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Enhancement of the interfacial reaction on mesoporous RuO_2 for next generation Li batteries

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HIGHLIGHTS

- Mesoporous RuO_2 shows higher discharge capacity than that of commercial RuO_2.
- The larger capacity of mesoporous RuO_2 is due to the enhanced interfacial reaction.
- Nano-size effects enable to improve the interfacial reaction.

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ABSTRACT

In order to develop high energy density Li rechargeable batteries, nano-sized materials have attracted attention as the active materials. Mesoporous materials consist of the micrometre-sized particles, and they have high surface area due to their mesopore and thin wall thickness of framework. Here, we synthesize a highly ordered mesoporous RuO_2 to investigate the effect that the mesoscopic structure has on the capacity and their corresponding reaction mechanism of Li rechargeable battery. The synthesized mesoporous RuO_2 shows an initial discharge capacity of 1366 mAh g^{-1} on mesoporous RuO_2, which is higher than that of commercial RuO_2. Our findings *via In situ* X-ray analysis techniques combined with electrochemical analysis demonstrate that the additional capacity of mesoporous RuO_2 is resulted from the enhanced interfacial reaction between Ru metal and Li_2O formed by conversion reaction of RuO_2. Nano-size effects of mesoporous structure such as high surface area, easy electron transport, and small domain would enable to improve the interfacial reaction of highly ordered mesoporous RuO_2. The understanding of this relationship between structural engineering and electrochemical properties provides the insight into development of high energy density anode materials in next generation Li rechargeable battery.

1. Introduction

The demands for high energy and power density of Li rechargeable battery are increasing due to the market growth in portable electronics, electronic vehicles, energy storage systems, etc [1–3]. Graphite as the anode material has the advantages such as flat and low working voltage, low cost, and good cycleability, but it shows the low power and energy density. Since commercialized graphite anode materials do not meet those requirements, it is necessary to develop new anode materials that replace the graphite anode. Extensive research has been conducted on transition metal oxides, silicon or metal alloying, and carbonaceous materials to overcome low energy and power density of the graphite anode [4–12]. They were able to achieve high energy density through the conversion and alloying reaction, but problems such as large volume expansion, poor cycle retention, etc. have to be solved before commercialized as the anode material [4–6]. One of the effective strategies for designing high energy density anode materials is the nanoscale engineering of the electrode materials [13,14]. A large surface area and short Li diffusion length of nano-sized materials provide a chance to achieve high energy density in Li-ion batteries. Mesoporous materials are one of the superior nanoscale engineering anode materials that have the high surface areas and can control pore size, framework thickness, and surface properties [15,16]. These materials show advantage as the electrode materials: Because highly ordered mesopore

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plays a role of the structural buffer of the huge volume expansion, mechanical strain by Li insertion/extraction into/from electrode materials can be relieved during electrochemical charge and discharge in the Li-ion batteries. Moreover, the thin walls of framework ensure the short Li diffusion path and easy electron transport, and high surface area enlarges the active surface area by increasing distribution of electrode surface in contact with electrolyte. Therefore, various mesoporous materials have been introduced as the electrode materials for Li-ion batteries [14,17–21].

RuO_2, one of the transition metal oxides, can store the Li up to 4 mol during discharge by the insertion and conversion reaction, theoretically. However, practical capacity of RuO_2 has been reported about 1130 mAh g^{-1} corresponding to Li storage of 5.6 mol. Because unexplainable additional capacity through the conventional reaction mechanism was revealed on RuO_2 anode in Li-ion battery, research has been focused on understanding the origin of additional capacity. The new Li storage mechanisms have been discovered on various transition metal oxides: (1) reversible formation and decomposition of the gel-like polymer on the surface of the electrode materials, (2) interfacial charge storage between conversion reaction products, (3) reversible formation of LiH and LiOH on −OH group containing surface, (4) formation of metallic Li-rich phase between Li intercalated transition metal oxides [22–26]. Particularly, there are two different discussions about the mechanism that explains the origin of additional capacity beyond theoretical capacity of RuO_2. First, additional Li are stored in the interface between nano-size Ru metal and Li_2O formed by conversion reaction [23,24]. Second, LiOH on surface of RuO_2 particle reacts with Li forming the LiH and Li_2O, meaning the further Li storage occurs [25]. We discovered in previous study that fast Li diffusion occurs after conversion reaction, and it is associated with additional Li consumption. Our finding demonstrated that because the additional Li accumulation into interface between nano-sized Ru metal and Li_2O offers the faster Li diffusion than conversion reaction, additional capacity of the RuO_2 is correlated with interfacial reaction [27].

Mesoporous RuO_2 reported here shows high specific capacity of about 1366 mAh g^{-1} in the 1st discharge, which is larger than the capacity of commercial RuO_2. The structural modification by the 3D network enhances the capacity, even though they have the same chemical composition. Here, we investigated why mesoporous RuO_2 shows higher capacity than commercial RuO_2 using the synchrotron based *in situ* X-ray analysis and electrochemical analysis.

2. Methods

2.1. Material preparation

Highly ordered mesoporous silica with 3D cubic I*a3d* mesoporous structure, named as KIT-6, was prepared followed by the previously reported methods [28,29]. To synthesize ordered mesoporous RuO_2, ordered mesoporous silica template should have the hydrophobic surface. For changing from the hydrophilic surface of KIT-6 to hydrophobic surface, 5 g of KIT-6 was put into the solution of 120 mL hexane and 0.5 g of hexamethyldisilane (HMDS), subsequently the mixture was stirred vigorously at 100 °C for an hour. The white precipitate (hydrophobic KIT-6, abbreviated as HP-KIT-6) was gathered and washed several times with hexane. Then, the powder was dried at 80 °C oven for a day. Ordered mesoporous RuO_2 was replicated using as-prepared HP-KIT-6 *via* nano-replication method. 0.80 g of $RuCl_3{\cdot}3H_2O$ (99.0%, Kojima) was dissolved in 3 g of deionized water. This precursor solution was infiltrated within the mesopores of HP-KIT-6, and the wetted powder ($RuCl_3$/HP-KIT-6) was dried at 80 °C oven for a day to evaporate the water. The obtained powder was annealed at 300 °C for 2 h in the air. This impregnation procedure was repeated once again. After two times impregnation of precursor, silica template was removed using 25 wt% of hydrofluoric acid (J.T.Baker) three times. The mixture was washed with deionized water for six times, and acetone for once, subsequently dried at 80 °C oven for a day. Ordered mesoporous RuO_2 was finally obtained. The commercial RuO_2 was prepared by annealing the anhydrous RuO_2 powder (electronic grade, 99.9%, Alfa Aesar) at 300 °C for 2 h in the air.

2.2. Electrochemical measurements

The electrode was prepared by mixing mesoporous RuO_2, Super P (Super P® carbon black, TimCal Graphite & Carbon), and PAI (polyamide-imide polymers, PAI, Solvay, Torlon® 4000 T) with weight ratio of 70:15:15 casted on Ti foil. And this electrode was dried at 80 °C for 2 h and heat treated at 200 °C for 2 h under vacuum. The Li half cells are assembled into coin-type CR2032 cell with a Celgard separator, metallic Li foil as a counter electrode, and Li conducting electrode of 1.0 M $LiPF_6$ and 0.3 M $LiBF_4$ dissolved in 3:7 ethylene carbonate (EC)/diethyl carbonate (DEC) in Ar filled glove box. The electrochemical tests were performed at constant current density of 100 mA g^{-1} within voltage range between 0.05 and 4.3 V. The galvanostatic intermittent titration technique (GITT) measurement was carried out applying a constant current flux of 100 mA g^{-1} for 30 min followed by open-circuit equilibration time for 3 h.

2.3. Structural characterization

The low and wide angle X-ray diffraction (XRD) patterns of the mesoporous silica template and mesoporous RuO_2 were measured from a Rigaku D/MAX-III, and the N_2 sorption isotherms was estimated on a Micromeritics ASAP 2000 at liquid N_2 temperature. The SEM images were obtained using Hitachi UHR S-5500 instrument at an accelerating voltage of 30 kV. The TEM images were collected from a G2 FE-TEM at operation voltage of 200 kV. *In situ* XRD patterns were collected at the 5 A MS-XRS beamline at Pohang Light Source-II (PLS-II) in Korea using a Mar-345 image plate detector with wavelength of 0.6927 Å. The 2θ angles of all the XRD patterns were converted to the corresponding angles for CuKα for easy comparison. *In situ* Ru K-edge X-ray absorption spectroscopy (XAS) spectra were obtained at 8C nano XAFS beamline at PLS-II using the Si solid-state detector and Si(111) double-crystal monochromator.

3. Results and discussion

The silica KIT-6 template with cubic I*a3d* mesostructure was used for synthesizing the mesoporous RuO_2 *via* nano-replication method. Low angle XRD pattern of mesoporous silica KIT-6 shows well-defined diffraction of (211), (220), and (332) reflections, which describes that this material has the highly ordered mesoporous structure (Fig. 1a). N_2 adsorption-desorption isotherms were measured for characterizing the specific surface area, pore size, and pore volume. In the N_2 adsorption-desorption isotherms, the type IV isotherm appears with the H1 hysteresis indicating the cylindrical pore array in Fig. 1b. The Brunauer-Emmett-Teller (BET) surface area of silica templates is about 770 $m^2 g^{-1}$, a total pore volume is 0.84 $cm^3 g^{-1}$, and the pore size of KIT-6 is 6.5 nm. The structural characteristics of the mesoporous RuO_2 replicated from this mesoporous hard template are represented in Fig. 1c and d. The (110) and (211) reflections in the low angle XRD pattern in Fig. 1c show that the highly ordered mesoporous RuO_2 has been successfully replicated from the 3D cubic KIT-6 template. The wide angle XRD pattern of mesoporous RuO_2 inserted in Fig. 1c is well corresponded with rutile structure with $P4_2/mnm$ space group. For comparison of the surface area between synthesized mesoporous RuO_2 and commercial RuO_2, we also measured the N_2 adsorption-desorption isotherms on both RuO_2. BET surface area of commercial RuO_2 is about 22 $m^2 g^{-1}$, and a total pore volume is 0.06 $cm^3 g^{-1}$. The ordered mesoporous RuO_2 has the high BET surface area of 113 $m^2 g^{-1}$, a total volume of 0.37 $cm^3 g^{-1}$. Moreover, there are dual pores of below 3 nm and of about 17 nm on ordered mesoporous RuO_2. Fig. 2a and b