



The Preparation of Iridium-Based Catalyst with Different Melting Point-Metal Nitrate and Its OER Performance in Acid Media

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Abstract. Oxygen evolution reaction (OER) is the main factor limiting the large-scale development of proton-exchange membrane (PEM) hydrogen production. It is urgent to develop catalysts with excellent OER catalytic performance and stability. Herein, several Iridium-based catalysts were prepared by simple mixing and calcination, the OER properties of catalysts with different melting points of nitrates as calcinating additives were investigated. The RbNO_3 treated catalyst displayed a low overpotential(η) of 297.6 mV versus RHE, which is lower than the catalyst calcinated without nitrate (323.8 mV vs. RHE). Moreover, the RbNO_3 treated catalyst displayed good acid stability over 20 h Chronopotentiometric test. The high OER catalytic activity and stability of RbNO_3 treated catalyst may be attribute to the smaller nanoparticle morphology, pure IrO_2 structure and high electrochemical surface area (ECSA), which increase the number of active sites and the intrinsic catalytic activity. This work indicated that the catalyst with excellent OER performance can be obtained by selecting nitrate with moderate melting point as the calcinating additive. Nitrates (like RbNO_3) treated catalyst with excellent catalytic activity and stability has good application prospect in hydrogen production of PEM water splitting.

Keywords: Oxygen evolution reaction · Nitrates · PEM water splitting

1 Introduction

Hydrogen energy [1–3] is a kind of renewable energy, which has the advantages of high energy density, environmental protection and pollution-free, so it has obtained the support of a number of national policies. At present, hydrogen production by proton-exchange membrane (PEM) electrocatalytic water splitting is regarded as a promising

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technical route. However its practical application is influenced by the slow kinetics [4, 5] of the oxygen evolution reaction (OER). Hence, it's urgent to develop catalysts with excellent OER performance.

Among OER catalysts, Iridium components are widely studied because of the good catalytic activity as well as acid stability. There are various IrO₂ preparation method such as Adams Fusion method [6, 7], sol-gel method [8, 9], liquid reduction method [10], template method [11] and so on. Adams Fusion method is a traditional method having the advantages of simple preparation process and low cost, but the catalyst's overpotential prepared by this method is relatively high compared with other method [7]. Traditional Adams Fusion method mixes metal chloride precursor with NaNO₃ and then calcinate at proper temperature, NaNO₃ acts as an oxidation in the formation of new oxides. The presence of chlorine in the precursors can adversely affect PEM, and many studies have shown that chlorine-contained precursor should be avoided in future work to get rid of Cl⁻ contaminations [12]. Catalyst with nano size often shows better catalytic performance. With the increase of calcinating temperature, the grain grows [13, 14]. Research [15] shows that the addition of salt has effect on crystal growth. In consequence, inspired by above researches, several nitrates with different melting points (low melting point nitrate: Fe and La nitrate; middle melting point nitrate: Na and Rb nitrate; high melting point nitrate: Mg and Ba nitrate) were introduced to control grain size. After simple mixing and calcination with Ir black, Iridium based catalysts were prepared.

In this work, we have developed an innovative additive oxidation process that on the one hand effectively inhibits particle size growth during calcinating and on the other hand extends the raw material from harmful chloride precursor to iridium black. The properties of different catalysts were studied by electrochemical measurement, and the reasons for the differences were explored by a series of characterization methods.

2 Experimental

2.1 Catalysts Preparation

The catalysts were prepared by mixed drying and calcination. Firstly, the nitrate and iridium black (Premetek, P40V40) were weighed at a mass ratio of 20:1, after which 20ml deionized water was added for ultrasonic mixing for 30 min. Then the solvent was evaporated and dried, the resulting mixture was placed in a crucible and transferred to a furnace with a temperature control system. The calcinating treatment was performed at 600 °C for 6 h with a heating time of 3 h. The obtained product was centrifuged, washed with deionized water three times, and then dried at 80 °C in a drying oven for 12 h. For comparison, the sample prepared by direct calcination without adding nitrates was used as the contrast.

2.2 Physical Characterization

X-ray diffraction (XRD) data were collected on a Rigaku D/MAX 2500 X-ray diffractometer equipped with a Cu K α source. The morphology and compositions of the samples were examined by scanning electron microscopy (SEM, SU8020) and transmission

electron microscopy (TEM) on a Tecnai G2 F30 configured with scanning transmission electron microscopy (STEM).

2.3 Electrochemical Analysis

The electrochemical performance (activity and stability) was performed in a typical three-electrode system by using CHI 660E instrument. The catalyst ink was prepared by adding 10 mg catalyst, and 100 μL Nafion (Alfa Aesar, D520 dispersion) into 1 mL ethanol and then ultrasonicated for 30 min. A certain amount of ink was loaded on the surface of the pre-polished glassy carbon electrode (GCE, $\varphi 3.0$ mm) or carbon paper for drying, and the load of the catalyst is 0.5 mg cm^{-2} . A catalyst-modified GCE or carbon paper was used as the working electrode, and a Pt wire and a saturated calomel electrode (SCE) electrode were used as the counter and reference electrodes, respectively. A 0.5 M H_2SO_4 solution was chosen as the electrolyte, and oxygen was bubbled into the electrolyte for at least 30 min to reach saturation before testing. The saturated calomel electrode was calibrated by the reversible hydrogen electrode (RHE), giving their conversion equation: $E(\text{RHE}) = E(\text{SCE}) + 0.059\text{PH} + 0.24 \text{ V}$. The current densities are normalized by the geometric area.

3 Results and Discussion

3.1 Structural Characterizations

Figure 1 shows the X-ray diffraction (XRD) patterns of the nitrate treated catalysts and the contrast. As can be seen from the figures, different phases were formed after calcinating with nitrates with different melting point ranges. As the temperature rises, the crystalline water is removed first at a relatively low temperature and then the decompose of nitrate occurs, the melting point of anhydrous nitrates is shown in the Table 1. As for the NaNO_3 and RbNO_3 treated catalyst and the contrast, the diffraction peaks correspond well to IrO_2 phase (PDF No. 43-1019, tetragonal, $P4_2/mnm$, and $a = b = 4.4983 \text{ \AA}$, $c = 3.1544 \text{ \AA}$). Additionally, with the addition of nitrates, XRD diffraction peak widened. As for low melting point $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, IrO_2 was observed, but the main phase is Fe_2O_3 for $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ treated catalyst and $\text{La}(\text{OH})_3$ for $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ treated catalyst. For high melting point nitrates, $\text{Ba}(\text{NO}_3)_2$ treated catalyst contains IrO_2 and $\text{BaIrO}_{2.73}$ phase, and $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ treated catalyst has IrO_2 and Ir phase. The XRD results proved that different structure may be formed by introducing different melting point nitrate. By introducing nitrates with appropriate melting points, pure IrO_2 can be synthesized.

Table 1. Melting points

	$\text{Fe}(\text{NO}_3)_3$	$\text{La}(\text{NO}_3)_3$	NaNO_3	RbNO_3	$\text{Mg}(\text{NO}_3)_2$	$\text{Ba}(\text{NO}_3)_2$
Melting point ($^\circ\text{C}$)	47.2	40	306.8	310	648	592

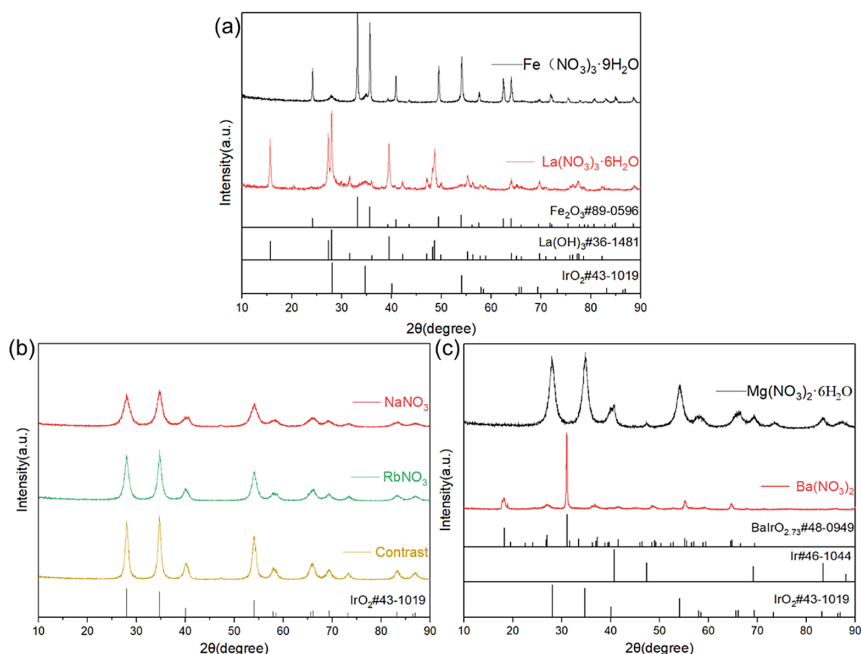


Fig. 1. X-ray diffraction (XRD) patterns of the catalysts.

The SEM images of the synthesized catalysts are shown in Fig. 2. As can be seen from the figures, the contrast showed a nanoparticle morphology. After adding sodium nitrate and rubidium nitrate with moderate melting points, the size of the particles is reduced. In order to further explore the morphology of catalyst, TEM and HRTEM images are shown in Fig. 3. Same as the morphology that observed by SEM, NaNO_3 , RbNO_3 treated catalyst and the contrast has the morphology of nanoparticle, the average particle size of RbNO_3 and NaNO_3 treated catalyst is about 8 and 11 nm, which is smaller than the contrast (about 16 nm). The HRTEM images of the two catalysts revealed a lattice fringe spacing of 0.318 nm, which correspond to the (1 1 0) plane of IrO_2 , which further verified the formation of pure IrO_2 .

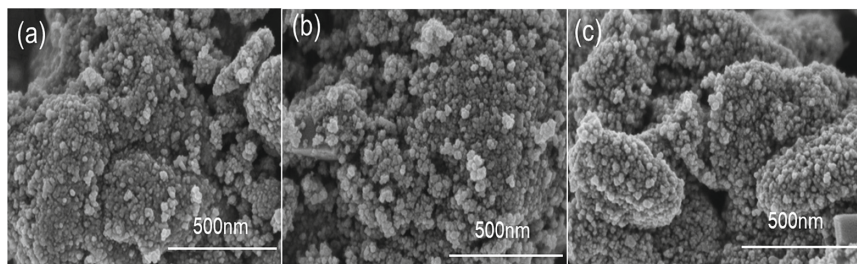


Fig. 2. SEM images of the catalysts. (a) NaNO_3 , (b) RbO_3 , (c) Contrast.

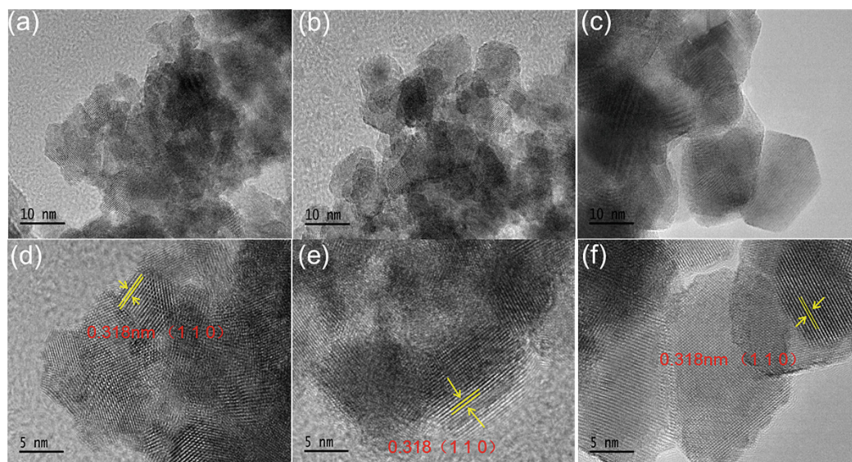


Fig. 3. TEM and HRTEM images of the catalysts. (a, d) NaNO_3 , (b, e) RbNO_3 , (c, f) Contrast.

3.2 Electrochemical Characterizations

To investigate the OER performance, the catalysts treated with several nitrates and the contrast were applied as anodic materials in a three-electrode system in 0.5 M H_2SO_4 . The mass loading of all samples is 0.5 mg cm^{-2} . The OER activities of all catalysts were evaluated by LSV with 85% iR -compensation. As shown in Fig. 4(a), catalyst treated with RbNO_3 displayed a low overpotential(η) of 297.6 mV at 10 mAcm^{-2} , which is lower than that of contrast (323.8 mV). Figure 4(b) gives the OER activity at 1.55 V (vs. RHE), the current density of RbNO_3 treated catalyst is the highest, about 3 times higher than that of the contrast one. And Nitrates of Fe and La have almost no catalytic performance, which may be because the calcinated material is basically oxide or hydroxide.

Tafel slope is a vital parameter for evaluating catalytic activity, as can be seen in Fig. 4(c) (the data is obtained from the LSV plots), these catalysts can be roughly divided into two classes according to the tafel value. Different tafel slope indicates that the catalyst has different rate-determining step (RDS) [16]. The contrast and RbNO_3 treated catalyst have a tafel slope approach 40 mV/dec, the NaNO_3 treated catalyst has a tafel slope about 60 mV/dec. The RbNO_3 treated catalyst's slope is much lower, which indicates a fast reaction kinetics. Moreover, cyclic voltammetry (CV) curves were constructed at different scan rate to obtain double-layer capacitance (C_{dl}), further evaluate electrochemical surface area (ECSA). RbNO_3 treated catalyst has a larger C_{dl} (73.32 mF cm^{-2}) than the contrast (23.52 mF cm^{-2}), implying the RbNO_3 treated catalyst has more active sites [17]. Due to that ECSA is a parameter to reflect intrinsic activity of the catalyst, it can conclude that RbNO_3 treated catalyst has a larger intrinsic catalytic area. Catalysts prepared with nitrates at different melting points showed different OER catalytic performance, RbNO_3 and NaNO_3 with moderate melting points are more superior, probably because they really act as calcinating aids at the calcinating temperature of $600 \text{ }^\circ\text{C}$.

In addition to electrocatalytic activity, stability is another crucial parameter to evaluate the performance of the catalyst. The stability of RbNO_3 treated catalyst and the

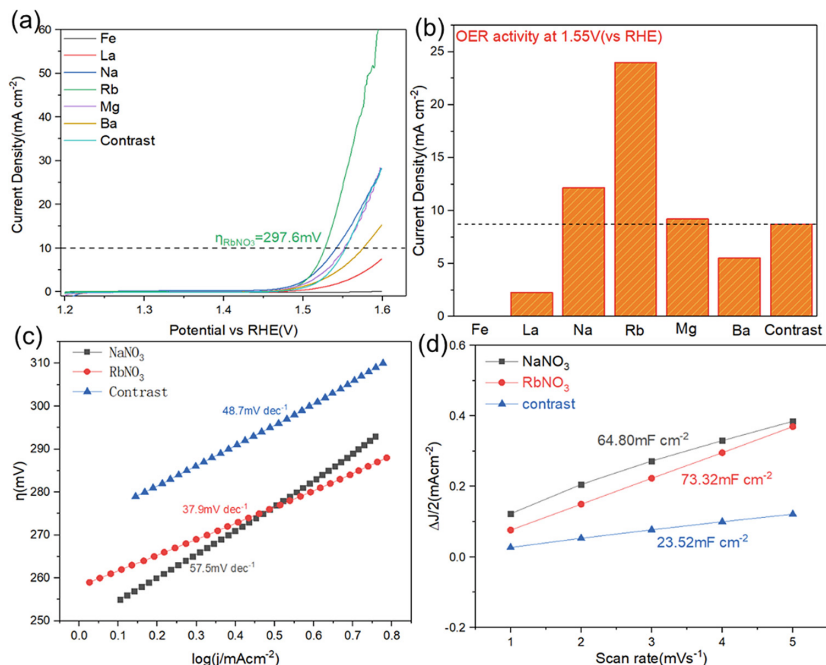


Fig. 4. Electrocatalytic properties of the catalysts (a) a LSV curves in 0.5 M H_2SO_4 solution with 85% iR-compensations. (b) OER activity at 1.55 V versus RHE. (c) Tafel plots obtained from lsv curves. (d) C_{dl} calculated from the obtained CV curves.

contrast were recorded by a chronopotentiometry technique. As can be seen in Fig. 5, the RbNO_3 treated catalyst is extremely stable during the 20 h test at 10 mAcm^{-2} , having a smaller voltage rise rate than the contrast. Chronopotentiometry test results indicated that the RbNO_3 treated catalyst has a good stability in acid media.

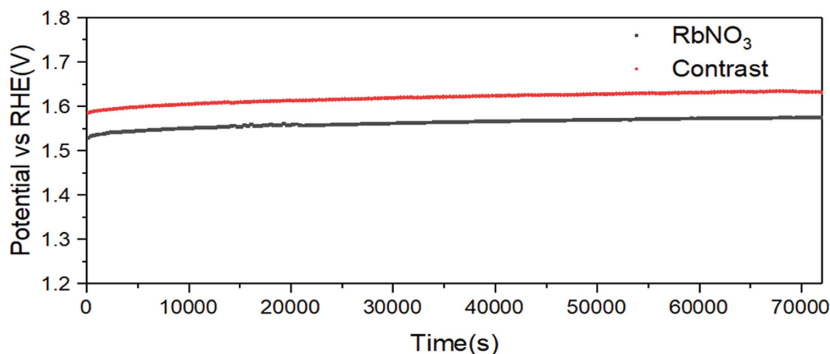


Fig. 5. Chronopotentiometric stability for RbNO_3 treated catalyst and the contrast (without iR compensations).

4 Conclusion

To summarize, we synthesized Iridium-based catalyst by introducing several nitrates with different melting point. The simple mixing and calcinating process makes the preparation of iridium-based catalysts easier for industrial operation. By introducing different melting point nitrates, different crystal structure characteristics were produced, which affected the performance of OER. The results revealed that the as-prepared catalysts exhibited different OER catalytic activity. The addition of moderate melting point nitrates facilitated the formation of pure IrO₂, achieving a low overpotential, especially for RbNO₃ ($\eta = 297.6$ mV vs. RHE). Meanwhile, RbNO₃ treated catalyst showed a long-term stability of 20 h. Sufficiently good catalytic activity and stability of RbNO₃ treated catalyst may attribute from the smaller nanoparticle morphology and high ESCA. This work put forward an innovative chlorine-free method to prepare high OER performance iridium-based catalyst, which can be well used in the acid media like PEM water splitting and other energy device applications.

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