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Communication

Engineering Ru(IV) charge density in Ru@RuO₂ core-shell electrocatalyst via tensile strain for efficient oxygen evolution in acidic media

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ARTICLE INFO

Article history:

Received 11 November 2019

Accepted 11 December 2019

Published 5 August 2020

Keywords:

Tensile strain

Core-shell structure

Ruthenium oxide

Charge density

Oxygen evolution reaction

Acidic media

ABSTRACT

The design of efficient Ru-based electrocatalysts with high intrinsic activities for acidic water oxidation is highly desirable and challenging for water splitting in proton exchange membrane electrolyzers. Here, for the first time, we engineer the charge density of Ru(IV) by creating tensile strains in the RuO₂ shell of Ru@RuO₂ core-shell nanoparticles, viz. Ru@RuO₂-L. High-resolution spectroscopic characterizations confirm the presence of av. 6% tensile strain in Ru–O bonds, which results in an effective reduction of the Ru(IV) charge density. The resultant Ru^{x+} (4 < x < 5) active sites greatly accelerate the oxygen evolution reaction (OER) in an acidic electrolyte, leading to a remarkably low overpotential of 191 mV at 10 mA cm⁻². These values are lower than those for the benchmark RuO₂ catalyst and are also among the lowest for efficient Ru-based electrocatalysts reported thus far. The specific activity and mass activity are also greatly enhanced 4.2-fold and 17.7-fold compared to those of RuO₂, respectively. The acidic OER activity improvement is ascribed to the lowered adsorption energy of *OOH, owing to the reduced charge density of Ru(IV), and the rapid charge transport owing to the Ru core. Ru@RuO₂-L also demonstrates high feasibility as the anode catalyst for the overall water splitting in acidic media.

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As an abundant and recyclable resource, water can be electrochemically split into clean hydrogen energy and chemical oxygen by an electrolyzer to achieve an environmentally friendly energy cycle [1]. Compared to alkaline electrolyzers, proton exchange membrane (PEM) electrolyzers offer significant advantages, such as higher current density, higher voltage efficiency, lower ohmic losses, and less unfavorable reactions, making them the most promising devices for producing hydrogen energy and oxygen [2]. As one of the semi-reactions of electrochemical water splitting, the oxygen evolution reaction (OER) is a four-electron and four-proton coupled multi-step electrochemical reaction, requiring higher energy to compen-

sate for its slower dynamic processes than hydrogen evolution reaction (HER), which is a two-electron transfer reaction [3]. The high anode potential and harsh corrosive environment in PEM electrolyzers set a high standard for anode electrocatalysts, while the scarcity of highly active and stable anode electrocatalysts limits the wide implementation of PEM electrolyzers [4]. The feasible catalysts used under such conditions are mainly limited to Ru Ir, and their derivatives [5], and it is more desirable to develop RuO₂-based catalysts owing to the low earth abundance and high cost of Ir [6]. Unfortunately, the OER overpotential of commercial RuO₂ electrocatalysts in acidic media is too high, and they are considerably less stable in acidic

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This work was supported by the National Natural Science Foundation of China (51572188, 51822106).

DOI: 10.1016/S1872-2067(20)63543-4 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 41, No. 8, August 2020

media than in alkaline media; thus, they do not meet the requirements for practical applications [7]. Moreover, from a practical perspective, improving the intrinsic activity of noble-metal Ru-based electrocatalysts is always highly desirable to reduce the amounts of catalysts required for practical applications. Therefore, improving the acidic water oxidation electrocatalysis over RuO₂ is urgent.

It has been confirmed that the formation of the active intermediate, *OOH, is the rate-determining step (RDS) for the OER in acidic media. However, the adsorption energy of *OOH is overly strong on the Ru⁴⁺ active sites in RuO₂ [8,9]; consequently, a large overpotential of about 300 mV is required to deliver an OER current density of 10 mA cm⁻² in an acidic electrolyte for commercial RuO₂ catalysts [7]. To reduce the adsorption energy of *OOH on Ru⁴⁺ active sites and reduce the RDS energy barrier, intensive efforts have been devoted to engineering the electronic structure of the Ru⁴⁺ site, including heteroatom doping and preparing Ru-based solid solutions. For instance, it was reported, very recently, that Na-doped Sr_{1-x}Na_xRuO₃ exhibited excellent OER activity in acidic media since the Na doping increased the valence state of Ru⁴⁺, thereby displacing the positive O *p*-band and Ru *d*-band centers, in turn weakening the Ru-adsorbate bonds [10]. Contrarily, it has been well established that the strain effect is an effective strategy for tuning the electronic structure of alloy catalysts [11]. Nevertheless, the formation of a stable strain in RuO₂ without introducing any heteroatoms remains a major challenge, and it would practically be more convenient to modulate the electronic structure of Ru⁴⁺ active sites in RuO₂ and enhance the acidic water oxidation electrocatalysis.

Here, for the first time, we effectively engineer the charge density of Ru⁴⁺ using the tensile strain in the RuO₂ shell of the Ru@RuO₂ core-shell nanoparticles without any heteroatom doping. The engineered catalyst exhibits substantially enhanced intrinsic activity and greatly lowered overpotential for acidic water oxidation, far surpassing the benchmark commercial RuO₂ catalyst. The highly efficient Ru@RuO₂-L electrocatalyst was simply synthesized via a one-step laser irradiation method. X-ray absorption fine structure (XAFS) spectroscopy revealed the presence of av. 6% tensile strain in the Ru–O bonds. High-resolution X-ray photoelectron spectroscopy (XPS) and electron energy loss spectroscopy (EELS) indicate a noticeable increase in the valence state of Ru⁴⁺. The Ru@RuO₂-L catalyst exhibits a very low OER overpotential of 191 mV at 10 mA cm⁻² in an acidic electrolyte, which is among the lowest values reported thus far for efficient Ru-based electrocatalysts that are normally modified with the aid of heteroatoms. Moreover, the specific activity and mass activity of Ru@RuO₂-L are 4-fold and 18-fold higher than those of the commercial RuO₂ catalyst, respectively. When using Ru@RuO₂-L as the anode catalyst for the overall water splitting in the acidic electrolyte, the two-electrode system requires an extremely low applied voltage of 1.45 V to achieve a current density of 10 mA cm⁻². The greatly improved acidic water oxidation activity can be attributed to the tensile-strain-induced reduction of the charge density of Ru⁴⁺. This results in weakened adsorption of *OOH over the Ru^{X+} (4 < X < 5) active sites in Ru@RuO₂-L, conse-

quently accelerating the OER kinetics in the acidic media.

Ru@RuO₂-L nanoparticles were synthesized by laser irradiation of commercial RuO₂ powders (RuO₂-C, Fig. S1) and characterized using a combination of scanning electron microscopy (SEM), transmission electron microscopy (TEM), and X-ray diffraction (XRD). As shown in Fig. 1a, the Ru@RuO₂-L nanoparticles are well dispersed and uniform with an average size of 21.7 nm (inset in Fig. 1a). In contrast, RuO₂-C is irregular with an average particle size of 100–300 nm (Figs. S1b and S1c). According to the TEM image (Fig. S2), the core-shell structure is clearly apparent by the contrast difference, and the diffraction rings in the selected area electron diffraction (SAED) pattern verify the Ru@RuO₂-L catalyst consisting of Ru and RuO₂ (inset in Fig. S2). High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) was employed to analyze the chemical distribution in a single core-shell structure. There are strong characteristic Ru signals that originate mainly from the core of the nanoparticle, while the O signals are mainly distributed on the shell with a thickness of 2–3 nm (Figs. 1c–1e), confirming the Ru@RuO₂ core-shell structure. As displayed in Fig. 1f, the high-resolution TEM (HRTEM) image clearly shows the core-shell structure with a shell thickness of 2–3 nm. Interestingly, the RuO₂ (110) lattice spacing for Ru@RuO₂-L is 0.338 nm, which is larger than that for the RuO₂-C (110) facet (0.318 nm) (Fig. 1g). This preliminarily reveals the existence of tensile strain in the RuO₂ shell. For alloy catalysts, the strain effect is a well-established strategy for tuning the *d*-band centers of metal atoms and for consequently tuning the adsorption energies of the reaction intermediates [12,13]. However, to date, the existence of tensile strain in RuO₂ has not been reported in the literature, and whether or not it would effectively modify the electrical struc-

Fig. 1. (a) SEM image of Ru@RuO₂-L, and the inset displays the particle size distribution. (b–e) HAADF-STEM image (b) and the corresponding EDX elemental maps (c–e) of Ru@RuO₂-L, in which red refers to O and green refers to Ru. (f, g) HRTEM images of Ru@RuO₂-L and RuO₂-C. (h) XRD patterns of Ru@RuO₂-L, Ru@RuO₂-A, RuO₂-A, and Ru@RuO₂-H.

ture of Ru^{4+} and enhance acidic OER activity deserve further investigations. Moreover, the XRD pattern (Fig. 1h) also confirms that $\text{Ru@RuO}_2\text{-L}$ is composed of Ru and RuO_2 .

X-ray absorption spectroscopy (XAS), XPS, and EELS were performed to obtain in-depth information on the bond length and Ru valence state. Fig. S3 shows the X-ray absorption near edge structure (XANES) of the Ru K-edge region of $\text{Ru@RuO}_2\text{-L}$. Commercial Ru metal powder (Ru-C) and RuO_2 powder ($\text{RuO}_2\text{-C}$) were also measured as references. As revealed in the enlarged white-line region of the Ru K-edge (Fig. S3, inset), the white line adsorption energy of $\text{Ru@RuO}_2\text{-L}$ is between Ru-C and $\text{RuO}_2\text{-C}$, implying that $\text{Ru@RuO}_2\text{-L}$ is a mixture of Ru and RuO_2 . This is consistent with the TEM and XRD data. Furthermore, the extended Ru K-edge X-ray absorption fine structure (EXAFS) spectra were recorded to obtain information on the bond length [14]. The corresponding Fourier transformed (FT) radial structure based on the k^2 -weighted EXAFS is displayed in Fig. 2a. The peak at 1.5033 Å for $\text{RuO}_2\text{-C}$ is attributed to the Ru–O bond, while the Ru–O bond length in $\text{Ru@RuO}_2\text{-L}$ is slightly elongated to 1.5953 Å, suggesting av. 6% tensile strain in the Ru–O bond for $\text{Ru@RuO}_2\text{-L}$. XPS was carried out to characterize the surface Ru valence state. As shown in Fig. 2b, the Ru^{4+} $3p_{3/2}$ and $3p_{1/2}$ peaks of $\text{RuO}_2\text{-C}$ are centered at 463.1 and 485.4 eV, respectively. However, the Ru^{4+} $3p_{3/2}$ and $3p_{1/2}$ peaks of $\text{Ru@RuO}_2\text{-L}$ are observed at 464.4 and 486.7 eV, respectively. The shift toward a higher binding energy observed with $\text{Ru@RuO}_2\text{-L}$, compared to the case with $\text{RuO}_2\text{-C}$, implies that the Ru valence state is higher than +4 for the RuO_2 shell of $\text{Ru@RuO}_2\text{-L}$; however, the positive shift is not high enough to reach the Ru^{5+} state [15,16]. Therefore, the Ru valence state for the RuO_2 shell of $\text{Ru@RuO}_2\text{-L}$ should be between 4 and 5, i.e., Ru^{X+} ($4 < X < 5$). Meanwhile, the Ru M-edge EELS signals for $\text{Ru@RuO}_2\text{-L}$ also shifted toward a higher energy loss range relative to $\text{RuO}_2\text{-C}$ (Fig. 2c), suggesting that the valence state of the Ru ions in $\text{Ru@RuO}_2\text{-L}$ is slightly higher than +4, which is in good agreement with the XPS results. The presence of Ru^{X+} ($X >$

4) enhances the OER catalytic activity in acidic media, as reported in many studies [10,17–19].

To thoroughly investigate the reason for the steady existence of tensile strain in RuO_2 , we analyzed the EXAFS data in detail. As shown in Fig. 2a, the Ru–Ru bond length of $\text{Ru@RuO}_2\text{-L}$ is observed to be 2.3930 Å, about 1.3% shorter than 2.4237 Å of the commercial Ru reference, namely Ru-C. The contraction of the Ru–Ru bond reflects the existence of compressive strain in the Ru core. This result is consistent with the reduced $\text{Ru}(101)$ lattice spacing in $\text{Ru@RuO}_2\text{-L}$ (Fig. S4). We speculate that the compressive strain of the Ru core may be the determining factor for the stability of the tensile strain in the RuO_2 shell. The Ru core with compressive strain tends to expand, while the RuO_2 shell with tensile strain tends to shrink. The confrontation between the Ru core and RuO_2 shell is balanced so that the tensile strain in the RuO_2 shell can exist stably.

To further verify the important role of the Ru core in stabilizing the tensile strain in the RuO_2 shell and also explore the correlation between the tensile strain and the presence of Ru^{X+} ($4 < X < 5$), control experiments were carried out. Firstly, the Ru core was removed by annealing $\text{Ru@RuO}_2\text{-L}$ at 800 °C in air for 6 h, and the as-prepared control sample was named $\text{RuO}_2\text{-A}$, in which the Ru core was completely oxidized to RuO_2 after annealing (Figs. 1h and S5). Meanwhile, the EXAFS spectra (Fig. 2a) show that the Ru–O bond length in $\text{RuO}_2\text{-A}$ is the same as that in $\text{RuO}_2\text{-C}$, implying the disappearance of the tensile strain in $\text{RuO}_2\text{-A}$ without the Ru core. Moreover, XPS and EELS data confirm that no peak shifts were observed for $\text{RuO}_2\text{-A}$ compared to $\text{RuO}_2\text{-C}$ (Figs. 2b and 2c), suggesting the absence of Ru^{X+} ($4 < X < 5$) in $\text{RuO}_2\text{-A}$ without the tensile strain. The above results confirm the importance of the Ru core in maintaining the tensile strain in the RuO_2 shell, and also further verify the correlation between the tensile strain and Ru^{X+} ($4 < X < 5$). Furthermore, to eliminate the probability that the 800 °C annealing process results in the disappearance of the tensile strain

Fig. 2. (a) Fourier-transform EXAFS spectra of Ru K-edge for $\text{Ru@RuO}_2\text{-L}$, $\text{Ru@RuO}_2\text{-A}$, $\text{RuO}_2\text{-A}$, $\text{Ru@RuO}_2\text{-H}$, and reference $\text{RuO}_2\text{-C}$, Ru-C. (b) Comparison of the Ru 3p XPS spectra of $\text{Ru@RuO}_2\text{-L}$, $\text{Ru@RuO}_2\text{-A}$, $\text{RuO}_2\text{-A}$, $\text{Ru@RuO}_2\text{-H}$, $\text{RuO}_2\text{-C}$, and Ru-C. (c) Ru M-edge EELS spectra of $\text{Ru@RuO}_2\text{-L}$, $\text{Ru@RuO}_2\text{-A}$, $\text{RuO}_2\text{-A}$, $\text{Ru@RuO}_2\text{-H}$, and $\text{RuO}_2\text{-C}$.

in RuO₂, another control sample, Ru@RuO₂-A, was prepared by annealing Ru@RuO₂-L at 800 °C in nitrogen gas for 6 h. After annealing, Ru@RuO₂-A retains the core-shell structure with the Ru core and RuO₂ shell (Figs. 1h and S6). More importantly, the elongated Ru–O bond length is still maintained as 1.5946 Å, and the shortened Ru–Ru bond length is also retained as 2.3931 Å (Fig. 2a). Therefore, it is strongly evidenced that the existence of the Ru core with 1.3% compressive strain is the main reason for the steady existence of a 6% tensile strain in the RuO₂ shell, even with high-temperature annealing processes. Moreover, for Ru@RuO₂-A, the Ru⁴⁺ 3p_{3/2} and 3p_{1/2} peaks shift toward a higher binding energy and Ru M-edge EELS peaks shift toward a higher energy loss range when compared to the case with RuO₂-C (Figs. 2b and 2c), confirming again that the tensile strain in Ru–O bond leads to the generation of Ru^{X+} (4 < X < 5) in RuO₂. The above experimental results strongly verify that the existence of Ru core plays a vital role in retaining the tensile strain in the RuO₂ shell. Additionally, we synthesized Ru@RuO₂ core-shell nanoparticles via a conventional chemical method (see Experimental Section for details), and the resultant sample is named Ru@RuO₂-H. Ru@RuO₂-H has a morphology and crystal structure similar to those of Ru@RuO₂-L prepared by laser irradiation (Figs. 1h and S7). However, no noticeable strain was found in the Ru–O and Ru–Ru bonds for Ru@RuO₂-H (Fig. 2a). Moreover, the XPS and EELS spectra indicate the absence of Ru^{X+} (4 < X < 5) in Ru@RuO₂-H (Figs. 2b and 2c). Consequently, the results of the control samples strongly support that the tensile strain in the Ru–O bond is responsible for the formation of favorable Ru^{X+} (4 < X < 5) active sites on the shell surface that would benefit the acidic OER activity enhancement [10,17].

Notably, also, the quenching effect of laser irradiation might be the reason for the generation of strains in Ru@RuO₂-L during the preparation process. We assume that, upon pulsed laser irradiation, the commercial RuO₂ powders absorb the laser energy and are heated abruptly, causing the Ru–O bonds to break. During the following rapid cooling process, some O atoms gather to form O–O bonds and subsequently escape as O₂, while the Ru atoms rapidly aggregate to form Ru nanocrystals containing compressive strain. The remaining O and Ru atoms form Ru–O bonds and continue to absorb the next laser pulse energy, resulting in elongated Ru–O bond lengths. Finally, the RuO₂ shell with tensile strain forms outside the Ru core, leading to the Ru@RuO₂ core-shell structure with strains. The unique role of laser irradiation in strain formation is also supported by the control experiments mentioned above, where Ru@RuO₂-H, prepared by a conventional chemical method, does not contain any strain.

Noteworthy, the samples possess oxygen vacancies (Fig. S8), which, however, are not relevant to the presence of the tensile strain in the RuO₂ shell. For instance, RuO₂-C has a higher number of oxygen vacancies than Ru@RuO₂-A (Table S1); however, no strain is found in the former, whereas tensile strain is present in the latter (Fig. 2a). The XPS survey spectra for all the samples are shown in Fig. S9.

Next, we evaluated the acidic OER activity of Ru@RuO₂-L in comparison with those of the control samples using a typical

three-electrode electrochemical system in O₂-saturated 0.5 mol L⁻¹ H₂SO₄ electrolyte. The Hg/Hg₂Cl₂ reference electrode was calibrated with respect to the reversible hydrogen electrode (RHE). The electrodes were prepared by drop-casting a water/isopropanol and Nafion-based ink on a glassy carbon electrode (more details in Experimental Section). Fig. 3a shows the OER linear sweep voltammetry (LSV) curves with *i*R-correction, where the rising current indicates the region where the OER occurs. The Ru@RuO₂-L catalyst exhibits excellent OER activity with a remarkably low overpotential of 191 mV, corresponding to a current density of 10 mA cm⁻², which is considerably lower than those of the control catalysts, e.g., the commercial RuO₂ catalyst (RuO₂-C, 293 mV), as listed in Table S2. In addition, these values are among the lowest reported thus far for efficient Ru-based electrocatalysts (Table S4). Moreover, Ru@RuO₂-L also has the smallest Tafel slope (48.9 mV dec⁻¹), indicating a greatly improved OER kinetics in acidic electrolytes (Fig. 3b). The EIS spectra in Fig. 3c shows that the Ru@RuO₂-L catalyst has the smallest semicircle radius, suggesting the highest charge transfer rate and once more confirming the largely accelerated OER kinetics [20]. Additionally, Ru@RuO₂-L has the highest electrochemical double-layer capacitance (*C*_{dl}) measured by cyclic voltammetry (CV) (Figs. 3d and S10). This suggests the presence of more active sites on Ru@RuO₂-L [21]. Considering the high cost of noble-metal-based electrocatalysts such as RuO₂, improving their intrinsic activities is always highly desirable to reduce the amount of catalysts required to achieve efficient water oxidation for practical applications. To further explore the intrinsic activity, we calculated the specific activity and mass activity of each catalyst at 1.5 V vs. RHE. As shown in Fig. 3e and Table S3, Ru@RuO₂-L has a substantially enhanced specific activity and mass activity, which are 3.8-fold and 8.8-fold higher than those of Ru@RuO₂-H without any strain. Ru@RuO₂-L shows a significant increase in mass activity by nearly 18 times compared to the case with RuO₂-C.

Based on the above electrochemical results, the acidic OER activity order for different catalysts is as follows: Ru@RuO₂-L > Ru@RuO₂-A > Ru@RuO₂-H > RuO₂-A > RuO₂-C. Benefiting from the reduced charge density of the Ru⁴⁺ active sites, i.e., Ru^{X+} (4 < X < 5), due to the tensile strain in Ru–O bonds, Ru@RuO₂-L exhibits a remarkably enhanced acidic water oxidation activity with extremely low overpotential and substantially improved OER kinetics and intrinsic activity. To further provide more evidence for the correlation between Ru^{X+} (4 < X < 5) and the OER activity, we adjusted the laser irradiation energy within the allowed energy range (108–518 mJ) for the laser apparatus, and the as-prepared samples were denoted as Ru@RuO₂-L-a, Ru@RuO₂-L-b, Ru@RuO₂-L-c, and Ru@RuO₂-L-d, corresponding to the laser energies of 108, 185, 250, and 409 mJ, respectively. Subsequently, these samples were subjected to XPS characterization and electrochemical measurements. As seen in Fig. S11, as the laser irradiation energy increases from 108 to 518 mJ, the XPS peak related to Ru⁴⁺ gradually shifts toward a higher binding energy region, indicating that the valence state of Ru⁴⁺ gradually increases with increasing irradiation energy. Meanwhile, the OER activity is also gradually improved as the

Fig. 3. Electrocatalytic OER performance test of the catalysts in O_2 -saturated 0.5 mol L^{-1} H_2SO_4 solution. (a) OER polarization curves of $Ru@RuO_2-L$, $Ru@RuO_2-A$, RuO_2-A , $Ru@RuO_2-H$, and RuO_2-C with the same mass loading. (b) The Tafel plots of $Ru@RuO_2-L$, $Ru@RuO_2-A$, RuO_2-A , $Ru@RuO_2-H$, and RuO_2-C . (c) Electrochemical impedance spectroscopy (EIS) Nyquist plots collected in a frequency range of 0.1– 10^6 Hz. (d) Capacitive current at 1.15 V (vs. RHE) against the scan rate and corresponding C_{dl} values estimated through the linear fitting of the plots. (e) OER specific activity and mass activity corresponding to the kinetic current at 1.5 V (vs. RHE), normalized by the electrochemical surface area (ECSA) of the catalysts. (f) Potential required to reach 5 $mA\ cm^{-2}$ for $Ru@RuO_2-L$ and RuO_2-C measured using chronopotentiometric holds.

Ru valence state increases for the laser-irradiated catalysts (Fig. S12). These results indicate that a high Ru^{X+} ($4 < X < 5$) valence state would result in enhanced OER activity, therefore confirming, once more, that Ru^{X+} ($4 < X < 5$) can enhance the acidic OER activity. The activity enhancements should be ascribed to the reduced adsorption energy of $*OOH$ on the Ru^{X+} ($4 < X < 5$) active site, as reported in the literature [10,17]. In addition, for $Ru@RuO_2-H$ and RuO_2-A , which do not have strains, it was noted that the former exhibits a higher OER activity than the latter, indicating that the Ru core might play an important role in improving the charge transport during the catalytic process. The reduced catalytic performance of $Ru@RuO_2-A$ compared to that of $Ru@RuO_2-L$ is attributed to particle growth and agglomeration during annealing at a high temperature.

Moreover, we used CV cycles and chronopotentiometry technique to evaluate the durability of $Ru@RuO_2-L$ and RuO_2-C . As shown in Fig. S13, for RuO_2-C , the overpotential (at 10 $mA\ cm^{-2}$) dramatically increased from 293 mV at the first cycle to 339 mV at the 1000th cycle. In contrast, $Ru@RuO_2-L$ exhibited a more stable OER performance, with only 7 mV overpotential increase (at 10 $mA\ cm^{-2}$) after 1000 cycles. It can be observed from Fig. 3f that $Ru@RuO_2-L$ has an overpotential increase of 97 mV during the durability test for 20 h to maintain a current density of 5 $mA\ cm^{-2}$, which is much lower than that of RuO_2-C , with an increase of 317 mV. Therefore, $Ru@RuO_2-L$ exhibits

improved OER stability compared to RuO_2-C . The increment in the potential may be attributed to the gradual loss of the RuO_2 catalyst, which is oxidized to soluble RuO_4 dissolved in the electrolyte at a certain voltage, and the spilling of the electrode material during the continuous evolution of O_2 bubbles [22]. In addition, we performed XPS characterization of $Ru@RuO_2-L$ after 1000 CV cycles. As shown in Fig. S14, the Ru 3p XPS spectra do not show observable variation before and after the stability test. Specifically, the peak for Ru^{X+} ($4 < X < 5$) is unchanged after the stability test, indicating that Ru^{X+} ($4 < X < 5$) and the corresponding strain probably remain in the catalyst after the stability test.

To demonstrate the practical applicability of $Ru@RuO_2-L$, it was employed as the anode catalyst along with Pt-C as the cathode catalyst ($Ru@RuO_2-L+Pt/C$) to form a two-electrode system in an N_2 saturated 0.5 mol L^{-1} H_2SO_4 acidic medium to evaluate the overall water splitting performance. A pair of RuO_2-C (anode) and Pt/C (cathode) catalysts were also tested for comparison (RuO_2-C+Pt/C). As revealed in Fig. 4a, $Ru@RuO_2-L+Pt/C$ requires a very low cell voltage of 1.45 V to drive a current density of 10 $mA\ cm^{-2}$. This is much lower than that for the benchmark commercial electrocatalyst (RuO_2-C+Pt/C : 1.56 V). In the durability test for 1000 cycles, $Ru@RuO_2-L+Pt/C$ exhibits considerably better durability with a positive shift of only 12 mV at a current density of 10 $mA\ cm^{-2}$

Fig. 4. (a) Overall water splitting performance of Ru@RuO₂-L+Pt/C and RuO₂-C+Pt/C in N₂-saturated 0.5 mol L⁻¹ H₂SO₄ solution with a two-electrode configuration. The inset shows the cell voltages at a current density of 10 mA cm⁻² of Ru@RuO₂-L+Pt/C and RuO₂-C+Pt/C. (b) Constant current chronopotentiometric stability tests for Ru@RuO₂-L+Pt/C and RuO₂-C+Pt/C for the overall water splitting at a current density of 5 mA cm⁻².

than RuO₂-C+Pt/C with a positive shift of 50 mV (Fig. S15). In addition, Ru@RuO₂-L+Pt/C remains stable at a current density of 5 mA cm⁻² for 20 h of continuous water electrolysis, and the battery voltage only increased by 147 mV (Fig. 4b). Therefore, the Ru@RuO₂-L catalysis shows high feasibility for achieving efficient and long-term use as an anode catalyst for an acid cell dual-electrode electrolysis water system.

In conclusion, we report a highly active OER electrocatalyst for acidic media, i.e., Ru@RuO₂ core-shell nanoparticles with av. 6% tensile strain in the RuO₂ shell (Ru@RuO₂-L), prepared by a simple one-step laser irradiation method. The generation of strain might be correlated to the quenching effect of pulsed laser irradiation. Control experiments confirm the important role of Ru core with av. 1.3% compressive strain in stabilizing the tensile strain in the RuO₂ shell. In addition, control experiments confirm the correlation between the tensile strain in the Ru–O bond and the presence of Ru^{X+} (4 < X < 5). Benefiting from the lowered adsorption energy of *OOH at the Ru^{X+} (4 < X < 5) active sites, Ru@RuO₂-L exhibits excellent OER activity in an acidic medium with an overpotential as low as 191 mV at 10 mA cm⁻², significantly surpassing those of commercial RuO₂ catalysts and most efficient Ru-based catalysts reported in lit-

eratures. Remarkably, the specific activity and mass activity are also substantially enhanced by nearly 5 and 18 times compared to those of RuO₂, respectively. Considerably improved stability is also achieved. Furthermore, as the anode catalyst for the overall water splitting in acidic medium, Ru@RuO₂-L requires a very low cell voltage of 1.45 V to deliver a current density of 10 mA cm⁻², which is much lower than that for the RuO₂-C+Pt/C couple (1.56 V). This work offers a novel strategy to effectively modify the electronic structure of ruthenium oxide electrocatalysts for efficient water splitting in acidic media.

Acknowledgments

The authors are thankful for the supports from the BSRF (Beijing Synchrotron Radiation Facility) for XAFS measurements.

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Graphical Abstract

Chin. J. Catal., 2020, 41: 1161–1167 doi: 10.1016/S1872-2067(20)63543-4

Engineering Ru(IV) charge density in Ru@RuO₂ core-shell electrocatalyst via tensile strain for efficient oxygen evolution in acidic media

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A high-performance OER catalyst was prepared by modulating the charge density of Ru⁴⁺ via the generation of tensile strain in the RuO₂ shell of Ru@RuO₂ core-shell nanoparticles without any heteroatom doping.

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通过拉伸应变调节Ru@RuO₂核壳纳米球中Ru(IV)的电荷密度并应用于酸性环境电解水产氧

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摘要: 水作为一种储量巨大且可循环利用的资源, 可以被电解槽电化学分解为清洁的氢能和化学品氧气, 从而实现环境友好的能源循环. 与碱性电解槽相比, 质子交换膜(PEM)电解槽具有明显优势, 例如更高的电流密度、更高的电压效率、更低的欧姆损耗和更少的不利反应, 使其成为生产氢能和氧气的最有希望的装置. 作为电催化水分解的半反应之一, 氧析出反应(OER)过程是一个四电子和四质子耦合的多步电化学反应, 与双电子转移的氢析出发应(HER)相比, 需要更高的能量来补偿缓慢的动力学过程. PEM电解槽中高的阳极电势和苛刻的腐蚀环境为阳极电催化剂设定了更高的选择标准, 同时由于缺乏高活性和高稳定性的阳极电催化剂, 限制了PEM电解槽的广泛应用. 在这种条件下, 适用的阳极电催化剂主要局限于钌(Ru)和铱(Ir)及其衍生物, 因为其固有的电子结构使之具有较高的催化活性. 然而, 由于Ir的低地球丰度和高成本, 人们更希望开发RuO₂基电催化剂. 遗憾的是, 商业RuO₂电催化剂在酸性介质中的OER过电位仍然过高, 稳定性也比在碱性介质中低得多, 无法满足实际应用的要求. 此外, 从实用角度出发, 研究者始终希望提高贵金属Ru基电催化剂的本征活性以减少实际应用所需的催化剂量. 因此, 迫切需要改性RuO₂基电催化剂以提升其在酸性介质中的析氧反应催化活性.

迄今, 研究已经证实活性中间体*OOH的形成是酸性介质中OER的速率决定步骤(RDS), 但是RuO₂基催化剂中Ru⁴⁺活性位点对活性中间体*OOH的吸附过强, 导致商用RuO₂具有约300 mV的过电势(10 mA cm⁻²). 为了减弱*OOH在Ru⁴⁺活性位点上的吸附能并降低RDS能垒, 研究人员做了大量的试验来调节Ru⁴⁺活性位点的电子结构, 包括杂原子掺杂和制备Ru基固溶体. 应变效应也是调整合金催化剂电子结构的有效策略. 在RuO₂中利用应变来调节Ru⁴⁺活性位点的电子结构进而增强其在酸性介质中的OER催化活性是一种简便的手段, 但是形成稳定的应变而不引入任何杂原子仍然是一个巨大的挑战.

本文首次在不掺杂任何杂原子的情况下, 采用一步激光辐照法合成了高效的Ru@RuO₂-L电催化剂, 利用Ru@RuO₂核壳纳米颗粒RuO₂壳层的拉伸应变, 有效调节了Ru⁴⁺的电荷密度, 其本征活性显著增强, 酸性水氧化的过电位大大降低, 远远低于商用RuO₂催化剂. X射线精细吸收结构(XAFS)显示Ru–O键中存在6%的拉伸应变, X射线光电子能谱(XPS)和电子能量损失谱(EELS)表明Ru⁴⁺的价态明显增加. Ru@RuO₂-L催化剂在酸性电解液中表现出191 mV的极低过电位(10 mA cm⁻²), 这是迄今为止报道的不借助杂原子修饰的高效Ru基电催化剂的最低值, 其面积比活性和质量比活性分别比商用RuO₂催化剂高4倍和18倍. 当使用Ru@RuO₂-L作为阳极催化剂在酸性电解液中进行整体水分解时, 双电极系统只需要1.45 V的极低的外加电压使系统达到10 mA cm⁻²电流密度. 酸性析氧活性的大幅度提高归因于由拉伸应变引起的Ru⁴⁺电荷密度的降低, 从而削弱了*OOH在Ru^{X+} (4 < X < 5)活性位点上的吸附能.

关键词: 拉伸应变; 核壳结构; 钌氧化物; 电荷密度; 析氧反应; 酸性介质

收稿日期: 2019-11-11. 接受日期: 2019-12-11. 出版日期: 2020-08-05.

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基金来源: 国家自然科学基金(51572188, 51822106).

本文的电子版全文由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).