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# Hierarchical nanostructure of $RuO_2$ hollow spheres with enhanced lithium ion storage and cyclic performance

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ABSTRACT

$RuO_2$ hollow spheres as a macroporous model structure for substituting a graphite anode in a lithium ion battery were successfully fabricated by utilizing the electrostatic attraction between exfoliated $RuO_2$ nanosheets and cationic polymers onto the polystyrene (PS) templates. According to the results of scanning electron microscopy, thin $RuO_2$ nanosheets were homogeneously covered onto the polystyrene beads before calcination. Transmission electron microscopy images clearly indicated complete removal of the PS templates after calcination at 500 °C for 2 h, leading to $RuO_2$ hollow spheres with a macroporous structure. Electrochemical charge/discharge experiments demonstrated a much larger lithium storage capacity for the $RuO_2$ hollow spheres described here (600 mAh/g) than that of bare rutile $RuO_2$ (340 mAh/g), highlighting the effectiveness of this synthetic technology.

## 1. Introduction

In recent years lithium ion batteries (LIBs) have attracted tremendous scientific and industrial research interests because of their high energy density and high electromotive force. In LIBs, $LiCoO_2$ and graphite are generally used as a cathode and an anode, respectively. Graphite is especially suitable as an anode material, as it shows a very stable and safe behavior during charge/discharge reactions. It has a theoretical discharge capacity of 372 mAh/g, which is attributed to the 1:6 ratio of lithium to carbon in the discharge state of $LiC_6$ [1–3]. As the demand for an energy storage device with high capacity increases, new anode materials—including transition metal oxides—have been explored. For example, typical anode materials based on transition metal oxides such as SnO and $SnO_2$ have theoretical discharge capacities of 875 and 782 mAh/g, respectively [4–6]. Such high discharge capacities found in transition metal oxides used in LIBs are ascribed to a large lithium storage due to alloying/dealloying and/or conversion reactions and they result in high-energy-density anodes [7,8]. However, one of the inherent disadvantages of using transition metal oxides as anodes is capacity fading upon successive cycles of charge/discharge reactions [9]. In the case of $SnO_2$, a huge volume change of ~300% accompanies the charge/discharge process, leading to pulverization and detachment of the active materials from the current collector [10,11]. In this regard, a flexible nanostructure was proposed to overcome such drawbacks of transition metal-containing anodes in LIBs. A $SnO_2$/graphene hybrid with a three-dimensionally delaminated structure is a representative example of this type of flexible anodes [12]. Preparing hollow spheres is another relevant method to endure large volume expansions during cycling of anodes in LIBs, as reviewed in reference [13]. Very recently, Zhang and co-workers fabricated metal oxide anodes of hollow nanostructures by using templates, in which both improved discharge capacities and cycling properties were guaranteed by hollow structures [14]. In this structure, nanosized pores in hollow spheres provide buffer spaces to avoid large volume changes, leading to a significant enhancement of the cyclic performance upon charge/discharge. The improved capacity retention of the hollow nanostructures showed that controlling the textural properties of the anode material could play an important role in developing new electrodes with improved discharge capacity [15]. It is worthwhile to note that the anodes with hollow nanostructures could provide the facileaccess of electrolytes and lithium ions, leading to the improved electrochemical performances. Also,

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the hollow spheres with very thin shells can effectively enhance the charge-transport properties of anodes by utilizing the reduced paths of charge transportation.

On the other hand, ruthenium oxide is one of the attractive candidates among the anodes of transition metal oxides in LIBs. $RuO_2$ exhibits fascinating characteristics such as good chemical stability, extraordinary metallic conductivity, and excellent discharge capacity [16–18]. Though $RuO_2$ is a relatively expensive material, it can be one of the potential candidates of anodes for the small-scale portable devices demanding large energy densities. Also, $RuO_2$ is still considered to be a model material for understanding the physicochemical properties for achieving the high discharge capacity and high Coulombic efficiency [19,20]. According to the reported paper on lithium intercalation into $RuO_2$, 5.6 mol of Li can be inserted per 1 mol of $RuO_2$, resulting in very high discharge capacity of 1130 mAh/g at the first cycle [16]. Recent experimental observation and theoretical calculation on $RuO_2$ in LIBs revealed that the lithium storage mechanism of $RuO_2$ via intercalation and conversion reaction can lead to the increased discharge capacity and electrochemical property of $RuO_2$ [20–22]. However, during the charge/discharge reaction of $RuO_2$, a volume expansion similar to that shown in $SnO_2$ is still observed, giving rise to electrical disconnections between the active material and the current collector [23].

The key strategy in this study is to minimize the demerit of large volume changes of transition metal oxide anodes upon successive charge/discharge cycles. Therefore, we tried to fabricate a hierarchical $RuO_2$ hollow sphere as a model structure, in which a large amount of void spaces in hollow sphere could be used as buffer spaces to circumvent volume expansion. It is highly plausible that a very thin $RuO_2$ hollow sphere with a curved surface could potentially afford enough space to overcome the large volume change upon charge/discharge cycling, leading to improved specific capacities. To the best of our knowledge, this is the first example of macroporous $RuO_2$ hollow sphere used in the LIB application. We chose layered ruthenic acid as the starting material because it can be effectively exfoliated into a very thin, single-layered nanosheet for layer-by-layer self-assembly [24]. Furthermore, the layered ruthenate is also known to have the highest metallic conductivity among transition metal oxides [25]. By using the intercalation of bulky organic cations such as tetrabutylammonium ($TBA^+$), exfoliated nanosheets of transition metal oxides could be stabilized to possess a negative surface charge in the colloidal state, allowing construction of a hierarchical nanostructure [26,27]. This exfoliated ruthenate nanosheet can be also hybridized with organic cations. As seen in Fig. 1, the exfoliated $RuO_2$ nanosheet with a negative charge was used as the building block in assembling the hierarchical $RuO_2$ hollow spheres on a polystyrene (PS) template. Positively charged polyethylenimine (PEI) was utilized as a polymeric glue between the PS template and exfoliated $RuO_2$ nanosheet. Repeated self-assembly between the oppositely charged components and the subsequent calcination that removes the organic moieties resulted in successful fabrication of the $RuO_2$ hollow spheres.

## 2. Experimental

### 2.1. Synthesis of the exfoliated ruthenium oxide nanosheets

The unilamellar nanosheets of ruthenium oxide were synthesized by the following procedure. First, the pristine $K_{0.2}RuO_{2.1}\cdot nH_2O$ (layered potassium ruthenate) was synthesized via a solid state reaction [24]. Potassium carbonate (Aldrich, $K_2CO_3$) and ruthenium dioxide (Aldrich, $RuO_2$) were mixed at a molar ratio of 5:8 in a mortar. This mixture was pelletized, and subsequently calcined at 850 °C for 12 h under an Ar atmosphere. The resultant powder was thoroughly washed with water to remove water-soluble impurities. The resulting potassium ruthenate was treated with an aqueous solution of 1 M HCl at room temperature for 72 h to synthesize the layered protonic ruthenate, $H_{0.2}RuO_{2.1}\cdot nH_2O$. The hydrochloric acid was replaced with a fresh batch every 24 h during this proton-exchange reaction. Next, ethylammonium ($EA^+$)-intercalated ruthenate was synthesized by reacting the layered protonic ruthenate with a 50% aqueous solution of ethylamine (EA) at room temperature for 24 h. The $EA^+$-intercalated ruthenate was collected by centrifugation, washed with water, and reacted with a 10% aqueous solution of tetrabutylammonium hydroxide ($TBA^+OH^-$) at room temperature for 120 h. Finally, this colloidal suspension of exfoliated $RuO_2$ was used for further self-assembly experiments.

### 2.2. Fabrication of the $RuO_2$ hollow spheres using layer-by-layer self-assembly

PS bead was synthesized by the previously reported procedure [28]. This PS bead (0.6 g) was suspended by sonication in the mixed solution of deionized water (150 mL) and 30 wt% of PEI aqueous solution (0.066 mL, Alfa Aesar: $M_w \sim 70000$). The solid, PEI-covered PS beads (PEI-PS) were collected by centrifugation, thoroughly washed with deionized water 3 times, and then re-dispersed in deionized water (150 mL). The colloidal dispersion of $RuO_2$ nanosheets (10 mL, 4 g/L concentration) described above was then added dropwise to this suspension containing PEI-PS while stirring. The resultant solid, $RuO_2$-covered PEI-PS ($(RuO_2/PEI)_1$-PS) spheres were gathered by centrifugation, and repeatedly subjected to the same procedure of layer-by-layer self-assembly for five more times to obtain $(RuO_2/PEI)_6$-PS. After six cycles that provided alternative coverage of exfoliated ruthenate and PEI, the solid product was collected by centrifugation, and heat-treated at 500 °C for 2 h under ambient atmosphere. In this heat-treatment step, organic parts such as the PEI and PS bead can be removed, resulting in the $RuO_2$ hollow spheres.

### 2.3. Characterization and charge/discharge experiment

X-ray diffraction (XRD) analysis of the samples was conducted by an X-ray diffractometer (Bruker D2 phaser, $\lambda = 1.5418$ Å). The morphology of the samples was monitored by scanning electron microscopy (SEM, Hitachi SU8220) using an acceleration voltage of ~30 keV. High-resolution transmission electron microscopy (HRTEM) studies were carried out with a Titan G2 ChemiSTEM (FEI Company) electron microscope with an acceleration voltage of 200 keV. To evaluate the lithium storage ability, charge/discharge experiments of the samples were conducted using battery test equipment (Maccor K4300). The slurry for active electrode was made by mixing of 70% active material, 20% conductive carbon (Super P), and 10% polyvinylidene fluoride in *N*-methyl-2-pyrrolidone (NMP). For $RuO_2$ hollow spheres, the composition of 50:40:10 (active material: carbon: binder) was also examined in charge/discharge. This slurry was cast onto a Cu current collector by using a doctor blade, dried under vacuum at 80 °C overnight, and then placed in an Ar-filled glovebox. A Swagelok-type cell, in which the electrolyte was 1 M $LiPF_6$ in a 1:1 volumetric mixture of ethylene carbonate and diethyl carbonate, was assembled using the active electrode and lithium foil counter electrode. A constant current was applied during the charge/discharge experiments, in which the voltage window was between 0.05 and 2.5 V and the current density was 50 mA/g. The specific capacity and the current density were calculated, based on the weight of the active material. The extended X-ray absorption fine structure (EXAFS) analysis for samples at Ru K-edge was performed at the beamline 8C in Pohang