Synthesis of Molybdenum Oxides and their Electrochemical Properties against Li

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Abstract
The need of high energy density battery leads to explore new materials for lithium ion batteries (LIBs). Recent study focused on the uses of molybdenum oxides as an alternate to carbon anode for LIBs. To obtain better electrochemical performance nano belts of MoO$_3$ were prepared using one step hydrothermal synthesis, whereas MoO$_2$ was prepared by heating MoO$_3$ in reducing atmosphere. Effect of binder selection on the performance of MoO$_3$ was studied and found that CMC binder exhibits better electrochemical performance compared to PVDF. It has also been observed that the cyclic stability of MoO$_3$ electrode using PVDF binder was improved dramatically when the electrode was heated above 220 °C in vacuum. A stable capacity of 600 mAh g$^{-1}$ was obtained for MoO$_3$ electrode using CMC binder. On the other hand a stable electrochemical performance was achieved for MoO$_2$. A reversible capacity of 680 mAh g$^{-1}$ was achieved after 30 cycles.

Keywords: Anode material; CMC binder; Lithium ion batteries; MoO$_3$; MoO$_2$

1. Introduction
One of the greatest challenges of the modern day electrochemistry is to develop high capacity energy-storage device by using low cost and environment friendly materials [1]. Due to this reason Li-ion battery (LIB) which provides the highest energy density as well as highest power density, attracts the attention of the researchers from various fields. But the energy density of LIBs are restricted due to the use of carbon as anode material (theoretical capacity of 372 mAh g$^{-1}$, correspond to 1 Li per 6 formula of Carbon) and LiCoO$_2$ as cathode (practical capacity of
140 mAh g⁻¹, correspond to 0.5 Li per formula of CoO₂). To improve the energy storage capacity, electrode material should be selected in such a way so that it can support more number of Li⁺. In the year 2000 nano-dimensional transition metal oxides unfold a new possibility to accommodate large no of Li⁺ through conversion reaction [2]. Most of the transitional metal oxides and sulphides follow the conversion reaction mechanism during electrochemical reaction with Li. Recent trends show plenty of ongoing work on the nanostructuring of conversion based materials to achieve better specific capacity and stable cyclic performance [3]. The main advantages of the conversion based electrodes are safe working potential (0.5-1.0 V), high specific capacity (800-1200 mAh g⁻¹) and better rate capability. The safety concerns associate with the existing carbon anode can be successfully removed by the use of conversion based transition metal oxides and sulphides. High practical capacity and good rate capability make these materials as ideal choice for next generation lithium ion batteries (LIBs). Due to these reasons several new conversion based materials were tested as anode materials [3-5]. Molybdenum trioxide is considered as one of the elite members of this conversion material family. α-MoO₃ can accommodate 6 Li⁺ through conversion reaction, which corresponds to a theoretical capacity of 1117 mAh g⁻¹. Though MoO₃ exhibits high initial capacity, the major drawback of this material is the first cycle irreversibility losses and poor cyclic life. Almost half of the Li-ion was found to be irreversible after first cycle. To obtain a better cyclic stability and good capacity retention several approaches has been demonstrated in the literature, which employed different synthesis techniques and electrode fabrication process. Ultra long nano-belts of α-MoO₃ demonstrated a stable capacity of 800 mAh g⁻¹ for more than 150 cycles at 0.2 C rate [6]. Porous MoO₂ film prepared by electrodeposition process reports a discharge capacity of 1000 mAh g⁻¹ at 70 mA g⁻¹ [7]. Due to one dimensional characteristics of α- MoO₃ nano-belts, it was also used to prepare free standing electrodes that exhibits a discharge capacity of 1000 mAh g⁻¹ at a current density of 50 mA g⁻¹ [8]. Better electrochemical performances were achieved using carbon coated MoO₃ electrode [9-11].

Molybdenum dioxide (MoO₂) is another stable oxide of molybdenum which also attracts great interest as anode material in LIBs. It can accommodate 4 Li⁺ and exhibits a theoretical capacity of 838 mAh g⁻¹. The reaction mechanism of MoO₂ and Li is not properly understood. According to some of the literature, MoO₂ undergoes conversion reaction [12-14] whereas other literature believes it to be intercalation [15-17]. But undoubtedly it has been observed that the bare MoO₂ electrode suffers from severe problem of cyclic instability. To overcome this issue, different carbon composites (such as CNT or graphene, in-situ carbonization) have been demonstrated in literature [13, 14]. But the performance of bare MoO₂ is yet to be achieved.

Current study focused on the potential use of molybdenum oxides (MoO₃ and MoO₂) as anode material for LIBs. Nano-belts of orthorhombic molybdenum trioxide (α-MoO₃) were prepared by one step hydrothermal reaction, whereas monoclinic molybdenum dioxide (α-MoO₂) was prepared by heating α-MoO₃ in reducing atmosphere. The growth of MoO₃ was studied in different acid medium. Herein, we have discussed a different approach to improve the electrochemistry of the material, by modifying the electrode fabrication process. A heat treatment approach has been used to improve the electrochemical performance of MoO₃ electrode prepared using PVDF binder. A superior electrochemical performance has been demonstrated using CMC (sodium salt of carboxy methyl cellulose) binder. The use of modified electrode fabrication process has demonstrated a new strategy to improve the electrochemical performance of the bare electrode material.

2. Experimental Section

2.1. Synthesis

A simple hydrothermal method was adopted to prepare α-MoO₃ nano-belts [18]. In a typical experimental procedure, 2.0 gm of Sodium molybdate (Na₂MoO₄.2H₂O, Merck) was dissolved in 10 ml of deionised water. 5 ml of 4(N) dilute acid (HClO₄/HNO₃/HCL) was added to the aqueous solution of sodium molybdate. At first a colourless solution was obtained which turned turbid after stirring for an hour. This solution was then transferred into a 35 ml Teflon-lined stainless steel autoclave which was kept inside a muffle furnace at 180 °C for 24 hours. A thick white coloured precipitate was obtained which was washed several times with distilled water and acetone and then dried in hot air oven at 60 °C for 12 hours. The products were named as (i), (ii) and (iii), obtained from three different acid medium namely HNO₃, HClO₄ and HCl respectively.

Molybdenum dioxide (MoO₂) was prepared by heating MoO₃ in reducing atmosphere. Firstly, MoO₃ was hand grinded with C (3:1) for half an hour and then placed inside a tube furnace with a constant flow of 5% H₂ (balanced
with N₂) to maintain a reducing atmosphere. To optimize the heating temperature MoO₃/C mixture was heated at 650 °C, 700 °C and 800 °C and compared with non-carbon mixed sample heated at 800 °C.

2.2. Characterization

All solid samples were systematically examined by X-Ray diffraction (XRD) measurements at room temperature (25°C) using a Philips X’pert diffractometer with Cu Kα radiation (λ = 1.5418 Å) at 40kV and 40 mA. A field emission gun scanning electron microscope (FEG-SEM, JEOL-7600F) with a resolution of about 1 nm was used to study the surface morphology of the samples. (FEG-TEM, JEOL-2100F) was done for high resolution imaging.

2.3. Cell Fabrication and Electrochemical Measurements

All the electrochemical performance of the materials was carried out in two-electrode Swagelok type cells in Li/Electrolyte/active material cell configuration. The complete cell was comprised with α-MoO₃ or MoO₂ as anode, borosilicate glass fibre sheet (Whatman GF/D) soaked with a 1 M LiPF₆ solution [in EC:DMC / 1:1 in mass ratio (LP-30, Merck, Germany)] as a separator and pure Lithium (Alfa Aesar) as a counter as well as reference electrode. The cells were assembled in an argon-filled glove box (Lab Star, Mbarun, Germany) with water and oxygen concentrations level of ~ 1 ppm. MoO₃ was hand ground with 20% of carbon black (Super C-65, Timcal, Switzerland) and 20% binder (PVDF or CMC) for half an hour. Slurry of the composite was prepared from the mixed powder by adding a few drops of NMP in case of PVDF binder while deionised water was used for CMC binder. The slurry was then tape casted on Cooper foil and finally dried at 120 °C (60 °C for CMC binder) under vacuum. MoO₂ electrodes were prepared by mixing the MoO₃/C mixture with 20 wt. % CMC and finally prepared the slurry using DI water.

Cycling voltammetry (CV) profile was obtained by measuring i-V response at scan rate of 0.2 mVs⁻¹ and cut off voltage was 0.01 V-3.0 V vs. Li/Li⁺. Electrochemical Impedance Spectroscopy (EIS) experiments were carried out at open circuit voltage (OCV) within the frequency ranges from 1 MHz-0.01 Hz. Bio-logic VMP-3 was used for CV and EIS measurements. The electrochemical charge-discharge experiments were performed in Arbin Instrument, USA (BT2000 model) with various current rates. All the electrochemical measurements were done at a constant temperature of 20 °C.

3. Result and Discussion

3.1. Structural characterization

The XRD pattern is shown in fig. 1a, which is indexed as orthorhombic phase of MoO₃ and a space group of Pbnm (JCPDS card No. 35-0609). It was also illustrated from fig. 1a that the pure phase of α-MoO₃ was obtained for all the three products prepared using three different acid medium. It has been observed that the product yield as well as structural uniformity depends upon two important factors (a) the acidifying agent (b) the acidification process. Though, the morphology of α-MoO₃ is unique nano-belts, however, the anisotropy of the belts were increase from HNO₃ to HClO₄ to HCl based synthesis (fig 1b-d). It has also been observed in fig. 1b-d that the MoO₃ nano belts are thinner and longer when HNO₃ was used as acidifying agent while shorter and irregular belts were obtained when HCl was used as the acidifying agent. MoO₃ prepared using HNO₃ (fig. 1b) was used for further characterization and electrochemical performance. Another important factor is the acidification process. It was observed that when acid was added drop wise (20 drops per minute) to the molybdate solution under constant stirring, thinner belts were obtained. But if the acid was directly poured into the solution, a thicker belt was found.
Fig. 1 (a) XRD of MoO₃ for different synthesis process (i) using HNO₃, (ii) using HClO₄ and (iii) using HCl, FEG-SEM images of α-MoO₃ prepared using different acid medium (b) HNO₃, (c) HClO₄ and (d) HCl.

XRD pattern shown in fig. 2a matches with JCPDS standard data of 36-0671 confirms the formation of monoclinic MoO₂. XRD pattern of all the four compounds are same to each other which confirmed that the reduction of MoO₃ to MoO₂ was started at 650 °C and it was remain unchanged till 800 °C. Presence of carbon does not affect the phase formation but helps in better mixing which improves the electrochemical performance of MoO₂ electrode. Carbon is also used reducing agent to reduce MoO₃ to MoO₂. MoO₂ prepared at 650 °C was used for further characterization and electrochemical performance. Fig. 2b illustrates that MoO₂ retain the morphology of the starting material and after the reduction process belt-like MoO₂ was obtained.

Fig. 2 (a) XRD of MoO₂ prepared at different temperature, (b) TEM image of as prepared MoO₂ at 650 °C.

3.2. Electrochemical performances

Cyclic Voltametry (CV) of MoO₂ is shown in fig. 3a demonstrates 4 prominent peaks in the first discharge curve. Peaks at 2.6 V and 2.3 V are due to the intercalation of Li ions into the interlayer spacing of [MoO₆] octahedral. The
peak around 0.5 V is due to conversion reaction between MoO$_3$ and Li. First discharge profile of MoO$_3$ shown in fig. 3c are also in good agreement with the CV results. A stable plateau was observed ~0.5 V which corresponds to conversion reaction while plateau at 2.3 V was due to intercalation of Li$^+$. In the oxidation reaction one broad peak at 1.7 V was observed which corresponds to delithiation process. Two additional peaks at 1.22V and 1.55 V were observed during the cathodic sweep from $2^{nd}$ cycle which are due Li intercalation in MoO$_2$ structure. As evident from the electrochemical data, after the first cycle both MoO$_3$ and MoO$_2$ were present in the system.

MoO$_2$ exhibits two strong peaks at 1.22 V and 1.53 V during cathodic sweep, similarly two strong peaks at 1.5 V and 1.74 V were observed during anodic peak (fig. 3b). The redox couple 1.22 V/1.5 V and 1.5 V/1.74 V were due to the reversible phase transitions (monoclinic–orthorhombic–monoclinic) of partially lithiated Li$_x$MoO$_2$ during Li insertion (discharge) and extraction (charge) process, which are in good agreement with previous reports [15-17]. Similar observations were also found during charge-discharge process (shown in fig. 3d). Two prominent plateaus at 1.25 V and 1.5 V were observed during discharge process whereas plateaus at 1.5 V and 1.8 V during charge process were due to deintercalation of Li$^+$ form MoO$_2$ lattice.

![Fig. 3: CV of (a) MoO$_3$ and (b) MoO$_2$ and the charge discharge profile of (c) MoO$_3$ and (d) MoO$_2$ are shown at 100 mA g$^{-1}$ rate for the potential window of 3.0 V to 0.1V.](image)

To get a better understanding of the electrochemical performance of MoO$_3$ three different electrodes were prepared using same active material and same electrode proportion (active material : binder : carbon = 60:20:20). First electrode was prepared using MoO$_3$ as active material, carbon as conductive additive and PVDF as binder and named as electrode-(I). Electrode-(I) was heated at 220 °C under vacuum and denoted as electrode-(II). Electrode-(III) was prepared using CMC binder instead of PVDF. All the three electrodes were tested against Li counter electrode at similar conditions. At a discharge rate of 100 mA g$^{-1}$ electrode-(III) exhibits best electrochemical stability whereas electrode-(I) exhibits least stability (fig. 4a). An initial discharge capacity of ~1200 mAh g$^{-1}$ was observed for all the three electrodes, but the irreversibility loss after first cycle was maximum for untreated PVDF
electrode (electrode-I) and minimum for heat treated PVDF electrode (electrode-II). The improved performance of electrode-(II) is due to the enhancement of binding property of PVDF due to heat treatment. It is assumed that due to heat treatment the adhesion between the electrode material and current collector improved [19-21]. PVDF (melting point 177 °C) is expected to meltdown while heated at 220 °C. Melted PVDF creates a better networking among the different component of the electrode and during cooling it rigidly bind with the active material and C, which leads to improvement in the electronic conductivity as well as electrochemical stability. EIS measurements was done on the different electrodes and shown in fig. 4b. It was observed that the charge transfer resistance of the PVDF electrode decreases after heat treatment which proves that due to heat treatment the adhesion among the electrode component increases that resulted an improvement in the electronic conductivity of the PVDF electrode. On the other hand CMC is known to be less electronic insulator than PVDF and as a result least impedance was observed for CMC electrode.

Due to better electronic conductivity and improved binding property, the electrochemical activity of electrode-(II) & (III) were improved. As shown in fig. 4a, the reversible discharge capacity of 180 mAh g⁻¹, 530 mAh g⁻¹ and 556 mAh g⁻¹ was achieved after 50 cycles with a fixed current discharge rate of 100 mA g⁻¹ for electrode-(I), (II) & (III) respectively. The superiority of CMC binder over PVDF is not fully understood. But different literature reports predicted that CMC provides a better networking between particles of conductive carbon and active material and presence of polar functional groups in the CMC molecule leads to formation of an effective chemical bonding with active material as well as current collector which enhance the stability of the electrode during cycling [19,22-24].
On the other hand MoO\textsubscript{2} electrode was prepared using CMC binder and tested as anode material for the potential range of 3.0 V to 0.01V. The MoO\textsubscript{2} electrode exhibits a good initial discharge capacity of 789 mAh g\textsuperscript{-1} in the first cycle which is close to 93\% of the theoretical capacity (fig. 5). The discharge capacity was decreased to 600 mAh g\textsuperscript{-1} in the second cycle. Discharge capacity was slightly increased in the consecutive cycles and reaches to ~ 690 mAh g\textsuperscript{-1} at the end of 30 cycles. Though a good discharge capacity was achieved for the bare material but the problem of cyclic stability is yet to resolve. The obtained results are very much similar to the results observed in the literature and the capacity values are also comparable with the literature results [12-17].

4. Conclusions

Present work represents a simple and scalable approach to prepare MoO\textsubscript{3} and MoO\textsubscript{2}. It was observed that the selection of inorganic acid for MoO\textsubscript{3} preparation plays an important role on the shape and size of the final product. Most importantly current work pointed out that the electrode fabrication process plays a pivotal role on the electrochemical performance. PVDF which is the most common binder for electrode preparation is not suitable for conversion reactions as conversion reaction deals with large no of Li intake which causes huge volume change. But if the same electrode was heated above the melting point of PVDF then the binding among the active material, carbon and binder sis increased and electrochemical performance of the electrode was improved significantly. It has also been observed that CMC provides better electrode stability towards conversion reaction in compare to PVDF binder.

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References


