Molybdenum Oxide as Cathode for High Voltage Rechargeable Aluminum Ion Battery

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A dense molybdenum oxide layer was fabricated on nickel foam (MoO2@Ni) and used as the cathode in the 1-ethyl-3-methylimidazolium chloride/AlCl3 eutectic salt electrolyte. The deposition was performed by a radio frequency (RF) magnetron sputtering system (KYKY Co., China) at 3 W cm−2. Firstly, the target was dipped into 10 wt% phosphoric acid for 30 min to remove the surface oxides. Then it was ultrasonically cleaned in acetone, ethanol and de-ionized water for 15 minutes, respectively, and dried under nitrogen flux. A nickel foam disc (Φ10 mm) was subjected to the same pretreatment as the molybdenum target and used as the substrate for molybdenum deposition. The deposition was performed by a radio frequency (RF) magnetron sputtering system (KYKY Co., China) at 3 W cm−2 power for 1 h at room temperature. After deposition, the nickel foam with MoO2 layer on its surface was placed into a horizontal tube furnace (Lindberg disc (Φ10 mm), respectively, and dried under nitrogen flux. A nickel foam disc (Φ10 mm) was subjected to the same pretreatment as the molybdenum target and used as the substrate for molybdenum deposition. The deposition was performed by a radio frequency (RF) magnetron sputtering system (KYKY Co., China) at 3 W cm−2 power for 1 h at room temperature. After deposition, the nickel foam with MoO2 layer on its surface was placed into a horizontal tube furnace (Lindberg Blue M, TF55030C, USA). First, a high purity argon (99.999%) was introduced into the tube and the sample was heated to 400 °C at a ramping rate of 10 °C min−1. After the target temperature was achieved, a purify oxygen flow was introduced at a flow rate of 2 mL min−1 and maintained for 1−2 min. Finally, the furnace was cooled to the room temperature naturally. The net mass increment of the foam was about 1.5 mg, and the loading of active material was about 1.91 mg cm−2 (calculated on the geometry area of nickel substrate). A high purity Mo foil disk (99.99%, Φ10 mm) was also treated by the same procedure and used as the reference sample.

Battery assembly.—A Swagelok type cell (Φ16 mm) was used to employ the electrochemical measurements in this work. Polytetrafluoroethylene (PTFE, Yangzhong Gongzheng Fluid Controls Co., China) was used as the battery shell. Two high purity (99.9%) molybdenum rods (Hebei Qingyuan Metal Materials Co., China) were used as current collectors. A rapid filtering paper (Toyo Roshi Kaisha Ltd., Japan) and a high purity electro-polished aluminum foil (99.999%, IMR, CAS, China) were used as the separator and the anode, respectively. All the assembling processes were performed in an Ar gas filled glove box where the oxygen and moisture were under 1 ppm.

Characterization.—The surface morphology of the sample was observed by scanning electron microscope (SEM, FEI INSPECT F50, USA). The composition of the sample was analyzed by energy-dispersive X-ray spectroscopy (EDX, X-Max Oxford, equipped with the SEM, UK). The crystal structure of the samples was detected by X-ray diffraction measurement (XRD, Rigaku D/Max 2500pc with Cu Kα radiation, λ = 1.5406Å, Japan). The galvanostatic charge/discharge (GCD) and cycling measurements were performed on an Arbin BT-2043 battery test system at a current density of 100 mA g−1. Cyclic voltammetry (CV) measurement was performed on an electrochemical working station (Zahner Zennium, Germany). Al was used as the counter and reference electrode. The scanning rate was 1 mV s−1 and the scanning voltage ranged from 0.3 to 2.5 V.

Results and Discussion

Fig. 1 shows the SEM images of the surface morphology of the pristine nickel foam and the foam after sputtering and heat-treatment. It can be seen clearly in Fig. 1b that a dense layer was formed. Fig. 1c shows the EDX spectra of the heat treated sample, and it can be found that other than those of Mo, Ni and O, no else element was detected. The XRD patterns of the foam after heat-treatment are presented in Fig. 1d. As is shown, three typical diffraction peaks locate at about 44.5° and 51.8° and 74.6° are belonging to the nickel foam substrate (JCPDS No. 04-0850). The rest diffraction peaks can be assigned to the Tugarinovite MoO2 phase (JCPDS No. 86-0135). Therefore, the

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Aluminum (Al) is the most abundant metal element in the earth’s crust and has the highest theoretical volumetric capacity of 8.04 mAh cm−3 among the metals, which makes it to be a hot candidate electrode material for modern society. However, it is difficult to fully use the high power densities of Al batteries due to some intrinsic restrictions such as Al passivation and harsh working condition.1,2 Recently, the rechargeable Al-ion battery has regained intensive attention because some ionic liquids for Al electro-deposition/stripping are used as the effective room temperature electrolytes. For example, 1-ethyl-3-methylimidazolium chloride (EMImCl)/AlCl3 eutectic salt is successfully used in Al-ion battery, Al-S and Al-O2 systems.3−8 There is no doubt that a better battery performance is strongly dependent on the properties of electrode materials in terms of charge efficiency, cycling stability, discharge voltage and specific capacity. Unfortunately, a low discharge voltage character (usually less than 1 V) is widely exhibited in most of the investigated Al battery systems in spite of the mezzo standard reduction potential of the Al (−1.68 V vs SHE).4−7 Thus it will be a significant drag on such fields as electrical vehicles, where high power supply is required. Although some carboneous materials exhibit high voltage and long cycle life, their limited specific discharge capacity remains a big challenge to meet the market needs. Therefore, it is worth exploring new cathode materials to satisfy the future application of rechargeable Al batteries.

Molybdenum oxide (MoO2) has long been investigated as a host material for lithium storage due to its high electrochemical activity and natural abundance.8,9,12 So far, various approaches have been adopted to fabricate novel structured MoO2 materials. Herein, we report a dense MoO2 layer fabricated by simple magnetron sputtering and heat-treatment. The electrochemical performance of the MoO2 layer in Al ion battery was also presented for the first time.

Experimental

Materials preparation.—A high purity molybdenum target (China Material Tech. Co., 99.99% purity, China) was used as molybdenum source for deposition. Firstly, the target was dipped into 10 wt% phosphoric acid for 30 min to remove the surface oxides. Then it was ultrasonically cleaned in acetone, ethanol and de-ionized water for 15 minutes, respectively, and dried under nitrogen flux. A nickel foam disc (Φ10 mm) was subjected to the same pretreatment as the molybdenum target and used as the substrate for molybdenum deposition. The deposition was performed by a radio frequency (RF) magnetron sputtering system (KYKY Co., China) at 3 W cm−2 power for 1 h at room temperature. After deposition, the nickel foam with MoO2 layer on its surface was placed into a horizontal tube furnace (Lindberg Blue M, TF55030C, USA). First, a high purity argon (99.999%) was introduced into the tube and the sample was heated to 400 °C at a ramping rate of 10 °C min−1. After the target temperature was achieved, a purify oxygen flow was introduced at a flow rate of 2 mL min−1 and maintained for 1−2 min. Finally, the furnace was cooled to the room temperature naturally. The net mass increment of the foam was about 1.5 mg, and the loading of active material was about 1.91 mg cm−2 (calculated on the geometry area of nickel substrate). A high purity Mo foil disk (99.99%, Φ10 mm) was also treated by the same procedure and used as the reference sample.

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composition of the sputtered layer can be determined to MoO$_2$. The composite is designated as MoO$_2$@Ni for brevity.

Fig. 2a shows the charge/discharge curves of the MoO$_2$@Ni at a constant current density of 100 mA g$^{-1}$ for the first, fifth and tenth cycles, respectively. Two discharge potential plateaus at about 1.95 V and 1.0 V can be seen clearly. The first charge/discharge capacities of the MoO$_2$@Ni were about 253 mAh g$^{-1}$ and 90 mAh g$^{-1}$, respectively. This means a large irreversible capacity loss occurred in the first cycle. The specific charge capacity decreased with the increase of cycle while the discharge specific capacity did not change dra-

Figure 1. SEM image of (a) pristine nickel foam and (b) sputtered and heat treated nickel foam; (c) EDX spectrum of the sputtered and heat treated nickel foam; (d) XRD pattern of the sputtered and heat treated nickel foam.

Figure 2. (a) Charge/discharge curves, (b) 100 cycles performance of the MoO$_2$@Ni electrode, (c) cyclic voltammogram of the MoO$_2$@Ni electrode and (d) CV profiles of the nickel, nickel sputtered Mo, nickel annealed electrode and blank electrolyte, respectively.
The 100-cycle stability performance is presented in Fig. 2b. As can be seen, the specific charge/discharge capacities were about 75 mAh g\(^{-1}\) for the 5th to 20th cycles. However, both of them decreased with the charge/discharge proceeding. There was only 25 mAh g\(^{-1}\) charge/discharge specific capacity left after 100 cycles, indicating a capacity decay. In addition, a low coulombic efficiency of 70% in average was kept through the entire cycles. Fig. 2c shows the CV curves of the MoO\(_2@Ni\) electrodes. For the first ten CV cycles, a clear pair of redox peaks at around 2.15 V and 1.91 V can be found invariably, which is in good agreement with the charge/discharge results. The asynchronous change of the CV peak intensity and discharge capacity may be ascribed to the difference of the activation degree during a given cycle between the batteries used for CV and GDC test, resulting from the difference of the charge-discharge regimes.

It has been pointed out by Reed and Nakayama et al., that the ionic liquid is a highly corrosive electrolyte.\(^{10,13}\) In order to confirm that the high discharge voltage is originated from the MoO\(_2\) and exclude the corrosion effect from the electrolyte and side reactions between the electrolyte and the cell components, we carried out two group of parallel experiments, respectively. In one group, a series CV measurements were performed on four type of batteries where the cathodes were nickel substrate, nickel substrate annealed at 400 \(\degree\)C, nickel substrate sputtered with Mo and blank electrolyte, respectively. The results are shown in Fig. 2d, no redox peaks can be found in all the CV curves and the electrolyte is stable at 1.9 V–2.2 V region, where the oxidation/reduction of MoO\(_2@Ni\) electrode occurred. Therefore, the contribution to the high discharge voltage from other materials but MoO\(_2\) can be excluded. In the other group, a high purity Mo disk foil was annealed to fabricate a dense MoO\(_2\) film under the same treatment as the MoO\(_2@Ni\) sample, which has been described in the Experimental section. The Mo foil covered with MoO\(_2\) film (referred as MoO\(_2@Mo\) for brevity) was assembled into a battery to study its electrochemical performance. The material characterization and battery performance are shown in Fig. 3. It can be seen in Fig. 3a that the surface of the Mo foil is composed of a particle-like MoO\(_2\) film, which can be evidenced by XRD results as shown in Fig. 3b. The MoO\(_2@Mo\) electrode exhibits a similar property of high voltage as the MoO\(_2@Ni\) and the better battery performance of the MoO\(_2@Ni\) electrode maybe results from the 3-D porosity network in nickel foam.\(^{17-19}\) Based on the above evidences, it can be solidly confirmed that the high voltage was ascribed to the MoO\(_2\) film.

To understand the reactions occurred on the MoO\(_2@Ni\) electrode, the battery after 100 charge/discharge cycles was disassembled in a glove box. The electrode and the separator were cleaned by anhydrous ethanol and examined by SEM, EDX and XRD. Fig. 4a shows the SEM image of the cathode after discharge. The morphology became roughness than that of the pristine electrode. The corresponding EDX spectra after long cycles. However, a beaded morphology and intensive Mo peaks can be found in the SEM image of the separator and the corresponding EDX spectra after...
discharge, as shown in Figs. 4b and 4d, respectively. It indicates that the Mo transferred from the electrode to the separator during the charge/discharge process, since no Mo was contained in the pristine separator, as shown in Fig. 4f. This can partially explain the specific capacity decay during the cycling. A similar phenomenon of Mo transfer is also found in the MoO2/Mo electrode after charge/discharge for a few cycles. The results are presented in Figs. 5a to 5d. The original dense particle-like morphology was destroyed and the Mo can be detected in the separator.

Since there is a capacity decay occurred in the cycling test. It is important to evaluate the stability of MoO2 in electrolyte in stationary condition. Therefore, a MoO2@Ni electrode was immersed into the ionic liquid for 24 h to observe the morphology changes as shown in Fig. 6a. The electrode was taken out and washed in anhydrous ethanol ultrasonically for a few minutes. The SEM image of the MoO2@Ni electrode after immersed is shown in Fig. 6b. It can be observed that the morphology of the MoO2@Ni electrode maintained the compact layer. The EDX spectrum also proved that the layer is mainly composed of Mo and O elements as seen in Fig. 6c. It is showed that the MoO2 was not corroded severely in the electrolyte without electric field applied although we do not exclude the possibility that small amount of MoO2 could be dissolved into the electrode in the stationary condition, and we believe that the stationary corrosion is not the main cause for the capacity decay.

It is also necessary to point out that the mechanism of the ionic liquid based Al-ion battery is quite complex for researchers to understand at present as our previous study demonstrated. Even so, some previous studies still obtained a similar dissolution phenomenon with our results. For example, Suto et al. used VCl3 and EMImCl/AlCl3 to construct a battery. They found that VCl3 could be dissolved into the EMImCl/AlCl3 electrolyte by X-ray absorption near-edge structure (XANES) examination, resulting in a poor cycling stability. Takuya et al. demonstrated a low voltage and poor cycling stability FeS2/Al battery. The dissolution of sulfides was the main reason for the sluggish performance, which was also proved by XANES. We believe this may help to understand the phenomenon in this work.

Fig. 7 shows the rate capability performance of the MoO2@Ni electrode Al-ion battery. Although the electrode showed a low rate-capability performance, the high discharge voltage of the MoO2@Ni...
Figure 5. (a) and (b) SEM images of pristine and after few cycled MoO$_2$/Mo electrode; (c) and (d) SEM image and corresponding EDX spectrum of cycled separator.

Figure 6. (a) Illustration of the MoO$_2$@Ni immersed into the electrolyte in stationary condition; (b) and (c) SEM image and EDX spectrum of the immersed MoO$_2$@Ni after cleansed thoroughly, respectively.
electrode under middle current density is still worth the further investigation, which should be conducted to explain the MoO$_2$ and EMImCl/AlCl$_3$ reaction mechanism in the future and prolong its cycle life.

Conclusions

A dense MoO$_2$ layer was fabricated on the surface of a Ni foam through magnetron sputtering and its electrochemical performance as the cathode of the rechargeable Al ion battery was investigated. The first discharge capacity was about 90 mAh g$^{-1}$ at a current density of 100 mAh g$^{-1}$ and the discharge potential plateau was about 1.9 V. Mo was transferred from the electrode to the separator during the charge/discharge process, resulting in a capacity decay of the battery. To our knowledge, it is the first time to obtain such a high discharge potential plateau for the metal oxide positive electrode in ionic liquid based Al-ion battery.

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