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Highly reversible insertion of lithium into MoO_2 as an anode material for lithium ion battery

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ABSTRACT

MoO_2 has gained renewed attention as a safe oxide anode host material for lithium ion insertion because of its high gravimetric/volumetric capacity and highly stable cycling behavior. However, these recent results are completely contrary to previous reports. To confirm that MoO_2 is an appropriate anode material as well as further understand lithium ion reactions when inserted into MoO_2, we combine electrochemical characterization of MoO_2 electrodes and *ex situ* X-ray diffraction analysis with first principle calculations. Theoretical capacity of the MoO_2 electrode (~209 mAh g^{-1}) and stable capacity retention up to 100 cycles are simultaneously attained using a proper particle size and type of binder. *Ex situ* XRD analysis with first principle calculations of the phase transformation of MoO_2 electrodes shows that MoO_2 undergoes reversible structural changes upon lithiation and subsequent delithiation, clearly demonstrating that nanostructured MoO_2 can be used as an anode material for highly reliable lithium ion batteries.

1. Introduction

Li-ion batteries (LIBs) are predominantly used as power sources for mobile electronic devices and are considered one of the most promising power sources for electric vehicles and large-scale electrical storage systems for renewable energies [1–3]. For these new applications, it is highly required to advance the technology of LIBs in terms of energy/power density, cycle life and reliability. In this regard, intensive research on the new electrode materials are pursued [4–7]. There is currently renewed interest in transition metal oxides [8–14] as anode materials because of the increased demand for alternative anode materials to meet the requirements of the aforementioned emerging applications [6,15–19]. In particular, spinel $Li_4Ti_5O_{12}$ (LTO) material [20–26] has been widely investigated as a promising anode material due to its excellent cycling performance and safer battery operation conditions than graphite anodes. LTO undergoes almost no change in volume during cycling, which ensures that LTO has excellent structural stability during cycling; this in turn increases the life cycle of the battery. In addition, the working voltage of LTO (about 1.5 V *vs.* Li/Li^+) is high enough to avoid lithium plating on the anode even under fast charging conditions, as well as unwanted side reactions such as electrolyte decomposition on the surface of the anode. However, the use of LTO is still limited by its low gravimetric/volumetric energy density (175 mAh g^{-1}, 630 mAh cc^{-1}). In the quest for reliable alternative anode materials with a greater energy density than LTO, several transition metal oxide materials such as TiO_2–B [21,26] and Ti–Nb [6,27,28] oxide have been suggested, and the results indicate that these materials show promising behavior as anode materials for Li-ion batteries.

MoO_2 with its distorted rutile structure can accommodate lithium ions through an insertion reaction to form $LiMoO_2$ with a theoretical capacity of 209 mAh g^{-1} [29–33], which is much higher than that of LTO. Moreover, its theoretical volumetric energy density (1357 mAh cc^{-1}) is much higher than that of LTO (630 mAh cc^{-1}) as shown in Fig. 1a. MoO_2 electrodes have two potential plateaus at about 1.5 V and 1.3 V (*vs.* Li/Li^+) for lithium insertion and 1.4 V and 1.7 V for lithium extraction, implying that the average working voltage of MoO_2 as an anode material is almost the same as that of LTO. These attractive features suggest that MoO_2 may be also an alternative anode material like LTO. However, it is widely accepted that MoO_2 as a host material for lithium ion insertion shows poor capacity retention because of irreversible phase transformation from MoO_2 to $LiMoO_2$. Recently, Sen et al.

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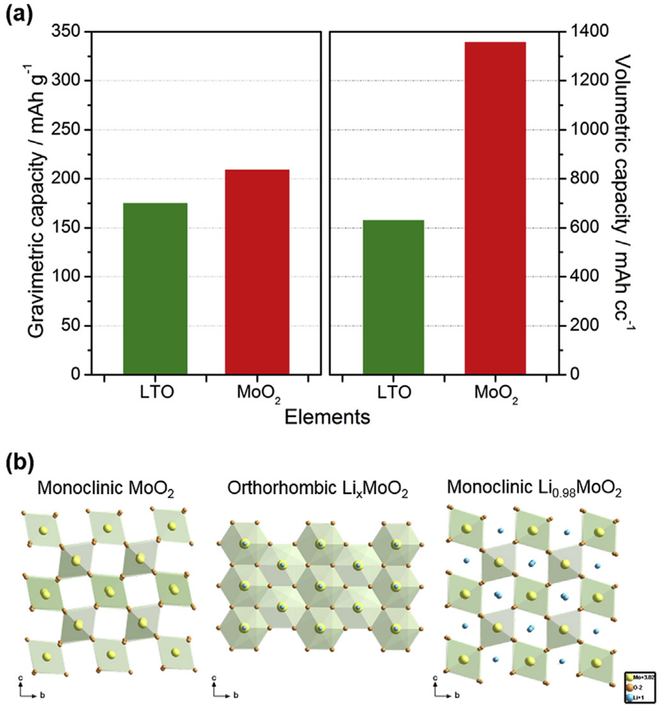

Fig. 1. (a) Theoretical gravimetric and volumetric energy density of MoO_2 and $Li_4Ti_5O_{12}$. (b) Crystal structure of monoclinic MoO_2, orthorhombic Li_xMoO_2 and $Li_{0.98}MoO_2$.

reported that MoO_2 nanobelt electrodes showed an excellent capacity of up to 200 cycles without significant capacity fading, which had not been reported in previous studies. They investigated phase transition of MoO_2 from monoclinic to orthorhombic was highly reversible during cycling using *ex situ* XRD analysis [34]. However, the MoO_2 nanobelt electrodes delivered a reversible capacity of about 180 mAh g^{-1}, which is only 90% of the theoretical capacity of MoO_2 electrodes. Park et al. reported that carbon-coated MoO_2 electrodes prepared by carbothermal reduction of MoO_3 nanobelts delivered a reversible capacity of 208 mAh g^{-1} with excellent capacity retention characteristics up to 100 cycles, as well as high rate capability [35]. These recent studies suggest that MoO_2 is potentially a highly reversible host material for lithium insertion reaction and that the theoretical capacity of MoO_2 electrodes can be realized by nano-engineering MoO_2 and/or creating a composite with carbon. However, given that the electrical conductivity of MoO_2 is much higher than that of $Li_4Ti_5O_{12}$ and TiO_2, which can deliver their theoretical capacity without carbon coating [6,9], it is reasonable to expect that MoO_2 without an additional conductive carbon phase could have a reversible capacity close to the theoretical capacity with stable long-term capacity retention characteristics. More importantly, it is still unclear why the MoO_2 electrodes characterized in recent studies showed highly stable capacity retention, in contrast with previous results. In particular, phase transformation of the MoO_2 electrode, which was shown in previous studies to be highly irreversible, needs to be further clarify. To address the aforementioned issues, we investigated phase transformation of MoO_2 electrodes using *ex situ* XRD analysis combined with first principles calculations. It should also be noted that the molar volume of $LiMoO_2$ is 13% higher than that of MoO_2, as shown in Fig. 1b, implying that the MoO_2 electrode undergoes repeated volume changes during cycling. Even though the extent of volume change is not severe compared to that of alloy-type materials such as Si, Sn, and Ge, one cannot rule out the possibility of degradation of the MoO_2 electrode caused by volume changes of MoO_2 associated with lithium insertion/removal. It is well known that the use of highly adhesive binder can significantly improve the battery performances of electrode materials that undergo volume changes during cycling. To gain further insights into the effects of various binders on the insertion reaction of lithium ions into MoO_2, we prepared various MoO_2 electrodes using two different sizes of MoO_2 particles and two types of polymeric binders (polyvinylidene-difluoride (PVDF) and polyimideamide (PAI)).

2. Experimental

2.1. Sample preparation

MoO_2 particles were prepared by carbothermal reduction of MoO_3 particles with urea. MoO_3 was prepared from the precipitation of 0.05 M ammonium molybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$) aqueous solution using nitric acid solution (5 ml, 40%) at 90 °C for 1 h. After drying of the precipitated MoO_3 particles at 80 °C for 6 h, the mixture of MoO_3 particles and urea (9:1, by weight) was pyrolyzed at 700 °C for 10 h under an N_2 atmosphere.

2.2. Materials characterization

The resulting particles were characterized using X-ray diffraction (XRD), elemental analysis, and scanning electron microscopy (SEM). Note that the amount of carbon in the MoO_2 particles was less than 1 wt% (Table S1). MoO_2 electrodes were prepared by casting a slurry composed of MoO_2 particles (80 wt%), carbon black as a conducing agent (10 wt%), and polyvinylidene fluoride in n-methyl-2-pyrrolidinone (NMP, 10 wt%) on Cu foil and dried in a vacuum oven at 120 °C for 12 h. Electrochemical properties of MoO_2 were characterized using coin-type cells (2016R), which were assembled in a dry room by stacking a separator (Celgard 2400 TM) containing liquid electrolyte (1.3 M $LiPF_6$ in EC:DEC (3:7, by volume)) between the MoO_2 electrode and lithium metal foil. The coin-type cells were cycled at a rate of 20 mA g^{-1} (about 0.1 C rate) between 1.0 and 3.0 V at 25 °C using a battery cycle tester (TOSCAT 3000 series, Toyo systems, Japan). Discharged and charged MoO_2 electrodes were analyzed by *ex situ* XRD analysis to investigate structural changes of the MoO_2 electrode during cycling. The cycled electrodes were detached from the coin cell, washed with diethyl carbonate, and coated with Kapton tape as a protective film.

First principles calculations based on density functional theory were performed using Vienna ab initio simulation package (VASP) code. Exchange-correlation interactions between electrons were described by the generalized gradient approximation (GGA), and projector-augmented wave (PAW) potentials were used to describe ion-electron interactions. The plane-wave cutoff energy was chosen to be 400 eV and k-points were sampled on 6 × 6 × 6 grids. Spin-polarization calculations were used for Li insertion structures. The conjugate gradient method for geometry optimization was used.

3. Results and discussion

Fig. 2 shows XRD patterns and SEM images of MoO_2 particles. Fig. 2a compares the XRD patterns of MoO_3 particles precipitated using ammonium molybdate tetrahydrate and nitric acid, MoO_2 particles from carbothermal reduction of MoO_3 particles with urea, and commercially available MoO_2 particles. All Bragg peaks shown in the XRD patterns of MoO_2 particles from carbothermal reduction of MoO_3 using urea corresponded to distorted rutile MoO_2 phase without any impurity phase. The nanoparticles and microparticles