Approaching the lithiation limit of MoS₂ while maintaining its layered crystalline structure to improve lithium storage

Zhu, Zhiqiang; Tang, Yuxin; Leow, Wan Ru; Xia, Huarong; Lv, Zhisheng; Wei, Jiaqi; Ge, Xiang; Cao, Shengkai; Zhang, Yanyan; Zhang, Wei; Zhang, Hongwei; Xi, Shibao; Du, Yonghua; Chen, Xiaodong

2019

Zhu, Z., Tang, Y., Leow, W. R., Xia, H., Lv, Z., Wei, J., . . . Chen, X. (2019). Approaching the Lithiation Limit of MoS₂ While Maintaining Its Layered Crystalline Structure to Improve Lithium Storage. *Angewandte Chemie International Edition*, 58(11), 3521–3526.
doi:10.1002/anie.201813698

<https://hdl.handle.net/10356/144550>

<https://doi.org/10.1002/anie.201813698>

This is the accepted version of the following article: Zhu, Z., Tang, Y., Leow, W. R., Xia, H., Lv, Z., Wei, J., . . . Chen, X. (2019). Approaching the Lithiation Limit of MoS₂ While Maintaining Its Layered Crystalline Structure to Improve Lithium Storage. *Angewandte Chemie International Edition*, 58(11), 3521–3526., which has been published in final form at doi:10.1002/anie.201813698. This article may be used for non-commercial purposes in accordance with the Wiley Self-Archiving Policy
[<https://authorservices.wiley.com/authorresources/Journal-Authors/licensing/self-archiving.html>].

Approaching the Lithiation Limit of MoS₂ While Maintaining Its Layered Crystalline Structure to Improve Lithium Storage

Zhiqiang Zhu, Yuxin Tang, Wan Ru Leow, Huarong Xia, Zhisheng Lv, Jiaqi Wei, Xiang Ge, Shengkai Cao, Yanyan Zhang, Wei Zhang, Hongwei Zhang, Shibo Xi, Yonghua Du*, and Xiaodong Chen*

Abstract: MoS₂ holds great promise as high-rate electrode for lithium ion batteries since its large interlayer can allow fast lithium diffusion in 3.0–1.0 V. However, the low theoretical capacity (167 mAh/g) limits its wide application. Here, by fine tuning the lithiation depth of MoS₂, we demonstrate that its parent layered structure can be preserved with expanded interlayers while cycling in 3.0–0.6 V. The deeper lithiation and maintained crystalline structure endows commercially micrometre-sized MoS₂ with a capacity of 232 mAh/g at 0.05 A/g and ~92% capacity retention after 1000 cycles at 1.0 A/g. Moreover, the enlarged interlayers enable MoS₂ to release a capacity of 165 mAh/g at 5.0 A/g, which is double the capacity obtained under 3.0–1.0 V at the same rate. Our strategy of controlling the lithiation depth of MoS₂ to avoid fracture ushers in new possibilities to enhance the lithium storage of layered transition metal dichalcogenides.

Lithium ion batteries (LIBs) with fast charging/discharging capability are urgently needed for portable/miniaturized electronic devices.^[1] However, the commercial anode material, graphite, cannot be used at high rates owing to its low lithiation potential (~0.1 V, the potential discussed in this manuscript is vs. Li⁺/Li, except in the case of the full cell) that may cause Li-dendrite growth as well as short circuits.^[2] Therefore, developing electrode materials with higher lithiation potential and good lithium mobility is essential. From this aspect, MoS₂ should be a promising candidate since its large interlayer space (0.62 nm) can allow fast lithium diffusion in 3.0–1.0 V.^[3] Additionally, the layered crystalline structure of MoS₂ can be well retained during repeated cycling, thus ensuring long cycle life.^[4] The main limitation of this reaction is its low theoretical capacity (167 mAh/g). Although some reports have shown that nanosized MoS₂ with expanded interlayers could offer higher capacity and faster reaction kinetics, the complicated synthetic procedures of these nanoscale materials are unsuitable for large-scale applications.^[5] In addition, nanosized materials are generally characterized by low volumetric energy density.^[6] Therefore, it is of great importance to exploit cheap and commercially micrometre-sized MoS₂ as electrode for LIBs.

A simple and widely used strategy to enhance the capacity of MoS₂ is to lower the discharging cutoff voltage from 1.0 to 0.01 V.^[7] This would induce its conversion to Mo and Li₂S, offering a

theoretical capacity of 669 mAh/g, almost twice that of commercial graphite anode.^[8] Unfortunately, such deep lithiation would cause the structural failure of MoS₂, leading to large volume changes (~103%) as well as poor cycle stability.^[9] To prolong the lifespan, the prevailing approach is to utilize nanostructured MoS₂ composites, but the issue of scale up synthesis still remains to be addressed.^[10] Hence, it is a critical challenge to realize the long-term cycling of micrometre-sized MoS₂ with enhanced capacity and kinetics.

To identify an alternative solution, we must first look at the lithium storage mechanism of MoS₂. Above 1.0 V, lithium ions are first stored in the interlayer of MoS₂, which is nondestructive to its pristine framework.^[3a, 3b] The following inserted lithium ions then begin to react with S atoms to form Li₂S.^[7c] With more and more S atoms are pulled away from the S–Mo–S skeleton, the crystalline structure of MoS₂ would start to crumble at a critical transition point, that is, the lithiation limit that can maintain its parent layered structure. We hypothesize that approaching this critical state can improve the capacity of MoS₂ without sacrificing its stability, since conversion reaction has already occurred at this point, but the parent layered structure of MoS₂ is retained (Scheme 1).

Here, by fine tuning the lithiation depth of MoS₂, we reveal that its parent layered structure can be retained when cycled in 3.0–0.6 V, and the interlayer remains expanded after de-lithiation. The deeper lithiation and well-maintained crystalline structure allows commercially micrometre-sized MoS₂ (~1.5 μm) to offer a capacity of 232 mAh/g at 0.05 A/g and a good capacity retention of ~92% even after 1000 cycles at 1.0 A/g. Moreover, owing to its enlarged interlayer space, a capacity of 165 mAh/g can be released at a high rate of 5.0 A/g (corresponding to ~2 min discharging/charging), which is double the capacity gained with 3.0–1.0 V at the same rate. Such remarkable rate performance is even comparable to that of heavily studied nanosized high-rate anodes such as Li₄Ti₅O₁₂, TiO₂, and Nb₂O₅.^[11] We further show that the full cell coupled with LiCoO₂ cathode can exhibit improved performance by controlling the lithiation depth of MoS₂, confirming the applicability of our strategy toward full cell applications.

In a typical experiment, micrometre-sized MoS₂ (~1.5 μm) purchased from Sigma-Aldrich was directly used as electrode materials (Figure S1). Our first aim is to find out the lowest discharging cutoff voltage at which MoS₂ has already undergone conversion reaction but still preserves its layered crystalline structure. To this end, we collected the powder X-ray diffraction (XRD) patterns (Figure 1a) and S K-edge X-ray absorption spectroscopy (XAS, Figure 1b) of MoS₂ electrodes discharged to different voltages at 0.05 A/g. To avoid air exposure during the XRD measurement, the cycled electrodes are sealed with Para film, which has little effect on the diffraction peaks of the active materials (Figure S2). As shown in Figure 1a, the ordered layered structure of pristine MoS₂ leads to a strong (002) reflection at 14.38°,^[12] which is shifted to a lower angle after discharging to 1.0 V. The intensity of the diffraction peaks around 40° becomes

[a] Dr. Z. Zhu, Dr. Y. Tang, Dr. W. Leow, Dr. H. Xia, Z. Lv, J. Wei, Dr. X. Ge, S. Cao, Dr. Y. Zhang, Dr. W. Zhang, Dr. H. Zhang, Prof. X. Chen

Innovative Centre for Flexible Devices (iFLEX), School of Materials Science and Engineering, Nanyang Technological University
50 Nanyang Avenue, Singapore 639798

E-mail: chenxd@ntu.edu.sg

[b] Dr. S. Xi, Dr. Y. Du
Institute of Chemical and Engineering Sciences, 1 Pesek Road,
Jurong Island, Singapore 627833
E-mail: du_yonghua@ices.a-star.edu.sg

Supporting information for this article is given via a link at the end of the document.

Scheme 1. Schematic of the proposed strategy. The deep conversion reaction of MoS_2 in 3.0-0.01 V yields higher capacity than that of the intercalation reaction in 3.0-1.0 V, but it causes structural collapse resulting in short lifespan. We propose that fine tuning the lithiation depth to avoid structural collapse of MoS_2 can improve its capacity without compromising its cycle stability.

much weaker than that of pristine MoS_2 , which should be ascribed to the intercalation induced phase change.^[13] Additionally, no peaks related to Li_2S are observed in the corresponding XAS spectrum (Figure 1b). This phenomenon agrees well with previous reports that only intercalation reaction takes place in 3.0-1.0 V, which enlarges the interlayer space.^[13] It is interesting to note that for the electrode discharged to 0.6 V, the (002) peak is still prominent in the XRD pattern, and the corresponding XAS spectrum exhibits a new peak centered at 2475.7 eV, which is originated from Li_2S .^[13] These results indicate that MoS_2 has undergone conversion at this moment, but its layered crystalline structure is well preserved. However, further discharging MoS_2 to 0.5 V results in structural degradation, as evidenced by the absence of the (002) peak in the XRD pattern. A more detailed XRD analysis reveals that the intensity of the (002) peak significantly decreases at 0.59 V (Figure S3), suggesting that the layered crystalline structure of MoS_2 has been partially destroyed. This means that 0.6 V should be the lowest discharging voltage at which MoS_2 can well preserve its parent layered structure. Similar results can be found in MoS_2 samples with different particle sizes (Figure S4). Thus we selected 3.0-0.6 V as the voltage window to control the lithiation depth of MoS_2 in order to avoid fracture. For comparison, we have also tested the lithium storage performance of MoS_2 with two other voltage ranges, 3.0-1.0 V (in which only intercalation occurs) and 3.0-0.5 V (in which deep lithiation destroys the layered crystalline structure).

The lithium storage property of MoS_2 was first investigated at 0.05 A/g in different voltage ranges. Figure 2a shows the initial differential capacity (dQ/dV) plots. During the discharging process, all cells exhibit a distinct peak at ~ 1.1 V, corresponding to the intercalation of Li^+ into the interlayer space to form Li_xMoS_2 .^[14] For the cells cycled in 3.0-0.6 V and 3.0-0.5 V, an additional peak located at ~ 0.6 V is related to the subsequent conversion reaction.^[15] However, the charging segment of the dQ/dV curve for the cell cycled between 3.0-0.5 V only features a prominent peak centered at ~ 2.2 V. This is different from that of the other two cells, which possess three small peaks located at ~ 1.9 , ~ 2.0 and ~ 2.5 V corresponding to the multistage de-intercalation process.^[5b, 13] Such differences are consistent with that among the voltage profiles (Figure S5) and cyclic voltammetry (CV) curves (Figure S6), and are also observed in the following dQ/dV curves (Figure S7). The dQ/dV curves of the cell cycled in 3.0-0.5 V is very similar to that of the cell cycled in 3.0-0.01 V (Figure S8), which has undergone full conversion reaction.^[16] Therefore we

Figure 1. a) XRD patterns and b) S K-edge XAS spectra of MoS_2 electrodes discharged to different voltages at 0.05 A/g. The peaks marked with “♦” in a) correspond to Para film. The results indicate that MoS_2 has undergone conversion reaction at 0.6 V, but its layered crystalline structure is preserved.

attribute the peak at ~ 2.2 V to the conversion reaction and the de-lithiation process of disordered MoS_2 . We note that this peak also appears in the dQ/dV curves of the cell cycled in 3.0-0.6 V, presumably due to some degree of conversion reaction under this voltage range. Based on the initial charging/discharging curves, we can calculate that about 20% conversion reaction has taken place in 3.0-0.6 V (see details in Figure S5).

Figure 2b shows the reversible capacity (obtained at the fifth cycle) of MoS_2 electrodes obtained in different voltage ranges at 0.05 A/g. In 3.0-1.0 V, the reversible capacity is 150 mAh/g, which increases to 232 and 425 mAh/g when the discharging cutoff voltage decreases to 0.6 V and 0.5 V, respectively. The increased capacity is mainly due to the conversion reaction happened below 1.0 V. However, deeper lithiation also has a significant effect on the cycle stability. Figure 2c presents the cycle performance of MoS_2 in different voltage ranges at 1.0 A/g. The cells have been cycled at 0.05 A/g in the initial five cycles. The initial Coulombic efficiencies (CEs) of the three cells are relatively low, which could be due to the partial side reaction and the possibility of traces of residual Li^+ inside the layers during the first cycle.^[5c, 13] However, the CEs of all the cells quickly increase to $>99.5\%$ after several cycles. Notably, MoS_2 can realize stable cycling in 3.0-1.0 V,^[13] but the reversible capacity of 110 mAh/g is relatively low. Although the cell cycled in 3.0-0.5 V delivers a much higher capacity of 375 mAh/g, it starts to decline after 200 cycles, retaining only a capacity of 140 mAh/g after 1000 cycles. In contrast, the cell cycled in 3.0-0.6 V demonstrates excellent cycle stability, with a capacity retention of $\sim 92\%$ after 1000 cycles. Moreover, its reversible capacity of 190 mAh/g is ~ 1.7 times the capacity obtained in 3.0-1.0 V. Similar phenomena are also found in the other two MoS_2 electrodes with different particle sizes (Figure S9). These results clearly validate our hypothesis that approaching the lithium storage limit that maintains the parent layered structure of MoS_2 can enhance its capacity without deteriorating its cycle stability.

In addition to raising the capacity, another merit of lowering the discharging cutoff voltage to 0.6 V is to promote the reaction kinetics. Since MoS_2 shows rapid capacity fade when cycled in 3.0-0.5 V, we only compared the rate capability of cells under the 3.0-1.0 V and 3.0-0.6 V ranges (Figure 2d). The typical voltage profiles are presented in Figure S10. For the cell cycled in 3.0-

1.0 V, the capacity gained at 0.05 A/g (150 mAh/g) is reduced to only 80 mAh/g when the current density increases to 5.0 A/g. In contrast, the cell cycled in 3.0–0.6 V delivers a much higher capacity of 165 mAh/g at 5.0 A/g (~2 mins discharging/charging). Such excellent rate performance is comparable or even better compared to that of reported nanostructured MoS₂ cycled in 3.0–1.0 V (Figure 2e and Table S1)^[5b] and state-of-the-art nanosized high-rate anode materials such as Li₄Ti₅O₁₂, TiO₂(B), and Nb₂O₅ (Figure 2e).^[11] Considering that the active materials investigated in this work are commercial micrometre-sized particles

without any further treatment, the achieved performance makes MoS₂ a promising candidate for high-power applications.

To understand the origin of the improved performance, XRD studies was conducted on the structure of the fully charged MoS₂ electrodes after cycling with different voltage ranges (Figure S11). The presence of a prominent (002) reflection peak in the XRD patterns of the electrodes cycled in 3.0–1.0 V and 3.0–0.6 V indicates that the layered crystalline structure is preserved. Interestingly, this peak is shifted to a lower angle, suggesting that the interlayer remains expanded even after de-lithiation (Figure 3a). This should be due to the remnant lithium trapped in MoS₂.^[13] The calculated *d*-spacing for the electrodes cycled in 3.0–1.0 V and 3.0–0.6 V are 0.63 and 0.64 nm, respectively. The larger interlayer distance for the latter may be due to structure defects induced by the conversion reaction. Note that the larger interlayer distance can facilitate lithium diffusion,^[17] as revealed by the transport measurements made with the galvanostatic intermittent titration technique (Figure S12). In contrast, MoS₂ becomes amorphous after cycling in 3.0–0.5 V, as can be seen from the disappearance of the (002) peak in the XRD pattern.

To further confirm our observations, transmission electron microscope (TEM) analysis was performed on the fully charged electrodes (Figure 3b–e), and the results coincides well with that of the XRD. The pristine MoS₂ shows distinct lamellar structure with *d*-spacing of 0.62 nm, which increases to 0.63 and 0.64 nm after cycling in 3.0–1.0 V and 3.0–0.6 V, respectively. By comparison, the MoS₂ electrode cycled in 3.0–0.5 V becomes highly disordered, which is consistent with previous reports that MoS₂ would transform to nanocrystals after undergoing deep conversion reaction.^[18] From the above results, we can conclude that MoS₂ could preserve its layered crystalline structure at potential above 0.6 V, thus ensuring long-term cycling (Figure 3f). The deeper lithiation and larger interlayer spacing respectively endow MoS₂ with higher capacity and faster kinetics between 3.0–0.6 V. However, further discharging MoS₂ to 0.5 V would cause structural failure, generating a large amount of disordered

Figure 2. Electrochemical performance of commercially micrometre-sized MoS₂ cycled in different voltage ranges. a) Initial dQ/dV curves at 0.05 A/g. The curves of the cell cycled in 3.0–0.5 V changes a lot due to the structural collapse. b) Statistical study of reversible capacity obtained at 0.05 A/g in the fifth cycle and capacity retention after cycling at 1.0 A/g for 1000 cycles. c) Cycling performance at 1.0 A/g. The cells have been cycled at 0.05 A/g in the initial five cycles. d) Rate capability of MoS₂ electrodes cycled in 3.0–1.0 V and 3.0–0.6 V. e) Comparison of the rate performance of our micrometre-sized MoS₂ with previously reported nanostructured MoS₂ electrodes cycled in 3.0–1.0 V and state-of-the-art nanosized high-rate anodes including Li₄Ti₅O₁₂, TiO₂(B) and Nb₂O₅.^[5b, 11]

nanocrystals. Although this could be beneficial to gain higher capacity,^[19] the huge structural change from bulky materials to nanocrystals would undoubtedly lead to large volume changes.^[20] Severe issues such as material pulverization and repeated solid-electrolyte interphase (SEI) formation would occur, finally causing rapid capacity decay.^[21]

To ascertain the aforementioned analysis, we further investigated the morphological changes of the MoS₂ electrodes after cycling in different voltage windows by scanning electron microscopy (SEM, Figure S13). The surface of MoS₂ particles cycled in 3.0–1.0 V and 3.0–0.6 V remain smooth even after 200 cycles, suggesting the formation of thin and stable SEI. However, a large amount of floccule appears on the surface of MoS₂ particles after cycling in 3.0–0.5 V for 200 cycles, which is indicative of successive SEI formation.^[22] This is supported by energy-dispersive X-ray spectroscopy (EDX, Figure S14) and X-ray photoelectron spectroscopy (XPS, Figure S15) analysis, which reveal that the composition of the SEI continues to change when the electrode is cycled in 3.0–0.5 V, while the SEI layers keep relatively constant for electrodes cycled in 3.0–1.0 V and 3.0–0.6 V. The thicker SEI could hinder charge transfer and consequently lead to large interfacial resistance,^[23] as shown by the impedance study (Figure S16). The above results clearly prove our conclusion that the structural degradation of MoS₂, which induces large volume changes, is responsible for capacity fading when cycling between 3.0–0.5 V.

The feasibility of our strategy for MoS₂ towards full cell application is affirmed by coupling with a LiCoO₂ cathode. To evaluate the performance of MoS₂, the cell is designed with the capacity limitation of MoS₂. As the negative electrode, the lithiation depth of MoS₂ in the full cell is controlled by the charging cutoff voltage. Accordingly, two voltage windows, 0.8–3.0 V and 0.8–3.4 V, have been tested, which respectively correspond to the discharging cutoff voltage of 1.0 and 0.6 V for MoS₂ in the half cell. As illustrated in Figure S17a, the cell cycled in 0.8–3.4 V shows a discharging capacity of 220 mAh/g with an average operation

Figure 3. a) Enlarged XRD patterns of the fully charged MoS₂ electrodes after cycling in different voltages for one cycle. The peaks marked with “♦” in a) correspond to Para film. b)–e) Corresponding TEM images with contrast profiles along the arrow-direction indicating average interlayer distance. f) Scheme for the structural changes and lithium storage performance of MoS₂ cycled in different voltage windows. MoS₂ can preserve its parent layered structure at potential above 0.6 V, thus ensuring long-term cycling. Additionally, the deeper lithiation and larger interlayer endow MoS₂ with higher capacity and faster kinetics in 3.0–0.6 V. In contrast, structural collapse takes place for the electrode cycled in 3.0–0.5 V, thus showing rapid capacity fading even though it can offer higher capacity.

voltage of 2.02 V at 0.05 A/g, higher than that of the cell cycled in 0.8–3.0 V (129 mAh/g and 1.92 V). Both cells demonstrate excellent cycle stability, with a capacity retention of ~90% after 1000 cycles at 1.0 A/g (Figure S17b). It should be highlighted that the rate capability of the cell cycled in 0.8–3.4 V is greatly improved, delivering a capacity of 125 mAh/g at 5.0 A/g, which is ~3 times the capacity obtained in 0.8–3.0 V (Figure S17c).

In summary, by fine tuning the lithiation depth of MoS₂, we revealed that its parent layered structure can be maintained when cycling in 3.0–0.6 V, along with the discovery of interlayer expansion after de-lithiation. The deeper lithiation, maintained crystalline structure, and enlarged interlayers allow commercially micrometre-sized MoS₂ to simultaneously achieve higher capacity, long lifespan, and fast rate capability. Specifically, the reversible capacity of commercial MoS₂ (~1.5 µm) reaches 232 mAh/g at 0.05 A/g, and ~92% of the capacity obtained at 1.0 A/g can be remained after 1000 cycles. Moreover, the commercial MoS₂ sample can release a capacity of 165 mAh/g in only ~2 mins (5.0 A/g), which is double the capacity gained in 3.0–1.0 V at the same rate. Such excellent rate performance is even comparable to that of heavily studied nanosized high-rate anodes such as Li₄Ti₅O₁₂, TiO₂, and Nb₂O₅. We also confirmed the feasibility of our approach towards full cell applications by constructing a LiCoO₂ paired full cell, even though there might be some other technical challenges in realizing the large-scale application of such system. Our results reveal the importance of controlling the lithiation depth of MoS₂ to avoid structural collapse towards improved lithium storage, offering a new avenue for developing other layered transition metal dichalcogenides as high performance electrodes for LIBs.

Acknowledgements

This work was supported by Singapore MOE Tier 2 (MOE2015-T2-1-110), Singapore National Research Foundation

(Nanomaterials for Energy and Water Management CREATE Programme).

Keywords: lithium ion batteries • commercial MoS₂ • layered crystalline structure • lithiation depth • high rate

- a) P. Simon, Y. Gogotsi, B. Dunn, *Science* **2014**, 343, 1210; b) Y. Tang, Y. Zhang, W. Li, B. Ma, X. Chen, *Chem. Soc. Rev.* **2015**, 44, 5926; c) C. Yan, Z. Fang, C. Lv, X. Zhou, G. Chen, G. Yu, *ACS Nano* **2018**, 12, 8670.
- a) T. Waldmann, B. I. Hogg, M. Wohlfahrt-Mehrens, *J. Power Sources* **2018**, 384, 107; b) Z. Yang, J. Zhang, M. C. W. Kintner-Meyer, X. Lu, D. Choi, J. P. Lemmon, J. Liu, *Chem. Rev.* **2011**, 111, 3577; c) H. G. Jung, S. T. Myung, C. S. Yoon, S. B. Son, K. H. Oh, K. Amine, B. Scrosati, Y. K. Sun, *Energy Environ. Sci.* **2011**, 4, 1345.
- a) P. J. Mulhern, *Can. J. Phys.* **1989**, 67, 1049; b) T. Stephenson, Z. Li, B. Olsen, D. Mitlin, *Energy Environ. Sci.* **2014**, 7, 209; c) L. Wang, Z. Xu, W. Wang, X. Bai, *J. Am. Chem. Soc.* **2014**, 136, 6693; d) Y. Chao, R. Jallili, Y. Ge, C. Wang, T. Zheng, K. Shu, G. G. Wallace, *Adv. Funct. Mater.* **2017**, 27, 1700234.
- a) M. Azhagurajan, T. Kajita, T. Itoh, Y. G. Kim, K. Itaya, *J. Am. Chem. Soc.* **2016**, 138, 3355; b) X. Fang, C. Hua, X. Guo, Y. Hu, Z. Wang, X. Gao, F. Wu, J. Wang, L. Chen, *Electrochim. Acta* **2012**, 81, 155.
- a) J. B. Cook, H. S. Kim, Y. Yan, J. S. Ko, S. Robbenolt, B. Dunn, S. H. Tolbert, *Adv. Energy Mater.* **2016**, 6, 1501937; b) J. B. Cook, H. S. Kim, T. C. Lin, C. Lai, B. Dunn, S. H. Tolbert, *Adv. Energy Mater.* **2017**, 7, 1601283; c) Z. Hu, Q. Liu, W. Sun, W. Li, Z. Tao, S. Chou, J. Chen, S. Dou, *Inorg. Chem. Front.* **2016**, 3, 532.
- K. J. Griffith, K. M. Wiaderek, G. Cibir, L. E. Marbella, C. P. Grey, *Nature* **2018**, 559, 556.
- a) X. Xu, W. Liu, Y. Kim, J. Cho, *Nano Today* **2014**, 9, 604; b) J. Wang, J. Liu, D. Chao, J. Yan, J. Lin, Z. Shen, *Adv. Mater.* **2014**, 26, 7162; c) T. Wang, S. Chen, H. Pang, H. Xue, Y. Yu, *Adv. Sci.* **2017**, 4, 1600289; d) B. Chen, E. Liu, T. Cao, F. He, C. Shi, C. He, L. Ma, Q. Li, J. Li, N. Zhao, *Nano Energy* **2017**, 33, 247; e) S. Wu, Y. Du, S. Sun, *Chem. Eng. J.* **2017**, 307, 189; e) W. Yang, L. He, X. Tian, M. Yan, H. Yuan, X. Liao, J. Meng, Z. Hao, L. Mai, *Small* **2017**, 13, 1700639.
- a) D. Kong, H. He, Q. Song, B. Wang, W. Lv, Q. Yang, L. Zhi, *Energy Environ. Sci.* **2014**, 7, 3320; b) P. Wang, H. Sun, Y. Ji, W. Li, X. Wang, *Adv. Mater.* **2014**, 26, 964; c) L. Zhou, K. Zhang, Z. Hu, Z. Tao, L. Mai, Y. M. Kang, S. Chou, J. Chen, *Adv. Energy Mater.* **2018**, 8, 1701415.
- a) F. Zhou, S. Xin, H. Liang, L. Song, S. Yu, *Angew. Chem. Int. Ed.* **2014**, 53, 11552; b) C. Zhu, X. Mu, P. A. van Aken, Y. Yu, J. Maier, *Angew. Chem.*

- Int. Ed.* **2014**, 53, 2152; c) X. Li, J. Zhang, R. Wang, H. Huang, C. Xie, Z. Li, J. Li, C. Niu, *Nano Lett.* **2015**, 15, 5268; d) T. Shan, S. Xin, Y. You, H. Cong, S. Yu, A. Manthiram, *Angew. Chem. Int. Ed.* **2016**, 55, 12783.
- [10] a) Y. Chen, X. Yu, Z. Li, U. Paik, X. Lou, *Sci. Adv.* **2016**, 2, e1600021; b) Y. Fang, Y. Lv, F. Gong, A. A. Elzatahry, G. Zheng, D. Zhao, *Adv. Mater.* **2016**, 28, 9385; c) Y. Wang, Z. Ma, Y. Chen, M. Zou, M. Yousaf, Y. Yang, L. Yang, A. Cao, R. Han, *Adv. Mater.* **2016**, 28, 10175; d) Z. Deng, H. Jiang, Y. Hu, Y. Liu, L. Zhang, H. Liu, C. Li, *Adv. Mater.* **2017**, 29, 1603020.
- [11] a) L. Shen, X. Zhang, E. Uchaker, C. Yuan, G. Cao, *Adv. Energy Mater.* **2012**, 2, 691; b) Y. Tang, Y. Zhang, J. Deng, D. Qi, W. R. Leow, J. Wei, S. Yin, Z. Dong, R. Yazami, Z. Chen, X. Chen, *Angew. Chem. Int. Ed.* **2014**, 53, 13488; c) V. Augustyn, J. Come, M. A. Lowe, J. W. Kim, P. L. Taberna, S. H. Tolbert, H. D. Abruña, P. Simon, B. Dunn, *Nat. Mater.* **2013**, 12, 518.
- [12] D. Xiao, J. Zhang, X. Li, D. Zhao, H. Huang, J. Huang, D. Cao, Z. Li, C. Niu, *ACS Nano* **2016**, 10, 9509.
- [13] L. Zhang, D. Sun, J. Kang, J. Feng, H. A. Bechtel, L. Wang, E. J. Cairns, J. Guo, *Nano Lett.* **2018**, 18, 1466.
- [14] a) L. Oakes, R. Carter, T. Hanken, A. P. Cohn, K. Share, B. Schmidt, C. L. Pint, *Nat. Commun.* **2016**, 7, 11796; b) J. Xiao, X. Wang, X. Yang, S. Xun, G. Liu, P. K. Koech, J. Liu, J. P. Lemmon, *Adv. Funct. Mater.* **2011**, 21, 2840; c) Y. Gong, S. Yang, L. Zhan, L. Ma, R. Vajtai, P. M. Ajayan, *Adv. Funct. Mater.* **2014**, 24, 125; d) J. Li, Y. Hou, X. Gao, D. Guan, Y. Xie, J. Chen, C. Yuan, *Nano Energy* **2015**, 16, 10; e) F. Xiong, Z. Cai, L. Qu, P. Zhang, Z. Yuan, O. K. Asare, W. Xu, C. Lin, L. Mai, *ACS Appl. Mater. Interfaces* **2015**, 7, 12625.
- [15] a) X. Zhou, L. Wan, Y. Guo, *Chem. Commun.* **2013**, 49, 1838; b) H. Jiang, D. Ren, H. Wang, Y. Hu, S. Guo, H. Yuan, P. Hu, L. Zhang, C. Li, *Adv. Mater.* **2015**, 27, 3687; c) X. Fang, X. Yu, S. Liao, Y. Shi, Y. Hu, Z. Wang, G. D. Stucky, L. Chen, *Microporous Mesoporous Mater.* **2012**, 151, 418; d) X. Li, J. Zai, S. Xiang, Y. Liu, X. He, Z. Xu, K. Wang, Z. Ma, X. Qian, *Adv. Energy Mater.* **2016**, 6, 1601056; e) J. Xiao, D. Choi, L. Cosimbescu, P. Koech, J. Liu, J. P. Lemmon, *Chem. Mater.* **2010**, 22, 4522.
- [16] a) C. George, A. J. Morris, M. H. Modarres, M. De Volder, *Chem. Mater.* **2016**, 28, 7304; b) J. Wan, W. Bao, Y. Liu, J. Dai, F. Shen, L. Zhou, X. Cai, D. Urban, Y. Li, K. Jungjohann, M. S. Fuhrer, L. Hu, *Adv. Energy Mater.* **2015**, 5, 1401742.
- [17] a) H. Hwang, H. Kim, J. Cho, *Nano Lett.* **2011**, 11, 4826; b) Z. Hu, L. Wang, K. Zhang, J. Wang, F. Cheng, Z. Tao, J. Chen, *Angew. Chem. Int. Ed.* **2014**, 53, 12794.
- [18] a) Q. Su, S. Wang, M. Feng, G. Du, B. Xu, *Sci. Rep.* **2017**, 7, 7275; b) Z. Zhu, X. Chen, *Nano Res.* **2017**, 10, 4115.
- [19] J. Jamnik, J. Maier, *Phys. Chem. Chem. Phys.* **2003**, 5, 5215.
- [20] a) H. Liu, D. Su, R. Zhou, B. Sun, G. Wang, S. Qiao, *Adv. Energy Mater.* **2012**, 2, 970; b) X. Wang, G. Li, M. H. Seo, F. M. Hassan, M. A. Hoque, Z. Chen, *Adv. Energy Mater.* **2015**, 5, 1501106.
- [21] a) J. Liu, N. Li, M. D. Goodman, H. Zhang, E. S. Epstein, B. Huang, Z. Pan, J. Kim, J. H. Choi, X. Huang, J. Liu, K. J. Hsia, S. J. Dillon, P. V. Braun, *ACS Nano* **2015**, 9, 1985; b) Y. Tang, D. Wu, S. Chen, F. Zhang, J. Jia, X. Feng, *Energy Environ. Sci.* **2013**, 6, 2447; c) M. Han, C. Zhu, Q. Zhao, C. Chen, Z. Tao, W. Xie, F. Cheng, J. Chen, *ACS Appl. Mater. Interfaces* **2017**, 9, 28620.
- [22] Y. Tang, J. Deng, W. Li, O. I. Malys, Y. Zhang, X. Zhou, S. Pan, J. Wei, Y. Cai, Z. Chen, X. Chen, *Adv. Mater.* **2017**, 29, 1701828.
- [23] Z. Zhu, Y. Tang, Z. Lv, J. Wei, Y. Zhang, R. Wang, W. Zhang, H. Xia, M. Ge, X. Chen, *Angew. Chem. Int. Ed.* **2018**, 57, 3656.

Entry for the Table of Contents

COMMUNICATION

Zhiqiang Zhu, Yuxin Tang, Wan Ru Leow, Huarong Xia, Zhisheng Lv, Jiaqi Wei, Xiang Ge, Shengkai Cao, Yanyan Zhang, Wei Zhang, Hongwei Zhang, Shibo Xi, Yonghua Du*, and Xiaodong Chen*

Page No. – Page No.

Approaching the Lithiation Limit of MoS₂ While Maintaining Its Layered Crystalline Structure to Improve Lithium Storage

By fine tuning the lithiation depth of MoS₂, we reveal that its layered crystalline structure can be well preserved when cycled in 3.0-0.6 V (vs. Li⁺/Li), which is accompanied with the expansion of the interlayer distance. These features enable the stable cycling of commercially micrometre-sized MoS₂ with higher capacity and faster rate capability, rendering itself a promising anode for fast charging lithium ion batteries.