Surfactant-free and controllable synthesis of hierarchically lithiated MoO₃ microspheres

1 | INTRODUCTION

Compared with traditional lead-acid batteries, lithium-ion batteries are highly favoured by academic community and practical industry by virtue of their light weight, high voltage and energy density, relatively long cycle life, and low self-discharge rate [1]. In recent years, new energy vehicles have been realized a leap-forward development, and lithium-ion batteries as the novel system of electrochemical energy storage have been experienced a new upsurge of scientific research and industrial application [2]. As one of the vital components of lithium batteries, cathode materials have played a crucial role on the performance of battery [3].

Molybdenum trioxides (MoO₃) has been used as functional materials in a wide range of applications such as synthetic sensitive components, display devices, and catalysts, because of its excellent properties of electrochromism, photochromism, photocatalytic degradation, and gas sensing [4]. Moreover, MoO₃ has also become a hot topic for researchers as potential electrode materials. There are three common phases of molybdenum trioxide: thermodynamically stable orthogonal phase, thermodynamically metastable hexagonal phase and monoclinic phase [5]. Moreover, tetrahedral and octahedral holes have been observed in their lattice structures, which formed the unique 2D layered structure, exhibiting alluring lithium ion insertion properties. On account of the open layered structure and the property of generating oxygen vacancies, the molybdenum trioxide crystal was characterized by high energy density (930 Wh/kg) and high theoretical electrochemical capacity (372 mAh/g) as the ideal cathode candidates for lithium ion batteries [6].

Various kinds of MoO₃ based materials have been prepared for different applications. Chu et al. obtained the bundles of α-MoO₃ nanowires by using (NH₄)₆Mo₇O₂₄⋅4H₂O as the Mo sources and aniline as the assembly-forming agent [7]. With the help of aniline, the α-MoO₃ nanowires can be attached together to form the hierarchical structures. The cycling stability of the α-MoO₃ can be enhanced through the assembly of α-MoO₃ nanowires. Qin et al. prepared the special arrays of α-MoO₃ nanowires. The large specific surface area and the exposure of the active crystal face in the single crystal of α-MoO₃ structures resulted in the high sensitivity for the detection of xylene. Zhang et al. modified MoO₃ nanobelts with the NiMoO₄ layers to form core/shell structures [9]. The abundance of active sites and the high porosity of the NiMoO₄ coating can act as the lithium reservoirs to improve the electrochemical performance of MoO₃ nanobelts. However, the hierarchical structures composed of primary MoO₃ plates have been rarely reported by using the surfactant-free method [10]. In this work, we have synthesized hierarchically lithiated MoO₃ structures as the cathode material for lithium ion battery, without the preparation and removal of organic templates. It was a simple synthetic method with low cost, which was relatively energy efficient and suitable for mass production.

2 | EXPERIMENTAL

2.1 | Synthetic procedures

First, the ethanol with the volumes of 0, 5, 10, 20, and 40 mL were weighed separately and mixed with 10 mL of distilled water. Then, 8 mmol (0.768 g) of metal molybdenum powder (Mo) were added with continuous stirring. After adding 5 mL of hydrogen peroxide (H₂O₂, 30 wt%) to the above five groups of suspensions, the mixture solutions were magnetically stirred for about 30 min. Lithium acetate (CH₃COOLi⋅2H₂O, 18 mmol, 1.834 g) and 5 mL of concentrated hydrochloric acid (HCl) were added dropwise to the reaction solution and stirred for around 30 minutes to prepare the lithiated MoO₃ structures. The resulting solutions were transferred to a Teflon-lined autoclave and kept at 180 °C for 24 h. Thereafter, the autoclave was left to cool and the precipitate was filtered and flushed for three times with deionized water and ethanol. The five groups of samples were dried at 80 °C for 12 h and then calcined in air at 600 °C for 10 h. However, when 0 mL of ethanol was added in the reaction system, no products can be obtained. The other four groups of the obtained samples were labelled as LMO-1, LMO-2, LMO-3 and LMO-4, respectively, when 5, 10, 20, and 40 mL of ethanol were used. Therefore, the volume ratios of H₂O/Ethanol was 2:1, 1:1, 1:2 and 1:4 for LMO-1, LMO-2, LMO-3 and LMO-4, respectively.
2.2 Materials characterization

The crystal structure of the sample was characterized by an X-ray powder diffractometer under Cu Kα radiation ranging from 5° to 70° at a scan rate 60°/min. The surface morphology and particle size were evaluated using a field-emitting scanning electron microscope (SEM, FEI Quanta 250). The mass ratio of Li:Mo in samples was measured via inductively coupled plasma optical emission spectroscopy (ICP-OES) (AGILENT ICPOES 730).

2.3 Electrochemical test

The electrochemical properties were investigated by 2032 coin-type cells assembled in an Ar-filled glovebox. The working electrodes were prepared by mixing 80 wt% active material, 10 wt% super P, and 10 wt% polyvinylidenefluoride (PVDF) in an appropriate amount of N-methyl-2-pyrrolidine with the assistance of ultrasound, which was then pasted on aluminium foil current collector and dried at 120 °C in a vacuum oven overnight. The thicknesses of the whole cathode plate and the Al foil were about 38 and 18 μm, respectively. The weights of the whole cathode plate and the Al foil (12 mm in diameter) were about 10.6 and 5.4 mg, respectively. Lithium foil was used as anode electrode and Celgard 2400 membrane as separator. An electrolyte of 1M LiPF₆ dissolved in ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1, v/v) was used. The galvanostatic charge–discharge cycles text was performed at various currents (0.03 A/g, 0.05 A/g, 0.2 A/g and 0.5 A/g) within a voltage range of 1.5–4.5V (vs. Li/Li⁺) at 25 °C. The electrochemical impedance spectroscopy (EIS) was conducted on VersaSTAT 3F electrochemical workstation with a voltage amplitude of 5 mV in the frequency range from 10 mHz to 100 kHz. The cyclic-voltammetry (CV) was performed at scan rates of 0.2 mA/s in the potential window of 1.5–4.2 V vs. Li/Li⁺, and it was also carried out on VersaSTAT 3F electrochemical workstation.

3 RESULTS AND DISCUSSION

To study the phase and crystallinity of the lithiated MoO₃ samples prepared in the presence of different amounts of ethanol, the XRD patterns were obtained as shown in Figure 1. The standard XRD patterns of MoO₃ (JCPDS: 65–2421) and Li₀.₀₄₂MoO₃ (JCPDS: 38–0045) were also shown for comparison. Three strongest diffraction peaks at 27.3°, 25.7° and 23.3° can be assigned to the (021), (040) and (110) planes of the orthorhombic MoO₃ phase (JCPDS: 65–2421). Other characteristic peaks of the orthorhombic MoO₃ phase can also be observed, such as (020) at 12.8°, (111) at 33.8°, (004) at 39.0°, (002) at 49.2° and (081) at 58.8°. When the XRD curves of lithiated MoO₃ samples were compared with the standard patterns of MoO₃ and Li₀.₀₄₂MoO₃, the intensity increase of the (040) peak (such as Sample LMO-1 and LMO-2) at 25.7° can be attributed to the successful lithiation of MoO₃ [11]. However, the intensity of (040) peak was decreased when more ethanol was added into the reaction system (such as Samples LMO-3 and LMO-4), indicating the negative influence of ethanol on the lithiation of MoO₃. In addition, the ICP results (Table 1) also indicated the decrease of lithium content in the samples with the increase of the adding amount of ethanol during the synthetic process.

The crystal morphology and size distribution of the obtained lithiated MoO₃ spheres were carefully studied by using their SEM images, as shown in Figures 2 and 3. The panoramic images (Figure 2) and their corresponding enlarged images (Figure 3) indicated that all the prepared products were composed by the lithiated MoO₃ micro-spheres of 2–6 μm. The existence of primary particles with the sizes of several hundred nanometres on the spherical surfaces indicated the hierarchical structures of lithiated MoO₃. The primary particles were little flakes with the thickness of several ten nanometres for Sample LMO-1, LMO-2 and LMO-3, while the primary particles of LMO-4 were composed of the larger rectangular prisms with the thickness of several hundred nanometres (Figure 4). During the synthesis process, the reaction between molybdenum and H₂O₂ resulted in the formation of the molybdenum oxides and hydrates in the solution. The interactions among molybdenum species including Vander Waals force and hydrogen bonding induced the aggregation and assembly of the nano-sized crystals [12]. Meanwhile, the continuous growth of molybdenum-based nano-crystals was also carried out in the presence of lithium ions. As a result, the hierarchical structures assembled by the lithiated molybdenum oxide particles can be formed through the hydrothermal reaction. The microsphere shape may be the most stable for the hierarchical structures due to the fact that the interfacial free energy of spherical structure is minimal [13].

At least 100 spheres of each sample were measured for calculating the size distribution of micro-spheres and primary particles, and the results were displayed in Figure 5(a,b), respectively. Based on the statistical analysis, the average sizes of the lithiated MoO₃ spheres and the primary particles on the spheres were further calculated to study the influence of ethanol.
TABLE 1  The mass ratio of Li/Mo, molar ratio of Li/Mo, the calculated molar percentage of Li$_{0.042}$MoO$_3$ [n(Li$_{0.042}$MoO$_3$)/n(Mo)] and kinetic parameters of LMO-1, LMO-2, LMO-3 and LMO-4

| Sample | LMO-1 | LMO-2 | LMO-3 | LMO-4 |
|--------|-------|-------|-------|-------|
| m(Li)/m(Mo) | 2.60 × 10$^{-4}$ | 1.92 × 10$^{-4}$ | 1.59 × 10$^{-4}$ | 1.00 × 10$^{-4}$ |
| n(Li)/n(Mo) | 3.60 × 10$^{-3}$ | 2.65 × 10$^{-3}$ | 2.20 × 10$^{-3}$ | 1.39 × 10$^{-3}$ |
| n(Li$_{0.042}$MoO$_3$)/n(Mo) | 8.58 % | 6.31 % | 5.23 % | 3.32 % |
| $R_s$ [Ω] | 4.45 ± 0.20 | 4.40 ± 0.13 | 2.82 ± 0.15 | 6.56 ± 0.18 |
| $R_{ct1}$ [Ω] | 49.6 ± 1.8 | 49.1 ± 1.8 | 24.6 ± 1.4 | 25.0 ± 2.1 |
| $R_{ct2}$ [Ω] | 127.9 ± 3.8 | 127.5 ± 3.1 | 102.8 ± 2.6 | 121.1 ± 3.6 |
| $D$ [cm$^2$/s] | 4.3 × 10$^{-15}$ | 8.2 × 10$^{-14}$ | 1.8 × 10$^{-13}$ | 8.7 × 10$^{-14}$ |

FIGURE 2  The panoramic SEM images. (a) LMO-1; (b) LMO-2; (c) LMO-3; (d) LMO-4

FIGURE 3  The enlarged SEM images of micro-spheres. (a) LMO-1; (b) LMO-2; (c) LMO-3; (d) LMO-4

addition on the morphology features of the resultant products (Figure 5(c,d)). The sphere size followed the order LMO-1 (3.44 μm) > LMO-2 (3.42 μm) > LMO-3 (3.28 μm) > LMO-4 (2.88 μm), while the size of primary particles increased in the order of LMO-1 (0.29 μm) < LMO-2 (0.31 μm) < LMO-3 (0.32 μm) < LMO-4 (0.83 μm). Therefore, increasing the ethanol adding amount during the fabrication process resulted in the increase of sphere size and size reduction of primary particles.

FIGURE 4  The enlarged SEM images of primary particles. (a) LMO-1; (b) LMO-2; (c) LMO-3; (d) LMO-4

The cycling performance of four lithiated MoO$_3$ samples was studied by the galvanostatic charge/discharge method, showing the initial capacities of nearly 300 mAh/g at 30 mA/g with the voltage range of 1.5–4.5 V (Figure 6(a)). The capacity losses of LMO-1, LMO-2, LMO-3 and LMO-4 were 40.8%, 38.7%, 26.7% and 33.3% in the first ten cycles, respectively. It was mainly because of the gradual collapse of the layered MoO$_3$ structure [5] and the irreversible insertion of lithium ions into the MoO$_3$ crystals during the electrochemical cycles [14]. With the cycling was carried out from the 11st to the 50th cycles, the discharging capacities were decreased more slowly than those in the first ten cycles. At the 50th cycles, the discharging capabilities of LMO-1, LMO-2, LMO-3 and LMO-4 were 75.6, 99.1, 155.9 and 111.3 mAh/g, respectively, indicating the capacity retention of 24.3%, 31.4%, 52.5% and 38.2%, respectively. The electrochemical reversibility of the lithiated MoO$_3$ samples was not very high, which may be due to the structural instability of MoO$_3$ [7] and inevitable dissolution of Mo in the organic electrolyte [15]. The rate capabilities of the lithiated MoO$_3$ samples were displayed in Figure 6(b) at different current densities of 30–500 mA/g. The increase of current...
FIGURE 5  The statistical analysis of particle size. (a) the size distribution of the lithiated MoO₃ spheres; (b) the size distribution of the primary particles on the spheres; (c) the comparison of the average sizes of lithiated MoO₃ spheres; (d) the size comparison of the primary particles on the spheres.

FIGURE 6  The electrochemical performances of four lithiated MoO₃ samples. (a) the cycling stability; (b) the rate performance; (c) the EIS plots; (d) the relationship between $Z''$ and $\omega^{-1/2}$. 
density resulted in the reduction of discharging capability, due to the enhanced polarization at higher rates [16]. LMO-3 showed the best rate performance, delivering the average capacities of 258.0, 184.0, 131.4, 84.2 and 41.8 mAh/g at 30, 50, 100, 200 and 500 mA/g.

In order to understand the electrochemical kinetics of the lithiated MoO₃ samples, their electrochemical impedance spectroscopy (EIS) tests were carried out in the frequency domain ranging from 100 kHz to 10 mHz. The typical Nyquist plots and their equivalent circuit model were given in Figure 6(c). The symbols of $R_s$, $R_{ct}$, $Z_{re}$ and $C_{dl}$ were used to represent the ohmic resistance of the electrode, the charge transfer resistance, the Warburg impedance and the double layer capacitance, respectively. The values of $R_s$, $R_{ct1}$ and $R_{ct2}$ were simulated by using the Zview software [17], as listed in Table 1. The $R_{ct1} + R_{ct2}$ values of LMO-1, LMO-2, LMO-3 and LMO-4 were 177.5, 176.62, 127.45 and 146.15 $\Omega$, respectively. The lithium content in the lithiated MoO₃ samples followed the order LMO-1 > LMO-2 > LMO-3 > LMO-4 (Table 1). Therefore, the $R_{ct1} + R_{ct2}$ values of the lithiated MoO₃ samples were first decreased and then increased. The Nyquist plots of all the samples exhibited similar shapes, including a depressed semicircle in the high-frequency region and a sloped line in the low-frequency region. The high-frequency semicircle can be assigned to the charge transfer resistance ($R_{ct}$), and the low-frequency line can be attributed to the Warburg diffusion process [18]. The values of lithium ion diffusion coefficient ($D_{Li^+}$) for the lithiated MoO₃ samples can be obtained by applying the following Equations (1) and (2) [19]:

$$D_{Li^+} = \frac{R^2T^2}{2A^2n^4F^4C^2\sigma^2} \quad (1)$$

$$Z_{re} = R_s + R_{ct} + \sigma\omega^{-1/2} \quad (2)$$

Herein, $R$ is the gas constant (8.314 J/K/mol), $T$ is the absolute temperature (298.15 K), $A$ is the surface area of the electrode (1.13 cm²), $n$ is the electron number per molecule during Li-ion insertion, $F$ is the Faraday constant (96,500 C/mol), $C$ is the concentration of Li ions, and $\sigma$ is the Warburg impedance coefficient associated with $Z_{re}$ (the real part of cell impedance) and $\omega$ (the angular frequency in the low-frequency region, $\omega = 2\pi f$). The plot of $Z_{re}$ against $\omega^{-1/2}$ in the low-frequency region was shown in Figure 6(d). The relationship between $Z_{re}$ and $\omega^{-1/2}$ can be fitted as the straight lines with the slope of $\sigma$ [20]. Therefore, the calculated values of $D_{Li^+}$ were $4.3 \times 10^{-15}$, $8.2 \times 10^{-14}$, $1.8 \times 10^{-13}$ and $8.7 \times 10^{-14}$ cm²/s.

The cyclic voltammograms (CV) was used at room temperature within the range from 1.5 to 4.2 V (vs Li/Li⁺) for studying the insertion and extraction process of lithium ions during the electrochemical cycling. The typical CV results of the Sample LMO-3 were shown in Figure 7, displaying the curves of the initial five consecutive cycles. The area of the CV curves represented the insertion amount of lithium ions [21]. The area percentages of the second, third, fourth and fifth cycles were 97.3%, 96.8%, 96.6% and 96.1% compared with the first cycle of sample, indicating the continuous decrease of capacity during the initial five cycles. It was in agreement with the results of the charge–discharge cycling.

4 | CONCLUSION

In summary, the hierarchically lithiated MoO₃ microspheres can be fabricated in the presence of the lithium salts without the use of any surfactant. The lithiated MoO₃ microspheres with the diameter of 2.88–3.44 $\mu$m were composed of nano-sized flakes or rectangular prisms and the shapes of their primary particles can be well controlled by adjusting the feeding amount of ethanol during their synthetic process. The discharging capacity of the lithiated MoO₃ microspheres can be nearly 300 mAh/g at 30 mA/g and the capacity retention was 52.5% after 50 cycles. The electrochemical performances were enhanced first, and then were reduced with the decrease of lithium content in the lithiated MoO₃ samples. In addition, the method in this work can be utilized for the fabrication of hierarchical structures of other oxide materials.

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REFERENCES

1. Armand, M., Tarascon, J.M.: Building better batteries. Nature 451(7179), 652–657 (2008)
2. Scrosati, B., Garche, J.: Lithium batteries: Status, prospects and future. J. Power Sources 195(9), 2419–2430 (2010)
3. Fergus, J.W.: Recent developments in cathode materials for lithium ion batteries. J. Power Sources 195(4), 939–954 (2010)
4. Dong, Y., et al.: Wrinkled-graphene enriched MoO3 nanobelts with increased conductivity and reduced stress for enhanced electrochemical performance. Phys. Chem. Chem. Phys. 15(40), 17165–17170 (2013)
5. Wang, Z., et al.: Ultralong alpha-MoO3 Nanobelts: Synthesis and Effect of Binder Choice on Their Lithium Storage Properties. J. Phys. Chem. C 116(23), 12508–12513 (2012)
6. Hu, X., et al.: Nanostructured Mo-based electrode materials for electrochemical energy storage. Chem. Soc. Rev. 44(8), 2376–2404 (2015)
7. Chu, Q., et al.: Alpha-MoO3 nanowire bundles fabricated from a self-assembled organic-inorganic precursor as cathodes for lithium-ion batteries. Mater. Res. Bull. 96, 419–424 (2017)
8. Qin, H., et al.: Solid-state chemical synthesis and xylene-sensing properties of alpha-MoO3 arrays assembled by nanoparticles. Sensor. Actuat. B 242, 769–776 (2017)
9. Zhang, X., et al.: Ultrathin mesoporous NiMoO4-modified MoO3 core/shell nanostructures: Enhanced capacitive storage and cycling performance for supercapacitors. Chem. Engin. J. 353, 615–625 (2018)
10. Chang, W.-C., et al.: Post-deposition annealing control of phase and texture for the sputtered MoO3 films. CrystEngComm 13(16), 5125–5132 (2011)
11. Shi, J., et al.: Cathode materials with mixed phases of orthorhombic MoO3 and Li0.042MoO3 for lithium-ion batteries. Can. J. Chem. 98(2), 106–113 (2020)
12. Xu, G., et al.: Fabrication of microsphere-like nano-MoO2 modified with silane coupling agent KH550. Mater. Res. Express 6(11), 115087 (2019)
13. Brijitta, J., et al.: Evolution of shape isotropy in silica microparticles induced by the base. Colloid Polym. Sci. 295(9), 1485–1490 (2017)
14. Xu, Y., et al.: Hydrothermal synthesis of hexagonal MoO3 and its reversible electrochemical behavior as a cathode for Li-ion batteries. Electron. Mater. Lett. 9(5), 693–696 (2013)
15. Takeda, N., et al.: Reversible Li storage for nanosize cation/anion-disordered rocksalt-type oxyfluorides: LiMoO2 · x LiF (0 ≤ x ≤ 2) binary system. J. Power Sources 367, 122–129 (2017)
16. Zhang, H., et al.: Coating of alpha-MoO3 on nitrogen-doped carbon nanotubes by electrodeposition as a high-performance cathode material for lithium-ion batteries. J. Power Sources 274, 1063–1069 (2015)
17. Shen, B., et al.: Mixed lithium ion and electron conducting LiAlPO3.93F1.07-coated LiCoO2 cathode with improved electrochemical performance. Electrochem. Commun. 83, 106–109 (2017)
18. Inamoto, J.-i., et al.: Insight into the state of the ZrO2 coating on a LiCoO2 thin-film electrode using the ferrocene redox reaction. J. Appl. Electrochem. 47(11), 1203–1211 (2017)
19. Shi, J., et al.: Titania and nitrogen-doped carbon co-modification: Their synergic effects on the electrochemical performance of LiFePO4. J. Alloys Compd. 750, 139–146 (2018)
20. Liu, H., et al.: Doping effects of zinc on LiFePO4 cathode material for lithium ion batteries. Electrochem. Commun. 8(10), 1553–1557 (2006)
21. Nadimicherla, R., et al.: Electrochemical performance of new alpha-MoO3 nanobelt cathode materials for rechargeable Li-ion batteries. Solid State Sci. 34, 43–48 (2014)