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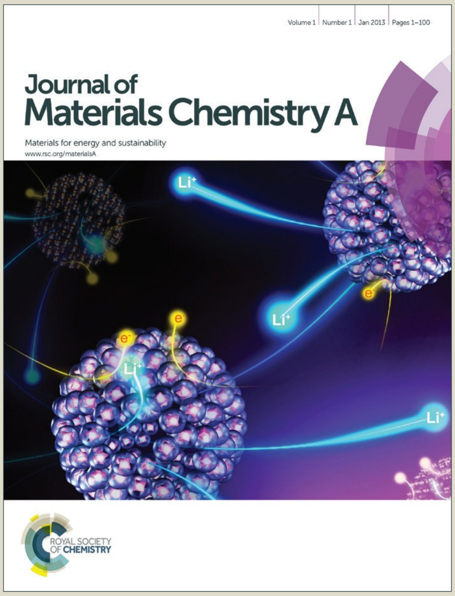

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All-solid-state MoS_2/Li_6PS_5Br/In-Li batteries as a novel type of Li/S batteries

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We demonstrate the first all-solid-state lithium secondary batteries that combines MoS_2 as cathode material with lithium argyrodite Li_6PS_5Br solid electrolyte. On first full discharge the battery turns into an all-solid-state Li/S battery with Mo nanoparticles of a size around 3 nm finely dispersed in the composite cathode. The cell achieves a competitive capacity retention of 85% over 700 cycles at rates in the range of C/5 to 1C, retaining a reversible capacity of 270 mAh/g at C/5 and 70 °C.

All-solid-state lithium secondary batteries present a pathway to high safety, high cyclability and high energy density energy storage systems, by replacing flammable organic liquid electrolyte with inorganic fast-ion conducting solids. Among the reported fast Li^+-ion conducting solids, lithium argyrodites Li_6PS_5X (X= Cl, Br)[1,2] are particularly promising candidates for solid electrolyte with high ionic conductivity,[3] high electrochemical stability[4] and easy fabrication.[5] However, only a few all-solid-state batteries using lithium argyrodites have been reported so far.[4,6,7] To ensure chemical compatibility of the solid electrolyte with the cathode, it appears straightforward to combine argyrodites (or other thiophosphate solid electrolytes) with sulfur-based electrodes.

The high specific capacity and energy density, low cost and low toxicity of sulfur has rendered rechargeable Li/S batteries attractive as potential next-generation energy storage system.[8] Besides the extremely low electronic and ionic conductivity of S and Li_2S, a key challenge limiting a wider application of the Li/S chemistry in liquid electrolyte batteries is the high solubility of intermediately formed polysulfides in liquid electrolytes. Various approaches have been proposed to mitigate this challenge, such as exploring encapsulation of sulfur in carbonaceous or transition metal compound shells,[9, 10] in metal organic frameworks,[11] retention at carbon surfaces and pores,[12] or optimizing the solid electrolyte interface by ionic liquids[13] as well as other additives.[14,15]

Despite the fact that various challenges of the otherwise attractive Li/S battery concept are linked to the use of liquid electrolytes, only a few groups developed all-solid-state Li/S batteries that can circumvent these problems.[16,17,18] Our group recently demonstrated an argyrodite-based all-solid-state Li/S battery achieving a reversible capacity of 1080 mAh/g after 50 cycles at room temperature.[19] Still as for most high capacity all-solid-state batteries it remains a challenge to achieve competitive power performance. Hence, we explore in this work the widening of the range of available high capacity high power performance electrode materials suitable for combination with argyrodites in all-solid-state batteries.

MoS_2 shows great potential as a cathode material for this application due to its high theoretical capacity (670 mAh/g), low cost and low toxicity. Recently, it has been reported that a MoS_2 liquid electrolyte battery turns into a Li/S battery after full discharge.[20,21] The Mo nanoparticles formed within the cathode provides electrically conducting paths, thus effectively mitigating the extremely low electronic conductivity of sulfur and Li_2S.[21] On the other hand, in the resulting Mo-S/Li batteries using liquid electrolytes intermediately formed polysulfides dissolve into the polar electrolytes which leads to essentially the same cycle life issues as discussed above for conventional Li/S batteries. Although Mo nanoparticles to some extent are reported to alleviate the dissolution by binding with polysulfides,[22] replacing liquid electrolytes with a solid electrolyte should be more effective in eliminating the root cause of this problem.

Still, in contrast to a range of in depth studies on MoS_2 as electrode materials for liquid electrolyte lithium or lithium-ion batteries, only few reports have been published on the application of MoS_2 in all-solid-state lithium batteries. In 1990s, Julien et al.[23,24] presented all-solid-state lithium batteries using disordered MoS_2 as the cathode in combination with B_2O_3-Li_2O-Li_2SO_4 solid electrolyte. The resulting battery showed an initial capacity of 160 mAh/g and 145 mAh/g up to 90 cycles, with a voltage range of 1.4 – 2.0 V at a low current of 15 $\mu A/cm^2$. It is noted that MoS_2 was not fully discharged at a voltage of 1.4 V. Therefore, these batteries were operating at the intercalation stage instead of transforming into Li/S batteries. To the best of our knowledge, despite of considerable studies in solid electrolytes, no further all-solid-state MoS_2 batteries have been reported in the following decades. In this study, we report a detailed study on the electrochemical performance of all-solid-state

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batteries using MoS_2 as cathode in combination with lithium argyrodite Li_6PS_5Br solid electrolyte. The cell becomes an all-solid-state Li/S cell with finely dispersed Mo nanoparticles in the composite cathode after full discharge. At room temperature, the cell showed an initial discharge capacity of 650 mAh/g between 0.1 – 3 V. When restricting the potential range to the more practical values of 1 – 3 V in subsequent cycles, a stable capacity was reached retaining reversible capacity of 190 mAh/g after 40 cycles at C/10 rate. At 70 °C, a reversible capacity of 270 mAh/g was achieved with a capacity retention of 85% after 700 cycles with C rates varying in the range of C/5 to 1C.

The MoS_2 composite cathode was prepared by ball milling the mixture of MoS_2, Li_6PS_5Br and super P carbon in a weight ratio of 40: 56: 4 at 500 rpm for 30 min (see experimental section in ESI). SEM images of the pristine MoS_2 powder and the MoS_2 composite cathode powder after ball milling are shown in Figure 1. In the layered crystal structure of MoS_2, Mo atoms are covalently bonded to S atoms in two adjacent S layers; the electroneutral MoS_2 slabs are held together by van der Waals interactions. Due to the weak interaction between the S-Mo-S layers, the slabs can be easily separated from each other, leading to a plate-like morphology: As demonstrated in Figure 1 (a), the diameter of the particles is within the range of 1-5 μm, while the thickness is much smaller (around 100 nm). After ball milling the MoS_2 powder with Li_6PS_5Br powder and carbon for 30 min at 500 rpm to prepare the composite cathode powder, no distinct variation of MoS_2 particles in either diameter or thickness can be discerned (see Figure 1 (b)), suggesting that to some extent MoS_2 can sustain high-energy mechanical milling without severe morphology change. So this ball milling should be seen more as an effective way to achieve a uniform mixing of the composite cathode powder: The MoS_2 plates are surrounded by solid electrolyte Li_6PS_5Br particles and carbon black particles, thus ensuring both efficient ionic and electronic conduction paths within the cathode.

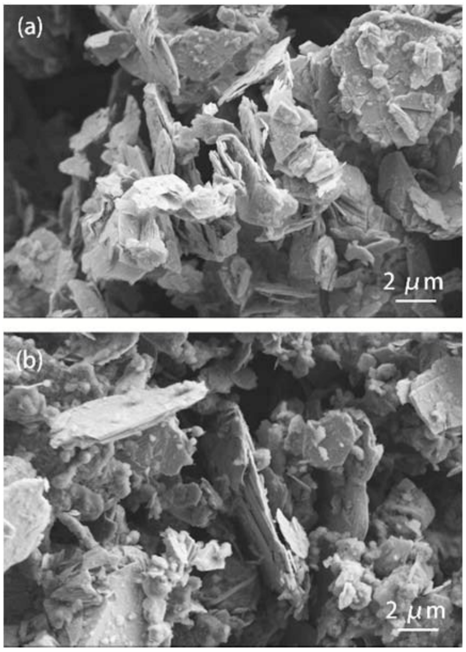

Figure 1 SEM images of the pristine MoS_2 powder and the MoS_2 composite cathode powder after ball milling.

Cyclic voltammetry (CV) was performed on the all-solid-state MoS_2/Li_6PS_5Br/In-Li cell between 0.1-3.1 V vs. Li/Li^+, as shown in Figure 2. The first reduction cycle showed two distinct cathodic peaks around 1.0 and 0.4 V. These peaks can be attributed to the intercalation reaction $MoS_2 + xLi \rightarrow Li_xMoS_2$, and the conversion reaction $Li_xMoS_2 + (4-x)Li \rightarrow Mo + 2Li_2S$ together with the interfacial lithium storage, in line with the reported literature data for liquid electrolyte MoS_2-based batteries.[21] Moreover, a minute peak at ca. 2.2 V occurred due to a minor impurity in the commercial MoS_2 (<< 1% of a Chevrel phase, as suggested from the XRD pattern), while a search for impurities by XPS only revealed minute amounts of Mo^{6+} from surface oxidation and Mo^{2+}, which may tentatively be ascribed to the Chevrel phase impurity. In subsequent reduction cycles, significant changes in the CV curves could be discerned. The peak at 1.0 V disappeared, while two new peaks around 1.8 V and 1.1 V occurred, supporting the new stepwise electrode reaction $nS_8 + 16Li \rightarrow 8Li_2S_n$ and $Li_2S_n + (2n-2)Li \rightarrow nLi_2S$. The peak at ca. 0.25 V corresponding to the interfacial lithium storage still existed though with a gradual reduction in intensity, which may be tentatively ascribed to reduction of the electroactive interface area, e.g. by coarsening or agglomeration of the Mo particles. In the oxidation step, the peaks referring to the two oxidation reactions overlap to a broad peak at nearly 2.4 V.

The formation of all-solid-state Li/S batteries with Mo nanoparticles dispersed in the fully charged composite cathode was verified by HRTEM. The all-solid-state batteries charged to 3 V after full discharge to 0.1 V was disassembled and the composite cathode was immersed in DI water. Since the lithium compounds in the composite cathode can react with and then dissolve in water, the Li_6PS_5Br solid electrolyte (and possibly Li_2S if it exists) was removed, leaving only the phases insoluble in water, such as molybdenum, sulfur, minor amounts of carbon and MoS_2/Li_xMoS_2 (if it forms again). Note that Li_xMoS_2 in contact with water will decompose into MoS_2 and soluble LiOH and thus it should be visible as MoS_2 in the TEM of a hydrolyzed sample.[25] TEM results of the resulting powder are demonstrated in Figure 3. Analysis of the selected area electron diffraction (SAED) pattern (Figure 3 (b)) clearly indicated that there are no signs of MoS_2, but the molybdenum is present as metallic

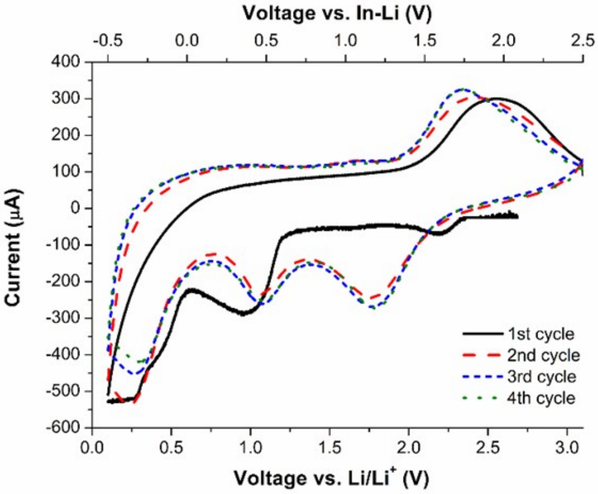

Figure 2 Cyclic voltammogram of all-solid-state MoS_2/Li_6PS_5Br/In-Li cell at a scanning rate of 0.05 mV/s. The voltage range is 0.1-3.1 V vs. Li/Li^+.

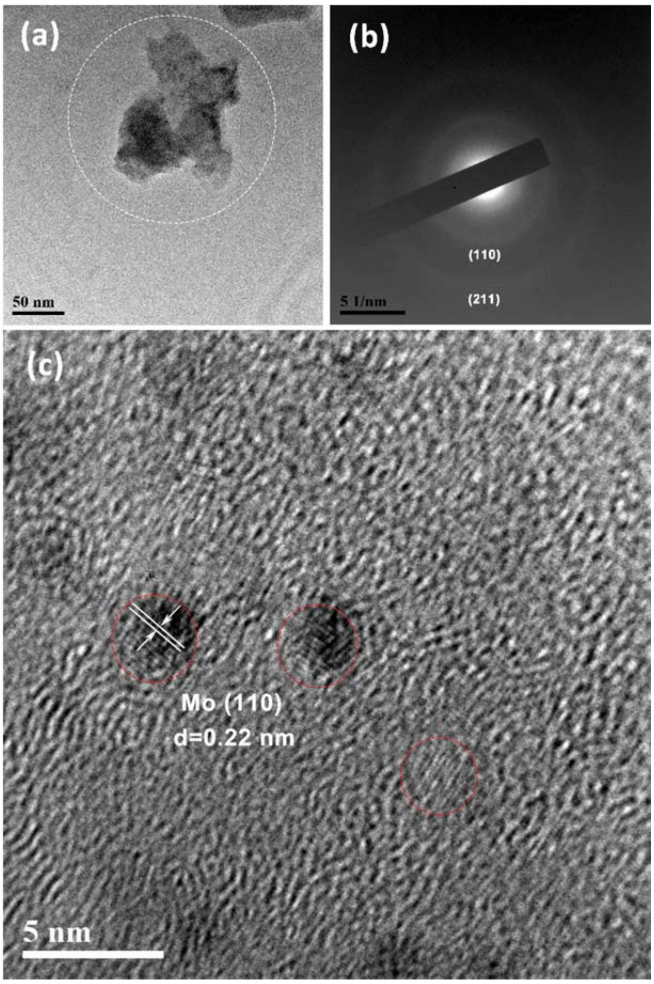

Figure 3 TEM results of the charged MoS_2 composite cathode powder after dissolving in DI water. (b) SAED pattern of the sample shown in the figure (a). (c) HRTEM image.

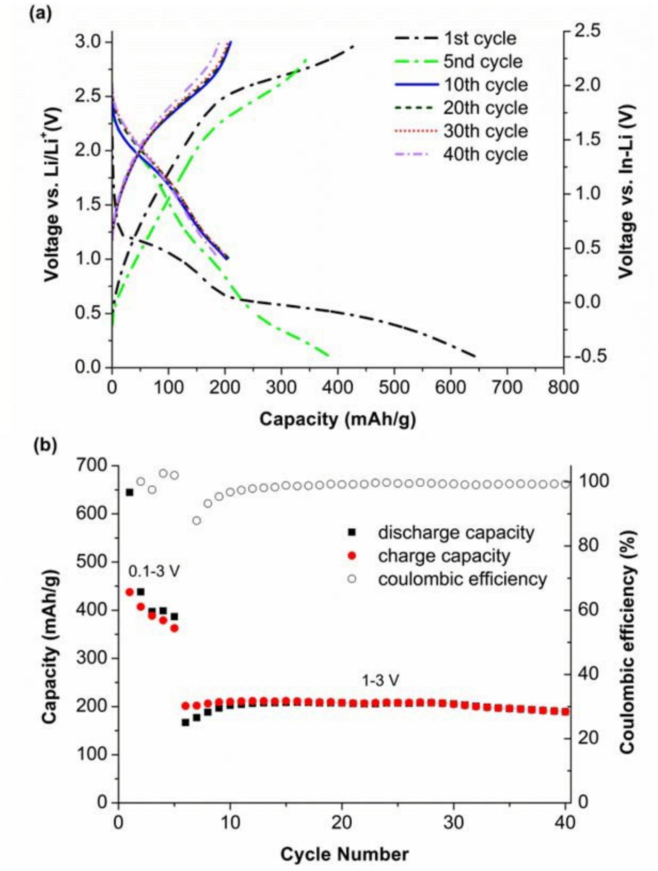

Figure 4 (a) Discharge-charge curves and (b) cyclic behavior of the all-solid-state MoS_2/Li_6PS_5Br/In-Li cell at room temperature at a rate of C/10. The voltage range was 0.1-3 V (vs. Li/Li^+) in the first 5 cycles and 1-3 V in the following cycles.

Mo nanoparticles. The HRTEM image (Figure 3 (c)) shows that the size of the Mo particles in the composite cathode is around 3 nm, similar to the 3-6 nm recently reported for discharged MoS_2 cathode in a liquid electrolyte half-cell.[21] Our TEM results of cathode materials in the charged state support that MoS_2/Li_xMoS_2 will not re-form in the following charge cycles once the battery is fully discharged. In other words, the all-solid-state MoS_2/Li_6PS_5Br/In-Li battery essentially turns into a Li/S battery with conductivity-enhancing Mo nanoparticles finely dispersed in the cathode.

Room temperature cyclic performance of the all-solid-state MoS_2/Li_6PS_5Br/In-Li cell was investigated at C/10 rate (corresponding to a current density of 67 mA/g) (see Figure 4). The voltage range of the first 5 cycles is 0.1-3 V vs. Li/Li^+ so as to “activate” the Li/S cell, while that of the following cycles is constrained to the more practical scale of 1-3 V vs. Li/Li^+. An initial discharge capacity of 650 mAh/g was obtained, close to the theoretical capacity of 670 mAh/g. Various MoS_2-based cells using liquid electrolyte have been reported in recent years with an initial discharge capacity exceeding the theoretical capacity[26,27]. This excess capacity can be ascribed to the high contribution of interfacial charge storage at the Li_2S/Mo interfaces, lithium intercalation in the conductive carbon and the SEI formation.[22] In most of these cases, a large amount of carbonaceous materials was employed in the MoS_2 electrode (e.g. MoS_2:C ≈ 3:1[26] or even 1:1[27]) and the resulting liquid electrolyte batteries were typically discharged to a relatively low voltage (e.g. 0 V). Consequently, the carbonaceous materials contributed to a significant amount of the practical capacity. Nevertheless, in our case, the carbon content is drastically reduced to a weight ratio of MoS_2:C=10:1, leading to the practical capacity with a value close to but not exceeding the theoretical capacity. During the first charge, however, a significant capacity drop to 460 mAh/g was observed, which can be tentatively attributed to the severe volume expansion of the overall electrode reaction $MoS_2 + 4Li \rightarrow Mo + 2Li_2S$. Thereafter, the capacity fading of the cell became moderate, leading to a reversible capacity of 385 mAh/g after 5 cycles within the full voltage range of 0.1 - 3.0 V. These 5 cycles should be seen more as a pre-treatment of the battery ensuring the complete conversion of MoS_2 into Mo and S/Li_2S.

From the 6th cycle onwards, the cell was then cycled over a practically useful voltage range of 1.0 – 3.0 V. Consequently, the capacity at the 6th cycle is considerably lower, since the lithium storage in the interfaces of Li_2S/Mo and in the carbon both occurs below 1 V vs. Li/Li^+ and is thus excluded by the choice of the voltage range.[28] With prolonged cycling, the capacity of the cell gradually recovered, probably due to the simultaneously improved electrical contact within the composite cathode. A reversible capacity of 190 mAh/g was achieved after 40 cycles. In addition, the cell showed a high coulombic efficiency after stabilization (19th cycle onwards), suggesting that there is hardly any side reaction during cycling.

High temperature cyclic performance of the all-solid-state MoS_2/Li_6PS_5Br/In-Li cell was studied at various C rates, i.e. C/5, C/2 and 1C, at a temperature of 70 °C (as shown in Figure 5). It should be noted that such rates are relatively high for all-solid-state lithium batteries, especially those using high capacity conversion electrodes. The voltage range was 0.1-3.1 V (vs. Li/Li^+) in the first cycle and 0.6-3.1 V in all following cycles. The discharge/charge rate was changed every 200 cycles. Similar to the cell cycling at room temperature, despite the inevitable capacity drop at the second cycle where the voltage range is narrowed, the cell gradually recovered in the following cycles and achieved a reversible capacity around 315 mAh/g for 200 cycles at C/5. Increasing the C rate reduces the discharge capacity, i.e. to 210 mAh/g at C/2 and to 95 mAh/g at 1C, but when the C rate is reduced back to C/5, a reversible capacity of 270 mAh/g is still maintained, indicating a capacity retention of ca. 85% after 700 cycles. With such a high capacity retention, Li/S-batteries using MoS_2 as the starting composite cathode material may be commercially viable products.

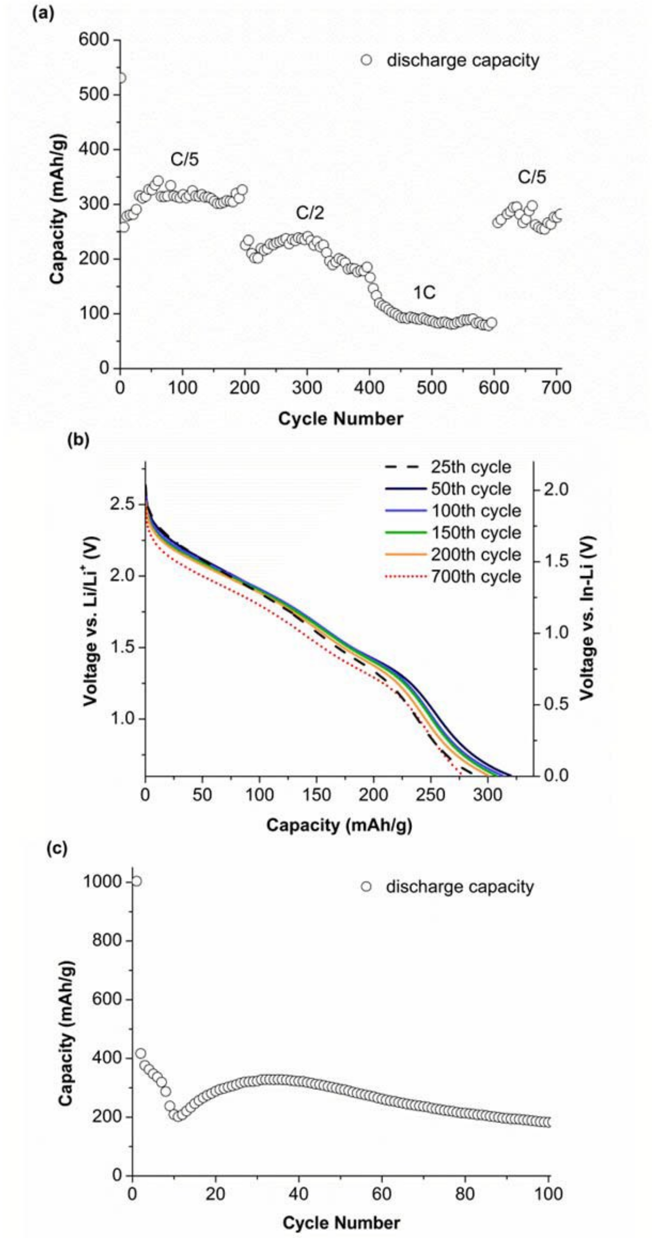

Figure 5 (a) Cycling behavior (b) discharge curves of all-solid-state MoS_2/Li_6PS_5Br/In-Li cell at 70 °C. The voltage range was 0.1-3.1 V vs. (Li/Li^+) at the first cycle and 0.6-3.1 V in the following cycles. The discharge/charge rate changed every 200 cycles from C/5, C/2 to 1C and then back to C/5. (c) Cyclic behavior of MoS_2 cell using liquid electrolyte at C/5 with the same voltage range up to 100 cycles.

For comparison, MoS_2 cells using liquid electrolyte was tested at C/5 within the same voltage range up to 100 cycles (see Figure 5 (c)). A higher initial discharge capacity of 1004 mAh/g was observed, which could be ascribed to the formation of solid electrolyte interface (SEI)[29]. After a rapid capacity drop followed by a partial capacity recovery (qualitatively similar to the observation for our all-solid-state cell), a capacity of 328 mAh/g was achieved around 31st cycle, close to that of the all-solid-state cell (309 mAh/g). However, the capacity of the liquid electrolyte cell started to fade soon after the 40th cycle, ending at a value of 182 mAh/g after 100 cycles. Similar fast capacity fading has been reported for liquid electrolyte batteries using bulk MoS_2 flakes.[26,30] This value is significantly lower than the one we found for our all-solid-state cell (even after 700 cycles), suggesting the effectiveness of the all-solid-state cell design in improving cyclability.

Conclusions

A novel type of all-solid-state Li/S batteries is achieved by fully discharging all-solid-state MoS_2/Li_6PS_5Br/In-Li batteries. This full discharge transforms the cell effectively into a Li/S cell with spherical Mo nanoparticles of about 3 nm in diameter finely dispersed in the composite cathode. At room temperature the cell showed a reversible capacity of 190 mAh/g up to 40 cycles at C/10 with a high coulombic efficiency when cycled in the practically useful voltage range 1 – 3 V. At non-ambient temperature of 70 °C, these cells exhibit a high rate capability up to 1C and high capacity retention of 85% up to 700 cycles with a reversible capacity of 270 mAh/g at C/5. The relatively large particle size of the employed MoS_2 is one of the limiting factors in enhancing the reversible capacity, despite of lower synthesis cost. In future, nano-structured MoS_2 will be prepared and their application in all-solid-state lithium secondary batteries will be investigated.

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References

1 H.-J. Deiseroth, S.-T. Kong, H. Eckert, J. Vannahme, C. Reiner, T. Zaiß and M. Schlosser, *Angew. Chem. Int. Ed.*, 2008, **47**, 755.
2 R.P. Rao and S. Adams, *Phys. Stat. Sol. A*, 2011, **208**, 1804.
3 R.P. Rayavarapu, N. Sharma, V.K. Peterson and S. Adams, *J. Solid State Electrochem.*, 2011, **16**, 1807.

4 M. Chen, R.P. Rao and S. Adams, *Solid State Ionics*, 2014, **262**, 183.
5 R. Prasada Rao, N. Sharma, V.K. Peterson, S. Adams, *Solid State Ionics*, 2013, **230**, 72.
6 F. Stadler and C. Fietzek, *ECS Trans.*, 2010, **25**,177.
7 M. Chen, R.P. Rao and S. Adams, *Solid State Ionics*, 2014, **268**, 300.
8 A. Manthiram, Y. Fu, S.-H. Chung, C. Zu and Y.-S. Su, *Chem. Rev.*, 2014, **114**, 11751.
9 X. Ji, K.T. Lee, L. F. Nazar, *Nat. Mater.*, 2009, **8**, 500.
10 Z. W. Seh, J. H. Yu, W. Li, P.-C. Hsu, H. Wang, Y. Sun, H. Yao, Q. Zhang and Yi Cui, *Nat. Commun.*, 2014, **5**, 5017.
11 J. Zheng, J. Tian, D. Wu, M. Gu, W. Xu, C. Wang, F. Gao, M.H. Engelhard, J.-G. Zhang, J. Liu and J. Xiao, *Nano Lett.*, 2014, **14**, 2345.
12 J. Zheng, M. Gu, M.J. Wagner, K.A. Hays, X. Li, P. Zuo, C. Wang, J.-G. Zhang, J. Liu and J. Xiao, *J. Electrochem. Soc.*, 2013, **160**, A1624.
13 J. Zheng, M. Gu, H. Chen, P. Meduri, M.H. Engelhard, J.-G. Zhang, J. Liu and J. Xiao, *J. Mater. Chem.* A, 2013, **1**, 8464.
14 D. Aurbach, E. Pollak, R. Elazari, G. Salitra, C.S. Kelley and J. Affinito, *J. Electrochem. Soc.*, 2009, **156**, A694.
15 Z. Lin, Z. Liu, W. Fu, N.J. Dudney and C. Liang, *Adv. Funct. Mater.*, 2013, **23**, 1064.
16 T. Kobayashi, Y. Imade, D. Shishihara, K. Homma, M. Nagao, R. Watanabe, T. Yokoi, A. Yamada, R. Kanno and T. Tatsumi, *J. Power Sources*, 2008, **182**, 621.
17 H. Nagata and Y. Chikusa, *J. Power Sources*, 2014, **264**, 206.
18 M. Nagao, A. Hayashi, M. Tatsumisago, *Energy Technol.*, 2013, **1**, 186.
19 M. Chen and S. Adams, *J. Solid State Electrochem.*, 2015, **19**, 697.
20 J. Xiao, X. Wang, X.-Q. Yang, S. Xun, G. Liu, P.K. Koech, J. Liu and J.P. Lemmon, *Adv. Funct. Mater.*, 2011, **21**, 2840.
21 X. Fang, X. Guo, Y. Mao, C. Hua, L. Shen, Y. Hu, Z. Wang, F. Wu and L. Chen, *Chem. Asian J.*, 2012, **7**, 1013.
22 T. Stephenson, Z. Li, B. Olsen and D. Mitlin, *Energy Environ. Sci.*, 2014, **7**, 209.
23 C. Julien, S.I. Saikh and M. Balkanski, *Mater. Sci. Eng. B*, 1992, **14**, 121.
24 C. Julien, *Ionics*, 1996, **2**, 169.
25 G. Du, Z. Guo, S. Wang, R. Zeng, Z. Chen and H. Liu, *Chem. Comm.*, 2010, **46**, 1106.
26 X. Zhou, L.-J. Wan and Y.-G. Guo, *Nanoscale*, 2012, **4**, 5868.
27 X. Zhou, L.-J. Wan and Y.-G. Guo, *Chem. Comm.*, 2013, **49**, 1838.
28 X. Fang, C. Hua, X. Guo, Y. Hu, Z. Wang, X. Gao, F. Wu, J. Wang and L. Chen, *Electrochim. Acta*, 2012, **82**, 155.
29 C. Zhu, X. Mu, P.A. van Aken, Y. Yu and J. Maier, *Angew. Chem. Int. Ed.*, 2014, **53**, 2152.
30 J.-M. Jeong, K.G. Lee, S.-J. Chang, J.W. Kim, Y.-K. Han, S.J. Lee and B.G. Choi, *Nanoscale*, 2015, **7**, 324.

High-performance all-solid-state Lithium/sulfur batteries stably running over 700 high-rate cycles are demonstrated by combining a MoS_2 precursor cathode with argyrodite-type solid electrolyte.