



Short communication

Quantitative analysis of oxygen-containing species adsorbed on the Pt surface of a polymer electrolyte fuel cell membrane electrode assembly electrode using stripping voltammetry

Nuttapol Limjeerajarus^a, Tatsunori Yanagimoto^a, Toshio Yamamoto^b, Taichi Ito^c, Takeo Yamaguchi^{a,c,*}

^a Department of Chemical System Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

^b Polymer Laboratory, UBE Industries, Ltd., Ichihara, Chiba 290-0045, Japan

^c Chemical Resources Laboratory, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

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ABSTRACT

The quantity of oxygen-containing species adsorbed on Pt surface of a single-cell polymer electrolyte fuel cell membrane electrode assembly (PEFC MEA) in the gas-phase system was measured by stripping voltammetry (SV), of which the adsorbed amount is considered in terms of the quantity of electric charge required for stripping. The effect of different experimental parameters on the adsorption quantity was analyzed and an optimum condition for applying SV to a PEFC MEA electrode was then suggested. The electric charge required for stripping was observed to be linearly proportional to the potential and arose from 0.7 V vs. RHE. The adsorption amount of oxygen-containing species for the PEFC MEA at a cell temperature of 60 °C was 384 $\mu\text{C cm}^{-2}$ -Pt at a potential of 1.0 V vs. RHE. More importantly, considering the effect of O₂ partial pressure on the adsorption in the gas-phase PEFC MEAs, water is suggested to be the main source of the oxygen in adsorbed oxygen-containing species. The present method is well applicable to quantitative studies of the oxygen-containing species adsorbed on electrodes of PEFC MEAs.

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1. Introduction

The polymer electrolyte fuel cells (PEFCs) are one of the strongest contenders as a power source because of their high-energy efficiency, low-pollution emission, and low noise, and in coming years they are expected to be more widely employed in various energy-conversion devices for mobile, stationary, and portable power applications [1–6]. However, the energy efficiency during practical operation of current PEFCs is still at low values because of the high cathode overpotential. Pt-oxides formation and/or adsorption of oxygen-containing species that poisons the Pt surface area at three-phase boundary are believed to be the main reasons of the high cathode overpotential, especially in the high potential region, and trim down both catalyst activity and durability.

Previous researches [7–9] before 1970s were concerned with the controversy on the nature of the Pt plate electrode surface at high potential whether it was covered by the Pt-oxides or adsorbed by oxygen-containing species. However, Reddy et al.

[10] showed that oxides are present on Pt electrodes in an acid solution (1N H₂SO₄) at potentials above 1 V. A subsequent study by Damjanovic and Brusic [11], which examined Pt electrodes in an HClO₄ solution (pH 1–3), observed that coverage of the electrode by oxygen-containing species was in the potential range of 1.0–0.6 V. Moreover, the coverage was found to be linearly dependent on the electrode potential. Similar results on the adsorption of oxygen-containing species were also noticed by other research groups, which proposed different adsorption mechanisms [12–15]. Most studies mentioned above have investigated the amount of adsorbed oxygen-containing species for Pt plate electrodes in aqueous solutions (liquid-phase systems), but not for the Pt/C catalyst introduced on MEA electrodes in a gas-phase system, which is practically used in PEFCs.

In the case of PEFC MEAs, a different approach, which is a qualitative analysis, can be more effective in analyzing the real adsorption mechanism. A recent study by Tada et al. [16] has been successful in determining the oxygen reduction reaction (ORR) mechanism on the cathode carbon-supported Pt catalyst of a PEFC MEA. By employing a novel time-gating quick X-ray absorption fine structure (QXAFS) technique accompanying with SPring-8, the third-generation (8 GeV) synchrotron radiation facility located in Japan, reaction kinetics and redox structural changes on a Pt cathode catalyst can be determined. However, this method cannot

* Corresponding author at: Chemical Resources Laboratory, Tokyo Institute of Technology, R1-17, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan. Tel.: +81 45 924 5254; fax: +81 45 924 5253.

E-mail address: yamag@res.titech.ac.jp (T. Yamaguchi).

quantify the adsorption amount of oxygen-containing species and unfortunately, it requires huge technical and financial supports, which restricts it from wide-scale use.

In this study, stripping voltammetry (SV) [17–20] has, therefore, been introduced to measure the quantity of electric charge required for stripping the oxygen-containing species (Q_{ox}) adsorbed on Pt/C cathode catalyst of a single-cell PEFC (gas-phase system). By this method, investigations on the amount of adsorbed oxygen-containing species can be carried out under conditions that close to the real operational conditions of PEFCs, and thus the knowledge obtained from surface science can be applied to the practical PEFCs. Furthermore, for a quantitative analysis of the adsorbed oxygen-containing species, the SV approach is a handy and convenient technique. A proper condition for SV and dependence of the amount of oxygen-containing species on experimental parameters such as holding time for SV, cell potential, cell temperatures and O_2 partial pressure, are also studied and discussed.

Note that there is a controversy on the effect of adsorption of oxygen-containing species whether it inhibits or enhances ORR. This is because previous works referred to different adsorptions, namely physical or chemical adsorption (sometimes considered as reaction), respectively. However, by the SV method, the physical and the chemical adsorptions cannot be distinguished. Nevertheless, using the SV under N_2 atmosphere, recent work by Ishikawa et al. [21] shows that Q_{ox} increases linearly with increasing relative humidity and contributes to the reduction in cell performance (OCV). Also, recent work by Tada et al. [16] show that the chemical adsorption exists at high potentials (1.0–1.4 V vs. RHE), and at such high potentials, Pt ions dissolve into electrolyte and lead to degradation of catalyst, and finally resulting in low cell performance. Based on the evidences mentioned above, the poisoning effect of the adsorption on ORR is considered in this work.

2. Experimental

Pt/C powder supplied by Tanaka Kikinokoku Co. Ltd. (Pt particle size: 2–3 nm, Pt/C ratio: 55.8 wt%) was used as the catalyst for both anode and cathode electrodes. The catalyst layer was formed on Teflon-coated carbon paper (EC-TP1-060, ElectroChem, Inc.) by the screen-printing method to make electrodes with a catalyst loading of 0.5 mg cm^{-2} -electrode for each electrode. Nafion® 112 was adopted as the electrolyte membrane. An MEA was fabricated by using a hot-pressing method at conditions of 2 kN and 130°C for 1 min. Pure H_2 gas and pure N_2 gas were humidified and pre-heated in deionized water baths at 58°C and 55°C , respectively. The pre-heated H_2 and N_2 were further supplied into anode and cathode with flow rates of 100 mL min^{-1} and 500 mL min^{-1} , respectively.

A single-cell MEA was fabricated and then connected to a potentiostat/galvanostat (P/G stat) (HZ-5000: HAG3001, Hokuto Denko Co. Ltd.) to perform the SV tests. Note that, unless otherwise stated, all experiments in this work were conducted using an SV sweep rate of 20 mV s^{-1} and a cell temperature of 60°C . The same instrument with the same experimental conditions as that of the SV test was used in cyclic voltammetry (CV) test to measure an electrochemical parameter called electrochemical surface area (ESA, $\text{cm}^2\text{-Pt cm}^{-2}$ -electrode) contributing to Pt utilization of the MEA electrode.

Other MEA performances such as polarization curves and IR loss were tested under the same conditions as mentioned above except O_2 was fed into the cathode instead of N_2 . The polarization curves were obtained by using a galvanostat (HJ1010SM8A, Hokuto Denko Co. Ltd.) and with current interruption method, the IR loss was measured by HZ3000: HAG5010 potentiostat/galvanostat.

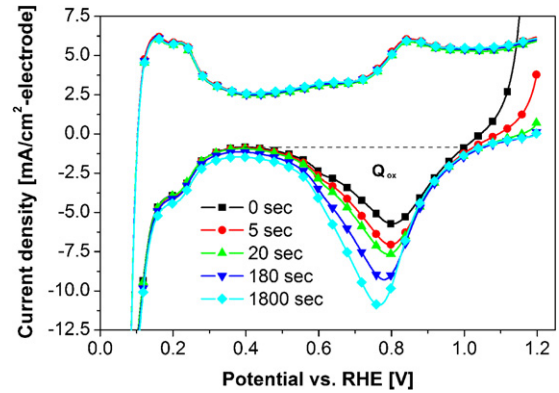


Fig. 1. Holding time dependence of the stripping voltammogram at a holding potential of 1.2 V vs. RHE.

3. Results and discussion

The principle of stripping voltammetry is to keep a uniform potential over a period of time before stripping so that oxygen-containing species can be adsorbed onto the Pt surface at the three-phase boundary. In this way, the electric charge required for stripping those adsorbed species can be measured afterwards. Therefore, an appropriate holding time allowing for the maximum adsorption at a particular potential is a very important parameter, and needs to be investigated.

Fig. 1 presents holding time dependence of stripping voltammograms at a holding potential of 1.2 V vs. RHE, and consequently Fig. 2 presents holding time dependence of electric charge required for stripping (Q_{ox}) at various potentials. The values of Q_{ox} presented in Fig. 2 is calculated from the integration of area under oxygen desorption peak of the stripping voltammograms (right-lower peak of Fig. 1) after subtracting the double layer charge. Although, there is a holding time dependence of the starting point of stripping voltammograms in the area of double layer charge, it does not affect the calculated results of Q_{ox} .

From Fig. 2, it can clearly be observed that at every potential, the quantity of electric charge required for stripping (in other words, the amount of adsorbed oxygen-containing species) rapidly increased when holding time was kept longer. The increase in electric charge continued until it reached a plateau at a holding time of 1800 s, and then the required electric charge became almost constant at any holding time. Thus, the following SV experiments were conducted at a holding time of 1800 s. In addition, it is worth noting that the anodic current peaks (right-upper peak) in the stripping voltammogram are identical for every holding time. This implies that using the SV method, the adsorbed oxygen-containing species

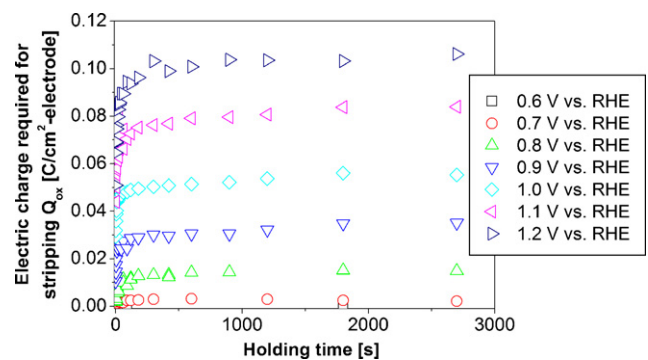


Fig. 2. Holding time dependence of the electric charge required for stripping at different potentials.

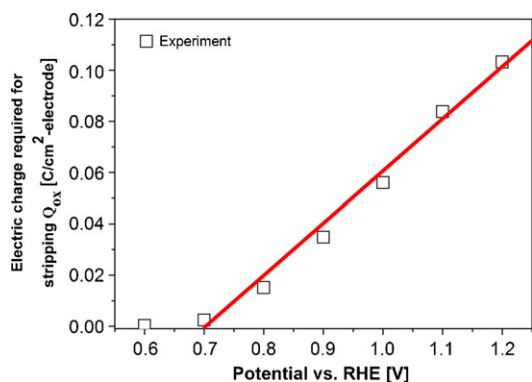


Fig. 3. Relationship between the electric charge required for stripping and the potential for a holding time of 1800 s.

were able to be completely stripped from the Pt surface and can be measured in each cycle.

The dependence of the electric charge required for stripping on the potential of an MEA operating at 60 °C is plotted in Fig. 3. The adsorption of the oxygen-containing species began at 0.7 V vs. RHE and was found to be linearly dependent to the potential from 0.7 V vs. RHE onwards. This finding matches with earlier reports by previous researchers, where different measurement methods for the Pt plate electrodes were employed [11,14,15]. In addition, at 1.2 V vs. RHE, which is close to the open circuit voltage (OCV) of PEFCs operating at 60 °C, the adsorption amount of oxygen-containing species was found to be 0.10 C/cm^2 -electrode. In this research, the SV was, however, carried out at potentials up to 1.2 V vs. RHE since in practice, the maximum cell voltage generated by a single-cell PEFC is always below 1.2 V (the theoretical electromotive force at 60 °C cell temperature is 1.191 V). Thus, it seems impractical to measure the quantity of adsorbed oxygen-containing species at potentials above 1.2 V. Moreover, at potentials above 1.0 V, the oxygen adsorption onto Pt surface becomes irreversible [10,11,16], and the Pt–O gradually dissolves into the electrolyte [16], resulting in a degradation of the cathode Pt catalyst.

To observe the effect of cell temperature on the electric charge required for stripping, SV was carried out at cell temperatures of 40 °C, 60 °C, and 80 °C and the results are shown in Fig. 4. For a comparison of the adsorbed amount of oxygen-containing species obtained in this work with that of previous reports, the amount of electric charge was considered per unit active surface area of Pt ($Q_{ox,Pt}$, $\mu C/cm^2$ -Pt), which was calculated by the

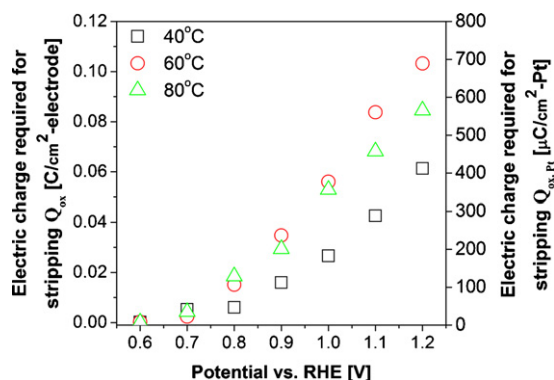


Fig. 4. Cell temperature dependence of the electric charge required for stripping per unit surface area of electrode (left axis) and per unit active surface area of Pt (right axis).

following equation:

$$Q_{ox,Pt} = \frac{Q_{ox}}{ESA}, \quad \text{where } ESA = \frac{Q_H}{Q_{Pt}} \quad (1)$$

where ESA is the value of electrochemical surface area (cm^2 -Pt cm^2 -electrode). In this work, the CV technique under the gas-phase system [22–26] was introduced for measuring the value of Q_H ($\mu C/cm^2$ -electrode), which is the area under the hydrogen desorption peak of a cyclic voltammogram (similar to the left-upper peak in Fig. 1) for the Pt catalyst after subtracting the double layer charge. Q_{Pt} is the charge associated to the oxidation of atomic hydrogen on a smooth surface of polycrystalline platinum, which is equal to 210 $\mu C/cm^2$ -Pt [27]. The calculated ESA of the MEA was 146 cm^2 -Pt cm^2 -electrode contributing to a Pt utilization of 23%.

The temperature dependence of the modified electric charge required for stripping in a unit of $\mu C/cm^2$ -Pt is also depicted in Fig. 4 (right axis). A comparison of the value of the $Q_{ox,Pt}$ to that of previous works is very difficult to be done because each work has its own experimental conditions, e.g. phase of the system, type of catalyst, temperature, etc., which significantly influence the $Q_{ox,Pt}$. For a reference, at a potential of 1 V vs. RHE, $Q_{ox,Pt}$ was about 115 $\mu C/cm^2$ -Pt for a Pt plate electrode experimented at room temperature in liquid-phase $HClO_4$ solution [11]. Compared to the value of $Q_{ox,Pt}$ in this work, which was 180 $\mu C/cm^2$ -Pt for a Pt catalyst in a single-cell PEFC MEA experimented at 40 °C in the gas-phase system, the obtained $Q_{ox,Pt}$ was reasonable and was in the same order of that of the previous work, which used a different measurement method.

Considering the data on the electric charge required for stripping shown in Fig. 4, the adsorption of oxygen-containing species looked increasing with the increasing cell temperature. However, by the SV used in this work, the increasing adsorption from 60 °C to 80 °C was not significantly observed.

Besides, from previous works [11–15], there are two main regions of Tafel slope, namely $-2.3RT/F$ at high potentials and $-2.3 \times 2RT/F$ at low potentials (F is the Faraday constant, R is the universal gas constant, and T is the temperature in Kelvin). This phenomenon so-called the double Tafel slope is believed to be due mainly to the effect of physical or chemical adsorption of oxygen-containing species, which diminishes the ORR activity of the Pt catalyst. The turning point of the double Tafel slope behavior is approximately at 0.7–0.8 V vs. RHE.

According to previous investigations [28–31], the Tafel slope is found to be dependent on the cell temperature in the low current density (high potential) region but it is independent of the cell temperature in the high current density (low potential) region. The explanation for the temperature dependence of the Tafel slope can be explained on the basis of the Bockris–Gochev theory [32]. This theory states that, in the presence of adsorbed oxygen-containing species, the Tafel slope is extensively affected by the configuration of molecules in the double layer, which changes with the cell temperature. This theory concurs with our results obtained from SV showing that the beginning of the adsorption is observed to be identical, i.e. at 0.7 V vs. RHE, for every cell temperature and in the high potential region (above 0.7 V vs. RHE), adsorption of oxygen-containing species, which influences the Tafel slope, was detected. On the other hand, in the low potential region (below 0.7 V vs. RHE), no adsorption was observed at any temperature. This is why Tafel slope is affected by the cell temperature only in the high potential region, and vice versa.

In addition, from the SV tests, the adsorption of oxygen-containing species was detected even though there was no O_2 supplied into the MEA system. Therefore, a hypothesis can be made that oxygen in the adsorption may come from the solely possible source, i.e., the water.

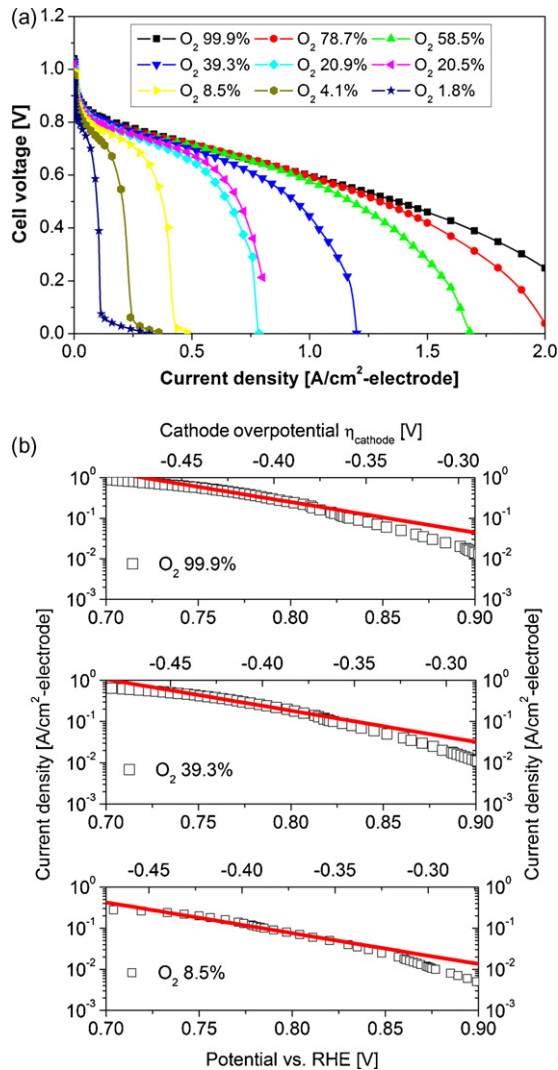


Fig. 5. (a) Polarization curves of the single-cell PEFC MEA supplied with various O_2 concentrations. (b) A comparison of the Tafel plots at O_2 concentrations of 8.5%, 39.3%, and 99.9%.

To verify this hypothesis, it is worth to investigate the effect of O_2 partial pressure on the adsorption of oxygen-containing species. However, SV test is not appropriate for this issue since the O_2 gas from cathode will react with H_2 gas supplied from the anode, resulting in complex phenomena.

Alternatively, we therefore investigated the effect of O_2 partial pressure on the double Tafel slope behavior, which takes place due mainly to the adsorption of oxygen-containing species [11–15]. In this way, the effect of O_2 partial pressure on the adsorption of oxygen-containing species can be examined indirectly.

Cell performance tests were conducted under different conditions of O_2 partial pressure considered in terms of O_2 concentration (the remaining concentration was N_2). The gas mixture was supplied to the cathode side of the selected MEA instead of pure N_2 used in the SV tests. Fig. 5a presents polarization curves of the MEA at various supplied O_2 concentrations. Consequently, to have a clear aspect of the effect of O_2 partial pressure on the change in Tafel slope, a comparison of the Tafel plots at selected O_2 concentrations of 8.5%, 39.3%, and 99.9% was analyzed and depicted in Fig. 5b. The cathode overpotential presented in the Tafel plots was calculated based on the IR loss obtained by the current interruption method, of which MEA resistance was $75 \text{ m}\Omega \text{ cm}^2\text{-electrode}$. From Fig. 5b, the

double Tafel slope phenomenon is observed at around 0.82 V for every O_2 concentration. We speculate that oxygen in adsorption process does not come from the supplied O_2 . Otherwise, for different O_2 concentrations, the Tafel slope should change at different potentials due to the change in the adsorption. In the concurrence with the results obtained from SV, a conclusion can, therefore, be made that oxygen in the adsorption may be sourced mainly by the water.

In addition, recent work by Ishikawa et al. [21] using SV test under N_2 atmosphere shows that Q_{ox} is linearly proportional to relative humidity leading to a conclusion, which concurs with that of the present work, that water is the main source of oxygen in the adsorbed oxygen-containing species.

As mentioned earlier, the adsorption of oxygen-containing species can poison the active Pt surface area at the three-phase boundary contributing to an increase in cathode overpotential. This is believed to be the main reason for the significantly reduced energy efficiency of PEFCs in the low current density region. Therefore, to achieve higher performance as well as longer durability of PEFCs, a quantification of the oxygen-containing species poisoning the Pt surface of an MEA is vital.

By the SV method, the adsorption of oxygen-containing species can be investigated under the similar conditions of the real PEFCs' operations. This approach can also contribute to the determination of the better catalytic material for PEFCs. Moreover, the quantification of the adsorbed oxygen-containing species poisoning the Pt surface is a key parameter in the future development of microscopic reaction modeling, which can improve the accuracy and predictability of the modeling approach for PEFCs.

The finding demonstrating that water may be the major source of oxygen in the adsorbed oxygen-containing species is very important for the future improvement in system and material design for PEFCs because if the fuel gas (O_2) itself is the source of oxygen-containing species, the overpotential caused by the adsorption, which greatly reduces cell performance, is inevitable. On the other hand, if the water is the source of oxygen-containing species as suggested by the present work, the better performance of PEFCs can be achieved by focusing development of operating conditions and material design, e.g., an improvement of an electrolyte, which can maintain high proton conductivity at the low humidity condition.

4. Conclusions

For a single-cell PEFC MEA in the gas-phase system, the amount of oxygen-containing species adsorbed on Pt catalyst has thoroughly been investigated. Experimental parameters dependence of the oxygen-containing species adsorbed on the cathode catalyst surface of the PEFC MEA has been systematically analyzed by the SV method. By considering the effect of the holding time on stripping voltammogram, the optimum condition was suggested to be at 1800 s, at which the adsorption can reach its saturated point. The adsorption first occurred at a potential of 0.7 V vs. RHE and had a linear correlation with the potential for every temperature. More importantly, the presence of oxygen-containing species detected by SV under N_2 atmosphere as well as the analysis of the effect of O_2 partial pressure on the double Tafel slope behavior imposed that the water may be the main source of oxygen in the adsorbed oxygen-containing species. For a quantitative analysis, stripping voltammetry is, therefore, considered a powerful approach for the estimation of adsorbed oxygen-containing species in PEFC MEAs.

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