Short Communication

Effect of trifluoromethanesulfonic acid on the ORR activity of Pt in acid medium

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In this paper, to study the effect of sulfonic groups on the ORR activity of Pt and exclude the effect of polytetrafluoroethylene (PTFE) backbone of Nafion, trifluoromethanesulfonic acid (CF_3SO_3H) was used to simulate the SO_3H-terminated side chains of Nafion. By using the CO displacement technique, it was predetermined that much more sulfonic groups are absorbed on the Pt surface in 50 mM CF_3SO_3H solution compared with that of 0 mM and 1 mM. The influence of sulfonic groups on the oxygen reduction reaction (ORR) activity of Pt is analyzed by using rotating Pt disk electrode (RDE) as work electrode in 0.1 M $HClO_4$ with various CF_3SO_3H contents. It is found that when the content of CF_3SO_3H is over 5 mM, the electrochemical active area of Pt decreases with increasing the content of CF_3SO_3H in solution, and the oxidation peak of Pt shifts to a higher potential. Meanwhile, the kinetic current loss of Pt increases apparently along with the increase of CF_3SO_3H content which is 40% for 10 mM and 71.3% for 50 mM at 0.9 V, respectively. The result shows that excess sulfonic groups of Nafion adsorbed on the surface of Pt will greatly lower the ORR activity of Pt.

1. INTRODUCTION

The relatively high demands of platinum in proton exchange membrane fuel cell (PEMFC) are still a bottleneck for its stationary and automotive applications. For achieving successful commercialization, a further reduction of Pt catalyst usage from ~30 g to ~10 g (80 kW stack) is necessary [1, 2]. Therefore, Pt catalytic activity should be fully utilized in PEMFC electrodes. The catalyst layers (CLs) of PEMFC is generally comprised by Pt/C powder and ionomer, and part of Pt surface directly contacts with ionomer to form three-phase interface which is considered to be the site

of electrochemical reactions and have a great effect to the Pt utilization.

Ionomers such as Nafion are an essential component in CLs which are used as binder and provide proton transport pathways [3]. However, hydrophilic ionomer side chain will be preferably oriented toward hydrophilic Pt surface [4], resulting in the adsorption of sulfonic anion on Pt surface. Researches by using RDE methods also indicated that Nafion would block other species from adsorbing on the surface of Pt which will affect the oxygen reduction reaction (ORR) activity of Pt, especially under low Pt loading [5, 6]. Subbaraman [5] first demonstrated that sulfonic anions of Nafion were specifically adsorbed on Pt single-crystal surfaces, and ORR was always affected by the ionomer layer on Nafion-covered surfaces irrespective of the surface orientation and/or the electronic properties of the surface atoms. Kodama [7] established a solid-state cell with a Pt single crystal electrode to study the adsorption and desorption of the sulfonic anions which found that the anion-adsorption/desorption peaks are shifted to lower potentials and the hydroxyl adsorption is more suppressed.

Although a lot of studies indicated that ionomer (e.g. Nafion) blocked the active sites on Pt catalyst and then slowed down the kinetics of ORR. The length of a single extended Nafion molecule with a molecular mass of 500,000 g will be 100 nm, and consists of hydrophobic PTFE backbones and hydrophilic sidechain which both affect Pt activity [8, 9]. Studies on Nafion coated on Pt surface suggested that sulfonate adsorption of Nafion was the main source that suppressed the ORR activity of Pt without considering the potential influence of the steric effect and the network structure of Nafion on Pt catalyst [10-14]. Thus, the intrinsic correlation between the adsorption of sulfonic groups on Pt catalyst and the activity of the catalyst remains elusive.

CF_3SO_3H has been applied to study the side chains of Nafion because it has the same molecular structure to the hydrophilic SO_3H-terminated side chains [15-17]. Ohma [18] reported that the Nafion coated Pt system and the 1.0 M CF_3SO_3H system had a close apparent activation energies and the fluorocarbon polymer network of Nafion might block O_2 adsorption. Murthi [19] investigated the ORR activity in carbon supported Pt and Pt alloy catalysts in 1 M and 6 M CF_3SO_3H solution to study the effect of water activity. The results showed that more peroxide yields for PtFe/C followed by Pt/C and then for PtCo/C in 6 M CF_3SO_3H solution than that in 1 M solution. Although a few studies about of the effect of CF_3SO_3H on the Pt electrodes and catalyst have been conducted [15, 20], the adsorption of sulfonic groups on Pt surface and its effect on the Pt kinetic loss has not been reported.

In this paper, CF_3SO_3H is used to study the effect of sulfonic groups on the ORR activity of Pt and exclude the effect of polytetrafluoroethylene (PTFE) backbone of Nafion. The impact of sulfonic groups adsorbed on the Pt surface has been studied using Pt rotating disk electrode in 0.1 M $HClO_4$ solution with various CF_3SO_3H contents. CO displacement method and Electrochemical methods have been used to analyze the adsorption of sulfonic groups on the Pt surface and the kinetic current loss of Pt electrode, respectively.

2. EXPERIMENTAL

2.1 CO displacement technique

The CO displacement technique was used to study the adsorption of anion on Pt surface, a constant potential is applied to the electrode when CO is introduced. As the zero-charge CO displaces

the adsorbing species on Pt, reductive current can be measured depending on the species being displaced. The Pt disk was kept under a potential of 0.34 V for 2 min in the N_2 saturated solution and a steady-state baseline current was established, then CO (10% CO, balance nitrogen) was bubbled into the solution, generated more rapid current transients until a new baseline was established. The current-time response was recorded during CO gas bubbling (Pine Instruments).

2.2 Electrochemical measurements

All electrochemical measurements were carried out using a conventional three-compartment electrochemical cell containing a working electrode (polycrystalline Pt disk), a counter electrode (platinum black electrode), and a reference electrode (reversible hydrogen electrode). The electrolyte was 0.1 M $HClO_4$ mixed with x mM CF_3SO_3H (x=0, 1, 5, 10, 30, 50) solution. RDE technique was used to perform the electrochemical measurements using a Pine RDE instrument. The geometric surface area of the polycrystalline Pt disk was 0.196 cm^2. Cyclic voltammograms (CVs) were obtained in a solution saturated with N_2 at a scan rate of 50 mV s^{-1} and collected in the potential range of 0.05-1.2V vs. RHE. Linear sweep voltammograms (LSV, ORR polarization curves) were taken in a solution saturated with O_2 at a scan rate of 50 mV s^{-1} with an electrode rotation of 1600 rpm and collected in the potential range of 0.1-1.1V vs. RHE. All current densities reported in this paper were normalized to the geometric surface area of the disk electrode. All electrochemical experiments were carried out at room temperature and ambient pressure.

3. RESULTS AND DISCUSSION

3.1 Adsorption of sulfonic anion

The CO displacement technique was developed to verify the adsorption of sulfonic groups on Pt surface. Since the adsorption of negatively charged species often occurs at a potential of >0.26 V vs. RHE [21, 22], the potential used in this study was 0.34V vs. RHE.
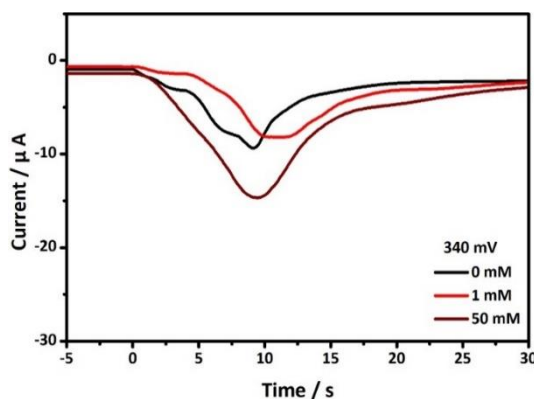

Figure 1. Current-time response as CO gas is being introduced to the solution during potential-hold experiments (Potential: 0.34V vs. RHE; 10% CO balanced by nitrogen)

Fig 1 shows the current responses after CO gas bubbling in various CF_3SO_3H content solutions. Although the adsorption peaks in 0 mM and 1 mM CF_3SO_3H solution are similar in peak intensity, a larger anion adsorption peak was showed in 50 mM CF_3SO_3H solution than that in 0 mM and 1 mM CF_3SO_3H solution. This indicates that the adsorption of sulfonic anion on platinum will take place in the CO displacement curve when the CF_3SO_3H content exceeds a certain value. However, when the CF_3SO_3H content is low, the competitive adsorption of ClO_4^- and sulfonate may keep the adsorption peak unchanged. This is consistent with the effect of CF_3SO_3H content on Pt oxygen reduction activity (See section 3.2.2).

3.2 Effect of CF_3SO_3H on catalytic ORR activity of Pt

3.2.1 Surface electrochemistry of Pt

Effect of sulfonic groups of CF_3SO_3H on the activity of Pt has been studied using RDE in 0.1 M $HClO_4$ with various concentrations of CF_3SO_3H.
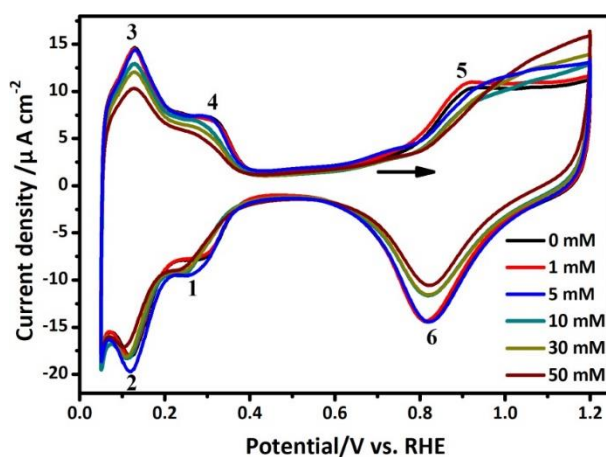
Figure 2. Cyclic voltammograms of the Pt disk in various CF_3SO_3H content solutions

Fig 2 shows the CVs of the Pt disk in various CF_3SO_3H content solutions saturated with N_2. Peak 1-4 are the adsorption/desorption peak of hydrogen. Among them, peak 1 and 4 are strong adsorption/desorption peak (about 0.25-0.4 V vs. RHE) and peak 2 and 3 are weak adsorption/desorption peak (about 0.05-0.25 V vs. RHE) [13, 23]. The sharp peak (peak 6) observed at 0.8 V vs. RHE is the reduction peak of oxide, and peak 5 is the oxidation peak of Pt. The onset potential of oxide formation started at about 0.65 V vs. RHE [6, 24]. When the content of CF_3SO_3H increased to more than 10mM, the oxidation peak of Pt shifted to higher potential. This may be due to the sulfonic groups adsorbed on the Pt surface blocks the formation of oxides [25, 26].

As shown in the inset of Fig. 3, the peak areas of hydrogen adsorption, strong hydrogen desorption and oxide reduction were defined as Area I, Area II and Area III, respectively. These areas are given by integration. After normalizatoin by setting the areas without CF_3SO_3H as 1, they are shown

in Fig.3. After excluding the influence of the hydrophobic PTFE backbone of Nafion, which has no electrochemical activity, the areas of hydrogen adsorption, strong hydrogen desorption and oxide reduction still decrease with the increase of CF_3SO_3H content.

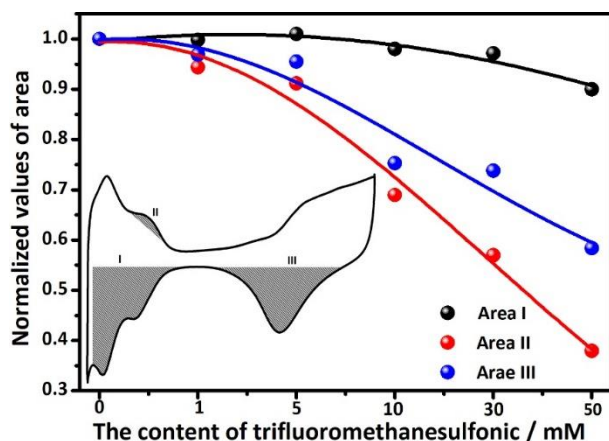**Figure 3.** Variations of the normalized peak areas with the content of CF_3SO_3H

This indicated that the sulfonic group itself had a significant reduction in the hydrogen adsorption and oxygen reduction activity of Pt surface. Although Area I did not obviously change with CF_3SO_3H content, Area II and Area III decreased significantly with it, especially when the content of CF_3SO_3H was higher than 5 mM. This means that the ORR activity of Pt may be greatly affected by the adsorption of sulfonic group on Pt surface.
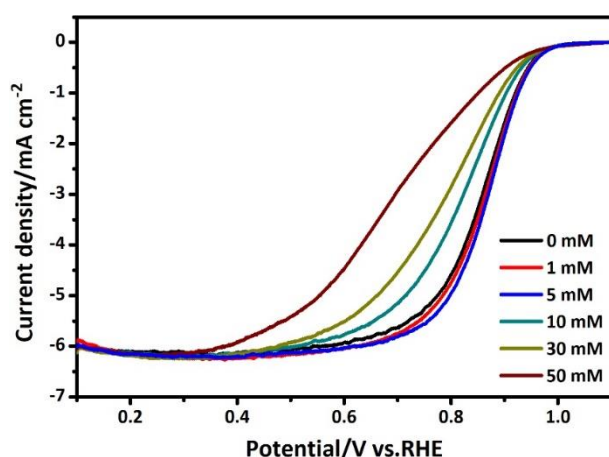
3.2.2 ORR activity of Pt

Figure 4. The ORR polarization curves of Pt disk in solution with various contents of CF_3SO_3H.

The ORR characteristics of Pt disk in solutions of different CF_3SO_3H content saturated with O_2 are shown in Fig 4. The limiting current plateaus at the potential range of 0.1-0.3 V vs. RHE were the same and close to the empirical value [2, 6]. But, their half-wave potential ($E_{1/2}$) obviously decreased with the increase of CF_3SO_3H content when the content of sulfonic groups exceeded 10 mM. This

indicated that the sulfonic groups adsorbed on the Pt surface reduced the ORR activity of Pt. Fig 5 shows the Tafel plots of Pt catalyst in different CF_3SO_3H content solutions. When the concentration of sulfonic groups was less than 5 mM, the Tafel slope did not change. But, the kinetic current with high concentration of CF_3SO_3H was significantly lower than the one without CF_3SO_3H at 0.9V vs. RHE, and the kinetic current density loss was 40% for 10 mM and 71.3% for 50 mM at 0.9 V vs. RHE (from 0.836 mA cm^{-2} to 0.502 and 0.24 mA cm^{-2}, respectively). With increasing the content of CF_3SO_3H in solution, the anion coverage on the Pt surface increased and the areas of oxide reduction decreased.

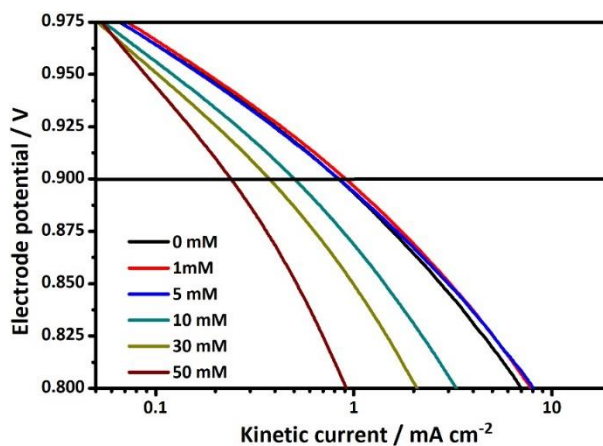**Figure 5.** The Tafel plots in different CF_3SO_3H content solutions.

These resulted in the reduction of ORR activity of Pt. Oxygen reduction active sites on platinum surface have been blocked and then diminished the kinetics of ORR. After studying the Nafion-capped surface (poly-Pt surface covered by a 2 μL aliquot of 0.025 wt % Nafion solution), Shinozaki [2] found that 70% of the kinetic current density at 0.9 V had been lost. It is approach to the result of the 50mM CF_3SO_3H solution in this study. This indicates that the adsorption of sulfonate on the Pt surface has a great effect to its ORR activity, and also is consistent with predecessors' results [5, 13, 14]. They covered the well-defined Pt surface with Nafion and found the ORR activity of Pt was reduced significantly. All of these indicate that the influence of Nafion on the catalytic activity of platinum for ORR mainly comes from the adsorption of sulfonic acid on platinum surface. In addition, it was obvious that the loss of activity with CF_3SO_3H in solution was less at higher potentials, that is mainly because that the sulfonic groups coverage was reduced by the growth of oxide at higher potential [27, 28].

4. CONCLUSION

In this study, the impact of sulfonate adsorption on the ORR activity of Pt is investigated in 0.1 M $HClO_4$ solution with various content of CF_3SO_3H. The CO displacement results showed that the sulfonic groups were adsorbed on the platinum surface when the content of CF_3SO_3H exceeded a certain value. When the content of CF_3SO_3H increased to more than 10 mM, the oxidation peak of Pt shifted to higher potential, the peak areas of strong hydrogen desorption and oxide reduction decreased significantly and it was clearly shown that the sulfonic groups adsorbed on the Pt surface reduced the

ORR activity of Pt. The kinetic current density loss was 40% for 10 mM CF_3SO_3H solution and 71.3% for 50 mM CF_3SO_3H solution at 0.9 V vs. RHE. With increasing the content of CF_3SO_3H in solution, oxygen reduction active sites on platinum surface have been blocked and then diminished the kinetics of ORR. This study excluded the effect of hydrophobic fluorocarbon backbones of Nafion and found that the influence of Nafion on the catalytic activity of platinum for ORR comes from the adsorption of sulfonic acid on platinum surface. Therefore, reducing the effect of sulfonic groups on the ORR activity of Pt is essential to increase the utilization of Pt catalyst, and more researches should be conducted to reduce the undesired effect of sulfonic groups to meet low Pt loading for PEMFCs.

COMPETING INTERESTS
We declare we have no competing interests.

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