Thermoelectrochemically Activated MoO₂ Powder Electrode for Lithium Secondary Batteries

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The high temperature lithiation behavior of the MoO₂ electrode is examined, which is lithiated by one-electron reduction (by addition reaction) at room temperature. At elevated temperatures, this electrode is lithiated with four-electron reduction by addition and continued conversion reaction. As a result of four-electron reduction, the initial crystalline MoO₂ phase is decomposed into a nanosized mixture of metallic Mo and Li₂O, which is in turn converted to nanosized MoO₂ upon forthcoming delithiation. An interesting feature here is that as-generated nanosized MoO₂ is now fully lithiated up to four-electron reduction even at room temperature. This phenomenon is named “thermoelectrochemical activation” because the extension from one- to four-electron reduction is achieved by a simple charge–discharge cycling made at elevated temperatures. The thermoelectrochemically activated MoO₂ electrode delivers a reversible specific capacity that is close to the theoretical four-electron capacity (838 mA h g⁻¹) with an excellent cycle performance at room temperature.

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Since the commercialization of lithium-ion batteries (LIBs) by SONY Corporation in the early 1990s, LIBs have been used as the major power source for portable electronic devices. 1,2 The recent issues of oil price and global warming drive a continuous development of cleaner and more fuel-efficient hybrid electric vehicles (HEVs), in which LIBs with their superior performance to nickel-metal hydride cells are now being considered as the future power source. The existing LIB technologies, however, still have serious cost and performance limitations with respect to energy density, safety, and cycle life, which hinders the widespread use of sophisticated electronic devices and HEVs.

To increase the energy density of LIBs, many electrode materials containing redox centers that accept more than one electron over a small voltage window have been highly sought. In this sense, a series of transition-metal oxides (M₂O₃, with M = Fe, Co, Ni, Cu, etc.) seems to be one of the candidate materials because the transition-metal components in these oxides are converted to their elemental state by more than one-electron reduction. 3,4 As a result of this reduction reaction, nanosized metal particles that are dispersed in the Li₂O matrix are formed (this is called conversion reaction) but restored to the original oxides by delithiation. 5,6 The number of electrons involved in this charge–discharge process is determined by the oxidation state of metallic components; for instance, four electrons for MoO₂. This conversion reaction is contrasted by the addition-type lithiation, in which the number of electrons involved in the redox reactions is commonly limited to less than 1 because Li inserts into the vacant sites of metal oxide frameworks without M–O bond cleavage. 5,6

When considered as the negative electrode for LIBs, the lithiation or metal oxides should take place at >0.0 V (vs Li/Li⁺) to prevent Li plating. Within this voltage window, the room-temperature lithiation behavior of metal oxides, which has been reported, can be classified into four groups: The first group does not show any lithiation activity; NbO and TiO. The extent of lithiation for the second group is limited to the addition-type reaction: TiO₂, V₂O₅, MoO₂. The third group is lithiated by the addition-type reaction in advance, which is followed by the conversion reaction; RuO₂. The final group is lithiated by the conversion reaction without the addition-type intermediate step; CoO, NiO, and CuO. The controlling factors for the room-temperature lithiation behavior must be, among others, the lattice structure of metal oxides, thermodynamic and kinetic parameters, and charge–discharge rates. That is, the lattice structure of oxides should provide vacant sites for Li for the addition-type lithiation. In a thermodynamic point of view, the equilibrium potential for lithiation should be at least >0.0 V. Even if this thermodynamic condition is met, the lithiation should not be hindered by any kinetic reasons. Otherwise, lithiation sometimes takes place below 0.0 V under transient charge–discharge cycling conditions, in particular, under a high rate cycling condition.

According to the literature, the lithiation of the MoO₂ electrode is limited to the addition reaction with one-electron reduction at room temperature. 5,12,13,16 That is, the conversion reaction does not take place in a normal cycling condition. Given that the conversion reaction is thermodynamically feasible at room temperature, the absence of this reaction must be attributed to a slower kinetics. Intuitively, one way to increase the conversion reaction rate is to raise the working temperature. An enlargement of surface and defect sites must be another measure to facilitate the conversion reaction because this reaction proceeds through heterogeneous charge-transfer reaction and solid-state Li⁺–ion diffusion. 5,11,16 With these two premises in mind, we examined the conversion reaction activity of the MoO₂ electrode at elevated temperatures. We also examined whether or not the conversion reaction is facilitated by ball-milling of the initial MoO₂ powder, with which an increase in the surface area and defect sites can be assumed.

Experimental

For the X-ray diffraction (XRD) and Raman and X-ray photoelectron spectroscopy (XPS) studies, a MoO₂-embedded Ag foil electrode was prepared by pressing (170 MPa) the MoO₂ powder (Aldrich) that was spread on a piece of Ag foil (1.0 cm² and ca. 0.25 mm thick). 10 With this configuration, any spectroscopic interferences that came from carbon additive and polymer binder was avoided. For the galvanostatic discharge/charge cycling, a composite electrode was prepared by spreading the slurry of the MoO₂ powder, Super-P (as a carbon additive for conductivity enhancement), and polyvinylidene fluoride (as a binder) (70:20:10 in weight ratio) on a piece of Cu foil, which was followed by drying in vacuum at 120°C for 12 h. The electrode plate was then pressed to enhance the interparticle contact and to ensure better adhesion to the current collector.

XRD patterns were obtained using a D8-Bruker diffractometer equipped with Cu Ka radiation (1.54056 Å). For the sample preparation, the cells were disassembled and electrodes were rinsed with dimethyl carbonate (DMC) and dried in an argon-filled dry box. All the XRD patterns were recorded at 3 kV and 20 mA using a continuous scanning mode with 1.0° min⁻¹. XPS measurements were...
made in an ultrahigh vacuum multipurpose surface analysis system (Sigma Probe, Thermo, U.K.) using an Al K\(_\alpha\) (1486.6 eV) anode operating at constant power (15 kV and 10 mA). During the data acquisition, the constant energy mode was employed at a pass energy of 30 eV and a step of 0.1 eV. Depth analysis was made by etching the samples with argon-ion beam (accelerating voltage of 3 kV and ion-beam current of 1 \(\mu\)A). For the postmortem high resolution transmission electron microscope (HR-TEM) analysis, the cells were disassembled and the powders in electrodes were dispersed in DMC by sonication in an argon-filled dry box before loading on the transmission electron microscopy (TEM) grid. All the procedures were carried out under inert atmosphere and the samples were transferred using a hermetically sealed bottle. TEM images and selected area electron diffraction (SAED) patterns were obtained using JEOL JEM-2100F and 2010 at 200 kV of acceleration voltage. The Raman study was made with a LabRam HR (Jobin-Yvon Co., France) spectrometer with a 514.5 nm Ar\(^+\) laser. Signals were collected by using a multichannel charge-coupled device detector cooled to 140 K. The Brunauer, Emmett, and Teller (BET) surface area was measured from the \(N_2\) adsorption isotherms that were obtained with a gas adsorption analyzer (Micromeritics, ASAP 2010). The particle morphology was examined using a field-emission scanning electron microscope (FE-SEM) (JEOL JSM-6700F).

The galvanostatic discharge/charge cycling was made in a temperature-controlled oven using a two-electrode 2032-type coin cell. Li metal foil was used as the counter electrode. To prevent Li plating and lithiation to Ag substrate, the lower cutoff voltage was set at \(85^\circ\text{C}\) because the PP was deformed at \(85^\circ\text{C}\) but a glass fiber sheet was used as the separator. To suppress an overcharge reaction that occurs above \(85^\circ\text{C}\), a Li metal foil was used as the counter electrode. To prevent Li plating and lithiation to Ag substrate, the lower cutoff voltage was set at \(85^\circ\text{C}\) because the PP was deformed at \(85^\circ\text{C}\) but a glass fiber sheet was used as the separator. To suppress an overcharge reaction that occurs above \(85^\circ\text{C}\), a Li metal foil was used as the counter electrode. To prevent Li plating and lithiation to Ag substrate, the lower cutoff voltage was set at \(85^\circ\text{C}\) because the PP was deformed at \(85^\circ\text{C}\) but a glass fiber sheet was used as the separator. To suppress an overcharge reaction that occurs above \(85^\circ\text{C}\), a Li metal foil was used as the counter electrode. To prevent Li plating and lithiation to Ag substrate, the lower cutoff voltage was set at \(85^\circ\text{C}\) because the PP was deformed at \(85^\circ\text{C}\) but a glass fiber sheet was used as the separator. To suppress an overcharge reaction that occurs above \(85^\circ\text{C}\), a Li metal foil was used as the counter electrode. To prevent Li plating and lithiation to Ag substrate, the lower cutoff voltage was set at \(85^\circ\text{C}\) because the PP was deformed at \(85^\circ\text{C}\) but a glass fiber sheet was used as the separator. To suppress an overcharge reaction that occurs above \(85^\circ\text{C}\), a Li metal foil was used as the counter electrode. To prevent Li plating and lithiation to Ag substrate, the lower cutoff voltage was set at \(85^\circ\text{C}\) because the PP was deformed at \(85^\circ\text{C}\) but a glass fiber sheet was used as the separator. To suppress an overcharge reaction that occurs above \(85^\circ\text{C}\), a Li metal foil was used as the counter electrode. To prevent Li plating and lithiation to Ag substrate, the lower cutoff voltage was set at \(85^\circ\text{C}\) because the PP was deformed at \(85^\circ\text{C}\) but a glass fiber sheet was used as the separator. To suppress an overcharge reaction that occurs above \(85^\circ\text{C}\), a Li metal foil was used as the counter electrode. To prevent Li plating and lithiation to Ag substrate, the lower cutoff voltage was set at \(85^\circ\text{C}\) because the PP was deformed at \(85^\circ\text{C}\) but a glass fiber sheet was used as the separator. To suppress an overcharge reaction that occurs above \(85^\circ\text{C}\), a Li metal foil was used as the counter electrode. To prevent Li plating and lithiation to Ag substrate, the lower cutoff voltage was set at \(85^\circ\text{C}\). To see if the conversion reaction occurs at elevated temperatures, the working temperature was varied from 25 to 120°C with \(10^\circ\text{C}\) intervals. The voltage profiles observed below \(75^\circ\text{C}\) were similar to that shown in Fig. 2a, whereas a somewhat different voltage profile was observed at 85–120°C (Fig. 2b). The voltage profile at 120°C is represented in Fig. 2c. The most apparent difference to that obtained at 25°C (Fig. 2a) is the additional voltage plateau evolving at 0.23–0.29 V (scans 4–6) at 85°C, which is absent at 25°C (Fig. 2a). This plateau is due to the formation of a stable, amorphous product, which is not present at 25°C. The most apparent difference to that obtained at 25°C (Fig. 2a) is the additional voltage plateau evolving at 0.23–0.29 V (scans 4–6) at 85°C, which is absent at 25°C (Fig. 2a). This plateau is due to the formation of a stable, amorphous product, which is not present at 25°C.

The particle morphology was examined using a field-emission scanning electron microscope (FE-SEM). The HR-TEM image of the (a) raw MoO\(_2\) and (b) ballmilled MoO\(_2\). The HR-TEM image of the (c) raw MoO\(_2\) and (d) SAED pattern.

Results and Discussion

Figure 1 shows the FE-SEM images of the raw and ballmilled MoO\(_2\) powder. The HR-TEM image and SAED pattern that are obtained with the raw MoO\(_2\) are also included. The apparent size of the raw MoO\(_2\) particles is 10–50 \(\mu\)m (inset of Fig. 1a), but each particle comprises the primary particles of 0.2–0.3 \(\mu\)m in size (Fig. 1a). The HR-TEM image ensures that the size of the primary particles in the raw MoO\(_2\) is in the range of 0.2–0.3 \(\mu\)m (Fig. 1c). The raw MoO\(_2\) powder is highly crystalline as seen from the SAED pattern, in which intense lattice fringes can be identified (Fig. 1d). The size reduction by ballmilling is ascertained from the FE-SEM image taken with the ballmilled sample (Fig. 1b), in which the primary particles of 0.1–0.2 \(\mu\)m can be located. From the irregular-shaped particle morphology and roughened surface of the ballmilled powder, an increase in the surface area and defect sites can be assumed.

Figure 2 shows the first galvanostatic discharge (lithiation, downward profiles) and charge (delithiation, upward) voltage profiles of the MoO\(_2\)/Li cell and the XRD patterns of MoO\(_2\) electrodes obtained at 25 and 120°C. At 25°C (Fig. 2a), the MoO\(_2\) electrode accepts ca. 1.7 Li/Mo but releases ca. 1.0 Li/Mo. The cyclic voltammetry scans shown in the inset illustrate that reversible Li\(^+\) uptake/extraction takes place at 1.0–2.0 V, but irreversible ones at two voltage regions (>2.0 and <1.0 V). The irreversible reaction at >2.0 V occurs only in the first cycle (solid line), but that appeared at <1.0 V is still observed in the second cycle (dotted line). Further study is continuing in this laboratory to identify the nature of these irreversible reactions. The XRD data (Fig. 2c) illustrate the Li\(^+\) uptake/extraction mechanism prevailing at 25°C. The most intense (111) diffraction line of the MoO\(_2\) phase (monoclinic, space group = \(P2_1/c\), JCPDS no. 00-032-0671) steadily moves to the smaller angle (scans 1–3) in the earlier stage of lithiation, indicative of a single-phase lithiation. A careful inspection on the diffraction profiles revealed that the MoO\(_2\) electrode is lithiated by an addition-type reaction with one-electron extraction at 25°C and restores to its initial crystalline MoO\(_2\) phase (scan 9). The maintenance of structural framework and no decomposition into the metallic state reflect that the conversion reaction does not take place at 25°C.

To see if the conversion reaction occurs at elevated temperatures, the working temperature was varied from 25 to 120°C with \(10^\circ\text{C}\) intervals. The voltage profiles observed below \(75^\circ\text{C}\) are similar to that shown in Fig. 2a, whereas a somewhat different voltage profile was observed at 85–120°C (Fig. 2b). The voltage profile at 120°C is represented in Fig. 2c. The most apparent difference to that obtained at 25°C (Fig. 2a) is the additional voltage plateau evolving at 0.23–0.29 V (scans 4–6) at 1.0 V in size. This phase is absent in this work. The formation of Li\(_{0.98}\)MoO\(_2\) has been assigned to Li\(_{0.98}\)MoO\(_2\) (JCPDS no. 01-087-0392) in this work. The other phase having a very close composition (LiMoO\(_2\)) can be discarded because the most intense diffraction peak at 2\(\theta = 17.2^\circ\) for this phase is absent in this work. The formation of Li\(_{0.98}\)MoO\(_2\) has been assigned to Li\(_{0.98}\)MoO\(_2\) (JCPDS no. 01-087-0392) in this work. The other phase having a very close composition (LiMoO\(_2\)) can be discarded because the most intense diffraction peak at 2\(\theta = 17.2^\circ\) for this phase is absent in this work. The formation of Li\(_{0.98}\)MoO\(_2\) has been assigned to Li\(_{0.98}\)MoO\(_2\) (JCPDS no. 01-087-0392) in this work. The other phase having a very close composition (LiMoO\(_2\)) can be discarded because the most intense diffraction peak at 2\(\theta = 17.2^\circ\) for this phase is absent in this work.
Decomposition into nanosized metal particles is a common observation for transition-metal oxides that undergo a conversion-type lithiation reaction.\textsuperscript{5–8} The evolution of the conversion reaction at the plateau region has been further confirmed by calculating the lithiation/delithiation capacity. In theory, 3.0 Li/Mo is required for the conversion reaction because 1.0 Li/Mo has already been consumed for the addition reaction. The experimentally observed lithiation capacity is 2.8 Li/Mo at the plateau region (0.23–0.16 V in Fig. 2b), which is close to the theoretical value. Another revealing feature in Fig. 2d is that the featureless XRD pattern is maintained upon delithiation (scans 5 and 6), reflecting that the delithiated products and any intermediates are also nanosized in nature.

The four-electron reduction to metallic Mo (one electron by addition and three electrons by conversion reaction) and four-electron oxidation back to MoO\textsubscript{2} have been evidenced by XPS study. The MoO\textsubscript{2} electrode that is lithiated down to 0.16 V clearly shows the presence of metallic Mo and the delithiated sample up to 3.0 V the MoO\textsubscript{2} phase (Fig. 3a). The restoration to the MoO\textsubscript{2} phase is further confirmed by Raman study (Fig. 3b). The delithiated electrode gives the same Raman peaks to those of the initial MoO\textsubscript{2} sample,\textsuperscript{22} suggesting that the Mo species generated by delithiation is nothing but the MoO\textsubscript{2} phase. One notable feature here is the redshift \( \Delta \nu \) in the Raman spectra for the nanosized MoO\textsubscript{2}, which has been evidenced by the redshift in the Raman spectra in the second cycle (Fig. 3b).

It is now interesting to see whether or not the same kinetic barrier prevails in the nanosized MoO\textsubscript{2} phase (less than 10 nm as seen later). Figure 4a compares the lithiation voltage profiles obtained in the first and second cycles at 120°C. The first profile corresponds to that for the initial MoO\textsubscript{2}, whereas the second one for the nanosized MoO\textsubscript{2}. An apparent feature in Fig. 4a is the higher plateau voltage for the conversion reaction (0.47 V) in the second cycle, reflecting that the conversion reaction is more facilitated in the nanosized MoO\textsubscript{2}. This favorable feature resulted from both thermodynamic (equilibrium potential for conversion reaction) and kinetic contributions (polarization). The galvanostatic intermittent titration technique (GITT) experiment made at the plateau region (Fig. 4b), however, illustrates that the kinetic contribution is dominant over the thermodynamic ones. That is, the quasi-equilibrium potential for the conversion reaction for the initial MoO\textsubscript{2} (the average value of six open circles) is 0.77 V, which is comparable to that (0.74 V) for the nanosized one. In contrast, there appears an appreciable difference in the overpotential values (difference between the quasi-equilibrium potential and transient value); 0.54 V for the initial MoO\textsubscript{2} and 0.27 V for the nanosized one. Clearly, the facilitated conversion reaction for the latter resulted from an enhanced kinetics.

As mentioned above, the heterogeneous charge transfer and solid-state Li\textsuperscript{+} or O\textsuperscript{2–} diffusion may be the kinetic barriers that impede the conversion reaction. Along this line, the enhanced kinetics for the nanosized MoO\textsubscript{2} can be ascribed to a transformation from the submicron-sized (0.2–0.3 \( \mu \)m for the raw MoO\textsubscript{2}) to the nanosized particles.\textsuperscript{25,17} The downsizing of particles and increase in defect sites in the latter seem to be favorable for the heterogeneous charge transfer and solid-state ion diffusion. Another kinetic barrier for the conversion reaction must be the M–O bond cleavage. In this sense, the enhanced conversion activity can also be attributed to a weaker M–O bond strength for the nanosized MoO\textsubscript{2}, which has been evidenced by the redshift in the Raman spectra (Fig. 3b).
The finding that the nanosized MoO$_2$ electrode exhibits an enhanced conversion activity led us to examine its lithiation activity at room temperature. To this end, a nanosized MoO$_2$ phase was generated by cycling at 120°C, as shown in Fig. 5a (dotted line), and then cycling at 25°C (solid line). Surprisingly, the extent of lithiation that was limited to the addition-type reaction at room temperature (Fig. 2a) is now extended to the conversion reaction. That is, the nanosized MoO$_2$ electrode is lithiated by an addition reaction at 2.0–1.0 V, which is followed by a conversion reaction at the 0.28 V plateau region (solid line in Fig. 5a). The lithiation and delithiation capacities amount to 912 and 842 mAh g$^{-1}$, respectively, which is close to the theoretical four-electron redox capacity of 838 mAh g$^{-1}$. The observed capacity is slightly larger than the theoretical value due to the contribution from carbon additive (Super P). In short, the submicron-sized MoO$_2$ powder that reacts by one-electron reduction at room temperature now reacts with four after being converted to the nanosized one by a cycling at 120°C. This phenomenon is named thermoelectrochemical activation because the electrode is activated from one- to four-electron reduction by a charge–discharge cycling made at elevated temperatures. Figure 5b shows the voltage profile that was obtained by another activation process, in which thermoelectrochemical activation was performed only by a lithiation at 120°C (dotted line). The forthcoming voltage profile obtained at 25°C (solid line) looks similar to that shown in Fig. 5a. This explains that the essential step for activation is the conversion process made at elevated temperatures, during which the initial bulkier MoO$_2$ particles are decomposed into the nanosized mixture of Mo and Li$_2$O. That is, once the nanosized Mo/Li$_2$O mixture is generated, the transformation to nanosized MoO$_2$ is ensured regardless of the delithiation temperature. Figure 5c presents the cycle performance of initial MoO$_2$ and two electrochemically activated ones (TEA1 and TEA2). The initial MoO$_2$ electrode delivers one-electron redox capacity with significant capacity decay. In contrast, two electrochemically activated ones show an excellent cycle performance with four-electron redox capacity.

As mentioned above, the onset temperature for the conversion reaction is near 85°C under the present cycling condition for the raw MoO$_2$ powder electrode. Upon considering that surface area and defect sites are important variables to affect the kinetics of conversion reaction, it is readily expected that the onset temperature can be lowered by ball milling the raw MoO$_2$ powder. As shown in Fig. 1b, the initial MoO$_2$ particles (0.2–0.3 μm in size) are mechanically crushed to be irregular-shaped ones with a decrease in size (0.1–0.2 μm). The separate BET measurement illustrates a slight decrease in surface area, which suggests that ball milling does not significantly affect the particle size of MoO$_2$.
increase in the surface area (from 4.4 to 8.7 m² g⁻¹) by ballmilling. Figure 6a displays the voltage profiles taken before and after the thermoelectrochemical activation. As expected, the onset temperature for thermoelectrochemical activation (that is, conversion reaction) is lowered down to 55°C with this ballmilled powder. The conversion reaction evolves as evidenced by the voltage plateau (\(\downarrow\)) and the electrode is lithiated by the addition and continuing conversion reaction at 25°C (solid line) after being activated at 55°C.

The formation of nanosized metallic Mo upon lithiation and restoration back to nanosized MoO₂ after delithiation during the 55°C activation period was ascertained from the HR-TEM images and SAED patterns shown in Fig. 6b-e. The points where the images are taken are indicated as * and ** in Fig. 6a. The TEM images taken after lithiation (Fig. 6b) and delithiation (Fig. 6d) illustrate the presence of nanosized particles (<10 nm), which were identified as the metallic Mo and MoO₂ from the lattice fringes (Fig. 6c and e), respectively.

Recently, we have reported the thermoelectrochemical activation behavior of a Cu–In intermetallic compound (Cu₇In₃) that does not show any lithiation activity at room temperature. The activation converts the initial Cu₇In₃ to CuIn phase. A common feature in two systems is that the thermoelectrochemical activation proceeds by two steps. In the first step, the initial phases are transformed to nanosized mixture (metallic Cu/Li/In for Cu₇In₃ and Mo/Li/O for MoO₂) by a conversion-type lithiation. In the second step, more reactive phases (CuIn phase and nanosized MoO₂) are generated in the forthcoming delithiation period. Both of the thermoelectrochemically activated materials are fully lithiated by conversion reaction at room temperature. The literature complain that a lot of chemically activated materials are fully lithiated by conversion reaction such as those discarded or underestimated materials (for instance, CuIn phase from Cu₇In₃ and nanosized MoO₂ from bulkier one).

**Conclusion**

This work demonstrates that the kinetically hindered conversion reaction in the MoO₂ electrode can be facilitated either by raising the working temperature or by decreasing the particle size. The onset temperature for conversion reaction shows a rough inverse relationship with the particle size; 85, 55, and <25°C for the raw MoO₂ (0.2–0.3 μm), ballmilled (0.1–0.2 μm), and nanosized (<10 nm) ones, respectively. This can be rationalized by an enhancement in the heterogeneous charge-transfer rate and solid-state
Li⁺ or O²⁻ diffusion. A weaker Mo–O bond strength in the nanosized MoO₂ as compared to that for the initial one can also explain the higher conversion reaction activity for this material. The point that should be more highlighted is, however, that the initial MoO₂, which is inactive for conversion reaction at room temperature, becomes active with an excellent cycle performance by thermoelectrochemical activation. The underlying activation mechanism is the generation of nanosized MoO₂ by a simple discharge–charge cycling made at elevated temperatures.

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