Gas Phase Hydrogen Electrooxidation Using an Integrated Ultramicroelectrode

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We have demonstrated a hydrogen electrooxidation in the gas phase by employing a Nafion-coated integrated ultramicroelectrode, which represents the three-phase interface of a membrane assembled electrode for a polymer electrolyte fuel cell. The limiting current of gas-phase hydrogen oxidation is proven to be more than ten times larger than that in hydrogen saturated water.

Polymer electrolyte fuel cell (PEFC) works on the basis of gaseous phase electrode reactions, i.e., anodic hydrogen oxidation and cathodic oxygen reduction.[1,2] The gas-phase reactions take place at so-called "three-phase interface" which is established among the reactant, polymer electrolyte and catalyst in the region of a porous electrode.[3] However, it is difficult to evaluate the electrode reaction quantitatively, especially at the porous membrane electrode assembly for practical uses, because of its complicated structure.[4–6] This report describes a research reproducing the three-phase interface by constructing an integrated ultramicroelectrode in combination with a polymer electrolyte film, and that of hydrogen electrooxidation in the gas phase at the ultramicroelectrode.

Three glass tubes of 1.2 mm-outer diameter were bound up, and then the tip was processed to a thin capillary by a burner work. A 25 μm-diameter Pt wire and 100 μm-diameter Pt wire each connected to a Cu lead wire were separately inserted into the glass tubes to the inside of the tip to form a working and a counter electrodes, respectively. Another 100 μm-diameter Pt of 3 mm length was inserted to the inside of the tip of the remaining glass tube for a liquid junction of the reference electrode.[7] Subsequently, the tip of the assembled tubes was heat-sealed, and then cut off and polished to a mirror finish. Finally, the tube for the reference electrode was filled with saturated KCl aqueous solution and a silver wire bearing AgCl on the surface. Thus assembled integrated ultramicroelectrode consists of three electrodes at the tip of about 500 μm in diameter as shown in Figure 1. The tip of the ultramicroelectrode was immersed in the Milli-Q water for 24 h; no ion from the reference electrode was detected in the water by using an Inductively Coupled Plasma Spectrometer (Varian, Vista). From a standpoint to reproduce the three-phase interface, we applied a Nafion thin layer, a proton exchange membrane, on the three-electrode-integrated tip by a dip-coating technique using Nafion 117 solution purchased from Sigma-Aldrich Japan, resulting in about 1 μm-thick polymer layer. The thickness was estimated by SEM side view. Thus prepared electrode is different from that for hydrogen gas sensing both in structure and concept.[8]

Electrochemical measurement was conducted employing the ultramicroelectrode in hydrogen gas atmosphere humidified by bubbling through Milli-Q water, by using a potentiostat (Hokuto Denko HA-150). The ultramicroelectrode was immersed in 0.5 M H_2SO_4 solution for 5 min to activate the Nafion layer immediately before the measurement. For a comparison, a set of three independent electrodes, including 25 μm-diameter Pt working electrode without a Nafion overcoat was utilized. All the measurements were carried out at room temperature (20 ± 2 °C).

Figures 2 (a) and (b) show cyclic voltammograms (CVs) at the Nafion-coated ultramicroelectrode measured in humidified gases and in gas-saturated Milli-Q water, respectively. Figure 2 (c) shows CVs at the independent electrodes in gas saturated 0.5 M H_2SO_4 aqueous solution for a comparison. All CVs showed a good reproducibility.

First of all, anodic current arises around –50 mV vs Ag/AgCl is observed in Figure 2 (a). The anodic current is considered as a result of gas phase electrooxidation of hydrogen, when compared to the CV profile with that of hydrogen oxidation at bare Pt in H_2SO_4 solution (see Figure 2 (c)). In addition, a negligible background current is obtained under humidified nitrogen gas as seen in Figure 2 (a); and, ultimately small current of sub-nano amperes at the integrated microelectrode without Nafion layer was observed under hydrogen gas phase. According to these results, the hydrogen electrooxidation takes place at the thin-film-coated Pt electrode, which clearly indicates that the Nafion-coated integrated microelectrode represents the three-phase interface. Moreover, the direct observation of the gas phase reaction is due to the integrated tip structure where the three small electrodes are conjugated with the

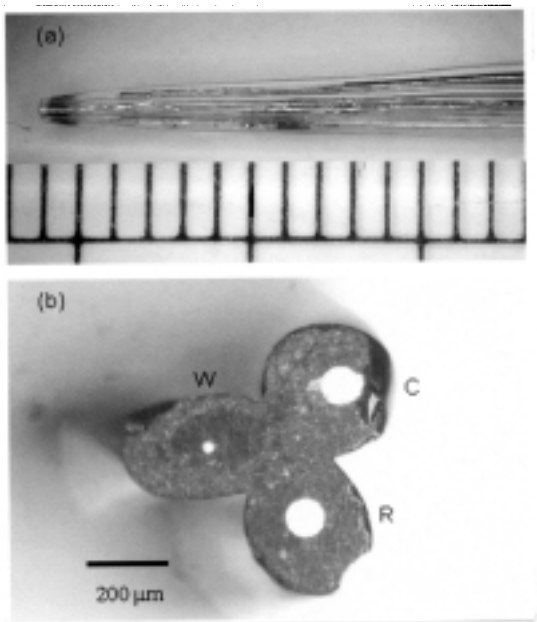

Figure 1. Photographs of the integrated ultramicroelectrode. (a): sideview, scale is 1 mm per division; (b): bottom view, scale bar is 200 μm. W, R and C indicate working, reference and counter electrodes, respectively.

polymer electrolyte.

In Figure 2 (a), a bell-shape CV for hydrogen oxidation is observed. The same kind of behavior is reported in other systems and explained in terms of platinum surface conditions controlled by adsorption[9,10] or mass transport process of the reactant which influences the electrode response.[11] Further study is needed to comprehend the mechanism in detail of the gas-phase hydrogen electrooxidation.

Figure 2 (b) shows a CV at the integrated microelectrode in hydrogen-saturated water with its background. In the figure, anodic current related to hydrogen oxidation is also indicated; however, the current is one order of magnitude smaller than that in the humidified hydrogen gas (see Figure 2 (a)). This difference is thought to be due to the difference in the bulk concentration of the reactant; 0.018 dm^3 hydrogen in 1 dm^3 water[12] and ca. 0.977 dm^3 in the humidified gas.[13] Moreover, the same kind of difference in cathodic current is observed between Figure 2 (a) and (b). The cathodic current is regarded as a result of reduction of the proton, which is generated by the hydrogen oxidation reaction. In this case, the magnitude of the cathodic current is considered to reflect the concentration of the reactant in the Nafion layer. In Figure 2 (b), the hydrogen oxidation current during cathodic scan exceeds the current during anodic scan, which is in disagreement with the well-known CV profile[9–11] including Figure 2 (c). This suggests the presence of a different mechanism for hydrogen oxidation.

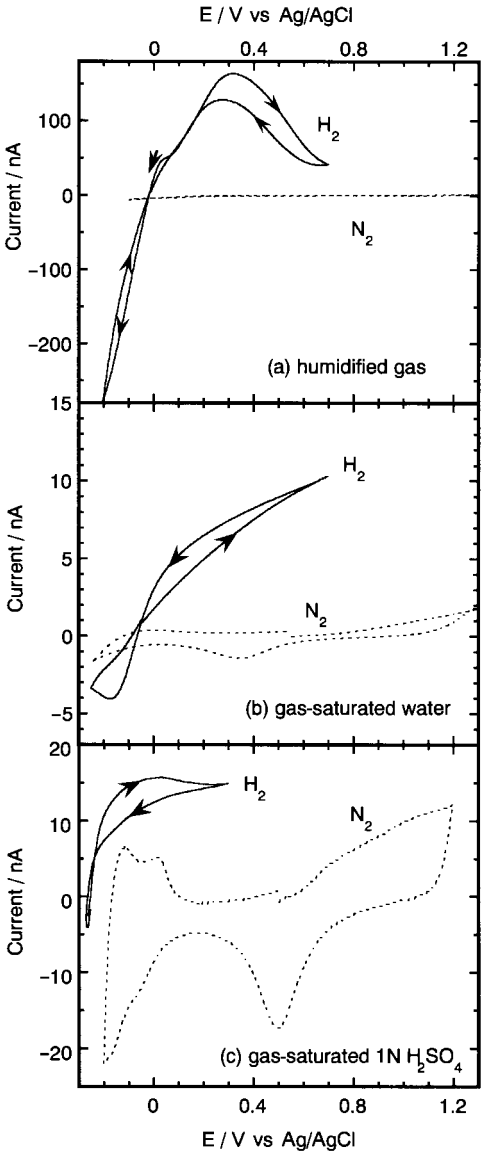

Figure 2. (a) Cyclic voltammograms at the Nafion-coated integrated ultramicroelectrode in humidified hydrogen or nitrogen gas; (b) cyclic voltammograms at the same ultramicroelectrode in hydrogen or nitrogen saturated water; and (c) cyclic voltammograms at independent 25-μm diameter Pt working electrode without a Nafion® layer in hydrogen or nitrogen saturated 0.5 M H_2SO_4 aqueous solution. Scan rate, 50 mV/s.

In conclusion, we have succeeded a direct observation of the hydrogen electrooxidation in the gas phase, by constructing a Nafion-coated integrated ultramicroelectrode. The prepared ultramicroelectrode can be regarded as representative of the three-phase interface of PEFC electrode. The limiting current of hydrogen oxidation in the humidified gas phase was found to be more than ten times larger than that in hydrogen saturated water.

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