Direct observation of pseudocapacitive sodium storage behavior in molybdenum dioxide anodes

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HIGHLIGHTS

- Introducing mesoporous and bulk MoO_2 anodes for sodium ion batteries.
- Excellent electrochemical performances using DME electrolyte.
- Pseudocapacitive sodium storage behavior is proposed based on CV measurements.
- Systematic validation by diverse structural analysis tools along with simulation.

GRAPHICAL ABSTRACT
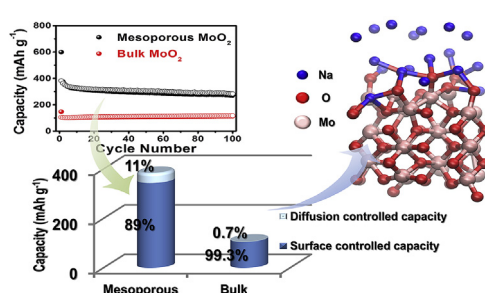
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ABSTRACT

Compared to research progress on cathode materials, progress on anode materials for sodium rechargeable batteries has been relatively slow. To bring sodium rechargeable batteries to a next level, it is necessary to explore feasible anode materials as well as understand clearly the reaction mechanism during electrochemical cycling. We herein introduce mesoporous and bulk molybdenum dioxide materials, which show excellent sodium storage performances under ether based electrolyte conditions, as anodes for sodium rechargeable batteries. Moreover, the pseudocapacitive sodium storage behavior in molybdenum dioxide anodes is proposed based on a quantitative analysis of the cyclic voltammetry responses. This result is systematically corroborated by using synchrotron radiation based analyses, X-ray photoelectron spectroscopy, scanning transmission electron microscope and *ab initio* molecular dynamics simulation. Comprehensive information on the electrochemical characterization as well as sodium storage mechanism of this transition metal oxide will provide a practical strategy to further advance anode materials for sodium rechargeable batteries.

1. Introduction

Although lithium rechargeable batteries have been largely successful in mobile electronics and hybrid electric vehicles, there are still several problems, such as the limited resources and increasing costs of lithium, that prevent the development of the large-scale energy storage systems [1]. Therefore, sodium rechargeable batteries have recently been recognized as alternative large-scale energy storage systems due to

the high abundance and low cost of sodium [2–5]. Layered transition metal oxides ($NaMnO_2$) [6,7], NASICON structure ($Na_3V_2(PO_4)_3$) [4,8], and olivine-type structure ($NaFePO_4$) [9,10] have been widely studied as cathode materials, and these studies have resulted in significant progress over the last decade in the development of sodium rechargeable batteries. However, the exploration of favorable anode materials and studies on their sodium storage mechanism have progressed slowly [11]. More recently, sodium intercalation compounds such as hard carbon [12], graphite [13,14], and $NaTiO_2$ [15] have been minutely studied as anode materials for sodium rechargeable batteries. However, these intercalation compounds have comparatively low energy density due to the limited sodium interstitial sites in the host structure [16]. Thus, metal oxide materials, which have mostly been studied as anode part for lithium rechargeable batteries with high specific capacity, are attractive as potential candidates for anode materials in sodium rechargeable batteries [17–23]. In Particular, molybdenum dioxide (MoO_2) is a very appealing alternative anode material due to its metallic electrical conductivity and high chemical stability [24–30]. In lithium based systems, it delivers a high theoretical capacity based on intercalation and/or conversion reaction (840 mAh g^{-1}) and shows a high density (6.5 g cm^{-3}), which enables more energy to be stored in a battery with the same size (graphite: 2.3 g cm^{-3}) [31,32]. However, according to several reported studies, the lithiation of MoO_2 is restricted to the addition reaction with a one-electron reduction at room temperature, which indicates that conversion reaction does not occur under a general cycling conditions [26,28,33–35]. Although conversion reaction of MoO_2 is thermodynamically feasible at room temperature [36], slow kinetics lead to the absence of conversion reaction during electrochemical cycling. Furthermore, large volume changes during the lithiation/delithiation process lead to electrical connectivity loss by the electrode pulverization [37,38]. To overcome these disadvantages, nanostructuring and carbon additives that improve the lithium insertion/extraction kinetics, structural stability and electronic conductivity are often used; thus, considerably enhanced electrochemical performances of metal oxides have been reported in several recent studies [39–45].

Mesoporous structure is one of the effective nanoscale-engineering methods, and numerous mesoporous metal oxide anode materials have been studied for lithium rechargeable batteries [21,29,46–49] In our previous work, we synthesized mesoporous MoO_2 with high and reversible specific capacity (1814 mAh g^{-1} for the first cycle and 1607 mAh g^{-1} after 50 cycles), and proposed a novel lithium storage mechanism, including intercalation reaction and the formation of lithium-rich phase, based on physicochemical analyses and computational modeling [50]. In recent years, nanostructured MoO_2 anodes in sodium based systems have been extensively studied by several research groups [51–55]. However, despite such reports, the sodium storage mechanism of MoO_2 anode is still unclear. Moreover, the selection of appropriate electrolytes has emerged as another hindrance to the development of anode materials for sodium based systems as reported in recent studies on graphite anodes [13,14,56].

In this study, we synthesized mesoporous MoO_2 by the same procedure described in our previous work [50] and prepared conventional bulk MoO_2 as a comparison. Subsequently, we conducted electrochemical characterizations under various electrolyte conditions and figured out that ether based dimethoxyethane (DME) electrolyte delivers the best performance for both MoO_2 anodes. Furthermore, we propose the pseudocapacitive sodium storage behavior of MoO_2 anodes in sodium rechargeable batteries by analyzing their electrochemical responses in cyclic voltammetry (CV) and provide direct evidences by using synchrotron radiation based analyses, X-ray photoelectron spectroscopy (XPS), scanning transmission electron microscope (STEM) and *ab initio* molecular dynamics (AIMD) simulation. These findings will provide a novel horizon for understanding sodium storage pathways in metal oxide based anode materials and enable a significant advancement in electrode materials for post energy storage systems.

2. Experimental

2.1. Materials

For synthesis of mesoporous MoO_2 material, KIT-6 with cubic *Ia3d* mesostructure was used as the silica template, and pluronic triblock copolymer P123 ($EO_{20}PO_{70}EO_{20}$, MW = 5800) was employed for KIT-6 synthesis as the structure-directing agent. 90.0 g of P123 was dissolved in a mixture (distilled water 3255 g, 99.7 wt% 1-BuOH (Aldrich) 90 g, and 35 wt% c-HCl (Aldrich) 177 g), and then stirred at 35 °C for 10 min. Simultaneously, under vigorous stirring condition, 193.5 g of tetraethylorthosilicate (98 wt%, Aldrich) was added to this solution. After stirring process at 35 °C for 24 h, the obtained mixture kept in an oven under static condition at 100 °C for 24 h. The solid product was filtered and washed with double distilled water, and then dried overnight in an oven at 100 °C. The resulting powder (white) was washed with EtOH, and dried in an oven at 80 °C for 12 h. Lastly, in order to remove the structure-directing agent, powder was calcined at 550 °C for 3 h under static air conditions (mesopore size of the KIT-6 template: 7.1 nm).

By the nano replication method using synthesized KIT-6 (mesoporous silica templates), mesoporous MoO_2 material was synthesized. Firstly, 5.9 g of ammonium molybdate tetrahydrate ((NH_4)$_6Mo_7O_{24}$■$4H_2O$, Aldrich) was dissolved in 8.4 g of distilled water, and then this solution was infiltrated into 10.0 g of the calcined KIT-6 template by an incipient wetness method. The obtained material was dried in an oven at 80 °C for 24 h, and then under nitrogen atmosphere condition, heated to 500 °C for 5 h for crystallization. After heat process, using a 20 wt% HF solution, the silica template was removed from the composite by a wet-etching process. Finally, mesoporous MoO_2 material, an end product, was washed several times using distilled water and acetone, and dried in an oven at 80 °C overnight. For a comparative analysis, conventional bulk MoO_2 (99%, Alfa Aesar) was prepared and used without any modification or post-treatment.

2.2. Electrochemical tests

Mesoporous and bulk MoO_2 electrodes were prepared by mixing the 70 wt% active material powder, 15 wt% carbon black (ketjen black, EC-300J) and 15 wt% binder (polyamideimide, PAI, Torlon 4000 T, Solvay) in solvent (N-methyl-2-pyrrolidone, Aldrich). The resulting slurry was uniformly casted onto a Cu foil current collector, and dried in an oven at 200 °C for 2 h under vacuum conditions. The mass loading of active material per mesoporous and bulk MoO_2 electrodes was ~1.24, ~2.04 mg cm^{-2}, respectively. The prepared electrodes were incorporated into coin cells (2032 type) with a metallic sodium foil as counter electrode and a glass fiber (grade GF/F, Whatman) as separator in the Ar filled glove box. The electrolytes were carefully prepared to maintain low H_2O contents (< 20 ppm). The $NaPF_6$ and molecular sieves (beads type, 4 Å (8–12 mesh), Aldrich) were stored in a vacuum oven at 150 °C before use. The dried sodium salts were dissolved in electrolyte solvents, including ethylene carbonate (EC), dimethyl carbonate (DMC), diethyl carbonate (DEC), diethylene glycol dimethyl ether (DEGDME), tetraethylene glycol dimethyl ether (TEGDME), and dimethoxyethane (DME) at 1 M and 1.3 M. The solutions were stirred at 60 °C for 24 h, and molecular sieves were used to remove residual H_2O from the electrolyte solutions. The discharge/charge profiles and cyclic voltammetry (CV) results were obtained using a WonATech Battery Cycler WBCS3000S, over a voltage range of 0.001–2.5 V.

2.3. Characterization

The X-ray diffraction (XRD) patterns were collected from Rigaku D/MAX-2200 Ultima instrument equipped with Cu-Kα radiation operating at 30 kV and 40 mA. N_2 sorption isotherms were measured under liquid N_2 temperature condition using a Micromeritics Tristar system after dry process of samples at 52 °C for 12 h. For calculating the surface areas