismatic MoS₂ (2H-MoS₂) to octahedral MoS₂ (1T-MoS₂).¹⁰ As the interlayer spacing is much larger than that of graphite, this will introduce less of a volume change regarding the intercalation process.¹⁴ Then with continuous Li⁺ intercalation, the structure of the 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 that for Li/S batteries. This presents the problem that MoS₂ should also come across the

difficulties encountered in Li/S batteries, such as the severe capacity loss owing to the active material dissolution, the polysulfide shuttling effect, and the side reaction between polysulfides and the electrolyte.^{18–20} So it is urgent to find an appropriate 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 a 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 interlayers. The as-prepared product showed an initial capacity of 1052 mA h g^{−1} and lasted for 100 cycles at 0.1 A g^{−1}.¹⁸ Although carbon coating leads to great improvement of MoS₂/Li batteries, the cycling performance is still hard to match to the need for commercialization, and the broadened voltage region (0.1–3.0 V) still suffers from safety issues like electrolyte decomposition, large volume change (203% after change), and the precipitation of lithium metal on the anode surface of LIBs. Thus to further improve the electrochemical performance of MoS₂, there should be more modification besides carbon coating and a nano-size design.

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

^aInstitute for Superconducting and Electronic Materials, Australian Institute for Innovative Materials, University of Wollongong, Innovation Campus, Squires Way, North Wollongong, NSW 2522, Australia. E-mail: shulei@uow.edu.au

^bKey Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), Nankai University, Tianjin, 300071, People's Republic of China. E-mail: taozh@nankai.edu.cn

^cCollaborative Innovation Center of Chemical Science and Engineering, Nankai University, Tianjin, 300071, People's Republic of China

†Electronic supplementary information (ESI) available: Experimental section, XRD, TEM, and electrochemical characterization. See DOI: 10.1039/c5qi00237k

Fig. 1 The typical charge and discharge curves of LiCoO_2 , MoS_2 , $\text{Li}_4\text{Ti}_5\text{O}_{12}$, and graphite.

known, high-voltage cathode materials (e.g. LiCoO_2 and $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$) always suffer from the risk of electrolyte decomposition when charging over 4.0 V in practical use. Fig. 1 shows the typical charge and discharge curves of the cathode material LiCoO_2 , and anode materials MoS_2 , $\text{Li}_4\text{Ti}_5\text{O}_{12}$, and graphite. Graphite is the most popular commercial anode material owing to its cheap price, relatively 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 the anode materials and then causes severe safety issues like short circuiting. However, materials such as MoS_2 and $\text{Li}_4\text{Ti}_5\text{O}_{12}$, which have much safer voltage regions from 1.0–3.0 V (half cell), can not only avoid safety issues like short circuiting and large volume changes during cycling (full cell) but also lower the risk of electrolyte decomposition when serving as the counter electrode of high voltage cathode materials.^{14,28} Nevertheless, until now there are only a few papers focusing on MoS_2/Li batteries with intercalation reactions.^{26,29–31}

Herein we have synthesized MoS_2 with expanded layers (H-MoS_2) through a hydrothermal process and freeze-drying method by modifying the experimental method of our previous work.²³ To preserve the layer structure, obtain a relatively 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 possible applications in commercial rechargeable lithium batteries and as anodes in rechargeable LIBs (full cell with LiCoO_2 as the counter electrode).

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 . The results show that the H-MoS_2 shows broadening characteristic peaks, and lower peak intensities. On the contrary, B-MoS_2 retains sharp and strong XRD peaks. Meanwhile the peak shift of the (002) crystal plane indicates that 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: the H-MoS_2 layers (layer dis-

tance of 0.69 nm) are in a disordered arrangement and are defect-rich, however B-MoS_2 possesses neatly restacked MoS_2 layers with a d -spacing of 0.62 nm. Through a 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 removed from the powders, the MoS_2 layers with expanded space could be preserved.

Then the electrochemical performances were tested using the ether-based electrolyte (1.0 M lithium bis(trifluoromethanesulfonyl)imide in tetraethylene glycol dimethyl ether). Fig. 2a and 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, H-MoS_2 has a higher discharge platform (~ 1.5 V) and more specific discharge capacity (260 mA h g^{-1}) than B-MoS_2 (~ 1.1 V and 181 mA h g^{-1}) because of the different d -spacing of (002). A larger layer distance facilitates the kinetics of Li^+ intercalation leading to a smaller energy barrier and more stable thermodynamics expressed as a stronger capacity for accommodating more Li^+ .^{33,34} From analysis of the cyclic data (Fig. 2b and S2b†), the capacities of the 2nd cycle reveal a slight decrease (the specific values are 195 and 108 mA h g^{-1} for H-MoS_2 and B-MoS_2 , respectively), which should be ascribed to the partial side reaction and the possibility of traces of residual Li^+ inside the layers. Then, the discharge capacity became a little higher ($5\text{--}10 \text{ mA h g}^{-1}$), which is a result of the activation of the electrode materials.¹⁰ What's more, after the 1st cycle the charge and discharge curves change a bit. The mechanism of the 1st discharge process is well investigated. The phase conversion from $\text{MoS}_2(2\text{H})$ to $\text{MoS}_2(1\text{T})$ should be the main reason for the curve changes.²⁶ Fig. 2b reveals the cyclic performance of H-MoS_2 . After the 1st cycle, the specific charge/discharge capacities are around 190 mA h g^{-1} . Then with gradual activation, the specific capacity remains stable at 205 mA h g^{-1} and after 1400 cycles

Fig. 2 Electrochemical performances of the as-prepared MoS_2 and the full cell assembled by LiCoO_2 with a cathode and MoS_2 as an anode. (a) Galvanostatic charge and discharge curves of MoS_2 at the 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).

the capacity retention is 96% (compared to the capacity of the second cycle). The coulombic efficiency has a low value in the 1st cycle (75%), and then gradually increases to near 100% and is stable for 1400 cycles. Fig. 2c shows the rate property of H-MoS₂. The discharge capacities at 0.2, 1, 2, and 3 A g⁻¹ are 200, 115, 70, 50 mA h g⁻¹, respectively. H-MoS₂ displays a high capacity at a low current density (0.2 A g⁻¹), and considerable capacity at 1 A g⁻¹. The H-MoS₂ battery can show a good recovery capability in high current density treatments: the discharge capacity can return back to 200 mA h 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 mA h g⁻¹ (4 electrons/Li⁺ ions reaction), the large volume change generated from the formation of the conversion products Mo and Li₂S leads capacity fade and worse reaction kinetics, which is proved by GITT characterization (Fig. S3 and S4†). It is clear that after the first discharge process, the H-MoS₂ battery cycling between 0.1–3.0 V shows sluggish ion diffusion (the lithium diffusion coefficient decreases by almost 1–2 orders of magnitude) leading to a large voltage polarization (Fig. S3b†). However the H-MoS₂ battery cycling from 1.0 to 3.0 V possesses a fast lithium migration ($\sim 10^{-9}$ cm² s⁻¹) ensuring the stable electrochemical performances mentioned above. An carbonate-based electrolyte (1M LiPF₆ ethylene carbonate and diethyl carbonate) is used to investigate the influence of the electrolyte. As shown in Fig. S5,† the Li/MoS₂ cell also performs well with good cycling stability. According to the above analysis, this means that the cut-off voltage is the most important factor for achieving long life.

To further investigate the possibility of using this material as an anode material, we have fabricated a full cell using LiCoO₂ as the cathode material and H-MoS₂ as the anode material. The electrochemical performances of the assembled full cell are estimated using the active mass of the cathode material and are tested under 0.1 C (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 the 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 mA h g⁻¹ with a coulombic efficiency of 82%. Then the coulombic efficiency improves to near 99% along with a capacity loss from 120 to 90.5 mA h g⁻¹. Analysis of a graphite/LiCoO₂ full cell is also performed (Fig. S6†). The charge and discharge platforms are at 4.0 and 3.6 V, respectively and the discharge capacity is 132 mA h g⁻¹. After cycling 30 times, the capacity retention is 91.6%. Thus the performance of the MoS₂/LiCoO₂ battery is comparable with that of a commercial type graphite/LiCoO₂ battery, and moreover MoS₂ possesses a 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 by designing high tapping density MoS₂ with high electrochemical performances. However this result shows the possibility of using MoS₂ as an anode material for LIBs.

The electrochemical impedance spectroscopy (EIS) measurements of H-MoS₂ at different voltage ranges were also characterized (Fig. S7†). Both EIS data from 1.0–3.0 V and 0.1–3.0 V exhibit one circle at high frequency and a line at low frequency. By comparing the different voltage ranges, the charge transfer resistance of the intercalation reaction is much smaller than that of the conversion reaction. Moreover H-MoS₂ shows smaller charge transfer resistance than B-MoS₂, resulting from the better nano-design that facilitates the electrochemical reaction kinetics.

Fig. 3 shows further investigations of the electrode material after cycling. Transmission electron microscopy (TEM) and HRTEM images of the MoS₂ electrode after cycling 100 times are shown in Fig. 3a and b. It is noticed that the graphite (conductive additive, KS-6) served as the carrier for the MoS₂ particles and as the conductive substrate between the collector and MoS₂ particles. We also find the MoS₂ layers preserved after cycling, which means that the conversion reaction does not happen when the terminal discharge voltage is set to 1.0 V. Energy dispersive X-ray spectroscopy (EDX) measurement was also employed to detect the elemental content of Mo and S. The results show that the atomic ratio of Mo *versus* S is about 1 : 2, however there is a loss of S of about 2%, which should be ascribed to systematic error and a partial over-discharge effect. Fig. 3d shows the electrode material after cycling 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 separation of Mo and Li₂S leading to a severe capacity loss.¹⁶

Fig. 3 TEM characterization of the electrode material (half cell) after cycling. (a) The TEM image, (b) HRTEM image, and (c) EDX of the MoS₂ electrode at 1.0 V after cycling between 1.0 V and 3.0 V 100 times. (d) HRTEM image of the MoS₂ electrode at 0.1 V after cycling at 0.1–3.0 V 10 times.

The overall characterization and discussion connect the proof of the excellent electrochemical properties of H-MoS₂ cycling in 1.0–3.0 V. Expanded layers provide better thermodynamics and kinetics, expressed as a higher discharge voltage and fast ionic conductivity. By eliminating the conversion reaction, the wholly preserved layer-structured MoS₂ ensures a rechargeable ability for MoS₂/Li and LiCoO₂/MoS₂ batteries. A smaller charge transfer resistance reveals improved kinetics leading to a smaller voltage polarization.

Conclusions

The as-prepared MoS₂ was synthesized through a hydrothermal process. By cutting off the terminal discharge voltage to 1.0 V in an ether-based electrolyte, H-MoS₂ exhibits a high discharge capacity of 200 mA h g⁻¹ at 0.2 A g⁻¹ with a stable charge and discharge platform of ~1.8 V and ~1.6 V, respectively. Regarding the cyclability, it can cycle 1400 times with almost no capacity fade. Thus controlling the terminal discharge voltage should be an effective way to improve conversion type materials with two key factors; an intercalation process that occurs before the conversion reaction happens, and easy-control voltage management. More attention should focus on the intercalation reaction so that MoS₂ can finally find promising applications as an anode material for rechargeable lithium ion batteries.

Acknowledgements

This work is financially supported by the Australian Research Council (ARC) through a Linkage Project (LP120200432) and the Commonwealth of Australia through the Automotive Australia 2020 Cooperative Research Centre (Auto CRC). The authors acknowledge use of the facilities at the UOW Electron Microscopy Centre funded by ARC grants (LE0882813 and LE0237478). The authors would also like to thank Dr Tania Silver for the critical reading of the manuscript.

Notes and references

- B. Dunn, H. Kamath and J.-M. Tarascon, *Science*, 2011, **334**, 928–935.
- K. Kang, Y. S. Meng, J. Bréger, C. P. Grey and G. Ceder, *Science*, 2006, **311**, 977–980.
- 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.
- Y. Sun, J. Zhu, L. Bai, Q. Li, X. Zhang, W. Tong and Y. Xie, *Inorg. Chem. Front.*, 2014, **1**, 58–64.
- S. Xu, S. Lau and L. A. Archer, *Inorg. Chem. Front.*, 2015, **2**, 1070–1079.
- J. Zhou, J. Qin, X. Zhang, C. Shi, E. Liu, J. Li, N. Zhao and C. He, *ACS Nano*, 2015, **9**, 3837–3848.
- R. Tenne, *Nat. Nanotechnol.*, 2006, **1**, 103–111.
- X. Huang, Z. Y. Zeng and H. Zhang, *Chem. Soc. Rev.*, 2013, **42**, 1934–1946.
- X. Cao, Y. Shi, W. Shi, X. Rui, Q. Yan, J. Kong and H. Zhang, *Small*, 2013, **9**, 3433–3438.
- H. Hwang, H. Kim and J. Cho, *Nano Lett.*, 2011, **11**, 4826–4830.
- K. Chang and W. X. Chen, *J. Mater. Chem.*, 2011, **21**, 17175–17184.
- 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.
- P. Sun, W. Zhang, X. Hu, L. Yuan and Y. Huang, *J. Mater. Chem. A*, 2014, **2**, 3498–3504.
- Z. Wu, B. Li, Y. Xue, J. Li, Y. Zhang and F. Gao, *J. Mater. Chem. A*, 2015, **3**, 19445–19454.
- Y. Gong, S. Yang, Z. Liu, L. Ma, R. Vajtai and P. M. Ajayan, *Adv. Mater.*, 2013, **25**, 3979–3984.
- T. Stephenson, Z. Li, B. Olsen and D. Mitlin, *Energy Environ. Sci.*, 2014, **7**, 209–231.
- Y. X. Wang, S. L. Chou, D. Wexler, H. K. Liu and S. X. Dou, *Chem. – Eur. J.*, 2014, **20**, 9607–9612.
- H. Liu, D. Su, R. Zhou, B. Sun, G. Wang and S. Z. Qiao, *Adv. Energy Mater.*, 2012, **2**, 970–975.
- J. Gao, M. A. Lowe, Y. Kiya and H. D. Abruña, *J. Phys. Chem. C*, 2011, **115**, 25132–25137.
- Y.-X. Yin, S. Xin, Y.-G. Guo and L.-J. Wan, *Angew. Chem., Int. Ed.*, 2013, **52**, 13186–13200.
- C. B. Zhu, X. K. Mu, P. A. van Aken, Y. Yu and J. Maier, *Angew. Chem., Int. Ed.*, 2014, **53**, 2152–2156.
- K. Zhang, X. Han, Z. Hu, X. Zhang, Z. Tao and J. Chen, *Chem. Soc. Rev.*, 2015, **44**, 699–728.
- Z. Hu, L. Wang, K. Zhang, J. Wang, F. Cheng, Z. Tao and J. Chen, *Angew. Chem., Int. Ed.*, 2014, **53**, 12794–12798.
- Z. Hu, Z. Zhu, F. Cheng, K. Zhang, J. Wang, C. Chen and J. Chen, *Energy Environ. Sci.*, 2015, **8**, 1309–1316.
- K. Zhang, Z. Hu, X. Liu, Z. Tao and J. Chen, *Adv. Mater.*, 2015, **27**, 3305–3309.
- M. A. Py and R. R. Haering, *Can. J. Phys.*, 1983, **61**, 76–84.
- Z. Hu, K. Zhang, Z. Zhu, Z. Tao and J. Chen, *J. Mater. Chem. A*, 2015, **3**, 12898–12904.
- Z. Zhu, F. Cheng and J. Chen, *J. Mater. Chem. A*, 2013, **1**, 9484–9490.
- N. Imanishi, K. Kanamura and Z. i. Takehara, *J. Electrochem. Soc.*, 1992, **139**, 2082–2087.
- C. Julien, S. I. Saikh and G. A. Nazri, *Mater. Sci. Eng., B*, 1992, **15**, 73–77.
- Y. Miki, D. Nakazato, H. Ikuta, T. Uchida and M. Wakihara, *J. Power Sources*, 1995, **54**, 508–510.
- L. Qian and H. Zhang, *J. Chem. Technol. Biotechnol.*, 2011, **86**, 172–184.
- 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.
- S. Q. Yang, D. X. Li, T. R. Zhang, Z. L. Tao and J. Chen, *J. Phys. Chem. C*, 2011, **116**, 1307–1312.