Excellent Electrochemical Properties of Yolk–Shell MoO₃ Microspheres Formed by Combustion of Molybdenum Oxide–Carbon Composite Microspheres

You Na Ko,[a, b] Seung Bin Park,[b] and Yun Chan Kang*[a]

Abstract: Yolk–shell MoO₃ microspheres are prepared by a two-step process in which molybdenum oxide–carbon (MoOₓ–C) composite microspheres are first obtained by spray pyrolysis, followed by combustion at 400°C in air. The yolk–shell microspheres exhibit excellent electrochemical properties and structural stability.

The fabrication of novel structures is a fundamental strategy for enhancing properties relating to shape and surface area of materials. Therefore, much effort has been devoted to the investigation of the fabrication of novel structures of metal oxides.[1–6] In particular, hollow structures with moveable cores, so-called yolk–shell structures, have attracted attention because of their interesting structural properties.[7–11]

Molybdenum oxide comprising mainly MoO₂ and MoO₃ is one of the most attractive materials with potential applications in energy storage.[12–15] The electrochemical properties of molybdenum oxide with various morphologies as anode materials for Li-ion batteries (LIBs) have been investigated.[16–24] However, the fabrication of molybdenum oxide with a yolk–shell structure has hardly been attempted. Only one approach has been reported on the synthesis and electrochemical performance of yolk–shell MoO₂ powders.[25] MoO₃ has also been considered a promising candidate as an anode material for LIBs because of its high theoretical capacity (1117 mAh g⁻¹) and high stability with a layered structure.[26–29] However, to the best of our knowledge, the preparation of MoO₃ material with a yolk–shell structure has not been reported previously. The low melting temperature of MoO₃ (795°C) makes it difficult to control its structure satisfactorily. The new preparation process of the yolk–shell structured materials was introduced in our previous report.[11] The scalable spray pyrolysis was successfully applied to the direct preparation of various types of metal oxides, such as V₂O₅, Co₃O₄, ZnCo₂O₄, LiMn₂O₄, and Li-NiₓMn₁₋ₓO₂.[30–34]

Herein, we report for the first time a facile synthesis of yolk–shell MoO₃ microspheres without using a template, and we demonstrate their application as an anode material for LIBs. The as-prepared molybdenum oxide–carbon (MoOₓ–C) composite microspheres (prepared by spray pyrolysis) were transformed through combustion in air into yolk–shell MoO₃ microspheres that consisted of nanocrystals. The yolk–shell MoO₃ microspheres exhibited excellent electrochemical properties at high current densities.

The yolk–shell MoO₃ microspheres were prepared through a two-step process. MoOₓ–C microspheres with a dense structure were first prepared by spray pyrolysis from the spray solution with sucrose at 900°C under a nitrogen atmosphere. The combustion of MoOₓ–C composite microspheres at 400°C in air resulted in the formation of yolk–shell MoO₃ microspheres with yolk–shell structure. Recombustion of the MoOₓ–C core part produced the final yolk–shell MoO₃ microsphere with configuration of MoO₃@void@MoO₃.

[a] Y. N. Ko, Prof. Y. C. Kang
Department of Chemical Engineering
Konkuk University
1 Hwayang-dong, Gwangjin-gu, Seoul 143-701 (Korea)
E-mail: yckang@konkuk.ac.kr
[b] Y. N. Ko, Prof. Dr. S. B. Park
Department of Chemical and Biomolecular Engineering
Korea Advanced Institute of Science and Technology
291 Daechak-ro, Yusong-gu, Daejeon 305-701 (Korea)
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Figure 1. The X-ray diffraction (XRD) pattern of the composite microspheres had main peaks of tetragonal MoO$_2$ and minor peaks of Mo$_{17}$O$_{47}$ and $\beta$-MoO$_3$ (Figure 1a). The enhanced reducing atmosphere caused by the presence of amorphous carbon formed through the polymerization and carbonization of sucrose resulted in composite microspheres with the main crystal structure of the MoO$_2$ phase. For the investigation of the thermal decomposition behaviors of MoO$_x$–C precursor microspheres, thermal gravimetric (TG) analysis was performed in a flowing air atmosphere from room temperature to 600 $^\circ$C (Figure 1b). The first weight loss below 200 $^\circ$C was associated with the loss of adsorbed water on the precursor microspheres. The slight weight increase observed from 200 to 330 $^\circ$C was related to the oxidation of MoO$_2$ and Mo$_{17}$O$_{47}$ to MoO$_3$. The formation of oxygen-rich MoO$_3$ phase as described in the explanation of Scheme 1 resulted in weight increase in the TG curve observed from 200 to 330 $^\circ$C. The large weight loss observed in the temperature range 330 to 500 $^\circ$C was associated with the decomposition of residual carbon components. The carbon content of the MoO$_x$–C composite microspheres as shown in Figure 1b was 13.3%. The precursor microspheres were spherical, non-aggregated, and of submicrometer size. Fine crystals of the molybdenum oxide dispersed in a carbon matrix and some rod-like crystals protruding from the surface were observed in the TEM images (Figure 1c). Dot-mapping images of the precursor microsphere clearly revealed that Mo and C components were dispersed uniformly inside the microsphere (Figure 1d). The amorphous and porous structures of the precursor microspheres resulted in a large BET surface area of 24 m$^2$ g$^{-1}$.

Combustion of the MoO$_x$–C composite precursor microspheres was performed at the optimum temperature of 400 $^\circ$C to fabricate the yolk–shell MoO$_3$ microspheres with a distinctive core@void@shell structure. The complete combustion of the precursor microspheres did not occur at a low temperature of 300 $^\circ$C (Figure S1a and S1b in the Supporting Information), while the microspheres combusted at a high temperature of 500 $^\circ$C had mainly hollow shape (Figure S1c and S1d in the Supporting Information). However, the oxidation of the MoO$_3$ phase into the oxygen-rich MoO$_3$ phase occurred at a temperature of 300 $^\circ$C, as described in the explanation of TG analysis in Figure 1b. The MoO$_3$–C microspheres obtained at a temperature of 300 $^\circ$C had a dense structure similar to that of the MoO$_x$–C precursor microspheres. The yolk–shell structure first formed through combustion and contraction was transformed into the hollow structure through the Ostwald ripening process at a high combustion temperature of 500 $^\circ$C. The XRD pattern of the yolk–shell MoO$_3$ microspheres combusted at 400 $^\circ$C (Figure 2) showed peaks associated with pure crystal-
spheres had yolk–shell structure without unburned carbon components. The BET surface area of the yolk–shell MoO₃ microspheres was 9 m² g⁻¹ (Figure S3 in the Supporting Information). The crystal growth of the MoO₃ phase and elimination of the carbon components decreased the BET surface area of the microspheres after combustion.

The electrochemical properties of the yolk–shell MoO₃ microspheres were investigated in the voltage range 0.001–3 V versus Li/Li⁺. Figure 3a shows the discharge/charge voltage profiles of the yolk–shell MoO₃ microspheres at a constant current density of 1000 mAg⁻¹. The initial discharge curve can be divided into two regions because it is believed that the lithiation of MoO₃ takes place in two steps. [27,28] The first lithiation process is generated in the voltage range above 1.5 V. The potential plateaus at around 2.7 and 2.3 V in the first discharge curve, which are seen as distinct cathodic peaks above 2.0 V in the first voltammogram, correspond to the intercalation of Li⁺ into the crystalline MoO₃ to form a LiₓMoO₃ solid solution. [36,37] As the potential decreases to below 1.5 V in the second lithiation process, the reaction of the LiₓMoO₃ solid solution with Li ions to form metallic Mo and 3Li₂O takes place, giving rise to a long plateau at around 0.4–0.5 V. [38] The potential plateaus and distinct cathodic peaks in the subsequent discharge curves and cyclic voltammograms, respectively, were not observed, because the crystalline structure of MoO₃ was transformed into an amorphous-like structure after the first discharge process through the conversion reaction given in Equation (1). [28,38]

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\text{MoO}_3 + 6\text{Li}^+ + 6\text{e}^- \rightleftharpoons 3\text{Li}_2\text{O} + \text{Mo}
\]  

From the second cycle onward, the cathodic and anodic peaks in the voltammogram tests overlapped substantially, indicating that the electrode of the yolk–shell MoO₃ microspheres showed outstanding cycle ability for the insertion and extraction of Li ions. Figure 3c shows the cycling performances of the yolk–shell and filled MoO₃ microspheres and Coulombic efficiencies of the yolk–shell microspheres at a constant current density of 1000 mAg⁻¹. The cycling performances of the filled structured MoO₃ microspheres are also shown in Figure 3c. The initial charge and charge capacities of the yolk–shell MoO₃ microspheres were 1481 and 998 mAhg⁻¹, respectively, and the corresponding first Coulombic efficiency was 67%. The initial capacity loss was attributed mainly to irreversible processes such as the irreversible trapping of Li ions in the crystal lattice, which is accompanied by the formation of a solid electrolyte interface (SEI) and electrolyte decomposition. [39] The Coulombic efficiency increased gradually in subsequent cycles and stabilized at more than 98% from the fifth cycle. The discharge capacity of the yolk–shell MoO₃ microspheres was as high as 835 mAhg⁻¹ even after 150 cycles, and the capacity retention measured after the first cycle was 81%. However, the discharge capacity of the filled structured MoO₃ microspheres was 606 mAhg⁻¹ after 150 cycles, and the capacity retention measured after the first cycle was 62%. The morphology of the yolk–shell MoO₃ microspheres after 150 cycles is shown in Figure S5 in the Supporting Information. The yolk–shell microspheres maintained their spherical structure despite repeated Li ion insertion and extraction processes. This result indicated that the yolk–shell MoO₃ microspheres had good structural stability even at a high current density of 1000 mAg⁻¹. Figure 3d shows the rate performance of the yolk–shell MoO₃ microspheres, in which the current densities were increased stepwise from 500 to 5000 mAg⁻¹ in the voltage range.
0.001–3 V. For each step, 20 cycles were measured to evaluate the rate performance. The yolk–shell MoO₃ microspheres exhibited final cycle capacities of 896, 729, 632, and 534 mAh g⁻¹ at current densities of 500, 1500, 3000, and 5000 mA g⁻¹, respectively. In spite of the cycling at high current densities, the discharge capacity recovered to 835 mAh g⁻¹ when the current density returned to 500 mA g⁻¹. The yolk–shell MoO₃ microspheres exhibit a superior rate performance because of their unique structure, composed of a porous core and shell, ensuring the facile diffusion of Li ions by offering them a short diffusion length and a void space between the core and the shell that is freely penetrated by the electrolyte.

A facile synthesis of yolk–shell MoO₃ microspheres without the use of a template and the application of these microspheres in anodes for Li ion batteries were introduced. The molybdenum oxide–carbon (MoO₃–C) composite microspheres obtained directly through spray pyrolysis were appropriate as the precursor material for the yolk–shell MoO₃ microspheres. Combustion of the MoO₃–C composite precursor microspheres was performed at an optimum temperature of 400°C to fabricate the yolk–shell α-MoO₂ microspheres with a distinctive core@void@shell structure. The yolk–shell α-MoO₂ microspheres exhibited excellent cycling and rate performances because of their unique structure and structural stability during cycling.

**Experimental Section**

**Material Synthesis**

The yolk–shell MoO₃ microspheres were prepared through a simplified two-step process involving spray pyrolysis and subsequent combustion in air at 400°C. The precursor solution was prepared by dissolving MoO₃ and sucrose in a mixture of hydrogen peroxide and distilled water with air at 400°C for 1 h. The spray pyrolysis system consisted of a droplet generator, a high-temperature tubular quartz reactor, and a Teflon bag filter (powder collector). A 1.7 MHz ultrasonic spray generator with six vibrators was used to generate aerosol droplets, which were then carried to the quartz reactor. A spray pyrolysis system consisted of a droplet generator, a high-temperature tubular quartz reactor, and a Teflon bag filter (powder collector). A 1.7 MHz ultrasonic spray generator with six vibrators was used to generate aerosol droplets, which were then carried to the quartz reactor. The obtained black MoO₃–C product was then combusted in air at 400°C for 1 h.

**Characterization**

The morphologies of the MoO₃–C composite and the yolk–shell MoO₃ microspheres were investigated through scanning electron microscopy (SEM, JEOL JSM-6060) and transmission electron microscopy (FE-TEM, JEOL-2100F). Thermal gravimetric analysis (TGA, SDT Q600) was performed in air at a heating rate of 10°C min⁻¹. The crystal structures of the microspheres were investigated through X-ray diffractometry (XRD, X'Pert PRO MPD) using Cu Kα radiation (λ = 1.5418 Å) at the Korea Basic Science Institute (Daegu). The surface areas of the microspheres were measured by the Brunauer–Emmett–Teller (BET) method with N₂ as the adsorbate gas.

**Electrochemical Measurements**

The electrochemical properties of the yolk–shell MoO₃ microspheres were analyzed in a 2032-type coin cell. The anode was prepared from a mixture of the MoO₃ active material, carbon black, and sodium carbonate in ethylene carbonate/dimethyl carbonate (EC/DMC; 1:1 v/v) with 2% vinylene carbonate. The discharge/charge characteristics of the samples were investigated through cycling in the voltage range of 0.001–3 V at various current densities. Cyclic voltammograms were measured at a scan rate of 0.1 mVs⁻¹.

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