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Short Communication

A Electrochemical Performance Analysis of High and Low Pt Loading in Pt/C Catalysts by Rotating Disk Electrode

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A series of Pt/C catalyst electrodes with different Pt loadings ranging from 12μg/cm^2 to 400μg/cm^2 was characterized in our experiments by rotational disk electrode (RDE) system. The influence of Pt loading on the performance of the catalyst was systematically analyzed. We found that if the Pt loading was very low, which the electrode thickness could be neglected, the H^+ in solution can be quickly penetrated into the electrode, the impact of mass transfer can be ignored and the electrochemical active area (*ECSA*) was equal to the inherent value; when the electrode thickness increases gradually with the increasing Pt loading, the mass transfer gets restricted as well as ohm potential drop in the solution, the electrode potential was to shift significantly as a result, and the *ECSA* was lower than the inherent value. Oxygen reduction reaction (ORR) performance also verified this point. The content of effective Pt loading in high Pt loading electrode (>100μg/cm^2, or electrode thickness >2.17μm) can be calculated by the ratio of *ECSA* for high to low Pt loading.

Keywords: Rotating disk electrode, Pt/C catalyst, Pt loading, Electrochemical active area, Oxygen reduction reaction

1. INTRODUCTION

As an electrochemical device that converts chemical energy from hydrogen and oxygen directly into electrical energy, proton exchange membrane fuel cell (PEMFC), which shows high energy conversion efficiency, environmentally friendly and produces only water (no hazardous gases, such as NO_x, SO_x and CO_2), has become an preferred clean and efficient power generation technology widely used in the world.[1-3] Currently, Pt/C catalysts are the most commonly used catalyst species for PEMFCs due to their high catalytic activity and stability.[4, 5] However, the lack of Pt resources and high cost has become a major problem which affects its further application. Therefore, the development of new catalysts with low Pt loading and high catalytic performance is particularly important.

The performance of PEMFC is limited by the kinetics of membrane electrode assembly (MEA) (the hydrogen oxidation and oxygen reduction), and the reaction rate of catalysts has played a decisive role during the reaction in fuel cells.[6] In the previous work, researchers found that the main reason of catalyst efficiency loss in the PEMFC is due to the low kinetics process of the oxygen reduction reaction at working temperature (-30~100℃).[7, 8] Moreover, the reaction rate of the oxygen reduction for the Pt catalysts is 6 orders of magnitude lower than the hydrogen oxidation, which means that a high Pt loading in the cathode is required to provide a sufficient rate of oxygen reduction reaction.[9] Usually, for the commercial Pt/C catalyst, the Pt loading in cathode is about $0.4mg/cm^2$, which is larger than the anode (about $0.1mg/cm^2$).[10] Therefore, studying the oxygen reduction performance is a more effectively method to reduce the Pt loading in the Pt/C catalyst.

Rotational disk electrode (RDE) technology, which is widely used for testing the electrochemical properties of catalysts in PEMFC, has become the first choice for most electrochemical researchers.[11, 12] Normally, in order to reduce the effect of mass transfer resistance, the study of oxygen reduction for Pt/C catalysts by RDE is mainly focused on the low Pt loading range ($4{\sim}36\mu g/cm^2$).[13] However, the actual Pt loading in cathode for PEMFC is usually up to $400\mu g/cm^2$, which is a large difference in the oxygen reduction test by RDE. Therefore, the traditional RDE test does not fully reflect the actual catalytic activity of the cathode catalyst in PEMFC. So it is of great scientific significance to test the actual Pt loading to predict the electrochemical performance of the fuel cell cathode catalyst by RDE test system.

The electrochemical active area (*ECSA*) is an important indicator for the performance of catalysts. However, researchers found that high Pt loading will result in smaller *ECSA*. Pozio et al. reported that some Pt particles were blocked in the carbon substrate and could not be exposed to the electrolyte solution with the Pt loading increasing ($28{\sim}900\mu g/cm^2$) (the electrode thickness growing, resulting in a gradual decrease in the *ECSA*.[5] But the authors didn't consider the effect of the mass transfer on Pt surface, which cannot be ignored because the surface of Pt is covered with a layer of ionomer. When the electrode thickness is very thin, the H^+ in solution can be quickly penetrated into the electrode, the impact of mass transfer can be ignored; when the electrode thickness increases gradually, the decrease of the H^+ permeation rate will cause the shortage of H^+ in the Pt catalyst surface, which would lower the measured electrode potential. Lin et al. found that the peak potential of hydrogen adsorption/desorption would appear a significant shift if the reaction of adsorption/desorption processes of H^+ in the Pt surface become very slow (or shortage).[14] This means that the peak potential shift of hydrogen adsorption/desorption can be observed in the CV curve (which is clearly observed in our laboratory) if hydrogen diffusion is restricted in high Pt loading electrode. Therefore, under the influence of mass transfer, it is important to reexamine the electrochemical performance of Pt/C catalysts with different Pt/C loading.

In this paper, the oxygen reduction performance of a series of Pt/C catalysts with Pt/C loading from $12\mu g/cm^2$ to $400\mu g/cm^2$ was investigated by using cyclic voltammetry (CV) and linear scan voltammetry (LSV). The main goal of this work is to study the effect of Pt loading on oxygen reduction activity at different stages, to explain the decrease of *ECSA* in the case of high Pt loading. Moreover, we propose a method to calculate the content of effective Pt loading under the condition of high Pt loading (>100μg/cm^2, or electrode thickness >2.17μm).

2. EXPERIMENTAL AND CHARACTERIZATION

In this work, a series of electrodes with different Pt loadings were prepared by using Pt/C catalyst ink with the same I/C ratio (the ratio of ionomer mass to carbon support mass) and characterized using CV and LSV. All of the electrochemical tests were performed using a three-electrode system on an electrochemical workstation (Shanghai Chenhua, CHI660E) and rotating disk equipment. The working electrode is a glassy carbon electrode with a diameter of 5mm (Russell Technology). The reference electrode is a home-made reversible hydrogen electrode and the counter electrode is Pt black (Russell Technology). The electrolyte was 0.1M $HClO_4$ (perchloric acid, analytical grade, Sinopharm 72.0%), and the experimental temperature was room temperature (24℃).

2.1 Preparation of the Electrode

Twelve electrodes with different Pt loading were prepared by using 57.9% commercial Pt/C catalysts (TKK Corporation, Japan) with the I/C ratio of 0.5. The Pt loading of electrodes were 12μg/cm^2 (thickness 0.26μm), 20μg/cm^2 (thickness 0.43μm), 40μg/cm^2 (thickness 0.87μm), 60μg/cm^2 (thickness 1.30μm), 80μg/cm^2 (thickness 1.73μm), 100μg/cm^2 (thickness 2.17μm), 150μg/cm^2 (thickness 3.25μm), 200μg/cm^2 (thickness 4.33μm), 250μg/cm^2 (thickness 5.12μm), 300μg/cm^2 (thickness 6.50μm), 350μg/cm^2 (thickness: 7.58μm) and 400μg/cm^2 (thickness: 8.67μm) respectively. To prepare the catalyst layer, a certain amount of Pt/C catalyst was taken into the 2mL sample tube. Following, 100μL of deionized water, 900μL of isopropyl alcohol (analytical grade, Sinopharm 99.7%) and 20μL of Nafion (DuPont 5wt%) solution were sequentially added in sample tube by pipetting. And then, the samples were put into an ultrasonic cell under ice-cooling conditions for 20 minutes to obtain a homogeneous dispersion of catalyst ink. Subsequently, a pipette gun was used to take different volumes of ink to the surface of the glassy carbon electrode, followed by drying the solution to form a homogeneous catalyst film. Before to test, the electrode coated the catalyst was immersed in the electrolyte solution for 30min.

2.2 Cyclic voltammetry (CV) analysis of the Pt/C catalyst

Before the experiment, the electrolyte was bubbled with 99.999% high-purity N_2 for 30 minutes to exclude O_2. And then, the electrodes were scanned for 80 cycles at a high scan rate (100mV/s) to remove the impurities on the electrode surface. The experimental voltage range is set to 0~1.2V (vs. RHE). According to the measured CV curve (Hydrogen adsorption peak area), the *ECSA* can be calculated using Equation 1:

$$ECSA = \frac{S}{2.1 \times V \times M} \tag{1}$$

V is the scan rate (V/s), $ECSA$ is the electrochemical active area (m^2/g_{Pt}), S is the integral area between the current and voltage in the hydrogen adsorption area (mA•V), M is the Pt loading (mg).

2.3 Linear scan voltammetry (LSV) analysis of the Pt/C catalyst

Similar to the CV test, the electrolyte was bubbled with 99.999% high-purity O_2 for 30min to achieve oxygen saturation. The experimental voltage range is set to 0~1.2V (vs. RHE) and the scan rate is 5mV/s.

In this paper, the reaction current at 0.9V is divided by the true surface area and the actual mass of the Pt to obtain the specific activity (*SA*). The reaction current at 0.9V is divided by the actual mass of the Pt to obtain the mass activity (*MA*). The *SA* is calculated using Equation 2:

$$SA = \frac{I_{0.9V}}{ECSA \times Pt_{Loading}} \tag{2}$$

The *MA* is calculated using Equation 3:

$$MA = \frac{I_{0.9V}}{Pt_{Loading}} \tag{3}$$

$I_{0.9V}$ is the reaction current in the LSV curve at 0.9V (mA), $Pt_{Loading}$ is the Pt loading of the catalyst electrode (mg).

3. RESULTS AND DISCUSSION

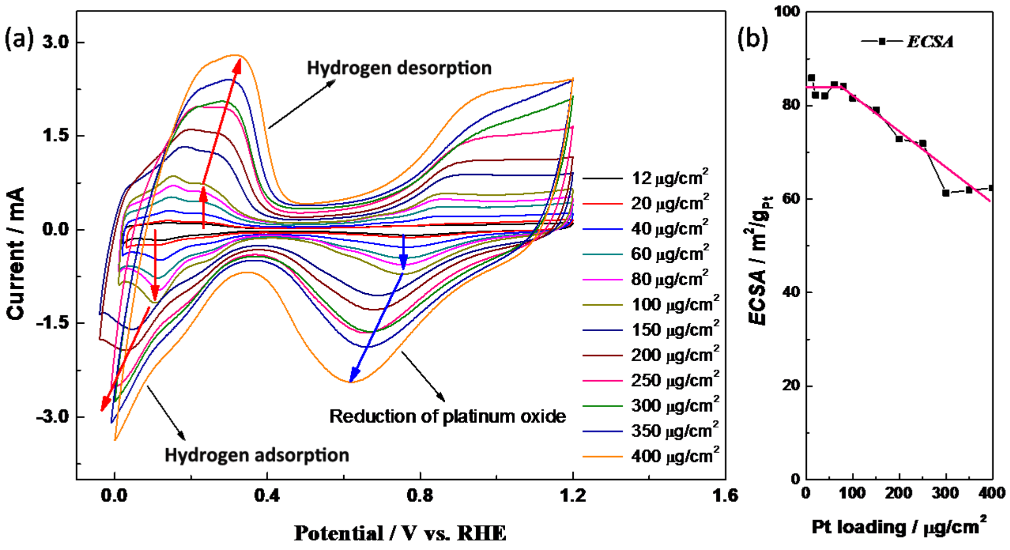

Figure 1. (a) The CV curves of a series of Pt/C catalyst electrodes with the same I/C ratio and different Pt loading; (b) Relationship between *ECSA* and Pt loading of Pt/C catalyst electrodes with the same I/C ratio and different Pt loadings. The testing condition was in 0.1M $HClO_4$ solution under nitrogen atmosphere, the voltage range was set to 0~1.2V (vs. RHE), scan rate was set to 50mV/s.

Figure1a shows the CV curves of Pt/C catalyst electrodes with the same I/C ratio and different Pt loading. The hydrogen adsorption/desorption peak is at about 0.2V, which is consistent with previous literature.[15] The hydrogen adsorption/desorption peak area (or total active area) is gradually increased with the increasing Pt loading (or thickness). According to the hydrogen absorption/desorption peak (potential: 0.05~0.4V vs.RHE) of the CV curves, the *ECSA* of Pt/C catalyst electrodes can be calculated by the eRec software and Equation 1. In our calculation, all Pt loadings in the electrode were considered to be electrochemically active. The results showed that the *ECSA* of Pt loadings (from 12μg/cm^2 to 400μg/cm^2) were 85.89m^2/g (12μg/cm^2), 82.24m^2/g (20μg/cm^2), 82.08m^2/g (40μg/cm^2), 84.52m^2/g (60μg/cm^2), 84.08m^2/g (80μg/cm^2), 81.55m^2/g (100μg/cm^2), 79.05m^2/g (150μg/cm^2), 72.81m^2/g (200μg/cm^2), 71.90m^2/g (250μg/cm^2), 61.31m^2/g (300μg/cm^2), 61.90m^2/g (350μg/cm^2), 62.36m^2/g (400μg/cm^2), respectively (as shown in Figure 1b and Table 1).

At low Pt loading region (<100μg/cm^2, or electrode thickness <2.17μm), we observed significant hydrogen adsorption/desorption peaks with longitudinal symmetry. This result indicated that the adsorption/desorption process of hydrogen on the electrode surface is reversible, and there is no mass transfer. Theoretically, under the same testing conditions, the *ECSA* of Pt/C catalysts with the same I/C ratio and preparation method are always same. As shown in Figure 1b, *ECSA* is about 85m^2/g in the low Pt loading range (<100μg/cm^2), as have been reported in many articles which gave range from 60 to 110 m^2/g$_{Pt}$,[16-22]indicating that the electrode does not experience mass transfer difficulties because the electrode thickness is small enough. Interestingly, when the Pt loading was further increased (>100μg/cm^2, or electrode thickness >2.17μm), the peak potential of hydrogen adsorption/desorption began to shift. Simultaneously, the *ECSA* started to decrease gradually and dropped to almost 60m^2/g$_{Pt}$. Yannick Garsany.et al had reported relatively low *ECSA* value for commercial Pt/C catalysts,[23]which could prove the accuracy of our experimental data. The impact of scan rates can be ignored because the scan rate used in this experiment (50mV/s) was very slow. Therefore, we believe that the peak shift at high electrode thickness was due to the incomplete H-adsorption process caused by the ohm potential drop in the solution, which resulted in the lower measured electrode potential compared to the low thickness electrode.

The hydrogen adsorption/desorption process on the surface of the electrode can be understood as the adsorption/desorption process of H$^+$ between the catalyst surface and the ionic solution. And the CV testing process can be equal to the oxidation/reduction process of H$^+$ on the catalyst surface, as shown in Equation 4:

$$\mathrm{H}_{ad}^{+} + e^{-} \rightleftharpoons \mathrm{H}_{ad} \tag{4}$$

H_{ad}^{+} is hydrogen ion adsorbed on the electrode surface, H_{ad} is hydrogen atom adsorbed on the electrode surface.

When the electrode thickness is very thin (low Pt loading), there is no mass transfer limitation for H$^+$ and electron-transfer reaction, the reaction shown in Equation 4 is very rapid and reversible. That is, the peak potential of adsorption/desorption is independent of the H$^+$ transfer rate (or the scan rate) in solution. So the peak potential of adsorption/desorption ($E_{P,low}$) does not shift. The peak current ($I_{P,low}$) can be calculated by Equation 5:

$$I_{P,low} = \frac{n^2 F^2 v A_r \Gamma^*}{4RT} \tag{5}$$

Where n is the stoichiometric number of electrons involved in the electrode reaction, F is the Faraday constant, A_r is the real surface area, Γ^* is the moles of adsorbed hydrogen atoms per unit Pt surface area, R and T are the gas constant and temperature, respectively. In the case of thin electrode thickness, same as low Pt loading, A_r is equal to the total surface area (A) in catalysts, and $I_{P,low}$ and A_r show a linear relationship. Therefore, *ECSA* values remain unchanged.

When the electrode thickness increased with the increasing Pt loading, the H^+ is difficult to transfer between the electrode surface and solution due to the shortage of H^+ inside the electrode, the electrical conversion reaction represented by Equation 4 significantly slowed down and got partially reversible. So the peak potential of adsorption/desorption is related to the H^+ transfer rate (or the scan rate) in solution. When the scan rate is constant, the H^+ transfer rate caused by electrode thickness will increase the mass transfer resistance. Thus the peak potential of adsorption/desorption ($E_{P,high}$) will shift. The peak current ($I_{P,high}$) can be calculated by Equation 6:

$$I_{P,high} = \frac{n\alpha n_a F^2 v A_r \Gamma^*}{2.718RT} \qquad (6)$$

Where a is the transfer coefficient and n_a is the number of electron transfer. When the thickness of the electrode increases gradually, that is, the loading of Pt increases, the ratio of the true surface area (A_r) to the total surface area (A) of catalysts will decrease gradually. It means that $I_{P,high}$ is directly proportional to a, n_a and A_r, resulting the drop of the *ECSA* value, gradually.

Moreover, in the high Pt loading electrode, some Pt particles are blocked in the carbon substrate and not exposed to the electrolyte solution. This means that the effective Pt loading ($Pt_{effective}$) is less than the actual Pt loading (Pt_{actual}). The $Pt_{effective}$ can be calculated by Equation7:

$$Pt_{real} = \frac{S_{high}}{2.1 \times V \times ECSA_{low}} \qquad (7)$$

$ECSA_{low}$ is the electrochemical active area in low Pt loading electrode (m^2/g_{Pt}), S_{high} is the integrated area between the current and voltage in the hydrogen desorption area in high Pt loading electrode (mA•V).

Thus, we propose the effective Pt loading (C) by Equation 8:

$$C = \frac{Pt_{real}}{Pt_{high}} = \frac{S_{high}}{2.1 \times V \times ECSA_{low} \times Pt_{high}} = \frac{ECSA_{high}}{ECSA_{low}} \qquad (8)$$

More interesting, the thickness of MEA which the Pt loading is 400μg/cm^2 in the fuel cell is normally 5~10μm, and the *ECSA* values for MEA in the fuel cell are around 60m^2/g, which is in agreement with the values obtained the catalyst of Pt loading greater than 250μg/cm^2 (or electrode thickness >5.12μm) as measured by a rotating disk electrode system.

Figure 2a showed the LSV curves of Pt/C catalyst electrodes with the same I/C ratio and different Pt loading. The limiting current obtained in the experiment fluctuates in the range of 1.0~1.2mA, and did not change with the Pt loading and electrode thickness. The half-wave potential increased with the increasing Pt loading. The current at 0.9V showed a positive correlation with the Pt loading. That is, with the increase of Pt loading, the current at 0.9V also increased. *MA* (see Figure 3a and Table 1) and *SA* (see Figure 3b and Table 1) were calculated by current at 0.9V, which were used to evaluate the oxygen reduction activity of the catalyst.

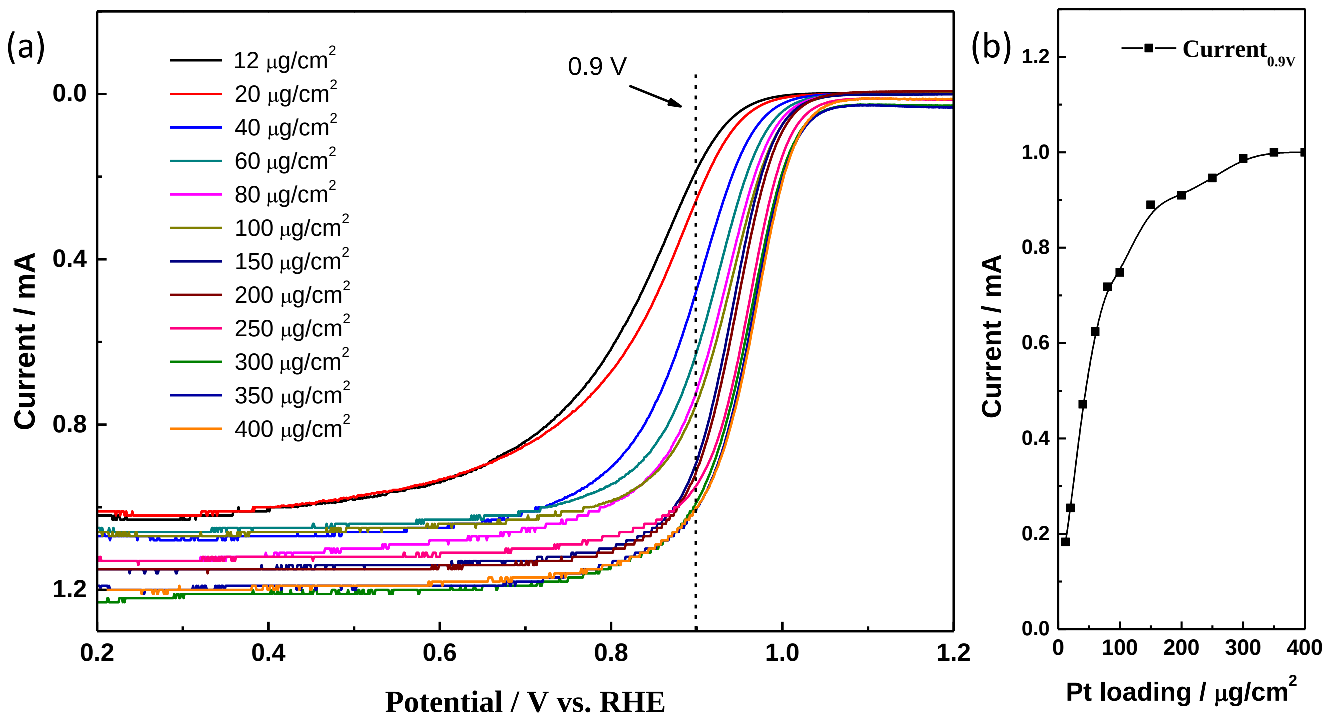

Figure 2. (a) The LSV curves of a series of Pt/C catalyst electrodes with the same I/C ratio and different Pt loading; (b) Relationship between current at 0.9V and Pt loading of Pt/C catalyst electrodes.

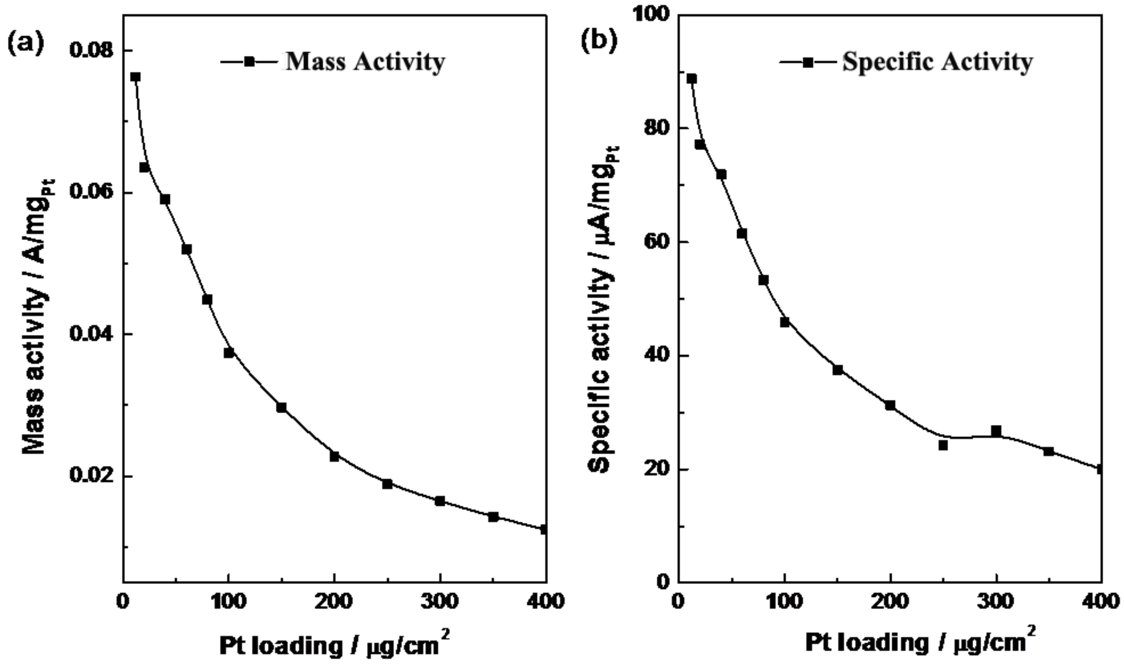

Figure 3. Relationship between *MA* and Pt loading of Pt/C catalyst electrodes (a) and *SA* and Pt loading of Pt/C catalyst electrodes (b).

Blizanac et al. announced that MA in their experiments was about 0.03A/mg_{Pt} at 0.9V.[24]While Huiyuan Zhu et al. reported that of commercial Pt/C catalysts was 0.035 A/mg_{Pt} and SA was 0.068 mA/cm^2 at 557mV (vs. Ag/AgCl), respectively.[25]However, there were still some literatures claimed higher value of MA and SA depending on the kinetics current at 0.9V,which is calculated from the current at 0.9V but larger.[26-29]It has been proved that the kinetics current at 0.9V would be more accurate at very low Pt loadings (<<100μg/cm^2),accounting for why we did not choose the current. [29-30] According to the ratio of *MA* to Pt loading and ratio of *SA* to Pt loading, it was clear to see that the *MA* and the *SA* decreased with the increase of Pt loading, which proved that the catalyst loading would have a significant impact on its activity. With the increase of the catalyst Pt loading, the internal mass transfer resistance of the catalyst increased, which further affected the active area of the catalyst.

Table 1. *ECSA*, current, *MA*, *SA* and limiting current of a series of Pt/C catalyst electrodes with the same I/C ratio and different Pt loading.

Pt loading μg/cm^2	Pt mass μg	*ECSA* m^2/g_{pt}	Limited Current mA	$I_{0.9V}$ mA	MA A/mg_{pt}	SA $\mu A/cm^2_{pt}$
12	2.4	85.89	1.00	0.183	0.0763	88.776
20	4	82.24	1.00	0.254	0.0635	77.213
40	8	82.08	1.07	0.472	0.0590	71.881
60	12	84.52	1.05	0.624	0.0520	61.523
80	16	84.08	1.12	0.718	0.0449	53.371
100	20	81.55	1.06	0.748	0.0374	45.861
150	30	79.05	1.15	0.890	0.0297	37.528
200	40	72.81	1.15	0.910	0.0228	31.245
250	50	77.90	1.12	0.946	0.0189	24.287
300	60	61.31	1.21	0.987	0.0165	26.830
350	70	61.90	1.19	1.000	0.0143	23.078
400	80	52.36	1.20	1.000	0.0125	20.044

4. CONCLUSION

In this paper, the electrochemical performance of Pt/C catalyst electrodes with the same I/C ratio and different Pt loadings were measured by the RDE system. We got the following conclusions:

(1) When the Pt loading (or thickness) is small enough (<100μg/cm^2, or <2.17μm), the measured *ECSA* was equal to the inherent value;

(2) In the high Pt loading electrode, the mass transfer was restricted as well as ohm potential drop in the solution, which resulted in the measured electrode potential shifting significantly. Moreover, the measured *ECSA* was lower than the inherent value;

(3) The concept of effective Pt loading in high Pt loading electrode (>100μg/cm^2, or electrode thickness >2.17μm) was proposed and could be defined as the ratio of *ECSA* for high to low Pt loading.

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