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Influence of underpotentially deposited Sb onto Pt anode surface on the performance of direct formic acid fuel cells

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ABSTRACT

We first reported on electrocatalytic activity and stability of antimony modified platinum ($PtSb_{upd}$) as anode catalyst in direct formic acid fuel cells. Sb modified Pt ($PtSb_{upd}$) was prepared by underpotential deposition technique applying constant potential of 0.2 V (vs. Ag/AgCl, 3M KCl) and its modified surface was characterized by XRD and XPS. The electrocatalytic oxidation activity by cyclic voltammograms and the single cell power performance of Sb modified Pt were measured and their results were compared with the data of unmodified Pt electrode. $PtSb_{upd}$ induced lower onset potential of formic acid oxidation and twice higher power density of 250 mW cm^{-2} was observed.

1. Introduction

Based on fundamental surface electrochemistry (i.e., three-electrode systems) of the influence of bismuth, antimony, lead etc. on electrocatalytic oxidation of formic acid has been extensively studied for last decade and dual path oxidation mechanism has been proposed to understand it [1–3]. A direct oxidation (i) of active surface intermediates to form CO_2 in parallel with an indirect oxidation (ii-1) and (ii-2) pathway involving dehydration and subsequent electro-oxidation of resulting strongly adsorbed carbon monoxide.

$$HCOOH \rightarrow \text{reactive intermediate} \rightarrow CO_2 \quad \text{(i)}$$

$$HCOOH \rightarrow CO_{ad} + H_2O \quad \text{(ii-1)}$$

$$CO_{ad} + H_2O \rightarrow CO_2 + 2H^+ + 2e^- \quad \text{(ii-2)}$$

The mechanism of formic acid electro-oxidation on Pt and selected Pt-modified surfaces in acid solution is reasonably studied. The interaction of HCOOH with Pt at potentials below 0.2 V is relatively weak, with only a small amount of spontaneous dehydration taking place upon immersion at 0.06 V. Very little current from either the dehydration or dehydrogenation reactions is observed until the potential is scanned above about 0.2 V, where there is the appearance of both reactions and solution-phase CO_2. Both the anodic current and CO_{ads} coverage reach a plateau on the anodic scan between 0.6 and 0.7 V. Above 0.7 V, the oxidation of CO_{ads} produced a large increase in total current and a decrease in CO_{ads} coverage [1].

The poisoning intermediates formed during the electro-oxidation of formic acid placed on the catalyst surface and decrease the activity by blocking of active sites and thus, many studies have been devoted to overcome poisoning problems on catalyst surface. In electro-oxidation of formic acid, surface modification is one possible way to enhance catalytic activity by reducing and/or eliminating the poisoning branch of the reaction. Surface modifiers such as Ru [4], Pd [5,6], As [7,8], Sb [9,10], Se [11], Bi [7,9,12–14], Pb [3,15] increase the apparent reaction rate and decrease oxidation overpotential. The enhanced activity could be explained as resulting from surface modification mechanism, i.e., the electronic and third-body effect on the Pt surface.

In this work, we tried to modify Pt surface via Sb UPD process and studied the influence of Sb surface modification on Pt with linear sweep voltammograms and I–V curves in cell operation of direct formic acid fuel cells.

2. Experimental

The Sb modification on Pt electrode was carried out by underpotential deposition (UPD). 1.0 mM Sb_2O_3 (Kanto) dissolved in 1.0 M H_2SO_4 (Aldrich) was used as electrolyte and +0.2 V (vs. Ag/AgCl, 3M KCl) is applied for 30 min. In order to investigate the electrocatalytic activity of Sb modified Pt electrode, half-cell tests were carried out. Working electrode of Pt, PtRu and Sb modified Pt electrodes with a

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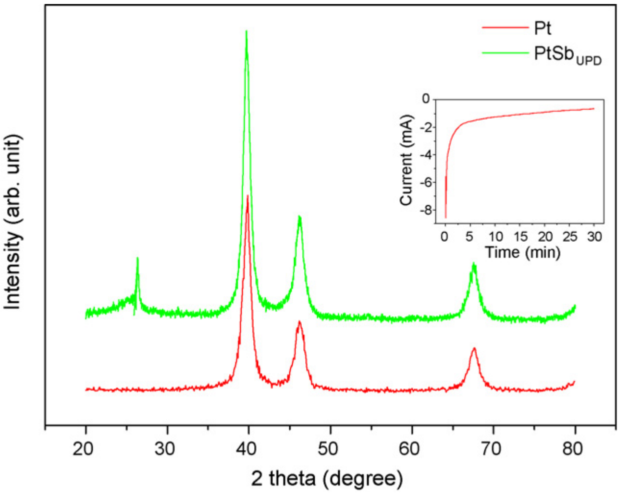

Fig. 1. XRD patterns of modified and unmodified Pt electrodes. (Inset figure: chronoamperometry curve for Sb modification.)

geometric area of 0.8 cm^2 was used. Platinized Pt mesh was used as counter electrode (CE) and Ag/AgCl, 3M KCl was used as reference electrode (RE). A Potentiostat/Galvanostat (Autolab, PGSTAT302N) was used for all linear sweep voltammetry (LSV) and chronoamperometry (CA). Surface condition of unmodified and Sb modified Pt electrode was also characterized by X-ray diffraction (XRD, D/MAX Uitima III) and X-ray photoelectron spectroscopy (XPS, Multilab 2000).

To compare the different materials, such as Pt black (Johnson Matthey, Hi-SPEC 1000), PtRu black (Pt:Ru;50:50 at.%, Johnson Matthey, Hi-SPEC 6000) and Sb modified Pt, were used as the anodes and Pt black was used as the cathode. All electrodes were prepared by dispersing appropriate amounts of unsupported catalysts powder in deionized water, 5% Nafion solution (Aldrich), 2-propanol and 1-propanol, sonicating the solution for 90 s and catalyst inks were coated on a GDL/carbon paper (SGL 24BC and 35BC). Then, additional ionomer solution was sprayed onto the catalyst layer of each electrode in order to decrease the contact resistance with polymer electrolyte membrane (Nafion 115, DuPont). The catalyst loading for the anode and cathode was approximately 3 mg cm^{-2} and the geometrically active area of the electrode was 5 cm^2. Membrane-electrode assemblies (MEAs) were prepared by hot pressing with Nafion 115 at a temperature of 140 °C and a pressure of 30 kg$_f$ cm^{-2} for 300 s. Current–voltage curves were measured galvanostatically by using an electronic load (PNCYS, ESL-300D).

3. Results and discussion

Fig. 1 shows the XRD patterns of unmodified Pt and Sb modified Pt electrodes. All peaks of Sb modified Pt electrode were consisted with those of unmodified Pt. Any peak was not observed for Sb or PtSb alloy among the XRD peaks. The peak of 26° is detected from GDL/carbon paper used as catalyst substrate. Considering the result of XRD analysis, Sb is highly dispersed in active structure on Pt catalyst layer and/or the deposited Sb is amorphous structure. In addition, the average particle size of unmodified Pt and Sb modified Pt particles are about 10 nm, according to the Debye-Scherrer calculation. Inset figure is current-time profile for underpotential deposition Sb on and /or into Pt surface.

The surface state of Sb modified Pt electrode was investigated by XPS. Fig. 2 shows the Pt 4f and Sb 3d regions of the XPS spectra of unmodified Pt and Sb modified Pt electrode. The binding energy of Pt 4f$_{7/2}$ peak of unmodified Pt electrode was located in 72 eV and the binding energy of Pt 4f$_{7/2}$ peak of Sb modified Pt was observed on 72.03 eV. According to Fig. 2(a), no shift in the binding energy of Pt 4f$_{7/2}$ in unmodified Pt and Sb modified Pt was observed. Fig. 2(b) shows XPS spectrum of the Sb 3d$_{5/2}$ region of Sb modified Pt electrode. The binding energy peak of Sb 3d$_{5/2}$ was located in 531.8 eV and it is not chemical state presenting Sb metal. Considering no shift of binding energy of Pt 4f$_{7/2}$, the chemical state of Sb 3d$_{5/2}$ of 531.8 eV corresponds to antimony oxides such as Sb_2O_3 or/and Sb_2O_5. Sb_2O_3 is an amphoteric oxide, dissolving in alkaline solution to give antimonites and in acid solution to give a range of polyantimonous acids [16]. It can be readily oxidized to antimony pentoxide or other antimony (V) compounds. Therefore, the chemical state of Sb on Sb modified Pt electrode might be existed as Sb_2O_5 or/and Sb_2O_3. According to XRD and XPS analyses, we could summarize that amorphous structure of antimony oxide, Sb_2O_5 or/and Sb_2O_3 is highly dispersed onto/into Pt nano-structured electrode. With

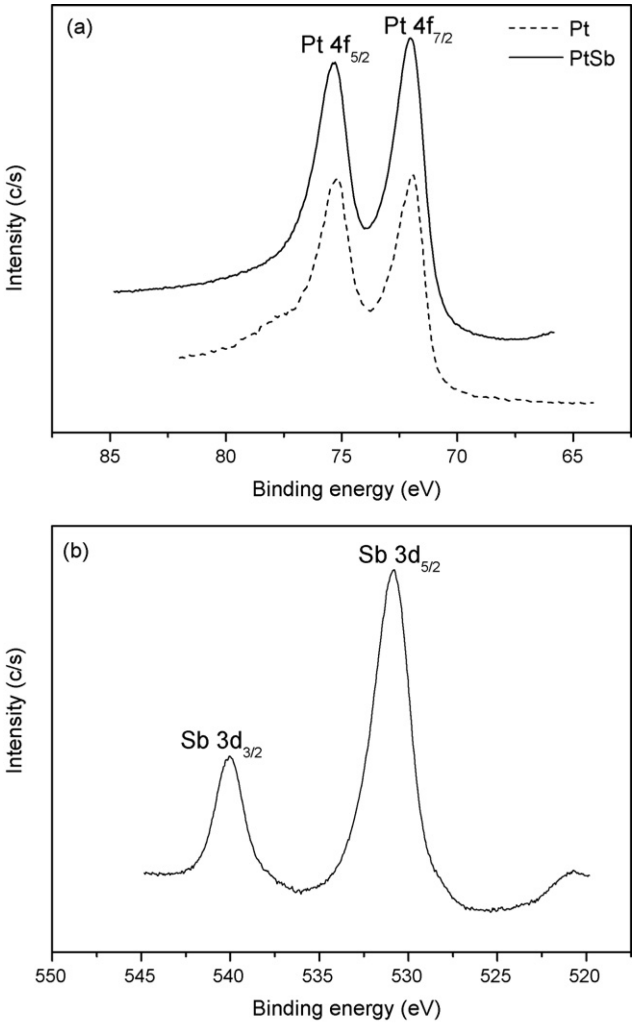

Fig. 2. XPS spectra of (a) Pt element of unmodified Pt and Sb modified Pt and (b) Sb element of Sb modified Pt electrode.

Table 1
The atomic ratio of Sb modified Pt electrode

Element	At.%
Pt	31.4%
Sb	27.39%
C	41.21%