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Estimation of Active Surface Area of Platinum by Electrochemical Impedance Spectroscopy

A.P. Yadav ^{1*}

1. Central Department of Chemistry, Tribhuvan University, Kirtipur, Kathmandu, Nepal
[Email: amar2y@yahoo.com]

Platinum is used as an electro-catalyst for the oxidation of hydrogen and reduction of oxygen in fuel cell. High surface area of platinum is achieved by using 2-5nm particle size. However, this also leads to loss of active surface area with the operation of fuel cell. In this study, active surface area of Pt in 0.5M H₂SO₄ solution was estimated from capacitance value measured by electrochemical impedance spectroscopy (EIS) and under potential deposited hydrogen (UPD-H) from CV and compared. The results showed that both the techniques gave similar trend in the variation of active surface area with the CV cycle. The active surface area estimated from capacitance value was slightly higher than that estimated from UPD-H value.

Keyword: PEFC, Pt Dissolution, Capacitance, electro-catalyst, UPD-H.

1. Introduction

The search for new electricity generation paths that preferentially use alternate fuels, with low environmental impact and high conversion efficiency, has led to the development of fuel cells. Polymer electrolyte fuel cell (PEFC) is particularly noteworthy due to its high versatility for mobile applications. At the hearth of a PEFC is the catalytic layer, which would normally be made with highly dispersed platinum crystallites on a conductive support that has a high surface area, such as carbon black. This is used as electro-catalyst for hydrogen oxidation and oxygen reduction reactions ^[1, 2]. Platinum is used due to its stability and because it enhances the hydrogen (H₂) oxidation and oxygen (O₂) reduction in an acid medium. However, it has been found that Pt dissolves under potential cycling conditions in operating PEFCs ^[3, 4] and under simulated conditions ^[5-8]. The best electroactive properties of Pt/C are obtained with Pt particles in the range from 2 to 5 nm, and C particles in the range from 30 to 100 nm diameter ^[9].

It has been reported that PEFCs operating under constant potential for thousands of hours gradually lose catalytic active surface area at cathode by nano-particle grain growth ^[10]. Recent testing indicates that

potential cycling accelerates the rate of surface area loss ^[11-14]. Patterson was the first to apply this method to investigate the Pt dissolution in a membrane-electrode-assembly (MEA) for use in PEFC to accelerate the loss of surface area for a Pt electrocatalyst and to predict the effect of this loss of electrochemical area on the PEFC cell performance ^[15]. The deposition of Pt in electrolyte membrane can lead to its decomposition or increase of resistance, therefore affecting the durability of PEFC. The loss of active surface area of Pt is estimated from the charged in hydrogen under-potential region (HUPD) of the cyclic voltammogram. For this, a well-defined HUPD region is necessary and therefore an erroneous active surface area maybe estimated in the absence of it. This study reports on the estimation of active surface area of Pt by measuring the capacitance with the help of electrochemical impedance spectroscopy (EIS). The purpose is to show how to use EIS for the estimation of active surface area and compare the results of active surface area estimated by CV and EIS.

2. Experimental

In this study, a planar AT-cut Au quartz crystal with a

fundamental frequency of 6 MHz in air was used as a substrate for electroplating Pt on it. Each crystal had a 1.45 cm² circular area on each side. One side of the QCM was electroplated with Pt in 2% H₂PtCl₆ solution at 0.2 V vs. SHE. The Pt-plated Au quartz crystal was then used as a working electrode. The thickness of the Pt coating was 65nm. The X-ray diffraction patterns showed the formation of a dominant (111) oriented Pt bulk phase with the average particle size of 40-60 nm^[5].

Electrochemical measurements were made in a one-compartment Teflon cell with 50 mL capacity. The cell had a special Teflon cover with holes designed to host the auxiliary and reference electrodes and degassing tubes. A KCl-saturated silver/silver chloride electrode (SSE) with a double junction was used as a reference electrode and Pt or Au wire was used as the counter electrode. The potential values are referred to SHE. All the measurements were made at 298 K with solutions prepared in doubly distilled water.

The active surface area of Pt-plated QCM electrode was evaluated by determining the double layer capacitance with EIS and from the amount of charge in the under potential deposited H region (UPD-H).

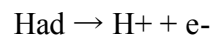
3. Results and Discussion

3.1 CV of Pt in 0.5 M H₂SO₄

The voltammetric response for the Pt in 0.5M H₂SO₄ solution at the scan rate of 0.01 V/s is shown in Fig.1. The potential was scanned from the immersion potential in the anodic direction in the potential range of 0.0-1.4 V vs. SHE. The current-potential response in between 0 ~ 1.4 V can be divided into three regions: UPD-H is observed between 0.05 and 0.4 V with two pairs of redox peaks at 0.27 and 0.12 V, which are attributed to strongly and weakly adsorbed H atoms at the Pt surfaces with (100) and (110) orientations^[16], respectively. The double-layer region having constant current is observed from 0.40 to 0.75 V. With a further positive shift in electrode potential, an oxidation wave appears at E>0.85 V, and a reduced peak appears around 0.8 V in the subsequent negative-going sweep. This pair of redox peak is attributed to the formation and reduction of Pt hydroxide/oxide (PtOH/PtOx) at the Pt electrode surface.

In the cathodic scan, during the reduction of platinum, protons from the acid are adsorbed at the surface of the electrode while during the anodic scan, these

atoms of hydrogen are desorbed according to the following electrochemical reaction:



The measure of the number of electrons liberated or taken during the oxidation or reduction of platinum for low potentials gives the number of hydrogen atoms desorbed or adsorbed and thus the number of adsorption sites present on the electrode's surface. This defines the active surface of the electrode. The total charge corresponding to the hydrogen desorption/adsorption can be related to the integral of the curve for a certain interval of potentials where the atoms are being desorbed. This is indicated in Fig. 1. The expression of the total charge of desorption/adsorption can be written as follows:

$$Q = \frac{1}{\nu} \int_{E_1}^{E_2} I. dE$$

Where ν is the scan rate. The contribution of capacitive current due to the double layer capacitance has to be subtracted.

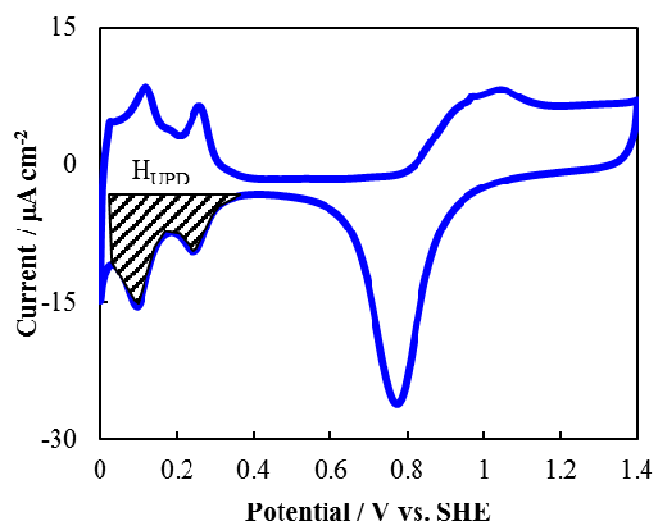


Fig 1: Cyclic voltammogram of Pt in 0.5M H₂SO₄ at the scan rate of 0.01V/s. The shaded area in UPD-H is used for the estimation of total charge due to adsorption of hydrogen.

The negative limit for the formation of a monolayer of the UPD-H atoms at Pt electrodes in 0.5 M H₂SO₄ is assumed to be 0.05 V^[16]. If Q_T is taken as the charge density for the adsorption of a monolayer of the UPD-H atoms on a Pt electrode in unit of

microcoulomb per square centimeter and Q_E is taken as the total charge estimated from the CV curve in Fig.1, the active surface area can be given as:

$$ECA = Q_E / Q_T$$

For a polycrystalline Pt electrode surface, a charge of about $210 \mu\text{C}/\text{cm}^2$ has been suggested for QS [16], therefore, from the calculated total charge (Q_E) the active surface area was estimated for 500 cycles of CV as shown in Fig 2.

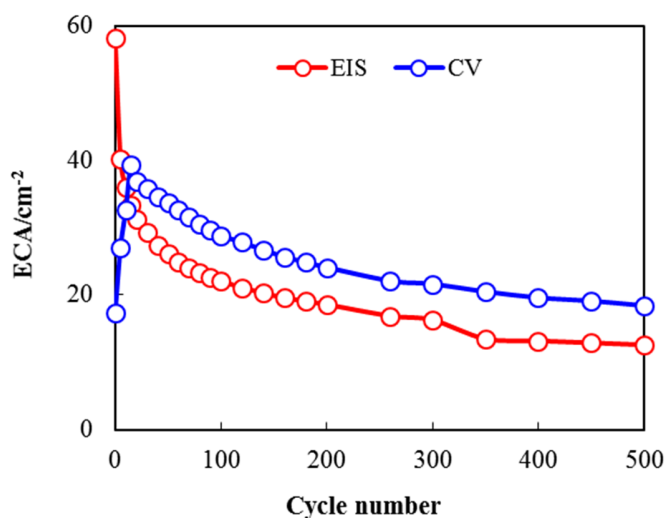


Fig 2: Variation of active surface of Pt in 0.5 M H_2SO_4 solution with the cycle number of CV. The active surface area was estimated from capacitance value and charge in UPD-H.

In the case of EIS technique, whole frequency impedance was measured from 10 kHz to 100mHz at open circuit potential (OCP) of Pt in 0.5M H_2SO_4 solution and is depicted in Fig. 3. From the Fig. 3, a frequency of 10 Hz was chosen for measuring impedance for the estimation of capacitance of Pt electrode after CV cycle. From the measured impedance at 10 Hz ($Z_{10\text{Hz}}$), the capacitance was estimated according to the relation:

$$C = \frac{1}{2\pi f \cdot Z_{10\text{Hz}}}$$

The active surface area was obtained from the calculated capacitance value by dividing it by capacitance value for per square centimeter area. The theoretical value for this was taken as $40 \mu\text{F}/\text{cm}^2$ in

the OCP region [17]. The active surface area estimated from the EIS method is plotted in Fig. 2 together with the active area estimated from the UPD-H.

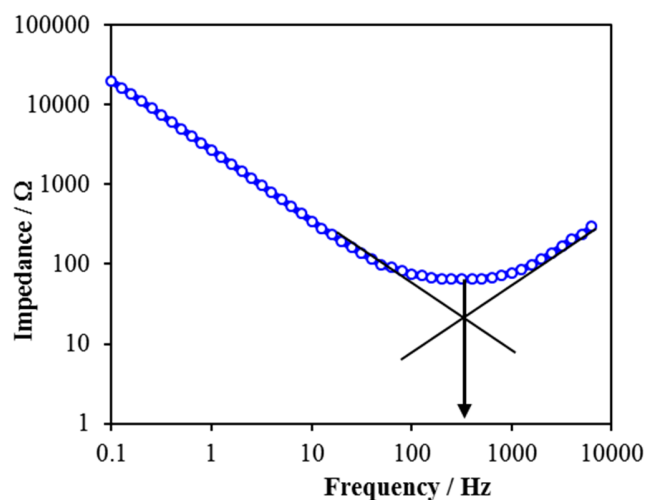


Fig 3: Bode plot for the Pt in 0.5 M H_2SO_4 solution. The frequency range was from 10 kHz to 100 mHz.

Comparing the active surface area obtained from EIS and UPD-H, it can be seen that both followed the same trend with cycle number till 500 cycles except that in the beginning the two values were in contrast. This can be explained by considering the effect of surface cleanliness on the adsorption-desorption of hydrogen. As the CV cycles progressed, the cleaning of the Pt surface took place and a well-defined adsorption-desorption peaks for hydrogen was observed. On the other hand, in the case of EIS method, the capacitance was estimated from the impedance value measured at OCP and it followed the gradual decreasing trend. The active surface area estimated from UPD-H was lower than that estimated from EIS. This shows that probably the capacitance value of $40 \mu\text{F}/\text{cm}^2$ in the OCP region is not the correct value. If the capacitance value is taken as $50 \mu\text{F}/\text{cm}^2$ in the OCP region, the active surface area estimated from both the methods are very close to each other. Therefore, it needs further study to evaluate the capacitance in the OCP region more accurately so that accurate estimation of active surface area may be achieved by EIS method. However, the active surface area estimated from UPD-H also needs to be carefully evaluated as the hydrogen adsorption-desorption peaks can also get affected by the type of Pt surface.

4. Conclusions

In this study, active surface area of Pt in 0.5 M H₂SO₄ solution was estimated from capacitance value measured by EIS and UPD-H from CV. The results showed that both the techniques gave similar trend in the variation of active surface area with the CV cycle. The active surface area estimated from UPD-H was slightly lower than that estimated from capacitance value.

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