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Research Progress of Ir and Ru-based Electrocatalysts for Hydrogen Production from PEM Acidic Water Electrolysis

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Abstract: PEM acid water electrolysis is the most prospective hydrogen production method in the terms of water electrolysis, which has garnered widespread attention due to its advantages of high current density, low ohmic impedance and high gas purity compared with alkaline water electrolysis. However, it has the serious problem of slow kinetics and high reaction barrier, and the key to overcoming this problem lies in finding a suitable catalyst. Although the best catalysts are Ir and Ru-based noble metal catalysts, they also have serious dissolution and defect problems under acid electrolysis conditions, so the development and synthesis of efficient electrocatalysts is essential to advance the development and industrialization of acid PEM water electrolysis. In this paper, we summarize the research progress of Ir and Ru-based catalysts for acidic electrolysis with excellent performance in last ten years, discuss them from the perspectives of element, oxide and alloy, and finally put forward our own insights and views on the synthesis and design of catalysts in the future.

Keywords: Noble Metal Electrocatalysts, PEM Acidic Water Electrolysis, Catalyst Design and Synthesis, Hydrogen Production

1. Introduction

With the rapid depletion of fossil fuels and growing climate concerns.,[1] transitioning to cleaner energy sources is critical for sustainable development. [2] Hydrogen, as an ideal energy carrier, offers an environmentally friendly alternative. [3-6] of all the hydrogen production methods, hydrogen production by water electrolysis is currently considered the most promising way to produce hydrogen due to its advantages in environmental friendliness and efficiency. [7-10] Among the many water electrolysis technologies, acidic electrolyzed water (PEM) has garnered widespread attention due to its superiorities of high current density, low ohmic impedance, low operating temperature, and high gas production purity. [11-13] The core reactions of water electrolysis to hydrogen include hydrogen evolution (HER) at the cathode and oxygen evolution (OER) at the anode [14-16]. In this process, the performance of the catalyst directly dominates the efficiency of hydrogen production through electrolysis of water, among which the noble metal catalyst Ru and Ir are widely used because of their efficient catalytic performance. However, under the long-term operation of high current density, precious metals and their oxide catalysts also face serious stability dissolution problems [17]. Therefore, finding a potent electrocatalyst in acidic electrolyte is the key to current research. In this paper, we summarize the research progress in the field of water electrolysis in last ten years, focusing on the synthesis and application of noble metal catalysts under acidic conditions, so as to provide reference and insights for the future application development in this field.

2. Iridium-based catalysts

2.1. Elemental iridium catalyst

Iridium has the best stability among all precious metals, but its scarcity seriously hinders the development and utilization of iridium catalysts, so decreasing the Ir concentration while ensuring the performance of the catalyst is a popular research direction at present [18].

The most commonly used method is the design and synthesis of nanocatalyst materials. For example, the amorphous Ir nanosheets (IrNSs) prepared by WU et al. have an overpotential of only 255 mV and a Tafel slope of only 40 at a current density of 10 mA/cm^2 (Fig. 2). In terms of stability, the degradation of the activity of amorphous Ir NSs after 5000 CV cycles is negligible, and it has extremely strong durability. [19] Li et al. prepared ultrafine iridium nanoparticles (1.6 nm)/carbon catalysts (Ir NPs/C). In the case of HER, the overpotential can be 13,57 mV at current densities of 10 and 100, respectively (Fig. 1(a)), and the Tafel slope is also only 28 mV dec-1. and extremely stable at 25 mV for 12 h (Fig. 1(b)). In terms of acidic OER, the catalyst requires minimum overpotentials of 361 and 400 mV to achieve current densities of 10 and 20 mA cm^{-2}, respectively, and the Ir NPs/C catalyst exhibits very high mass activity of up to 5.9 and 30 A mg^{-1} at overpotentials of 350 and 450 mV, respectively, compared to commercial IrO_2 catalysts, which are 983-fold and 478-fold, respectively [20].

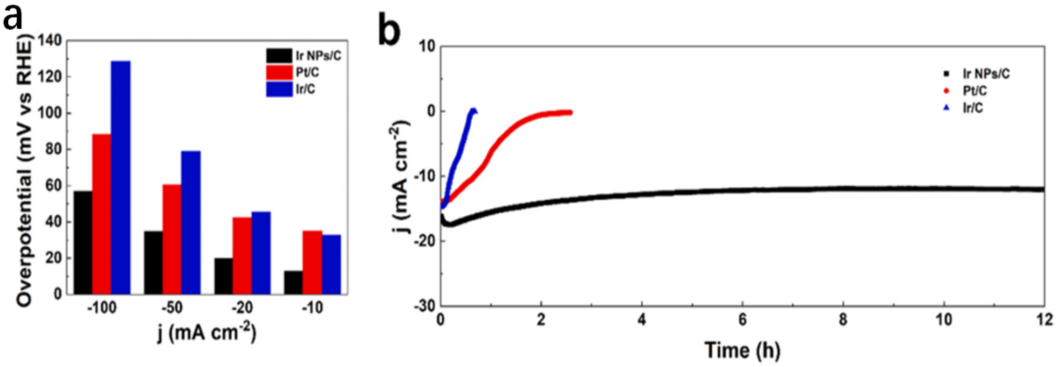

Figure 1: Performance and stability of Ir NPs/C

Improving the dispersion of Ir atoms and increasing the reactivity of catalysts is also an extremely effective strategy,which could greatly reduce the amount of Ir used and significantly increase the mass activity of the catalyst. [21] Zhu et al. synthesized a spinel phase Co_3O_4 (Ir-Co_3O_4) with uniformly dispersed Ir. The overpotential of the catalyst is only 236 mV at 10 mA/cm^{-2} current density in the test, (Fig. 2(a)) and the Tafel slope is only 526 mV/dec^{-1} (Fig. 2(b)). What's even more striking, Ir- Co_3O_4 can be stabilized for 30 hours at an experimental conditions of 10mA/cm^{-2} and shows excellent stability. CV scan measurements showed that isolated Ir unit points were able to activate spinel Co oxide more persistently in harsh OER environments (Fig. 2(d)). Later studies further showed that leaching preferentially occurs at the Co species in Ir- Co_3O_4, but that the dispersion of a single site of Ir during the OER reaction attenuates the dissolving effect of carrying Co_3O_4, hence Ir-Co_3O_4 has better acidic OER stability than ordinary catalysts [22].

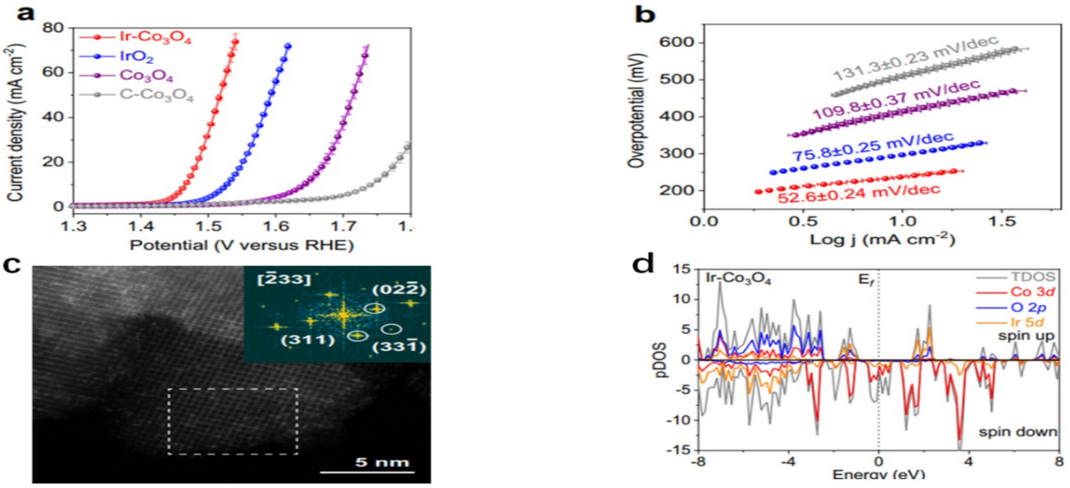

Figure 2: Structure and properties of Ir-CO3O4

2.2. Iridium oxide catalyst

Not only can Ir be used as an efficient acid catalyst, but IrO$_2$ and other Ir-based oxides also have good catalytic activity in acidic media.

A novel 3R-phase IrO2 material was successfully developed by Fan et al., which exhibits an extremely low overpotential of only 188 mV at a current density of 10 mA/cm² (Fig. 3(b)), which is significantly lower than that of the traditional rutile IrO2 (387 mV). In an acidic electrolyte environment, the 3R-phase IrO2 material is able to maintain a stable operating state at a current density of 10 mA/cm² for up to 511 hours, during which time its overpotential offset is only about 30 mV (Fig. 3(c)), thus demonstrating outstanding performance in terms of electrochemical stability and durability.[23]

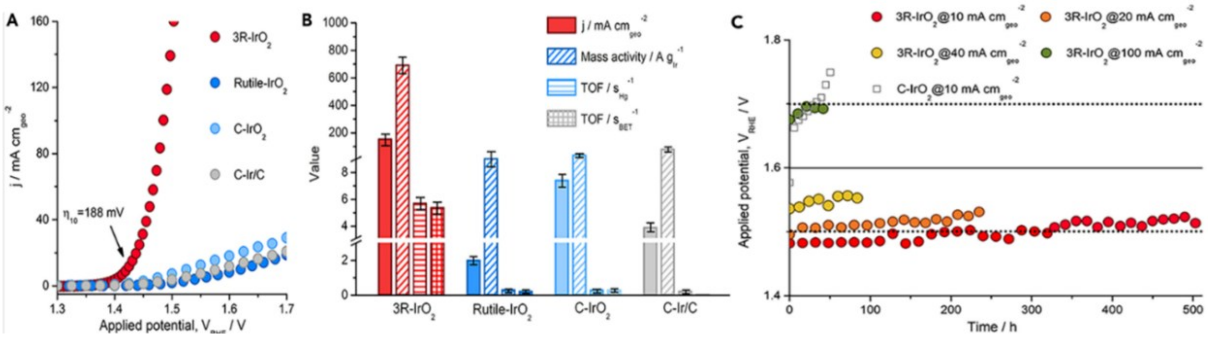

Figure 3: Performance and stability of 3R phase IrO2

The Ir-doped $A_2Ru_2O_7$ in pyroxene materials enhances the RuO_6-IrO_6 interaction through O-A-O bonds, which significantly improves the catalytic performance. The $Y_2Ru_{1.2}Ir_{0.8}O_7$ synthesized by Liu's team exhibited a low overpotential of 220mV at 10 mA/cm² and was stable for 2000 hours, which was attributed to the low oxidation state of the Ir-O/Ru-O bond, which promoted OOH* generation and enhanced RuO_x-IrO_x synergy[24]. In addition, the $Sr_7Ir_6CoO_x$ prepared by Zhao et al. had an overpotential of 245 mV under the same conditions, and its mass activity was better than that of $SrIrO_x$ and commercial IrO_2, and its stability was excellent at 200 mA/cm², and the performance degradation rate was as low as 0.21 mV/h [25].

2.3. Iridium-based alloy catalysts

Alloying can precisely modulate the electronic band structure and surface physicochemical properties of reactive metals, and is also an exceptional method to improve the intrinsic catalytic activity of metals.

Pi et al. have innovatively prepared a carbon-based supported highly diffuse iridium-nickel nanocluster (IrNi NCs) catalyst, which exhibits extraordinary catalytic activity in the processes of oxygen evolution reaction (OER) and hydrogen evolution reaction (HER). Specifically, in the electrochemical environment of 0.5 M H2SO4, IrNi NCs only need to apply a potential of 1.58 V to drive a current density of 10 mA cm^{-2}. Furthermore, in the stability test of 0.1 M HClO4, the current density maintenance rate of IrNi NCs after continuous electrolysis for 10 hours under the condition of constant 5 mA cm^{-2} current density is excellent, which is significantly higher than that of Ir NCs catalysts (about 230%), and is nearly 20 times higher than that of commercial platinum-carbon catalysts (Pt/C), which fully verifies its excellent electrochemical durability. [26].

The high-performance W-Ir-B alloy catalyst developed by Li et al. exhibited excellent catalytic activity with an overpotential of 291 mV at a current density of 10 mA/cm^2 (Fig. 4(a)) and an increase of 497 mV at 2 A/cm^2 and a Tafel slope of 78 mV dec^{-1} (Fig. 4(b)). It is stable for more than 120 hours at a current density of 100 mA/cm^2 and ultra-stable after 800 hours of continuous testing, with great application potential (Fig. 4(c)) [27].

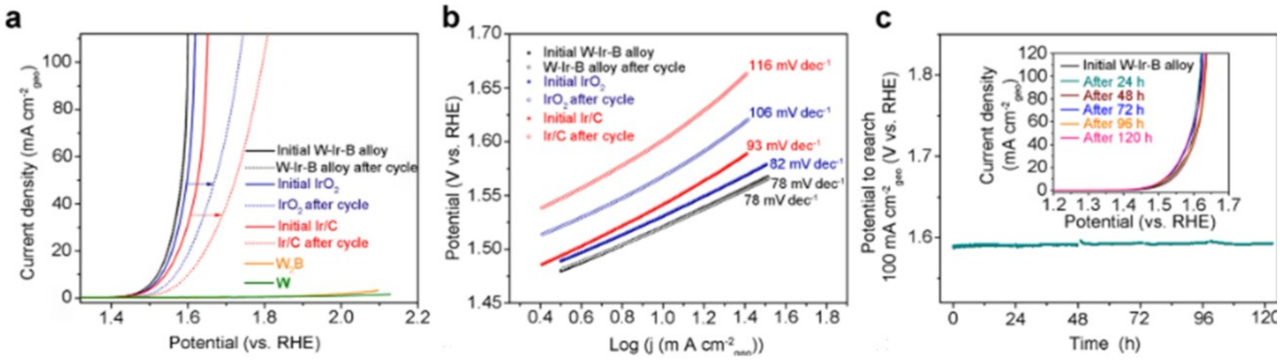

Figure 4: Performance and stability of W-Ir-B alloys

3. Ruthenium-based catalysts

3.1. Elemental ruthenium catalyst

Ruthenium (Ru) is the most catalytically active metal, and its reserves are richer than iridium, and its price is lower than that of Ir, making it an ideal electrocatalyst [28]. However, Ru is very easy to be corroded under acidic conditions, and Ru atoms are prone to peroxidation at high potential to form RuO4 or H2RuO5, resulting in a decrease in activity. [29] At present, the research on elemental ruthenium catalysts is mainly similar to the two major directions of elemental iridium catalysts.

Hu et al. designed a hybrid amorphous/crystalline FeCoNi LDH-supported stable single-ruthenium atom catalyst (Ru SAs/AC-FeCoNi), with an OER overpotential as low as 205 mV at 10 mA cm^{-2} and a Tafel slope of 40 mV dec^{-1}, which is better than Ru SAs/C-FeCoNi, AC-FeCoNi and RuO2(Fig. 5(a)(b)). DFT calculations revealed that Ru atom was the active site with the weakest OH* adsorption energy, and the OER path was optimized (Fig. 5(c)). The catalyst exhibited virtually no degradation of activity during a 48-hour stability test [30].

Kong et al. successfully prepared independent two-dimensional (2D) ruthenium nanosheets through advanced synthesis strategies. The new 2D ruthenium nanosheets exhibit excellent performance in OER, with an overpotential of only about 20 mV at a current density of 10 mA mg^{-1}, which is much lower than conventional ruthenium powder and commercial platinum (Pt) catalysts. At the same time, the electrochemical impedance spectroscopy (EIS) test results show that the interfacial charge transfer resistance of 2D ruthenium nanosheets is much lower than that of commercial Pt catalysts, which provides strong support for their application in electrochemical water splitting reactions [31].

In addition, Lin et al. reported a ruthenium-based electrocatalyst (Ru/MnO2) supported on a crystalline α-MnO2 support. The catalyst also performs well in OER, especially at a current density of 10 mA cm^{-2}, with an overpotential of only 161 mV and a Tafel slope as low as 29.4 mV/dec. Through systematic research, they found that the intrinsic OER activity of ruthenium atoms in Ru/MnO2 was significantly improved by more than 600 times compared with traditional RuO2 catalysts. In terms of stability evaluation, Ru/MnO2 also showed excellent performance, and after 200 hours of continuous operation at a current density of 10 mA cm^{-2}, the overpotential increased, but the degradation amplitude was relatively small, and the overall stability was good [32].

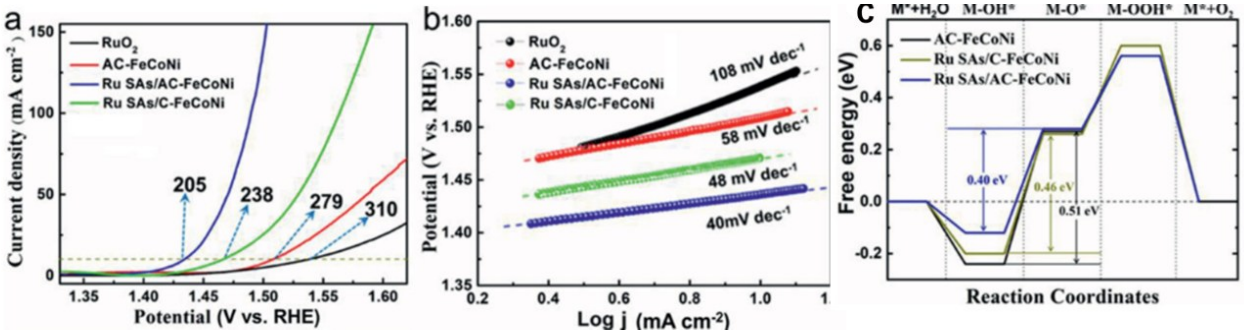

Figure 5: Correlation performance and stability of Ru SAs/AC-FeCoNi

3.2. Ruthenium-based oxide catalysts

Not only Ru has good catalytic activity, but its oxide also has excellent acidic catalytic activity. For example, Zhao's team synthesized ultrathin RuO2 nanosheets (RuO2 NSs) with a low overpotential of 199 mV and a Tafel slope of 38.2 mV dec^{-1} at a current density of 10 mA/cm^2 and a load of 125 μg/cm^2 in the OER reaction (Fig.6(a)). DFT analysis revealed that the Ru vacancies on the surface of RuO2 NSs optimized the binding energy of O and OOH intermediates, and significantly improved the performance of OER. In the stability test, RuO_2 NSs showed limited overpotential increase after 6 hours of testing at a current density of 1 mA/cm^2, and the morphology was well maintained, and it also showed high stability at 10 mA/cm^2(Fig.6(b)) [33]. The Ru@V-RuO2/C HMS electrocatalyst prepared by Li et al. has an overpotential of only 176 mV at a current density of 10 mA/cm^2 in 0.5 M H_2SO_4 dielectric, which is better than that of commercial RuO_2 at 277 mV. Its Tafel slope of 45.6 mV/dec is also lower than that of RuO_2 at 104.9 mV/dec. After 5000 cycles, the performance of the catalyst has little attenuation, and the stability of continuous electrolysis is good for 15 hours [34].

Wu et al. reported a Ni-RuO2 catalyst. It exhibits a low overpotential of 214 mV at 10 mA/cm^2, which is better than that of RuO2, with a Tafel slope of 42.6 mV/dec. The catalyst has the potential to stabilize water electrolysis for more than 1000 hours at 10 mA/cm^2 and when combined with the Pt/C catalyst in the PEM electrolyzer, it has the potential to stabilize water electrolysis for more than 1000 hours at 200 mA/cm^2(Fig.6(c)). Ni doping enhances lattice stability.[35] Liu et al. reported an Nb-stable RuO_2 catalyst, $Nb_{0.1}Ru_{0.9}O_2$. The catalyst rhas an overpotential of only 204 mV at 10 mA/cm^2 and a Tafel slope of 47.9 mV/dec. The 200 mA/cm^2 constant current test lasted for 360 hours, and the potential attenuation was only 9 mV, which was much lower than the attenuation rate of conventional Ru-based catalysts.[36]

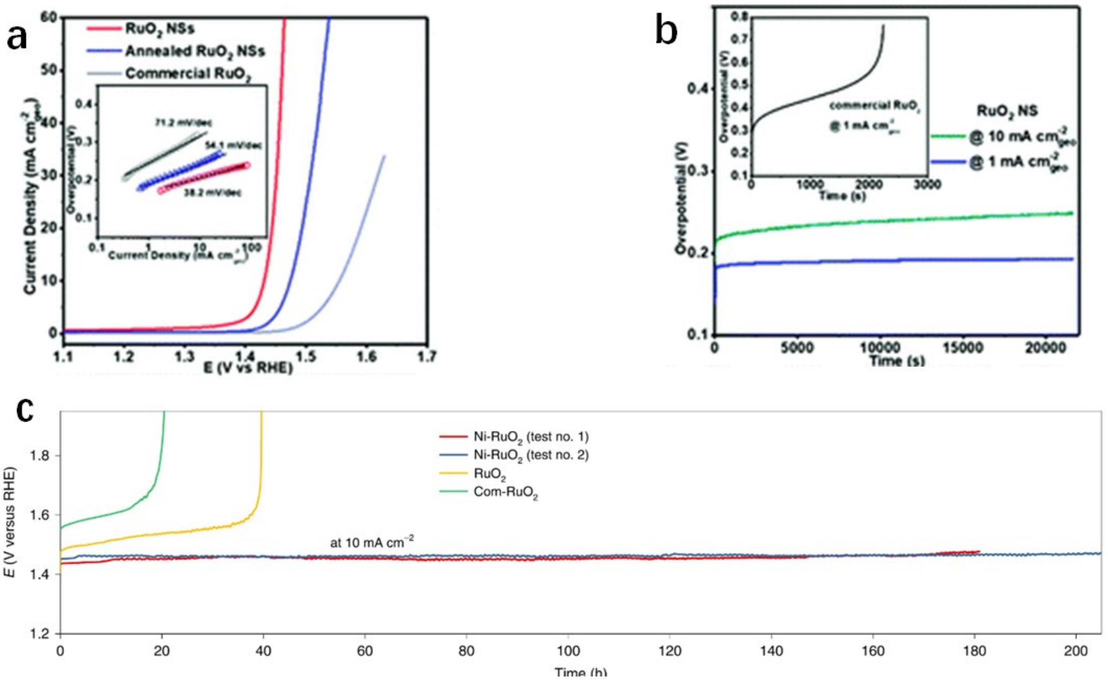

Figure 6: Catalytic performance of a,b RuO2 NSs, c excellent stability of Ni-RuO2

3.3. Ruthenium-based alloy catalysts

Ru is also frequently alloyed with other transition metals to improve the catalytic activity and stability of the catalyst. At present, the transition metals commonly alloyed with Ru are Ni, Co, Fe, Cu, Mn and Mo [37-38].

The Ru_1-Pt_3Cu catalyst synthesized by Yao et al. exhibited a low overpotential of 220 mV at a current density of 10 mA/cm², which was significantly lower than that of PtRu NPs and the corresponding PtCu catalysts (Figure 8(a))., revealing that Ru embedded in the Pt-Cu alloy promoted OER activity. During the 28-hour stability test, Ru1-Pt3Cu remained nearly constant (Figure 8(b)). The results show that the Pt-Cu alloy inhibits the excessive transfer of electrons from Ru to the oxygen-containing ligand, thereby enhancing the stability of the catalyst. [39]

Zhang et al. reported an electrocatalytic Mo@Ru-3 of Mo-doped hexagonal tightly packed Ru. The catalyst has excellent performance in HER, with an overpotential of 30.5 mV at 10 mA/cm², a Tafel slope of 36.4 mV/dec, and good stability after 5000 CV cycles and 10 hours of electrolysis test (Figure 8(d)) [40]. Lee et al. synthesized a superior $Co_{72}Ru_{28}$ catalyst with a very low overpotential of 26.4 mV at a current density of 10 mA/cm^2 and exhibited higher mass activity than other reported Ru-based catalysts. In terms of stability, at 0.5 M H_2SO_4, after 5000 CV cycles, $Co_{72}Ru_{28}$t has only a 5.7 mV increase in potential, and showed only a slight increase in overpotential (27-35 mV) after 50 hours of operation at a current density of 10 mA/cm^2 (Figure 8(d)), representing its excellent durability [41]

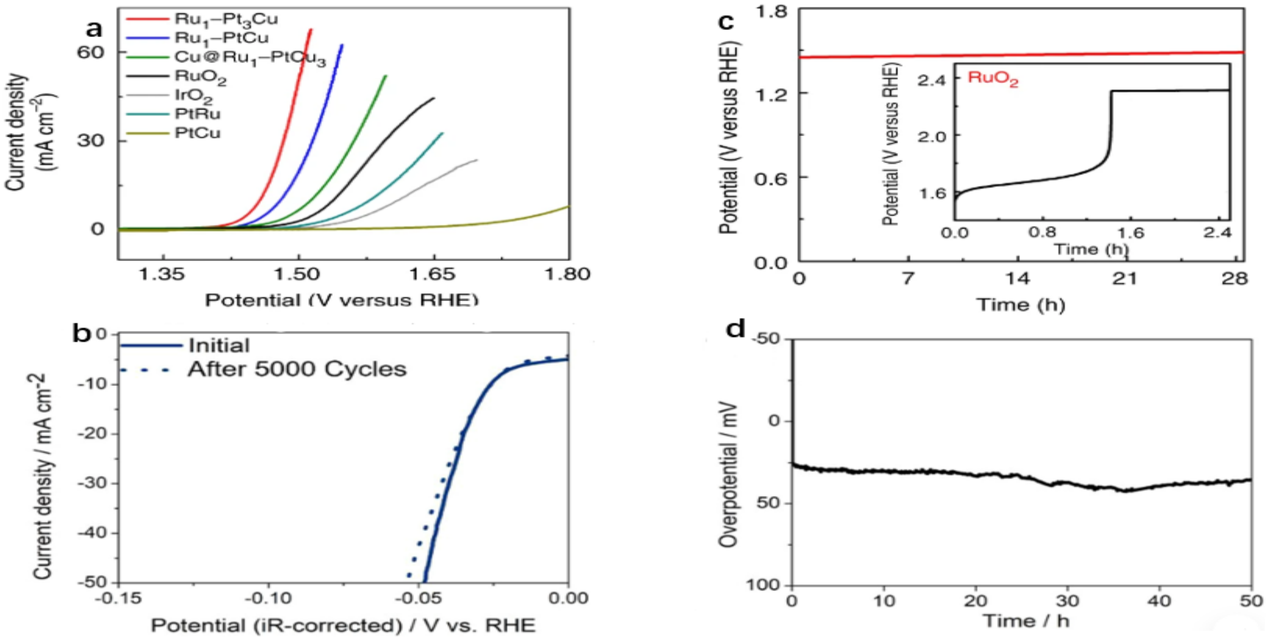

Figure 8: (a), (b) Performance of Ru1-Pt3Cu. (c), (d), Co-Ru performance and stability

4. Conclusion

Efficient and stable electrocatalysts play a pivotal role in the production of hydrogen from water electrolysis by acid PEM. In this paper, we briefly summarize the research progress of precious metal Ru and Ir-based catalysts in last ten years, discuss the synthesis design of Ir-based and Ru-based catalysts from three main aspects, and introduce the synthesis strategies of related catalysts. At present, a major breakthrough has been made in the research of acid water electrolysis catalysts, which can be operated under industrial conditions in laboratory tests. In the future, the research of catalysts should achieve stable operation in a higher current density and more demanding acidic environment, so as to accelerate the process of industrialization. However, there are still many challenges and problems that need to be solved urgently, so I put forward some insights on the future development of acid water electrolysis catalysts, hoping to provide some reference and inspiration for researchers.

First of all, current testing does not allow for a comprehensive and accurate assessment of catalyst performance. Therefore, researchers should explore the performance of catalysts in more depth from many aspects. A wider range of parameters such as ECSA, TOF, MA and other parameters are used to assess the performance of catalysts. and the use of more advanced characterization detection techniques. Such as XPS, XAS, infrared spectroscopy, Raman spectroscopy, etc., with the help of these technologies, we can better detect the transient changes of catalysts in real time, so as to better elucidate the catalytic reaction mechanism.

Second, the interface between the catalyst and the electrolyte is not yet well understood. Under the condition of acidic electrolysis of water, the surface of the catalyst is very likely to dissolve and collapse, which makes the surface structure of the catalyst evolve and greatly change the performance of the catalyst. Therefore, researchers should pay attention to the interface effects in the reaction process, deepen the study of the dissolution mechanism of the catalyst and the interaction between the catalyst and the test environment, so as to design better acid electrocatalysts.

Finally, the current catalyst structure is limited, which severely limits the synthesis design of more efficient catalysts. Therefore, researchers need to explore more strategies to expose the active sites of catalysts. For example, new nanostructures, one-dimensional three-dimensional structures and other new catalytic structures. In addition, choosing the right catalyst load, such as metal-organic frameworks (MOFs), is also an effective strategy.

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