The stability of PEMFC electrodes : platinum dissolution vs potential and temperature investigated by quartz crystal microbalance

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The Stability of PEMFC Electrodes

Platinum Dissolution vs Potential and Temperature Investigated by Quartz Crystal Microbalance

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The stability of platinum in proton exchange membrane fuel cell (PEMFC) electrodes has been investigated by determining the dissolution of platinum from a thin platinum film deposited on a gold substrate in 1 M HClO₄ at different temperatures ranging between 40 and 80°C and potentials between 0.85 and 1.4 V vs reversible hydrogen electrode (RHE). The loss of Pt during the dissolution process is monitored in situ with the highly sensitive quartz crystal microbalance. By combining the microbalance with the electrochemical cell, the dynamic change of the electrode weight can be observed in situ. It is shown that first an oxide layer is formed, which can be dissolved depending on temperature and potential. The dissolution rate is found to be strongly dependent on the potential and temperature. At a potential close to 1.15 V vs RHE, the dissolution rate becomes saturated at 80°C due to the protection of a passivating surface platinum oxide layer at high potential. At 80°C, the dissolution rate starts to diminish when the potential is higher than 1.15 V.

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Degradation of proton exchange membrane fuel cells (PEMFCs) performance has been getting increasing attention for the last couple of years. Among the degradation mechanisms, loss of platinum leading to a reduced electrochemically active surface area of the catalyst layers has been considered as an important cause of loss of fuel cell performance. The Pt loss especially takes place when high electrode potentials occur,¹⁻⁶ e.g., during load cycles, shutdown of the fuel cells, or under fuel starvation.^{7,8}

Loss of platinum can occur due to the oxidation of platinum itself or due to the corrosion of the carbon support.⁹ In either case, the active surface area on which oxygen reduction takes place is reduced. Poisoning of the membrane as a result of platinum diffusion into the PEM can take place as well.¹⁰ In highly acidic medium, under the operating voltage, Pt can also be dissolved and then migrates and redeposits on other Pt particles in the catalyst layer to form larger particles (sintering or Ostwald ripening). The mechanism of the Pt dissolution phenomenon has been suggested in detail in Ref. 11-13.

Furthermore, the dissolved platinum can also be removed and diffused to other parts of the membrane electrode assembly (MEA) following the coalescence mechanism.¹² The magnitude of the Pt dissolution and redeposition phenomenon depends strongly on the fuel cell operating voltage. The influence of potential at low temperatures on Pt dissolution has been reported by Wang and Kawahara.^{14,15}

To date, Pt dissolution has only been studied ex situ by determining the Pt concentration after the dissolution process.^{14,15} In this paper we present a different method to directly investigate the dissolution of Pt thin film under potentiostatic conditions in 1 M HClO₄ at different temperatures ranging from 40 to 80°C. By using the conventional electrochemical cell in combination with a quartz crystal microbalance, the weight of the Pt electrode is in situ monitored with high sensitivity during the dissolution process. This method gives an opportunity to investigate in detail the elementary steps of the dissolution mechanism, including formation of the surface Pt oxide layer and its further dissolution, thus giving a better insight into dynamics of the Pt dissolution in the fuel cell.

Experimental

A commercial quartz crystal purchased from Maxtex which has a thin polished gold electrode with an area of 1.37 cm² was used as a

substrate for Pt deposition. Before deposition of Pt, the gold electrode was electrochemically cleaned in 0.5 M H₂SO₄ by applying a cycling potential between 0.02 and 1.7 V vs reversible hydrogen electrode (RHE) for at least 30 min.

A Pt thin film on the gold electrode was obtained from a mixture of 0.02 mM H₂PtCl₆ and 0.02 M Na₂HPO₄. The film was electrochemically deposited under a constant current regime of 1 mA on the cleaned gold electrode. The thickness of the Pt film varied depending on the deposition time, which was typically between 3 and 5 min.

After deposition, the Pt electrode was rinsed with distilled water to remove the residue of the deposition solution. The electrode was further annealed in 1 M HClO₄, which is prepared from chloride-free HClO₄ 70% (Suprapur, Merck) and ultrapure 18 MΩ cm Millipore water, by applying a cycling potential between 0.05 and 1.3 V vs RHE for at least 20 cycles to stabilize the morphology and surface state of the Pt electrode. All cyclic voltammograms (CVs) were performed at a sweep rate of 50 mV/s.

The electrochemical cell, which is used for applying a constant potential, consists of the deposited Pt electrode as a working electrode, a Pt disk as a counter electrode, and a Hg/HgSO₄ reference electrode. All electrode potential values in this paper are reported vs RHE. In this setup the working electrode, which is at the same time an electrode for the microbalance, was separated from the counter electrode by a separate glass membrane. The volume of the compartment for the working electrode is about 230 mL. Before the experiment, the dissolution solution, 1 M HClO₄, was purged with purified argon to remove dissolved oxygen. During experiments, the temperature of the dissolution batch was stabilized and controlled by a thermostat. Before the dissolution experiment, the electrode is subjected to potential cycling between 0.05 and 1.3 V to remove all native oxide on the surface until the electrode cyclic voltammogram becomes unchanged. The cyclic voltammetry is stopped at an end potential of 0.45 V, thus the dissolution experiments are started on an oxygen-free platinum surface. The dissolution of the Pt electrode was performed at a constant electrode potential by applying a step potential from 0.45 V to the required potential, while the electrode weight was simultaneously monitored with the microbalance. The mass of the electrode is set at zero when the dissolution process is started. For each set of measurements done at the same potential, a fresh electrode was prepared. The experiments at the same potential but at different temperatures were measured with the same electrode. Between these experiments, the preconditioning procedure was the same, i.e., potential cycling in order to obtain a clean and reproducible platinum surface.

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Figure 1. Dependence of the electrode weight on the applied potential during cyclic voltammetry in 1 M HClO₄ with sweep rate of 50 mV/s.

The time of the dissolution experiment was taken such that the oxide layer buildup and dissolution could be measured accurately. Consequently, the measuring times were not the same for all experiments, i.e., much shorter for high temperatures and at the same temperature shorter for higher potentials. The dissolution was studied in the potential range between 0.85 and 1.4 V at temperatures between 40 and 80°C.

Results

During the platinum deposition on the gold substrate, the total weight of Pt deposited on the electrode linearly increases with deposition time. After 4 min of deposition, approximately 63 μg of Pt has been deposited on the gold electrode. After the Pt deposition, a CV of this electrode is taken in 1 M HClO₄ and shows only oxidation and reduction peaks of Pt oxide and hydrogen adsorption and desorption on Pt. No peaks for gold and gold oxide are observed.

In Fig. 1, dependence of the electrode weight on the applied potential during cyclic voltammetry at a sweep rate of 50 mV/s is plotted. The arrows in the graph show the direction of the sweeping potential. Compared with the CV plotted in the same figure, it is clear that at a potential higher than 0.45 V, the weight of the electrode increases when the Pt oxide layer is formed and decreases when the reduction of the oxide layer occurs. At further potential reduction from 0.45 to 0.05 V, the weight of the electrode decreases in spite of hydrogen adsorption occurring. The same phenomenon was observed by Birss et al.,¹⁶ who explained this by the desorption of water when the electrode potential is lowered from 0.45 to 0.05 V. In a potential range close to 0 V, the desorption-adsorption of water at the electrode surface becomes stabilized while the mass of the electrode stays unchanged. The complete desorption of water results in 0.24 μg loss in the electrode mass. Upon increase of the potential up to 0.45 V, adsorbed water again replaces adsorbed hydrogen.

From the H-adsorption region in the electrode CV, assuming 0.210 mC per "real" cm² of Pt,¹⁷ the electrode surface area was calculated to be about 24 cm². According to the electrode mass change during oxidation by scanning the potential from 0.45 to 1.3 V, each surface platinum atom is covered by 0.44 O atoms, using 1.31×10^{15} atoms per cm² for the density of platinum atoms on the polycrystalline Pt surface.¹⁷ This surface coverage is lower than that calculated from the coulombs passed to reduce the oxide, which amounts to 0.54 O atoms per surface platinum atom. The mass changes of the Pt electrode during the dissolution process under potentiostatic conditions, in 1 M HClO₄ at 80°C are presented in Fig. 2.

Figure 2A shows the change in the mass of the working electrode for the experiment at 0.85 V and 80°C. Two regions can clearly be discerned. In the first 150 min, the mass of the electrode increased up to a certain maximum. The gain in the electrode mass is much higher than can be obtained from the water adsorption (see Fig. 1).

After 150 min, the mass started to decrease, while the electrode potential was maintained. The decrease rate of the mass remained almost constant for a long period of time.

A similar increase of mass followed by a decrease was also observed at higher dissolution potentials. In Fig. 2B-2E, measured changes in electrode weights at dissolution potentials ranging from 0.95 to 1.4 V are plotted. The measuring time of these experiments is varied depending on how fast the dissolution occurs. As can be seen in these figures, both the rate of increase of the mass as well as the rate of decrease is accelerated with increasing the electrode potential. Comparison of data in Fig. 1 and 2 strongly suggests that the mass increase is a result of net oxide formation, whereas the decrease can be related to net dissolution. The oxidation of Pt can proceed according to¹⁸

Depending on the potential, PtO and PtO₂ are formed, resulting in an increase of the electrode mass as seen in the oxidation region of Fig. 2A-2E. The rate of the oxide-layer formation depends on the applied potential. Pt dissolution can occur via the dissolution of the surface oxide layer or even from metallic platinum as follows

Assuming a Butler-Volmer relation between the equilibrium potential and the reaction rate for Reactions 4 and 5, the Pt dissolution rate strongly depends on the potential and concentration of Pt ions in the solution. When the dissolution time is long enough, the dissolution process can be inhibited due a rising of the equilibrium concentration of Pt in the solution, which is typically observed at the dissolution curve at 0.95 V (see Fig. 2B). The maximum mass measured at a certain condition is the result of the mass increase due to oxide formation and the loss of mass caused by its dissolution. The fact that the mass maximum does not continuously increase with increasing potential shows that the mechanism of oxide growth and dissolution is rather complex. The mass change is thus a combination of mass increase due to oxide layer growth and a mass decrease due to dissolution. As the exact mechanism is unknown, no corrections have been made in the reported dissolution rates by taking into account these simultaneous phenomena.

In Fig. 2F, the steady-state current at the electrode during dissolution at 1.4 V is plotted. The charge transfer in the cell during 30 min calculated from this curve in the dissolution region in Fig. 2F is estimated to be about 19.43 mC. The measured amount of dissolved platinum amounted to 7.29 μg as shown in Fig. 2E. According to Faraday's law and assuming a reaction with two electrons involved, this amount of mass change would correspond to a charge of 7.21 mC, which is much lower than the actual number of 19.43 mC. This means that platinum oxide is still formed during its dissolution. Even if the dissolution of platinum is a four-electron process, i.e., PtO₂ dissolves as Pt⁴⁺, still more charge is passed. In case platinum dissolves from its platinum oxide, a new layer of oxide is formed subsequently.

When the dissolution temperature was lowered to 60°C, the whole dissolution process happened at a lower rate. At a potential of 0.85 V, only an increase of the electrode mass was observed without subsequent decrease. For the dissolution temperature of 40°C, even at a potential of 1.2 V, no dissolution was observed after 90 h (see Fig. 3). Therefore, it can be concluded that the Pt dissolution can only occur under a favorable condition, which is a combination of oxide layer thickness, temperature, and potential. While the thickness of the oxide layer is a result of the potential and the duration of

Figure 2. Time dependence of the electrode weight measured in 1 M HClO_4 and at 80°C at different dissolution potentials: (A) 0.85, (B) 0.95, (C) 1.05, (D) 1.15, and (E) 1.4; (F) time dependence of the steady-state current during dissolution at a potential of 1.4 V.

the exposure to this potential and temperature, the rate of dissolution of this oxide layer depends on temperature and potential as well.

Just after finishing the dissolution process at 60°C as described above, the CV of the electrode, which starts from a potential of 1.0 V and scans negatively, is immediately taken. Irrespective of the potential at which the dissolution was measured, the scan in the negative direction was started at 1.0 V to be able to compare the different reduction charges. As the time of the dissolution experi-

ment depended on the dissolution rate, the data shown in Fig. 4 are illustrative for the oxide present after dissolution. It does not enable a direct insight in the dependence of oxide layer thickness vs potential. The CV taken after 22 h of dissolution at 1.25 V shows a huge oxide reduction peak (Fig. 4A). This again confirms that the surface oxide layer is still present and is continuously formed during the dissolution. The surface oxide layer becomes thinner, resulting in a smaller oxide reduction peak as the second CV is done.

Figure 3. Time dependence of the electrode weight measured in 1 M HClO_4 at 40°C and 1.2 V.

Comparing the first CVs, which are taken after the dissolution experiments at 1.05, 1.15, and 1.25 V at 60°C and generated from the same starting potential of 1.0 V, the higher the dissolution potential, the larger oxide reduction peak is seen (Fig. 4B). The in-

crease in the Pt oxidation peaks is also observed in the same order. From data presented in Fig. 4A and 4B, the number of surface platinum oxide layers present on the electrode before and after taking 1, 2, and 5 CVs is calculated and shown in Fig. 4C. It shows that during the dissolution, the surface oxide layer in the Pt electrode is thicker when a higher electrode potential is applied. During the dissolution at a potential lower or close to 1.15 V, the electrode is covered with a monolayer of PtO. This oxide layer can partly be removed by applying one potential cycling. When the dissolution potential increases up to 1.25 V, more than two PtO layers are found on the electrode surface. Based on our experiments, no distinction can be made between a single layer of PtO_2 or two layers of PtO. The formation of a full monolayer of PtO corresponds to $0.42 \text{ mC cm}^{-2} \text{ Pt}$. As the electrode surface was 24 cm^2 , 10 mC of charge is passed for complete coverage of our electrode with PtO. Adding to this the charge corresponding to the mass change resulting from platinum dissolution (7.3 µg , 7.21 mC), and comparing it to the total charge measured during dissolution, 19.4 mC, and the fact that after a dissolution experiment more than a full monolayer of PtO layer can be reduced, the dissolution is very likely a two-electron process, as otherwise a even higher charge should have been measured.

From data such as presented in Fig. 2 the dissolution rate of the Pt electrode at different potentials and temperatures of 60 and 80°C

Figure 4. (Color online) CVs of the Pt electrode, which start at a potential of 1.0 V and scans negatively, after dissolution at potentials of (A) 1.25 and (B) 1.05, 1.15, and 1.25 V at 60°C ; (C) number of surface platinum oxide layers after taking 1, 2, and 5 CVs, depending on dissolution potentials.

Figure 5. Pt dissolution rate vs dissolution potential and temperature. The real surface area of the electrode is 24 cm².

was calculated from the slope of the decreasing part of the mass-time curve. The results are displayed in Fig. 5 and Table I. At the temperature of 40°C, the data is not available because only the oxidation is observed.

The logarithm of the dissolution rate was found to increase linearly with increasing potential up to 1.15 V. The dissolution rate increased about 54 times as the potential increased from 0.85 to 1.15 V. However, at 80°C, the dissolution rate reached a maximum at a potential close to 1.15 V. It also can be predicted by the data presented in Fig. 4C, which is explained by a presence of the platinum oxide layer. The platinum surface becomes more passive by the oxide layer when the potential reaches 1.15 V. When the potential increases further, Pt is fully protected by platinum oxide.¹⁹ The thickness of the protecting platinum oxide increased sharply above 1.15 V as shown in Fig. 4C. Therefore, the dissolution rate decreases at potentials higher than 1.15 V, as observed in Fig. 5. All measured dissolution rates shown in Fig. 5 are summarized and presented in Table I.

The data of our experiments seem to be in good agreement with the model of Darling and Meyers,²⁰ who calculated the buildup of platinum oxide and the dissolution of platinum for linear-sweep experiments. Exact comparison is difficult as our measurements are at constant potential.

Note that the dissolution rates in Table I should be compared to the amount of Pt deposited on the gold substrate, which is typically between 63 and 80 μg. Taking the dissolution rate at 1.15 V and 80°C, the electrode with a mass of 63 μg can be completely dissolved after 1 h 40 min, yielding a platinum concentration of 1.4 μM. In comparison with previously published results on bulk Pt dissolution,¹⁴ which reports the potential dependence of the Pt concentration resulting from platinum dissolution, the obtained data on

the dissolution rate presented in Table I have a similar potential dependence. The dissolution rate reported by Wang et al.¹⁴ at 0.9 V and 23°C, $1.4 \cdot 10^{-14}$ g cm⁻² s⁻¹, is the same as that reported in Table I at 0.95 V and 60°C, which translates into $1.5 \cdot 10^{-14}$ g cm⁻² s⁻¹. Although our method is different from that of Wang et al., comparison of the two numbers would lead to the conclusion that especially at temperatures higher than 60°C, the dissolution rate increases dramatically.

As stated before, the mass change is a combination of mass increase due to oxide-layer growth and a mass decrease due to dissolution. The reported dissolution rates can in fact be larger than reported in this paper. The dissolution rate presented in this paper is caused by the surface roughness and thin-film nature of the Pt layer, which is close in nature to the fuel cell catalyst.

Conclusions

To our knowledge, this paper shows for the first time a dynamic method to estimate the dissolution rate of the Pt thin film during potentiostatic conditions at elevated temperatures by combining the conventional electrochemical setup with a quartz crystal microbalance. Besides information obtained from the electrochemical measurements, this method allows the in situ observation of the dynamic change of the electrode weight. It can differentiate the oxidation and dissolution during the real-time Pt dissolution. For that reason, this technique gives extra advantages in comparison with previously presented techniques in literature, where the dissolution rate is only determined ex situ.

By using this technique, the Pt dissolution in 1 M HClO₄ during potentiostatic conditions has been investigated at different potentials and temperatures. The dissolution rate was found to be strongly dependent on the dissolution potential and temperature according to the Nernst equation. The dissolution was accelerated with increasing temperature. At the dissolution temperature of 80°C and potential higher than 1.15 V, the observed saturation of the dissolution rate is considered to be due to the protected surface platinum oxide at high potential. A reduction in the dissolution rate has been observed at the dissolution potential close to 1.4 V. The dissolution rates found for the thin-film Pt are higher than that previously published on bulk Pt dissolution, due to its surface and thin-film nature. Due to the characteristics of the electrode used in this study with high surface roughness and thin-film nature, the data are relevant for dissolution rates for PEMFC catalysts.

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Table I. Platinum dissolution rate per square centimeter of electrochemically active surface area vs potential and temperature.

Potential vs RHE (V)	60°C (ng/h cm ²)	80°C (μg/h cm ²)
0.85		0.03
0.95	0.05	0.10
1.05	0.45	0.22
1.15	0.87	1.58
1.25	2.09	—
1.40	—	0.60

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