

The study of Pt-based anode catalysis for formic acid full cell

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Abstract. The mechanism of the catalysts for electro-catalysis of formic acid fuel cell is introduced, the recent advances of the Platinum(Pt)-based anode catalysis and the influence of the catalytic activity of formic acid fuel cells are analyzed, providing direction of selecting the potential Pt-based anode catalysts of formic acid fuel cell.

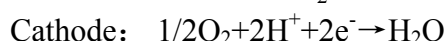
1. Introduction

As the growth of energy demand in daily life, research on new energy sources has attracted most attention in the past few years [1]. Formic acid fuel cell belong to proton exchange membrane fuel cell, using formic acid as fuel. To compare with other proton exchange membrane fuel cells. For example, methanol or hydrogen as energy source for fuel cell [2]. It is studied widely, due to its easily be transported and stored, has high energy conversion rate, has fast response speed, is less poisoning to Pt-based anode catalysts and environmental friendly [3].

The catalyst is an important part of the fuel cell. The research about fuel cell catalysts is a hot issue of this field. Pt nanoparticles show high catalytic activity on the anodic oxidation reaction of formic acid. However, the formic acid fuel cell anode catalyst suffers from some problems, such as high cost, the low catalytic activity, easily poisoned by carbon monoxide (CO), which is one of the intermediate products of the fuel cells [4]. In order to solve these problems, over the past few decades, some effective methods including incorporating transition metals into Pt, the addition of transition metal oxides and sulfides and using supporting substrate have been successfully used to enhance catalytic activity and showed their excellent electrochemical properties.

2. The mechanism of the direct formic acid fuel cells

Formic acid is a strong electrolyte, expected to promote the transport of electrons and protons on the anode of the fuel cell. Formic acid full cell uses oxygen (O₂) as cathode. On the cathode, by getting two electrons, O₂ transform into water by reduction reaction. On the anode, each molecular formic acid is oxidized to provide two electrons. The cathode, anode and total reaction are as shown in the following equations[5,6]:



The working principle of formic acid fuel cell refer to Fig.1 [7]

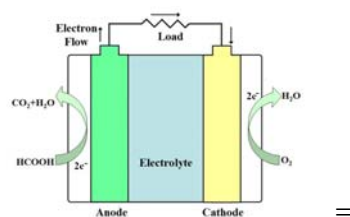


Fig.1 The working principle diagram of formic acid fuel cell

The theoretical open circuit potential (OCP) for DFAFCs from the Gibbs free energy, is 1.48 V.

$$E^{\theta} = -\Delta G^{\theta} / nF = 1.48(V)$$

OCP for formic acid full cell is higher than the direct methanol fuel cell. From the point of dynamics, only with two protons a molecular formic acid could be oxidized, in some cases, it can be done in one step reaction, so the electrochemical polarization is smaller than direct methanol fuel cells. Compared with the other proton exchange membrane fuel cells, formic acid showed many advantages as a fuel. Electro-oxidation of formic acid on Pt has attracted much attention, in the early research, the electro-oxidation of formic acid proved to be occurred via difunctional mechanism, including dehydrogenation (direct pathway), and dehydration (indirect pathway). In the direct pathway, formic acid is directly oxidized to form CO₂ via dehydrogenation reaction without forming CO intermediate (CO_{ads}) on the anode. In the indirect pathway, the formic acid first generates CO_{ads}, because of the weekly adsorption capacity, the CO is easily oxidized to CO₂. The reaction is as follows[5,6]:

Direct pathway: $\text{HCOOH} \rightarrow \text{CO}_2 + 2\text{H}^+ + 2\text{e}^-$

Indirect pathway: $\text{HCOOH} \rightarrow \text{CO}_{\text{ads}} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 2\text{H}^+ + 2\text{e}^-$

CO_{ads} produced in dehydration reaction, is easily to be adsorbed on Pt, which could lead to poison the Pt catalyst and decrease its catalytic activity. Because the potentials for indirect pathway is higher than the potential for the direct pathway, active sites of Pt is covered by CO_{ads}, so decrease of poison is an important research trend towards Pt-based anode catalysts of formic acid oxidation. In order to overcome this problem, researchers did a lot of work to improve the performance of formic acid fuel cell. The purpose of this work is to introduce the catalytic activity of different Pt-based anode catalysts.

3. Pt-based anode catalysts

There is agreement that Pt is a good catalyst, but the active sites of Pt are rapidly poisoned by a strongly adsorb CO_{ads}. High catalytic activity and tolerance to CO_{ads} poisoning have been achieved on Pt-based anode catalysts at relevant potentials. The improvement of CO tolerance of the Pt due to the decrease in the number of active sites available for CO_{ads}.

3.1 Pt/ transition metals

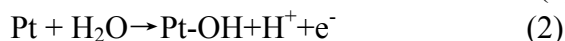
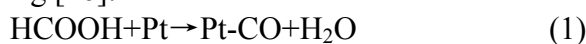
By adding transition metals to Pt, various Pt-based bimetallic nano-catalysts, such as PtRu[8], PtFe [9], PtCu [10], PtMn [11] and PtAu [12] etc., have been formed. Recent reports indicate that the catalytic activity and electrochemical properties of these Pt-based bimetallic nano-catalysts are exceeded to those of Pt alone catalysts. Pt-based bimetallic nano-catalysts have enhanced catalytic activity, electrochemical properties and improved tolerance to CO_{ads} poisoning due to difunctional mechanism.

As is known to all, the electro-oxidation of formic acid occurred via difunctional mechanism. But PtRu cannot change the way of catalyst on the oxidation, its main role is to accelerate oxidation speed on the oxidation of CO_{ads}, thus improve the electrochemical properties of formic acid [13]. For PtAu, the main effect is to reduce the adsorption quantity of CO_{ads}, so formic acid mainly oxidized in the direct pathway. Although significant progress has been made in the synthesis of Pt-based bimetallic nano-catalysts, some problems and unsolved challenges still remain, the catalyst can be difficult to be achieved commercial [14].

3.2Pt/ compounds

To further reduce the use of Pt, transition metal oxides and sulfides have also been studied as catalysts.

For instance, NiO_x-modified Pt catalyst was developed for electro-oxidation of formic acid. This modification resulted in high catalytic activity via direct pathway transform formic acid to CO₂, which might reduce the accumulation of CO_{ads} on the active sites of Pt, NiO_x is believed to against the CO_{ads} poisoning [15]. The catalytic enhancement and the high current density were observed stability. The stability of current is actually because the decrease of CO_{ads} poisoning. The CO oxidation proceeds as following [16]:



Therefore, metal oxides or sulfides-modified Pt will facilitate the electron transfer, hence, will support the electrode with a high catalytic activity and stability, show perfect electrochemical properties.

3.3Pt/ support

Carbon materials and heteroatom-doped carbon materials are as the support of Pt. In recent years, it has been found that carbon materials and N, P, B-doped carbon materials, such as carbon black [17], carbon nanotubes [18], graphene [19], show highly decentralized and highly catalytic activity. Such carbon materials demonstrate promising applications in formic acid fuel cell, that can reduce the size of the Pt particle and decrease the use of Pt, which lead to low price and high CO_{ads} tolerance.

For instance, N-doped graphene show their advantages compared with pristine graphene, due to the affect of the nitrogen dopant. Using N-doped graphene as the support can enhance catalytic activity and improve electrochemical properties of Pt. The nitrogen doped in the graphene depositing Pt particles uniformly. Therefore, the introduction of the support is of great importance that will not only reduce the use of Pt but also increase the catalytic activity and stability of Pt-based anode catalysts [20].

4. Summary

In general, Pt-based anode catalysts show promising applications in formic acid fuel cell. In recent years, there are great progresses on the synthesis. However, it is a long way to find other methods to realize their applications. We mentioned is commonly the formic acid oxidation under acid condition, the pH value of the solution become an important question in formic acid oxidation [21]. So more efforts have to be done on further reduce the use of Pt and improve the activity of catalyst.

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