Self-assembled lamellar *alpha*-molybdenum trioxide as high performing anode material for lithium-ion batteries

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HIGHLIGHTS

- Self-assembled lamellar α-MoO$_3$ is prepared by solvothermal method.
- Lamellar α-MoO$_3$ exhibits superior electrochemical reversible capacity.
- The material shows good rate capability even at higher rates.
- Excellent structural stability during lithiation and delithiation process.

GRAPHICAL ABSTRACT
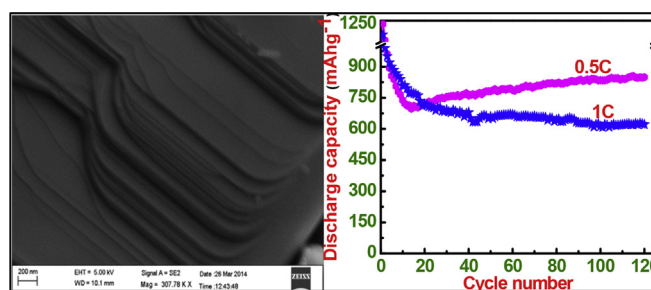
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ABSTRACT

Self-assembled lamellar *alpha*-molybdenum trioxide (α-MoO$_3$) has been prepared using facile polymer (polyvinyl pyrrolidone) assisted solvothermal method. Field-emission scanning electron microscopy (FESEM) studies reveal that the lamellar hexagonal particles are formed by close staking of 20–30 nm thin flakes (nanosheets). When used as lithium-ion battery electrode lamellar α-MoO$_3$ shows superior electrochemical reversibility and excellent rate capability. For example after 50 cycles, a capacity value of 1027 mA h g^{-1} can be extracted at 0.2C rate while at 2C rate it shows capacity of 700 mA h g^{-1}, which is higher than the theoretical capacity of conventional graphite anode. exsitu XRD and FESEM studies on electrochemically cycled samples show that the crystalline phase irreversibly changes to amorphous phase during the first discharge whereas the particle morphology remains unaltered even after 100 charge–discharge cycles. The superior electrochemical performance of α-MoO$_3$ is attributed to its lamellar-like morphology which allows faster lithium ion diffusion in addition to buffering the volume changes during lithiation/de-lithiation.

1. Introduction

Energy storage for electric mobility and grid applications has become one of the most important challenges of the 21st century. The Li-ion battery technology which has already conquered the portable electronics market is also found to be the suitable choice for powering electric vehicles and for storing the renewable energy. However, new electrode materials and new mechanisms need to be discovered to build a battery that can deliver high power and high energy required for such applications with due attention to safety and cost [1,2]. Also the major concern in Li-ion battery fabrication is to ensure that the electrodes do not degrade or pulverize during charge–discharge cycles so as to achieve good capacity retention and long calendar life [3]. Although currently graphite is the most

widely used anode with a theoretical capacity of 372 mA h g^{-1}, it is not suitable for high power applications owing to its poor rate capability as well as safety issues related to dendrite formation. Recently transition metal oxides have attracted considerable attention due to their higher theoretical capacities and intrinsic safety by avoiding formation of lithium dendrites [4–6]. For instance transition metal oxides like Fe$_3$O$_4$, Co$_3$O$_4$ can react reversibly with 6 Li per formula unit by conversion mechanism resulting in high capacities [7,8]. However transition metal oxides (TMO's) show poor electrical and ionic conductivities as well as suffer from structural instability during cycling causing polarization and pulverization of electrode [9]. Nevertheless nanostructuring of such materials indeed has shown to enhance diffusion kinetics and can also provide better stability during charge–discharge.

Molybdenum trioxide (MoO$_3$) is well known two-dimensional layered lithium insertion compound which has been investigated as electrode for lithium ion batteries [10–12] because of its good electrical conductivity [13], high thermal and chemical stability. MoO$_3$ commonly exists in three polymorphs, viz. orthorhombic α-MoO$_3$, monoclinic β-MoO$_3$ and hexagonal MoO$_3$ [14], out of which α-form is the most stable one. The lithiation in MoO$_3$ believed to happen in two stages; above 1.5 V insertion of Li$^+$ between MoO$_3$ layers takes place (stage I) [40] and below 0.7 V (stage II) conversion type reduction reaction occurs [41]. On the basis of insertion reaction mechanism MoO$_3$ was extensively explored as cathode material exhibiting a capacity of 200–300 mA h g^{-1} in the voltage range 3.5–1.5 V [15–17]. On the other hand, MoO$_3$ can show a high theoretical capacity (1117 mA h g^{-1}) through the conversion reaction, but it suffers from poor structural stability and sluggish kinetics. MoO$_3$ nanostructures viz. nanowires, nanorods, nanobelts and nanoparticles [18–26] have been shown to exhibit high initial discharge capacities, however, still severe capacity fading was observed. So preparation of nanoarchitectured α-MoO$_3$ exhibiting good cyclability and rate capability has remained a major challenge.

Herein we have successfully synthesized self-assembled lamellar like α-MoO$_3$ by employing simple polymer assisted solvothermal method by using ammonium heptamolybdate as starting material, ethylene glycol as solvent and polyvinylpyrrolidone as soft template and structure modifying agent. Amphiphilic molecules such as surfactants can self-assemble into lamellar micelles under some suitable conditions and consequently multilayered structures can be produced. When investigated as electrode material for Li-ion batteries, lamellar α-MoO$_3$ showed superior electrochemical cycling performance and enhanced lithium storage capacity. The outstanding electrochemical performance is mainly attributed to the lamellar like structure that buffer volume change during lithium insertion-deinsertion and also provides fast Li$^+$ ion diffusion path.

2. Experimental

2.1. Materials preparation

For the synthesis of self-assembled lamellar α-MoO$_3$, all the chemicals used were analytical grade without further purification. Ammonium heptamolybdate tetrahydrate (AHM, (NH$_4$)$_6$Mo$_7$O$_{24}$.4H$_2$O, Merck), ethylene glycol (SRL Chemicals) and polyvinylpyrrolidone (PVP, average MW = 3,500, Acros organics) were used as starting materials. In a typical synthesis, 0.2 g of PVP was dissolved in 35 mL of ethylene glycol by vigorous stirring at room temperature. Then 1.75 g of AHM was added and kept at 70 °C with continuous stirring for 30 min. The resulting pale yellow precursor solution with p^H ~6 was transferred to 50 mL Teflon-lined stainless steel autoclave and kept at 180 °C for 24 h in closed

condition. After being cooled to ambient temperature, the yellow precipitate of Mo-glycolate complex was collected by suction filtration and washed with de-ionized water several times and finally with absolute ethanol to remove excess ethylene glycol. The glycolate product was dried in the oven 80 °C for 6 h, then transferred to furnace and calcined in air at 500 °C for 3 h (heating rate 5 °C min^{-1}) to get molybdenum oxide.

2.2. Material characterization

XRD analyses were performed on Bruker D8 advance Davinci diffractometer equipped with Cu Kα radiation (λ = 1.5418 Å) at a generator voltage of 40 kV and current of 30 mA with a scanning speed of 2° min^{-1}. The product morphology and microstructure was examined by using field-emission scanning electron microscope (FESEM; Carl Ziess, SUPRA55VP, Germany). Infrared spectra was recorded in MIR region on FT-IR spectrometer, Bruker Optick GmbH with KBr pressed disks. Raman spectra were recorded using Renishaw laser Raman microscope. Thermo-gravimetric analysis (TGA) was carried out using a thermogravimetric analyzer (TG/DSC, Model STA449F3, NETZSCH Germany) with a heating rate of 5 °C min^{-1}in air.

2.3. Electrochemical characterization

The working electrode was fabricated by mixing active material (α-MoO$_3$), conducting carbon black (super-P) and sodium carboxymethyl cellulose (Na-CMC) binder in a weight ratio of 70:20:10. The mixture was coated on a Cu foil of thickness 15 μm and dried in air at 100 °C for 5 h. Thickness of the coated electrode is 60 μm and porosity of the electrode is found to be 17%. The electrodes were assembled into coin type test cells (CR 2032) with pure Li as both counter electrode and reference electrode. A porous glass microfiber filter (GF/D, Whatmann Int. Ltd.) used as a separator and the electrolyte used was 1.0 M LiPF$_6$ in ethylene carbonate (EC)/diethyl carbonate (DEC)/dimethyl carbonate (DMC) (2:1:2 by volume). The geometrical area and total electrode weight were 2 cm^2 and ca. 3 mg respectively, while the mass of active material (self-assembled lamellar α-MoO$_3$) is ca.1.05 mg cm^{-2} measured by ultra-micro analytical balance. Tap density of as prepared self-assembled lamellar α-MoO$_3$ is 0.914 g cm^{-3}.

Coin cell preparation was carried out inside Ar filled glove box (MBRAUN, Germany) where the moisture and oxygen concentrations were strictly limited to below 1 ppm. The cyclic voltammetry (0.1 mV s^{-1}) and galvanostatic charge–discharge cycling tests were carried at various current rates in the voltage window of 0.01–3.0 V at ambient temperature. Electrochemical impedance studies were performed over a frequency range of 400 kHz to 10 mHz with a perturbation of 20 mV applied Vs. Li/Li$^+$ at room temperature. All the electrochemical tests were carried out using VMP3Z (Biologic) multichannel potentiostat/galvanostat.

3. Results and discussion

3.1. Formation mechanism of self-assembled lamellar α-MoO$_3$

Scheme 1 illustrates the synthesis mechanism of multilayered lamellar α-MoO$_3$ structures. The amphiphilic nature of PVP (polyvinyl pyrrolidone) soft template and the formation of molybdenum glycolate complex during the initial step are the key parameters responsible for obtaining lamellar-like morphology. The surfactants having amphiphilic nature can self-assemble into multi-lamellar micelles in some conditions. It is known that PVP can coordinate to the metal ion (molybdenum ion) through N or/and O atoms. During the hydrothermal process the polymer supported chains of