Communication

Effect of Structure-Controlled Ruthenium Oxide by Nanocasting in Electrocatalytic Oxygen and Chlorine Evolution Reactions in Acidic Conditions

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Abstract: RuO2 has been used for various applications because of its good catalytic properties. To further improve its electrocatalytic properties, we used a nanocasting technique. By using this technique, we obtained structure-controlled (SC) RuO2 with a high surface area and an ordered porous structure, which created enhanced electrocatalytic properties over commercial RuO2 nanoparticles for both oxygen and chlorine evolution reactions.

Keywords: ruthenium oxide; KIT-6; nanocasting; oxygen evolution reaction; chlorine evolution reaction

1. Introduction

The oxygen evolution reaction (OER) is an important core reaction for electrochemical energy conversion systems such as fuel cells, water splitting, and metal–air batteries [1,2]. The chlorine evolution reaction (CER) is also an essential reaction in the chlor–alkali process for the chemical industry, which uses chlorine as the main raw material. [3]. RuO2 is considered as a highly active metal oxide material for both the OER and CER [4,5]. However, RuO2 has the fatal problem of a very high unit price due to low reserves. Therefore, many research techniques have been developed to reduce its usage by enhancing its electrocatalytic properties [6–9]. Among these techniques, nanocasting is a facile and versatile structure design technique for synthesizing various nanostructures through replication of the microporous or mesoporous siliceous or non-siliceous materials for use as hard or soft templates. The nanocasting technique is a process by which the structure of the replicate can be obtained by filling the pores of the template with a metal precursor, followed by optional treatment and final removal of the template [10–13]. In this work, we demonstrate a structurally controlled ordered mesoporous RuO2 replica through the nanocasting technique with mesoporous KIT-6 silica material as a template; the results reveal highly enhanced electrocatalytic activity and stability for OER and CER over commercial RuO2 nanoparticles.

2. Results and Discussion

Figure 1a–c show representative transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images of the KIT-6 template. These images display a well-ordered mesoporous KIT-6 structure. Figure 1d shows the small-angle X-ray scattering (SAXS) pattern of the KIT-6 in
the range of $2\theta = 0.3-5.0^\circ$. Characteristic peaks of the crystalline KIT-6 phase (211), (220) and (332) planes appeared at 0.9°, 1.04° and 1.71°, respectively. This SAXS result can be assigned to a cubic ordered three-dimensional $Ia\overline{3}d$ symmetry structure [14,15], indicating that the obtained KIT-6 template has a well-ordered pore structure. The mesoporous properties of KIT-6, namely the pore-volume (0.975 cc g$^{-1}$), the pore size (9.056 nm) and the surface area (868.3 m$^2$ g$^{-1}$), were revealed by a nitrogen adsorption–desorption isotherm (Figure 1e).

Figure 1. (a) TEM image, (b and c) HRTEM images, (d) SAXS pattern and (e) nitrogen adsorption–desorption isotherm (right: pore size distribution) of the KIT-6.

Figure 2 compares the structural properties of the structure-controlled (SC) RuO$_2$ obtained using the KIT-6 template and the commercial RuO$_2$ (Figure 2). Unlike RuO$_2$, which shows an aggregated spherical particle structure with a particle size of about 26 nm in TEM and HRTEM images (Figure 2a), SC RuO$_2$ shows the shape of a framework structure and the same cubic symmetry as the KIT-6 template (Figure 2b). Furthermore, the particle wall thickness of SC RuO$_2$ is almost the same as the pore size of the KIT-6 template (KIT-6 pore size: 9.056 nm and particle wall thickness of SC RuO$_2$: approximately 9 nm). The X-ray diffraction (XRD) patterns of both SC RuO$_2$ and commercial RuO$_2$ (Figure 2c) exhibit a crystalline phase of RuO$_2$ (JCPDS No. 43-1027).
1.1 V for CER at frequencies from 100 kHz to 0.1 Hz with an amplitude of 5 mV to compare the charge transport ability between SC RuO$_2$ and RuO$_2$ during the OER (Figure 3c) and CER (Figure 3d). In addition, the current density of SC RuO$_2$ for CER reached 616.4 mA cm$^{-2}$, which is 1.75 times higher than that of RuO$_2$ (352.1 mA cm$^{-2}$). EIS analysis was also performed at a constant voltage of 1.2 V for OER and 1.1 V for CER at frequencies from 100 kHz to 0.1 Hz with an amplitude of 5 mV to compare the charge transport ability between SC RuO$_2$ and RuO$_2$ during the OER (Figure 3c) and CER (Figure 3d). In the Nyquist plot, the quasi-semicircle is related to the Faradaic reactions at the electrode surface, and the diameter refers to the charge transfer resistance (R$_{ct}$) \cite{18,19}.

Figure 2. TEM and HRTEM image of (a) RuO$_2$ and (b) structure-controlled (SC) RuO$_2$. (c) XRD patterns, (d) nitrogen adsorption–desorption isotherm (inset: pore size distribution of SC RuO$_2$), (e) SAXS patterns of RuO$_2$ and SC RuO$_2$. (f) EDS spectra of KIT-6, RuO$_2$ and SC RuO$_2$.

To confirm the mesoporosity and long-range pore order of SC RuO$_2$, nitrogen adsorption–desorption isotherm and SAXS analysis were performed, respectively. SC RuO$_2$ possesses a typical mesoporosity with a type IV isotherm hysteresis loop \cite{16} and a pore size between 2 nm and 50 nm (SC RuO$_2$: 20.7 nm), while RuO$_2$ exhibits nonporous properties (Figure 2d). It is noteworthy that the surface area of SC RuO$_2$ (69.1 m$^2$ g$^{-1}$) is seven times higher than that of RuO$_2$ (9.5 m$^2$ g$^{-1}$). In SAXS patterns (Figure 2e), only SC RuO$_2$ shows two typical peaks of the long-range pore order properties between 20 = 0.5$^\circ$ and 1.0$^\circ$ \cite{17}. Through energy dispersive X-ray spectrometer (EDS) analysis (Figure 2f), we confirmed that the KIT-6 was completely removed in the SC RuO$_2$ material.

The electrochemical analyses (linear sweep voltammetry (LSV), electrochemical impedance spectroscopy (EIS) and chronoamperometry (CA)) for OER and CER over the prepared catalysts were performed in a 0.5 M H$_2$SO$_4$ solution and a 5 M NaCl + 0.01 M HCl solution, respectively (Figure 3). LSV analyses were performed at a scan rate of 10 mV s$^{-1}$ for OER (Figure 3a) and CER (Figure 3b) to estimate the electrocatalytic activities. Even though the onset potentials were the same for each catalyst (1.2 V and 1.1 V vs. Ag/AgCl for OER and CER, respectively), the peak current density of SC RuO$_2$ for OER was 272.7 mA cm$^{-2}$, which is 1.77 times higher than that of RuO$_2$ (154.1 mA cm$^{-2}$). In addition, the current density of SC RuO$_2$ for CER reached 616.4 mA cm$^{-2}$, which is 1.75 times higher than that of RuO$_2$ (352.1 mA cm$^{-2}$). EIS analysis was also performed at a constant voltage of 1.2 V for OER and 1.1 V for CER at frequencies from 100 kHz to 0.1 Hz with an amplitude of 5 mV to compare the charge transport ability between SC RuO$_2$ and RuO$_2$ during the OER (Figure 3c) and CER (Figure 3d). In the Nyquist plot, the quasi-semicircle is related to the Faradaic reactions at the electrode surface, and the diameter refers to the charge transfer resistance (R$_{ct}$) \cite{18,19}.
Figure 3. (a, c and e) OER in a 0.5 M H$_2$SO$_4$ solution and (b, d and f) CER in a 5 M NaCl + 0.01 M HCl solution over SC RuO$_2$ and RuO$_2$. (a, b) LSV curves at a scan rate of 10 mV s$^{-1}$. Nyquist plots at a constant voltage of (c) 1.2 V and (d) 1.1 V at frequencies from 100 kHz to 0.1 Hz with an amplitude of 5 mV. CA curves at a constant voltage of (e) 1.25 V and (f) 1.15 V.

In both reactions, the Nyquist plots obtained via EIS analysis show smaller semicircles for SC RuO$_2$ than for RuO$_2$, which is related to the enhanced charge transfer ability of SC RuO$_2$. The obtained electrolyte resistance ($R_s$) and the $R_{ct}$ for OER ($R_s$: 11.2 Ω, $R_{ct}$: 430.6 Ω) and CER ($R_s$: 5.1 Ω, $R_{ct}$: 144.9 Ω) of SC RuO$_2$ were lower than those of RuO$_2$ ($R_s$: 12.0 Ω, $R_{ct}$: 589.4 Ω for OER and $R_s$: 6.1 Ω, $R_{ct}$: 170.9 Ω for CER). Finally, CA tests were performed to examine the stability of SC RuO$_2$ and RuO$_2$ during OER and CER. Constant voltages of 1.25 V and 1.15 V vs. Ag/AgCl for the OER and CER, respectively, were applied for 60 min. As Figure 3e,f show, the current density of the OER and CER remains higher than that of SC RuO$_2$ during the reaction time, which suggests that the SC RuO$_2$ catalyst has high stability in both reactions. These electrochemical property results suggest that the potential
for initiating each reaction is the same due to the same constituent elements in both RuO$_2$ catalysts, but the reaction rate and the stability of the SC RuO$_2$ are much better than that of the RuO$_2$ because of the distinct structural properties of SC RuO$_2$, namely, its high surface area and mesoporosity.

3. Materials and Methods

3.1. Synthesis of KIT-6 Nanoparticles

Mesoporous silica KIT-6 nanoparticles were prepared following a reported study in the literature [20]. Pluronic P123 (33.8 g, Aldrich, Saint Louis, MO, USA) was dissolved in distilled water (1220 mL), and hydrochloric acid (54.2 mL, 35%, Aldrich, Saint Louis, MO, USA) and 1-buthanol (45.9 mL, Aldrich, Saint Louis, MO, USA) were added. Then, 92.8 mL of tetraethyl orthosilicate (TEOS, 98%, ACROS, Belgium) was added and the mixture was continuously stirred at 35 °C for 24 h. The final mixture was heated at 100 °C for 24 h. The white solid product was obtained by filtration and calcined at 550 °C for 6 h in air.

3.2. Preparation of Structure-Controlled RuO$_2$ (SC RuO$_2$) Catalyst

The replication process of the SC RuO$_2$ from KIT-6 as a template is depicted in Scheme 1. The replica was prepared by an incipient wetness impregnation (IWI) method using a RuCl$_3$·xH$_2$O precursor (Aldrich, Saint Louis, MO, USA) and as-prepared KIT-6. The ruthenium precursor (1.09 g) was dissolved in 10 mL of ethanol. This mixture was infused into 0.3 g of KIT-6. After the ethanol was evaporated, the sample was exposed to 28% ammonia vapor at 60 °C and calcined at 500 °C for 3 h [21]. After being calcined, the obtained powder was added to a 1 M NaOH solution to remove the KIT-6 template. The template-free product was collected by centrifugation, washed with distilled water and dried at 60 °C.

Scheme 1. Replication process for synthesizing SC RuO$_2$ by the nanocasting technique using KIT-6 nanoparticles.

3.3. Characterization

The crystal structure was characterized by SAXS (Rigaku, SmartLab, Japan) and an XRD (Rigaku, Ultima IV, Japan) equipped with a 2D detector (Hypix-3000) using Cu K-alpha (λ = 0.154 nm, 1.5401 Å). HRTEM (TECNAI, G2 T-20S, Japan) equipped with an EDS was used to verify the structural morphology and elemental composition of the prepared catalysts. Nitrogen adsorption–desorption analysis was conducted at 77 K using a physical adsorption instrument (Micromeritics, ASAP 2020, Norcross, GA, USA). To calculate the apparent surface area and the pore size distributions, the Brunauer–Emmett–Teller (BET) method and the Barret–Joyner–Halenda (BJT) theory were used, respectively. Electrochemical properties were investigated using LSV, EIS and CA techniques. These electrochemical analyses were carried out using a three electrode half-cell system connected to a potentiostat (ZIVE MP2A, WonATech, Seoul, Korea). A glassy carbon (0.196 cm$^2$), an Ag/AgCl (1 M KCl) and a Pt wire (diameter: 0.5 mm, length: 50 mm, surface area: 0.7 cm$^2$) were used as a working electrode, a reference electrode and a counter electrode, respectively. The catalysts were mixed with a 5 wt% Nafion solution (catalyst: Nafion = 90:10 wt%) and loaded onto the glassy carbon electrode (0.2 mg cm$^{-1}$).
4. Conclusions

In this study, we successfully synthesized a well-ordered mesoporous SC RuO$_2$ catalyst via a nanocasting technique using a KIT-6 template. SC RuO$_2$ exhibited highly improved electrocatalytic properties in terms of both activity and stability for the oxygen and chlorine evolution reactions over the commercial RuO$_2$ catalyst. The improved electrochemical performance of SC RuO$_2$ could be attributed to the following unique structural features: (i) well-distributed pores could promote electrolyte permeability for faster reactant migration, and (ii) framework structures with thin walls could accelerate electrocatalytic reactions by enlarging the surface area.

Author Contributions: J.H. conducted electrochemical analyses and contributed to the writing of the original manuscript. H.J.A. and T.-W.K. contributed to the synthesis of catalysts. K.-Y.L. and H.J.K. contributed to the physicochemical characterizations of catalysts. Y.K. and H.-J.C. designed and supervised the research.

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References

1. Tahir, M.; Pan, L.; Idrees, F.; Zhang, X.; Wang, L.; Zou, J.-J.; Wang, Z.L. Electrocatalytic oxygen evolution reaction for energy conversion and storage: A comprehensive review. Nano. Energy 2017, 37, 136–157.
2. Delgado, D.; Minakshi, M.; McGinnity, J.; Kim, D.-J. Co/Mo bimetallic addition to electrolytic manganese dioxide for oxygen generation in acid medium. Sci. Rep. 2015, 5, 15208. [CrossRef] [PubMed]
3. Hansen, H.A.; Man, I.C.; Studt, F.; Abild-Pedersen, F.; Bligaard, T.; Rossmeisl, J. Electrochemical chlorine evolution at rutile oxide (110) surfaces. Phys. Chem. Chem. Phys. 2010, 12, 283–290. [CrossRef] [PubMed]
4. Exner, K.S.; Anton, J.; Jacob, T.; Over, H. Controlling selectivity in the chlorine evolution reaction over RuO2 based catalysts. Angew. Chem. Int. Ed. 2014, 53, 11032–11035. [CrossRef] [PubMed]
5. Reier, T.; Oezaslan, M.; Strasser, P. Electrocatalytic oxygen evolution reaction (OER) on Ru, Ir, and Pt catalysts: A comparative study of nanoparticles and bulk materials. ACS Catal. 2012, 2, 1765–1772. [CrossRef]
6. Xiong, K.; Peng, L.; Wang, Y.; Liu, L.; Deng, Z. In situ growth of RuO2-TiO2 catalyst with flower-like morphologies on the Ti substrate as a binder-free integrated anode for chlorine evolution. J. Appl. Electrochem. 2016, 46, 841–849. [CrossRef]
7. Nazir, R.; Basak, U.; Pande, S. Synthesis of one-dimensional RuO2 nanorod for hydrogen and oxygen evolution reaction: An efficient and stable electrocatalyst. Colloids. Surf. A. 2019, 560, 141–148. [CrossRef]
8. Panic, V.V.; Dekanski, A.B.; Mitric, M.; Milanovic, S.K.; Miskovic-Stankovic, V.B.; Nikolic, B.Z. The effect of the addition of colloidal iridium oxide into sol-gel obtained titanium and ruthenium oxide coatings on titanium on their electrochemical properties. Phys. Chem. Chem. Phys. 2010, 12, 7521–7528. [CrossRef]
9. Petrykin, V.; Macounová, K.; Okube, M.; Mekerje, S.; Krtíl, P. Local structure of Co doped RuO2 nanocrystalline electrocatalytic materials for chlorine and oxygen evolution. Catal. Today. 2013, 202, 63–69. [CrossRef]
10. Lu, A.-H.; Schüth, F. Nanocasting: A versatile strategy for creating nanostructured porous materials. Adv. Mater. 2006, 18, 1793–1805. [CrossRef]
11. Schüth, F. Non-siliceous mesostructured and mesoporous materials. Chem. Mater. 2001, 13, 3184–3195. [CrossRef]
12. Gu, D.; Schüth, F. Synthesis of non-siliceous mesoporous oxides. Chem. Soc. Rev. 2014, 43, 313–344. [CrossRef] [PubMed]
13. Ren, Y.; Ma, Z.; Bruce, P.G. Ordered mesoporous metal oxides: synthesis and applications. Chem. Soc. Rev. 2012, 41, 4909–4927. [CrossRef] [PubMed]
14. Suzuki, N.; Kiba, S.; Yamauchi, Y. Fabrication of mesoporous silica KIT-6/polymer composite and its low thermal expansion property. Mater. Lett. 2011, 65, 544–547. [CrossRef]
15. Klett, F.; Choi, S.H.; Ryoo, R. Cubic $Ia3d$ large mesoporous silica: synthesis and replication to platinum nanowires, carbon nanorods and carbon nanotubes. Chem. Commun. 2003, 17, 2136. [CrossRef]
16. Grewe, T.; Deng, X.; Tüysüz, H. A Study on the growth of Cr2O3 in ordered mesoporous silica and its replication. Chem. Eur. J. 2014, 20, 7692–7697. [CrossRef] [PubMed]

17. Kim, T.-W.; Solovyov, L.A. Synthesis and characterization of large-pore ordered mesoporous carbons using gyroidal silica template. J. Mater. Chem. 2006, 16, 1445–1455. [CrossRef]

18. Verma, M.L.; Minakshi, M.; Singh, N.K. Synthesis and characterization of solid polymer electrolyte based on activated carbon for solid state capacitor. Electrochim. Acta. 2014, 137, 497–503. [CrossRef]

19. Verma, M.L.; Minakshi, M.; Singh, N.K. Structural and electrochemical properties of nanocomposite polymer electrolyte for electrochemical devices. Ind. Eng. Chem. Res. 2014, 53, 14993–15001. [CrossRef]

20. Kim, T.-W.; Kleitz, F.; Paul, B.; Ryoo, R. MCM-48 like large mesoporous silicas with tailored pore structure: facile synthesis domain in a ternary triblock copolymer-butanol-water system. J. Am. Chem. Soc. 2005, 127, 7601–7610. [CrossRef]

21. Cui, X.; Zhou, J.; Ye, Z.; Chen, H.; Li, L.; Ruan, M.; Shi, J. Selective catalytic oxidation of ammonia to nitrogen over mesoporous CuO/RuO2 synthesized by co-nanocasting-replication method. J. Catal. 2010, 270, 310–317. [CrossRef]

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