

Progress of ammonia electro-oxidation catalysts for direct ammonia alkaline fuel cells

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Abstract. At present, hydrogen fuel cells are one of the effective means to solve energy and environmental problems, but the problem of hydrogen storage and transportation is difficult to break through. Ammonia is a carbon-free hydrogen-rich compound, which also has the advantages of high bulk density and easy storage and transportation, and is an ideal fuel to replace hydrogen as a battery. However, at present, the preferred ammonia electro-oxidation catalyst for direct ammonia alkaline fuel cells is still platinum, and its expensive price is the main problem that hinders the wide application of direct ammonia alkaline fuel cells. Therefore, the design of low-cost and high-efficiency catalysts is a necessary task for commercializing direct ammonia fuel cells. In this paper, we firstly review the progress of researchers in ammonia electrooxidation mechanism in recent years, focus on reviewing the current research status of Pt catalysts and non-Pt catalysts for direct ammonia alkaline fuel cells, and finally suggest future research approaches to address the existing problems, aiming to provide ideas for designing more efficient, stable and cheap ammonia electrooxidation catalysts in the future.

Keywords: Ammonia Electro-oxidation Catalyst, Fuel Cell, Ammonia Fuel.

1. Introduction

In recent years, countries are making great efforts to develop clean energy to overcome the problems of rising global average temperature, atmospheric pollution, and climate anomalies caused by fossil fuels. Hydrogen is recognized as the most promising clean energy source because of its high calorific value, abundant reserves, diverse sources and environmental friendliness. However, hydrogen is not liquefied effortlessly at room temperature and atmospheric pressure, colorless, odorless and flammable and explosive, which makes it more challenging to store and transport [1-3]. Ammonia is a carbon-free, hydrogen-rich compound, a colorless, alkaline gas with an irritating odor, and is much less expensive to produce than hydrogen [4]. At the same time, ammonia has the properties of high bulk density, easy liquefaction and easy storage and transportation [5].

Fuel cell is a equipment that converts the chemical energy of fuel directly into electrical power, with the advantages of high power generation efficiency, no common pollutant (SO_x, NO_x) emissions, long service life, etc [6-8]. Currently, hydrogen is the main fuel used in this technology, and to compensate for the lack of hydrogen as a fuel, ammonia is considered to be an ideal fuel to replace hydrogen as a fuel cell [9]. In utilizing ammonia as a fuel, indirect ammonia fuel cells decompose to generate nitrogen and hydrogen in an external unit and subsequently use the reformed hydrogen as a fuel; direct ammonia fuel cells use ammonia directly as a fuel without an external unit, thus also providing convenience for various applications.

Among ammonia fuel cells, direct ammonia alkaline fuel cells have attracted extensive attention from many researchers by virtue of their simple structure, low-cost, high-energy density and fast starting speed [10]. However, the kinetic process of ammonia electrocatalytic oxidation in direct ammonia alkaline fuel cells is slow at room temperature, and Pt is still the preferred catalyst. Therefore, the disadvantages of low Pt reserves and high price are the most important reasons to limit the commercialization of direct ammonia alkaline fuel cells. How to improve Pt catalytic capacities and develop low-Pt catalysts or even non-Pt catalysts are hot research topics in this field.

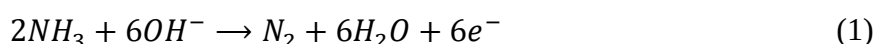
In this paper, we firstly introduce the generator theory of direct ammonia alkaline fuel cell, review the current research status of Pt catalysts and non-Pt catalysts for AFC ammonia electro-oxidation,

outline and prospect the future research directions, aiming to provide research directions on how to design cheap and efficient catalysts for universal application of direct ammonia alkaline fuel cell.

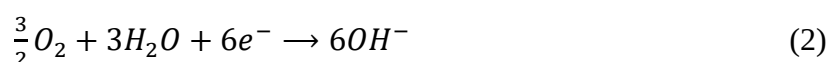
2. Mechanism of ammonia electrochemical oxidation reaction

In a direct ammonia alkaline fuel cell, ammonia is fed directly to the anode side for the AOR, which combines hydroxide ions to produce nitrogen and water, and oxygen is fed to the cathode side for the ORR, which combines water molecules to produce hydroxide. The specific reaction equation is as follows.

Anodic reaction:



Cathodic reaction:



Overall respons:



The reaction kinetics of this anode reaction process is slower than the hydrogen oxidation reaction of the hydrogen-oxygen fuel cell, and the intermediate materials (*N, *NO) they produce being heavily adsorbed to the catalyst's surface to occupy the active sites, catalyst poisoning results [11]. Therefore, exploring the AOR mechanism can help to understand the nature of catalyst poisoning and provide directions for designing more efficient catalysts.

Early researchers interpreted the results as a mechanism similar to the decomposition of the gas ammonia into nitrogen and hydrogen by Oswin and Salomon [12] in 1963, a stepwise dehydrogenation mechanism (referred to as the O-S mechanism) was proposed. This mechanism states that ammonia gradually reacts with adsorption-activated OH⁻ to gradually dehydrogenate atoms to form *N, and finally *N-*N dimerizes to form N₂ molecules. It should be noted that the dehydrogenation of *NH₂ to *NH is a rate-determining step in the reaction at low current densities; the dimerization of two *N into N₂ molecules is a rate-determining step in the reaction at high current densities.[11-13]. In a subsequent development, Gerischer and Mauerer [14] provided the guiding key mechanism (referred to as the G-M mechanism) in 1970. The mechanism states that substances partially dehydrogenated by ammonia (*NH, *NH₂) will dimerize to form *N₂H_x (x=2,3,4) substances and finally dehydrogenate to produce product N₂ molecules, without the involvement of *N in the process. In this mechanism, the *NH_x dimerization reaction is additionally pointed out as the rate-determining step, while the substance that renders the catalyst inactive is considered to be the *N substance that is completely dehydrogenated [11,14]. The reaction paths of the above two mechanisms are shown in Figure 1.

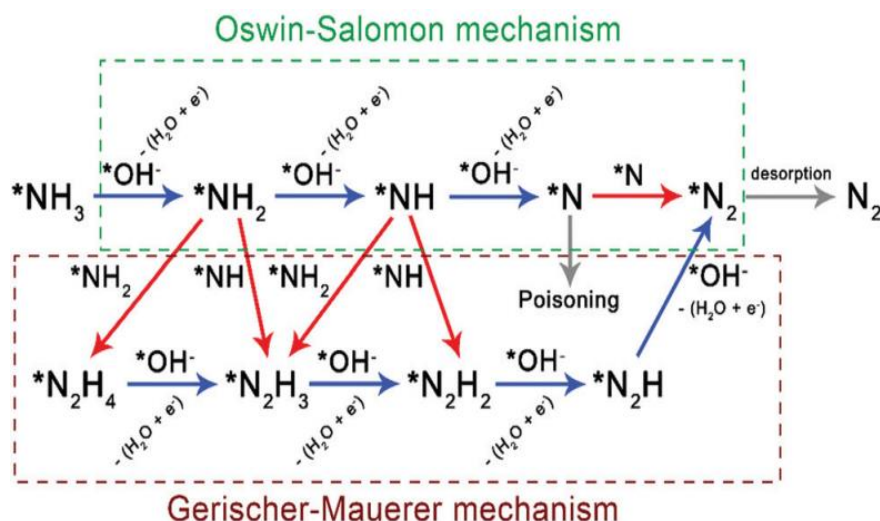


Figure 1. Mechanism of ammonia oxidation reaction [15]

The G-M mechanism is more representative than the O-S mechanism and has been verified experimentally by many scholars. On the one hand, in situ characterization techniques, which can reflect the states in the reaction, are indispensable for catalytic reactions and have a crucial position for the mechanistic study of AOR processes. J. F. E. Gootzen et al. [16] used CV and DEMS to study the AOR process at Pt electrodes and the intermediate substance for N₂ generation was found to be most likely *NH, and the toxic effect of *N on the catalyst surface was also confirmed. de Vooy et al. [17] studied the active intermediates of AOR using DEMS and CV methods and found that *NH₂ is also an active intermediate. Vidal-Iglesias et al. [18] studied the AOR process on Pt electrodes using surface-enhanced Raman spectroscopy (SERS) and found that the azide anion (N₃⁻), which can be formed by the recombination of *NH, *N₂H_x, would be involved in the generation of N₂, confirming the G-M mechanism. Matsui et al. [19] used in situ ATR-IR to detect *N₂H₄ on Pt electrodes for the first time, confirming the possibility of *N₂H₄ as a reactive intermediate and further demonstrating the G-M mechanism.

On the other hand, theoretical calculations are of remarkable importance in mechanistic analysis problems, and density functional theory calculations are a common technical tool to study AOR processes. Novell-Leruth et al. [20] investigated the morphology, site distribution and relative stability of adsorbed ammonia and its intermediate derivatives on a low refractive index Pt surface and elucidated the potential reasons for the excellent catalytic capacities of Pt (100), while the experimental results partially supported the G-M mechanism. Skachkov et al. [21] also did a similar computational study and found that at high potentials the reaction follows the O-S mechanism and at low potentials the two mechanisms compete with each other but the activity is lower compared to that at high potentials. In a recent study, Yang et al. [22] researched the stepwise dehydrogenation of ammonia at the Pt (100) crystal plane based on DFT calculations combining molecular dynamics and slow growth of free energy sampling, pointing out that the adsorbed *OH may be the true reactive species rather than the OH⁻ in the water molecule. This finding is proposed to bring new insights to future studies on the mechanism of the AOR process.

Although Pt has high catalytic capacities compared to other catalysts, its disadvantages such as high price limit its large-scale application. Accordingly, the use of new catalysts with non-precious metals or composites is crucial. Therefore, it is not enough to learn about the mechanism of the AOR process of ammonia on Pt alone, but it is still necessary to learn about the mechanism of the AOR process of ammonia on other materials. Herron et al. [23] researched the AOR process of ammonia on a range of metal surfaces like Au, Ag, and Cu under two mechanisms using DFT calculations and found that the dimerization of two *N into N₂ always has a very high activation potential, which indicates that *N formation leads to catalyst poisoning. Meanwhile, the initial potential of ammonia on the tightly packed surface of transition metals estimated by the authors shows that the metals with weaker N binding energy than Pt are more likely to form N-N bonds on the surface, leading to the

poisoning of the AOR process; the initial potential of the G-M mechanism of Ni and Co metals with stronger N binding energy than Pt is lower than that of the O-S mechanism, which means that the catalyst will not be inactivated at low potentials, so Ni and Co might also be excellent catalysts, but Co is experimentally proven to be inactive, while the remaining metals such as Rh are poisoned in the experiment. In addition, this author also presented Figure 2 of AOR catalytic capacities versus metal catalyst binding energy to N, which pointed out that the activity of metal G-M mechanism with stronger N binding energy than Cu is much higher than the activity of O-S mechanism by several orders of magnitude, while for Cu it shows high activity but poor effect. According to Fig 2, it has been pointed out that the catalyst for the optimal AOR should have a moderate binding strength between Pt and Cu [11,15,24]. These findings point to the alloying of catalysts as a good way to employ new catalysts. Experiments by Daramola et al. [25] also corroborate this claim, stating that the Ir mix into the Pt electrode helps the AOR process to occur in a more favorable pathway.

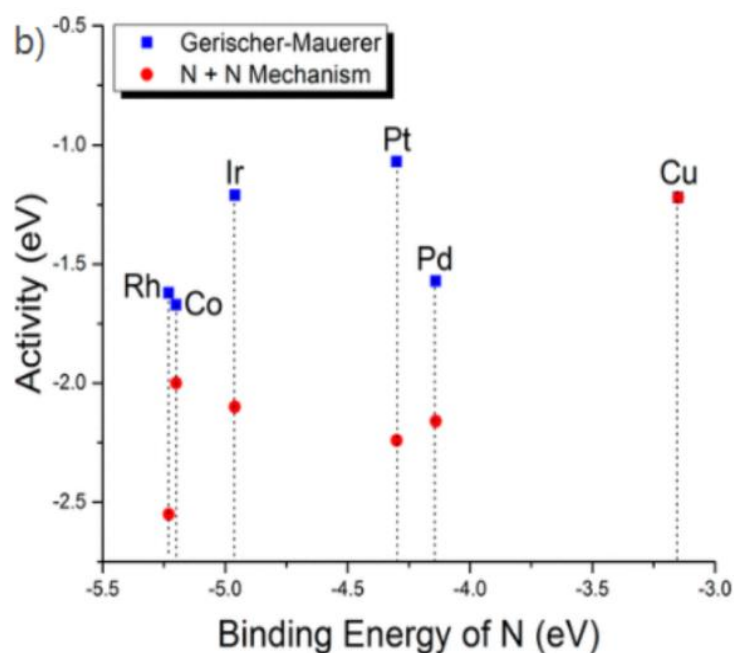


Figure 2. AOR catalytic capacities versus metal catalyst binding energy for N [23]

3. Ammonia electrochemical oxidation catalyst

AOR catalysts can be categorized into three groups: pure Pt metal catalysts, alloy catalysts composed of Pt and other metals such as Ir and Ru, and non-Pt catalysts. It is worth pointing out that the catalyst preparation method also affects its performance. [26]. This section only briefly reviews the results of researchers in recent years from the perspective of catalyst types to provide ideas for the design of new ammonia electrooxidation catalysts.

3.1. Pure Pt metal catalysts

Currently, despite the disadvantages of Pt such as expensive and limited reserves, a large number of experimental studies indicate [17,23,27] that the most active singlet metal for catalytic AOR is still Pt. Therefore, it is especially important to improve the catalytic capacities, stability and anti-toxicity ability of Pt catalysts. The current research mainly focuses on crystal surface modulation, reasonable control of Pt particle size and morphology, and addition of hydroxide or oxide surface modification to increase the catalytic capacities of pure Pt metal catalysts.

Vidal-Iglesias et al. [28-29] discovered that the AOR process occurs almost exclusively at the Pt (100) site contrast to the Pt (111) and Pt (110) sites and that the peak current obtained rises as the number of Pt(100) sites rises. This shows that a viable method to boost the activity of Pt catalysts is to maximize the percentage of Pt (100) sites on the Pt surface. Along this strategy, Fu et al. [30] prepared

Pt nanobellicies surrounded by Pt (100) crystalline facets. It was shown that the Pt nanoribbons were highly active for AOR and had better activation performance than commercial Pt black catalysts. On the other hand, changing the size and morphology of Pt particles also affects the catalytic capacities. Liu et al. [31] found that lamellar and flower-like Pt nanoparticles exhibited higher AOR activity compared to spherical ones. In addition, this author also looked into the connection between Pt morphology and Pt (100) sites, and came to the conclusion that shifting Pt particles from spherical to cubic shapes enhances the proportion of Pt (100) sites and the catalytic capabilities; meanwhile, a (100) crystalline surface selectively oriented Pt nanocube was prepared using periodic square wave potential electrochemistry, which also exhibited very high catalytic capacities for AOR [32]. This suggests a potential connection between different morphologies and the (100) crystalline plane occupancy, further demonstrating the importance of choosing the right morphology and size. In addition, Eguchi et al. [33-34] modified the Pt catalyst surface with rare earth oxides (CeO_2 , Y_2O_3 , La_2O_3 , Sm_2O_3) and found that the AOR peak current density increased for all of them, with CeO_2 modified Pt catalyst showing the best activity with 3.5 times higher AOR peak current density than the Pt catalyst. Figure 3 illustrates that the Pt oxidation charge of each oxide modified catalyst is higher than that of the unmodified catalyst, reflecting the rise of OHad species on the catalyst surface, which led this author to the conclusion that the AOR activity increased with the quantity of OHad species. This suggests that the addition of oxides for Pt catalyst surface modification is likewise one of the effective strategies to improve the electrocatalytic performance.

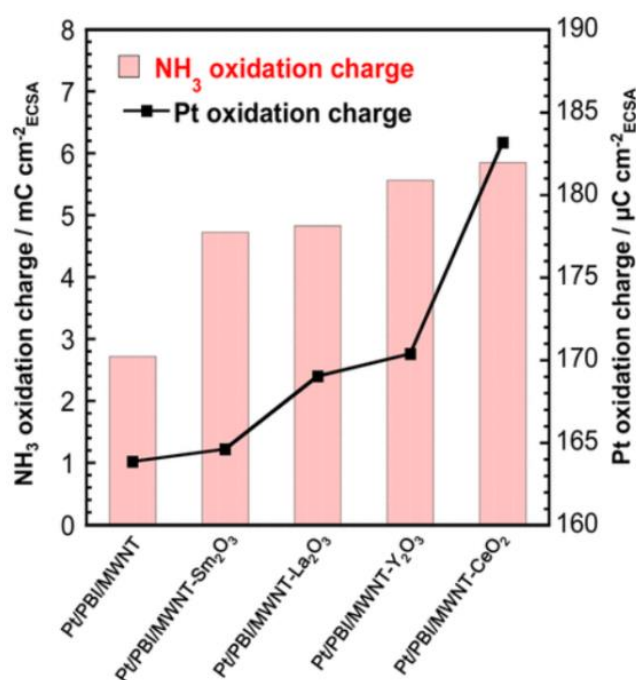


Figure 3. Relationship between Pt oxidation charge and NH_3 oxidation charge of Pt/PBI/MWNT electrocatalysts [33]

3.2. Pt-Based binary or ternary catalysts

Alloying of Pt catalysts can neutralize the advantages of other metals and is a feasible way to improve the catalysts' resistance to toxicization. The elements that can be alloyed with Pt that are currently being explored the most are Ir and Ru, and from the results of the studies, more satisfactory results have been obtained. As early as in the 1960s, McKee et al. [35] found that Pt-Ir alloys were more effective as catalysts than Pt alone as a catalyst, and that the open circuit voltage increased with increasing Ir content. Imbeault et al. [36] evaluated the catalytic performance of a range of $\text{Pt}_x\text{-Ir}_{100-x}$ alloys for AOR and found that these alloys were more resistant to toxicity than Pt alone, with $\text{Pt}_{89}\text{-Ir}_{11}$ having similar electrocatalytic capacities as Pt and also being more tolerant to the intermediate toxicants generated during AOR with the best results. Endo et al. [37] prepared various $\text{Pt}_{1-x}\text{-M}_x$

(M=Ir,Ru or Ni) binary alloys by thermal decomposition and investigated their electrocatalytic activity in AOR process, and found that the saturation current densities on $Pt_{1-x}Ir_x$ ($x<0.8$) or $Pt_{1-x}Ru_x$ ($x<0.4$) were significantly higher at low oxidation potentials than when pure Pt was used as catalyst, suggesting a possible positive synergy between Pt and Ir or Ru in AOR. There may be a positive synergistic effect in the AOR. The second component, according to this author's analysis, boosts the electrocatalytic capabilities of AOR at low potentials and aids in the dehydrogenation of ammonia at a potential lower than Pt. Vitse et al. [38] used Pt-M (M = Ru and Ir) deposited alloy catalysts for the electrolysis of ammonia to make hydrogen and found that the AOR catalytic capacities of Pt-Ru was superior to that of Pt black. Unfortunately, despite the good catalytic capacities of the above alloys, Ir and Ru are also noble metals and do not solve the cost problem, while the study indicates that Pt with less expensive metals like Ni or Cu has not shown promising results so far. It is also important to note that the effect of subcomponent elements on Pt seems to be related to the electrochemical test conditions and the use of cyclic voltammetry tends to give negative results. Vidal-Iglesias et al. [39] studied ammonia electrooxidation over different Pt-M (M=Ir, Rh, Pd, Ru) alloy catalysts using CV tests and showed that the peak AOR current density was significantly reduced by the addition of subcomponents. According to Figure 4, the peak current density rapidly falls as the content of subcomponents rises. As a result, when employing Pt alloys, careful attention should be made to the working conditions.

On the other hand, Pt ternary alloy catalysts were formed by adding a third metal to Pt binary alloy catalysts, which also have high catalytic capacities for AOR. Bonnin et al. [40] evaluated the catalytic performance of PtIrRh electroplated on carbon fiber-based materials, and the results indicated that PtIrRh is the most promising catalyst under low concentration ammonia electrolysis. Huang [41] tested the electrochemical characteristics of PtPdRh alloy catalysts for AOR and showed that the catalytic performance of PtPdRh electrocatalytic materials was significantly improved by the combination of peak surface current density and potential electrochemical characterization, and that PtPdRh alloy catalysts were crucial to the AOR process. Jiang [42] modified Pt-Ir and Pt using Zn, and showed that doing so considerably increased their AOR catalytic capabilities. Recently, Lin et al. [43] prepared PtIrCu hyperbranched concave octahedra with high refractive index facets, which are characterized by strong strain effect and open structure, and their AOR activity and stability are better than other forms of Pt-based catalysts (PtIrNi, PtCu, PtIr, etc.).

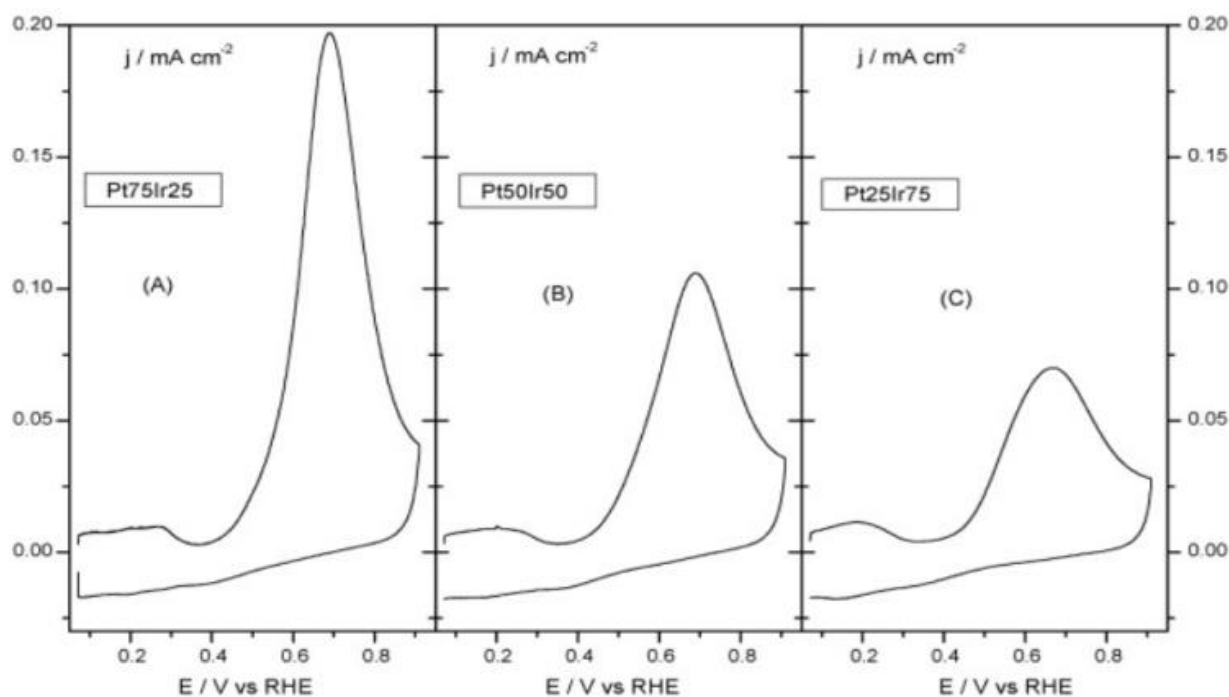


Figure 4. AOR cyclic voltammogram on Pt₇₅Ir₂₅, Pt₅₀Ir₅₀, Pt₂₅Ir₇₅[39]

3.3. Non-Pt catalysts

The use of inexpensive metal catalysts without Pt is an effective means to reduce the cost and achieve technically large-scale applications. The DFT calculation shows that the AOR onset site of Ni is 0.33V, which is very close to that of Pt at 0.28V. Therefore, Ni is one of the elements that has the best chance of replacing Pt in AOR catalyst applications. Earlier experiments concluded that pure Ni is inactive for AOR [44], while Kapałka et al. [45] reported that Ni electrodes in NaClO₄ solution can form a surface Ni(OH)₂ layer, and this layer can adsorb oxygen for AOR process. This author also discovered that AOR is substantially pH-dependent, primarily at pH>7, and occurs in the potential range of Ni(II)/Ni(III) redox activity, indicating that the substance oxidized on Ni(OH)₂ is NH₃ rather than NH₄⁺. Also, this author predicted that the formation of N₂ molecules is through a direct electron transfer mechanism from ammonia to Ni(III), while the nitrate production may be due to the oxygen transfer mechanism of water molecules. These findings suggest that Ni-based materials have different reaction pathways from Pt-based materials, but related studies are very limited. Currently, the biggest factors limiting the efficiency of Ni materials are their corrosion problems and the production of oxygenated nitrogen species, and researchers have addressed this issue for improvement. For example, Xu et al. [46] prepared hybrid NiCu hydroxide nanowires (Figure. 5) by doping with Cu elements and obtained an optimal Ni/Cu ratio of 0.8:0.2. Meanwhile, this author performed CV tests on pure Ni(OH)₂ and Ni_{0.8}Cu_{0.2} and discovered that the former's current density was seven times more than the latter. Zhang et al. [47] investigated the performance of NiCu nanoparticles loaded with carbon nanotubes applied to direct ammonia microfluidic fuel cells and discovered that NiCu's catalytic capabilities are higher than those of pure Ni and pure Cu, which is attributed to the formation of NiCu hydroxide. the doping of Cu can increase the surface-active sites of Ni, and in addition there is a positive synergistic effect with Ni, which can significantly increase the current density of AOR. Chen et al. [48] designed a novel class of Ni and Co metal nitride nanosheets for AOR electrocatalysis. After experimental characterization and DFT calculations by the authors, the electron acceptor in NiCo₂N nanosheets is accompanied by a strong metal-ammonia bonding interaction, which greatly promotes the formation of NH_x⁺ cation radicals and significantly improves the catalytic performance. In addition, Zott et al. [49] reported the satisfactory performance of the Fe mediated [(bpyPy₂Me) Fe (MeCN)₂]²⁺ molecular system in AOR, which exhibited enhanced catalyst stability and higher catalytic capacities, with a turnover number of up to 149 after further improvement by the authors. The authors also point out that Fe is a promising metal that is abundant on Earth and can be used to mediate molecular systems for AOR catalysis.

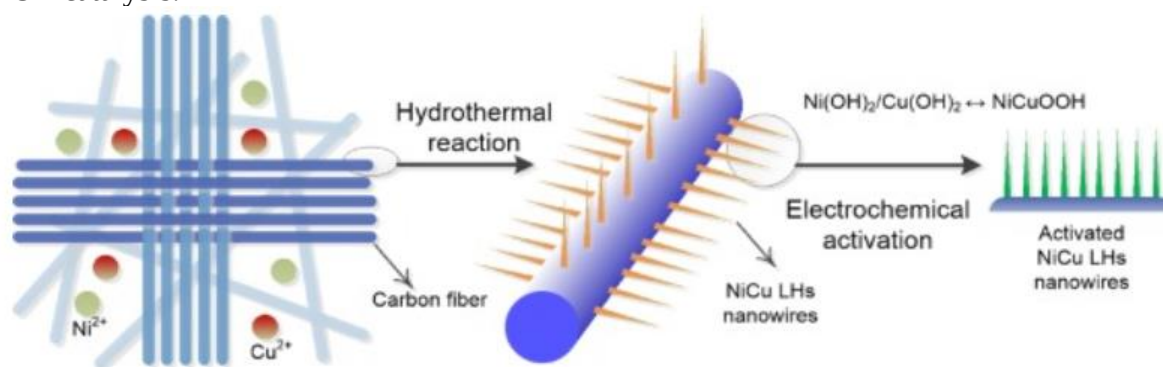


Figure 5. catalyst preparation of NiCu LH nanowires and electrochemical activation [47]

4. Conclusion and outlook

In recent years, it is difficult to make a big breakthrough in hydrogen storage and transportation, and ammonia as a hydrogen-rich carrier has entered the vision of researchers by virtue of its low cost, high bulk density and easy storage. Fuel cells are one of the pathways to efficiently utilize ammonia energy, however, mechanistically, it is still controversial what mechanism is followed in the ammonia

oxidation process of direct ammonia alkaline fuel cells, and the intrinsic mechanism of some new catalysts is still unclear, and some experimenters have reported new intermediate products, indicating that ammonia oxidation should have a more complex mechanism. In terms of catalysts, Pt metals are still the preferred catalysts by experimentalists, with excellent high performance, but their resistance to toxicity still needs to be improved. By increasing the percentage of selectively oriented Pt (100) crystalline surfaces on the catalyst surface, controlling the catalyst morphology and adding oxides for surface modification, researchers have improved the anti-toxicity of Pt catalysts, thereby increased the catalysts capacities, while also reduced the amount of Pt used. Alloying is also one of the areas of importance for researchers. The addition of component elements can improve the anti-toxicity of catalysts, but different operating conditions may lead to a decrease in the activity of alloyed catalysts, and the component elements incorporated are all precious metals, which cannot effectively reduce the cost. For non-Pt metal catalysts, no major breakthroughs have been made, and the most promising Ni-based catalysts have very few experiments and DFT calculations on ammonia oxidation mechanism, and the mechanism is so far vague and not very active. Although Ni-based alloy catalysts can improve the activity, they are still far from the activity of noble metal catalysts.

Direct ammonia alkaline fuel cells are still in the laboratory stage and cannot be commercialized, despite the significant advancements made by researchers in recent years. To address the problems of ammonia electrochemical oxidation catalysts in direct ammonia alkaline fuel cells, in-depth research can be carried out in the following four aspects in the future: (1) in situ characterization techniques can be used to explore the intermediate products and combine with DFT theory to calculate the N binding energy to further reveal the mechanism of the AOR; (2) explore the effect of alloying on the AOR of Pt electrodes. Currently, although many alloyed catalysts are reported to have high catalytic capacities experimentally, the study of their intrinsic mechanisms still lacks information. The mechanism can be revealed by coupling DFT theoretical calculations and experimental phases to provide a theoretical basis for finding the optimal subcomponent elements; (3) development of new size and shape of catalysts. The mechanism of these previously reported nanomaterials for AOR is still unclear and can be further investigated in the hope of bringing new breakthroughs; (4) exploring the mechanism of catalyst poisoning and providing a theoretical basis for how to inhibit the poisoning effect.

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