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Lithium storage in commercial MoS_2 in different potential ranges

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ABSTRACT

Transition metal sulfides are regarded as another type of high-performance anode materials following the transition metal oxides for lithium ion batteries. However, the lithium storage mechanisms of these sulfides are complicated. This work is intended to evaluate the electrochemical performances of molybdenum disulfide (MoS_2) and find out its lithium storage mechanism at different lithium insertion stages. It is found that although the MoS_2 shows excellent cycling stability in different voltage ranges, its structural transition is irreversible in the initial cycling. In contrast to the traditional beliefs, metallic Mo is found inert and Li_2S/S is the redox couple in a deeply discharged MoS_2/Li cell (0.01 V vs. Li/Li^+). The metallic Mo nanoparticles are believed to be responsible for the enhanced cycling stability of the cell and act as the electronically conducting phase in the capacitive energy storage on the interfaces or grain boundaries of Mo/Li_2S_x nanocomposite. In addition, the Mo/Li_2S nanocomposite can be used as a cathode material for lithium–sulfur batteries.

1. Introduction

Transition metal (TM) sulfides [1,2] are important cathode materials in primary lithium cells. Their electrochemical performances and lithium storage mechanisms have been well understood. They store lithium by the well-known intercalation/de-intercalation of lithium in their lattices. Since the discovery that TM oxides could be promising anode materials for lithium ion batteries [3], much attention has been paid to TM sulfides as another type of promising anode materials due to their low cost, high safety and easy synthesis [4–6]. Recently, Liu et al. [5] reported that restacked molybdenum disulfide (MoS_2 with enlarged *c*-axis spacing) electrodes exhibit high reversible lithium storage capacity (800 $mA\,h\,g^{-1}$) and superior rate capability. However, much less attention has been paid to examine the lithium storage performances of MoS_2 in different voltage ranges. Even fewer authors tried to explain why (or have ever noticed that) the actual capacity of MoS_2 should be significantly higher than its theoretical value when it is discharged to 0.00 V (800 $mA\,h\,g^{-1}$ for experimental observation vs. 669 $mA\,h\,g^{-1}$ for calculation based on reaction, $MoS_2 + 4Li^+ + 4e^- \leftrightarrow 2Li_2S + Mo$ [5,7,8]).

In this paper, we evaluate the electrochemical performances of commercial MoS_2 and explore its lithium storage mechanism in various voltage ranges. It will be seen that the commercial MoS_2 follows a lithium storage mechanism different from that of most other metal sulfides or oxides [5]. The reduced metallic Mo does not participate in the subsequent cycling. Rather it plays important roles in improving the cycling stability of the actual sulfur electrode and in realizing the interfacial capacitive lithium storage. These findings provide helpful guidance to improving the electrochemical performances of the sulfur electrode in Li–S batteries and support the interfacial capacitive lithium storage beliefs.

2. Experimental

Commercial MoS_2 powder (purity >99%, Alfa) was used as the active material for the test cell. The working electrode was prepared by casting a slurry of the active material (80 wt.%), carbon black (10 wt.%) and polyvinylidene fluoride (10 wt.%) dissolved in *N*-methylpyrrolidone as the binder on a clean Cu current collector. In an Ar-filled glove box (MBraun, Lab Master 130), button-type test cells were assembled with the commercial MoS_2 as the working electrode, fresh Li foil as the counter electrode, 1 $mol\,L^{-1}$ $LiPF_6$ in ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 in volume) as the electrolyte, and Celgard 2400 as the separator. The specific capacity and the cycling performances were evaluated on Land BT2000 battery tester (Wuhan, China) at room temperature.

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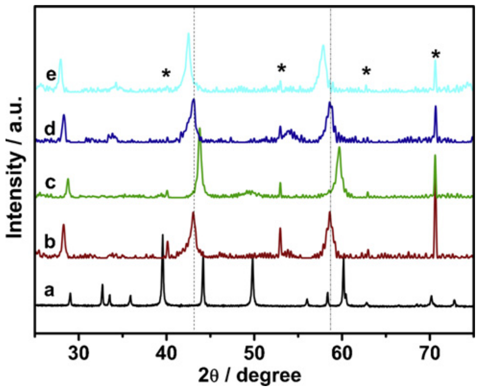

Fig. 1. The XRD patterns of the commercial MoS_2 at various states: as-received (a), the commerial MoS_2 initially discharged to 0.80 V (b), then recharged to 3.00 V (c), further discharged to 1.15 V (d) and continuously discharged to 0.80 V (e). The peaks with asterisks are for the diffractions of the Ti current collectors.

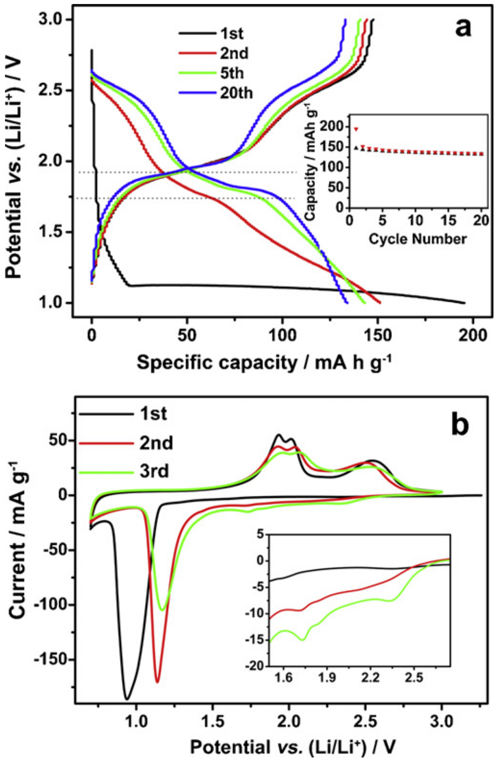

Fig. 2. The voltage profiles between 3.00 and 1.00 V (a) and the cyclic voltammetry between 3.00 V and 0.75 V (b) of the commercial MoS_2. The inset in (a) is for the cycling performance while the inset in (b) is for the selected CV between 1.50 and 2.70 V.

The cyclic voltammetry (CV) tests were carried out on CHI660A electrochemical workstation (Shanghai, China) at room temperature. The electrode was taken out of the cycled cells and rinsed with DMC before characterized by X-ray diffraction (XRD, X'Pert Pro MPD X-ray diffractometer (Philips, Holland) with Cu Kα1 radiation ($\lambda = 0.15405$ nm)) and Fourier-transformed infrared (FTIR, Bruker Optics, EQUINOX 55) spectroscopic techniques. For the *in situ* XRD measurements, stainless steel mesh was used as the current collector and the window was covered by a layer of Mylar film. The X-ray diffraction was performed on a Bruker AXS D8 Advance diffractometer with Cu Kα radiation (0.15405 nm).

3. Results and discussion

SEM imaging indicates that the commercial MoS_2 is sheet-like with a thickness of ca. 200 nm [9]. XRD analysis (Fig. 1a) shows that all the diffraction peaks can be indexed to pure MoS_2.

In a MoS_2/Li cell cycled between 1.00 and 3.00 V vs. Li/Li^+, the MoS_2 delivers a discharge capacity of ca. 200 mA h g^{-1}, most of which comes from a long discharge plateau at around 1.10 V (Fig. 2a). The reversible capacity of the material is around 150 mA h g^{-1}, corresponding to a coulombic efficiency of ca. 75%. The voltage profile of the 2nd discharge is drastically different from that of the first discharge. The long voltage plateau in the initial discharge is replaced with two plateaus in the 2nd and subsequent discharges. These plateaus become more obvious with continuous cycling. Meanwhile, the charge voltage plateaus keep symmetric to the corresponding discharge plateaus. These indicate the high structural reversibility of MoS_2 after the initial discharge and agree with its excellent cycling performances between 1.00 and 3.00 V (inset of Fig. 2a). The reversible capacity maintains at 140 mA h g^{-1} after 20 cycles. However, the cycling performance of the material quickly decays if the discharge cutoff voltage is lowered to 0.80 V (not shown).

Feng et al. [10] ascribed the plateau in the initial discharge to the lithium intercalation on the layer sites of MoS_2 and the formation of Li_xMoS_2 based on their elemental analysis. However, they did not carry out any structural characterization to the products. Fig. 3 shows in the structural evolution of the MoS_2 electrode initially cycled between 3.00 and 0.80 V by *in situ* XRD. With discharge, the intensity of the diffraction peaks of MoS_2 decreases but their positions keep unchanged. Meanwhile, three new peaks appear at 14.59°, 43.60° and 59.22°. These peaks grow in intensity but their positions keep stable with continuous discharge. At 0.80 V, all the diffraction peaks of MoS_2 disappear but the intensities of the new peaks reach their maximum. This means that the lithium intercalation into MoS_2 is a two-phase process above 0.80 V in the initial discharge. This agrees with the presence of the long discharge plateau in the initial discharge. However, these new diffraction peaks cannot be indexed to any known Li–Mo–S species (the 1T Li_xMoS_2 [11,12] β-Li_xMoS_2 (JCPDS Card No. 44-1078), $LiMoS_2$ (JCPDS Card No. 18-0752)). Further analysis is required to determine its structure.

As the cell is recharged backward, the diffraction peaks move towards the lower angle side. The *d*-spacing reaches its maximum at 2.10 V (14.59° → 14.42°, 43.60° → 43.04°, 59.22° → 58.29°) but no new diffraction peaks come into being. Clearly, this is a single phase transition process. When the cell is further charged, the 14.42° and 58.29° peaks shift back to 14.50° and 59.00°, respectively. This indicates that the lattice parameter increases at first and then decreases as the cell is recharged. The new peaks at 14.79° and 60.05° are attributed to residual MoS_2 at 3.00 V (due to kinetic reasons, not all the MoS_2 has been fully reacted or experienced the above phase transition when the MoS_2/Li cell is discharged to 0.80 V or recharged to 3.00 V). As a result, two phases co-exist when the cell is charged to 3.00 V, one is the MoS_2 and the other is the unknown (Li–)Mo–S, most of the lithium of which has been extracted.

The above *in situ* XRD analysis indicates that only the structure of some residual MoS_2 keeps reversible when the MoS_2 electrode is discharged to 0.8 V. The structural irreversibility becomes even more significant when the XRD patterns of the MoS_2 electrode having experienced different cycles are compared (Fig. 1b vs. Fig. 1e). The commercial MoS_2 cannot return to itself at the end of recharge (Fig. 1a vs. Fig. 1c). Fig. 1 also shows that the XRD patterns of the commercial MoS_2 initially discharged to 0.80 V are more like that of the electrode discharged to 1.15 V rather than the one discharged to 0.80 V in the 2nd discharge though these three patterns can be indexed to the same phase. This discrepancy might be related to the