Nanoporous Ag and Ag–Sn anodes for energy conversion in photochemical fuel cells

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Abstract
Nanoporous Ag and Ag–Sn anodes made from chemical dealloying and electrochemical processes were studied for energy conversion in photochemical fuel cells. The porous materials possess better catalytic performance than their nonporous counterparts. Photochemical fuel cells were made using ethanol and ethylene glycol as fuels and the porous Ag and Ag–Sn as anodes. Open circuit voltage test results show that the porous anodes are sensitive to UV light. It is concluded that the nanoporous Ag and Ag–Sn materials with high surface areas can be used for photochemical fuel cell anodes.

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1. Introduction
Direct methanol fuel cell (DMFC) has been studied extensively and considered as a possible power source for electric vehicles. However, the fuel, methanol, is toxic and volatile. Such properties make it unsuitable for many applications. Other organic fuels such as ethanol [1–4], 1- and 2-propanol [5–8], ethylene glycol [9,10], dimethoxymethane and trimethoxymethane [11,12] have been tested for direct liquid fuel cell applications. As one of the alternatives, ethanol is safer, easily produced and has more energy density compared to methanol (8.01 kWh/kg vs. 6.09 kWh/kg) [13]. It is of significant importance to develop new anode electrocatalysts for ethanol electro-oxidation in order to enhance the performance of direct ethanol fuel cells (DEFCs). It has been reported that Pt-based bimetallic and trimetallic anode catalysts, such as Pt–Sn [14], Pt–Ru [15,16], Pt–Ru–Sn [17], Pt–Pd–Au [18] and non-Pt based Pd–Ru [19], Ir3SnC [20] have good electrocatalytic properties for ethanol electro-oxidation. Interestingly, anodes with porous structures were found to have activity for ethanol oxidation. Porous structured anodes can accelerate the anode reaction kinetics because of their high surface areas. It is reported that porous Pb–Ag anode [21], porous Ni–Pd or Co–Pd [22] have high performances in direct ethanol fuel cell.

In this work, we prepared nanoporous Ag and Ag–Sn electrocatalysts via chemical and electrochemical processing. The surface morphology of the porous Ag and Ag–Sn was examined by scanning electron microscopy (SEM). Their electrocatalytic behaviors were studied via cyclic voltammetry (CV). We made photochemical fuel cell using the porous Ag and alloy as the anodes, ethanol and ethylene glycol as the fuels. The open circuit voltages were measured under UV light.

2. Experimental
Ag–Sn wire with 1.5 mm diameter has the composition of 96 wt% Sn and 4 wt% Ag. The porous Ag–Sn anodes were made through chemical dealloying and electrochemical dealloying.
For chemical dealloying, the Ag–Sn alloy was directly immersed into 5% hydrochloric acid for 24 h to form the porous anode. For electrochemical dealloying, the Ag–Sn alloy was selectively etched to increase the surface area in an electrolyte consisting of 5% hydrochloric acid, 75% ethanol and water. The pure Ag also has the diameter of 1.5 mm. The porous Ag anode was formed using the same electrolyte as above. The installation for electrochemical dealloying consists of three electrodes: the Ag–Sn or Ag work electrode (W), platinum counter electrode (C) and Ag/AgCl reference electrode (R). These three electrodes were connected to the CHI400A Quartz Microbalance Electrochemical Analyzer. After the liner sweep potential scan from 0 to 1 V for one cycle, both Ag–Sn and Ag became porous with increased surface areas.

Morphological observations were done by scanning electron microscopy. The electrocatalysis behaviors of the untreated Ag–Sn, porous Ag–Sn via chemical treatment, porous Ag–Sn alloy from electrochemical dealloying and porous Ag anode were examined by cyclic voltammetry tests in two solutions: 3% hydrochloric acid+50% ethanol, and 3% hydrochloric acid+80% ethanol. Photochemical property tests were performed in H3PO4+20% ethanol and ethylene glycol under UV irradiation. Before the tests, the anodes were heat treated at 150°C for 3 h to form oxides. The open circuit voltage was measured as a function of time when the UV lamp was ON and OFF repeatedly.

3. Results and discussion

3.1. Morphological features

The morphologies of the original pure Ag and the electrochemically etched Ag are illustrated in Fig. 1. Fig. 1a reveals the surface of the Ag before the electrochemical treatment. It can be observed that the surface is relatively smooth with some parallel rolling marks from the mechanical machining. Fig. 1b–d exhibits the morphology of the Ag after electrochemical etching. Two types of morphological features are found on the Ag anode electrocatalyst. The small particles are found near the boundary between electrolyte and air. The average diameter of these particles is about 200 nm. The pores below these particles were formed due to the dissolution of Ag. The dissolved silver ions were then reacted with chlorine ions and precipitated as AgCl. Part of the silver ions was reduced to silver particles and set on the top of the surface, resulting in the increase in the surface area of the Ag anode. Fig. 1c shows other morphological features found at the deeper location in the electrolyte at the silver anode. The small Ag crystals with different orientations were exposed after the electrochemical etching and only a small amount of fine particles were formed on the top of these silver grains. The existence of the fine particles can be explained by the lower current density in dealloying at this location. The composition of these particles was verified by the EDX analysis as shown in Fig. 1d. The weight ratio of Cl to Ag elements is 9.13–90.87%. The normal stoichiometric weight ratio of Cl to Ag in AgCl should be about 1:3. The excessive amount of Ag is mainly due to the reduction of silver ions. The deeper penetration of electron beam at the relatively high acceleration voltage of 20 kV could also result in the extra silver signal.

The surface features of Ag–Sn anode electrocatalyst after the electrochemical dealloying are shown in Fig. 2. Fig. 2a illustrates the porous surface with varied pore diameters from nanometer to micrometer. Numerous pores in the nanoscale level lead to a significant increase in the surface area. This is...
expected to enhance the anode electrocatalytic performance. Fig. 2b displays the magnified pores with 100 nm to 1 μm diameters. Fig. 2c shows the pores with the size range from 3 μm to 8 μm. In order to confirm the selective removal of Sn element from the Ag–Sn alloy, quantitative analysis of elemental content was performed and the results are shown in Fig. 2d. Stoichiometrically, the usual weight ratio of Ag versus Cl should be 3:1. In this case, the ratio is higher than 23:1 indicating the main component of the selected point is Ag with a small amount of AgCl. This evidently shows that Sn was dissolved, leaving Ag behind. Since the electrode surface was oxidized during dealloying, it is reasonable that oxygen exists. That is why the oxygen signal was detected by the EDX analysis.

3.2. Electrochemical catalysis behavior

The electrochemical oxidation behavior of different nanoporous anode catalysts was studied. The cyclic voltammetry (CV) test results show that for the nanoporous Ag anode, the current density reached a maximum value of 155 mA/cm² at 0.6 V in the electrolyte containing 3% hydrochloric acid and 80% ethanol. On the other hand, the non-porous Ag anode shows much lower current density in the ethanol-based electrolyte. For the Ag–Sn anode catalysts in the electrolyte with 3% hydrochloric acid, 50% ethanol and water, it was observed that the porous Ag–Sn made from both electrochemical and chemical dealloying have obvious higher current densities than the untreated anode. The highest current density for all three specimens achieved at 1.0 V. The highest current density is 91 mA/cm² for the electrochemically dealloyed Ag–Sn anode. The highest current density is 77 mA/cm² for the chemically dealloyed one. The highest current density is only around 13 mA/cm² for the pristine Ag–Sn anode. The electrocatalytic performance of the chemically treated porous Ag–Sn anode is not as good as that of the electrochemically treated porous one.

3.3. Photochemical fuel cell performance

The results of the fuel cell performance test show that the porous Ag anode is UV-sensitive in the H₃PO₄+ethanol solutions. The electrochemically dealloyed Ag–Sn anode is also UV sensitive in the H₃PO₄+ethanol solution. The principle for the decomposition of the fuel lies in the holes and electrons generated by the illumination of UV light. Because a photon of UV light has large energy, the hole and electron pairs were generated in the surface layer of the Ag₂O exposed to the irradiation. The electrons contribute to the change in the open circuit voltage, while the ethanol fuel received the generated holes. This resulted in the decomposition of the fuel and produced water and carbon dioxide as described in [23]. The increased surface areas associated with the nanoporous structure can help to generate holes and electrons more efficiently under UV irradiation.

The UV-sensitive property of the porous Ag anode in ethylene glycol solution is shown in Fig. 3. To further prove this property, three ON-OFF intervals were used in the tests: 10 s, 20 s and 35 s. It is obvious to see that when the UV light was ON, the potential, E, suddenly shifted away from the equilibrium value of 77 mV. When the UV light was OFF, the potential went back. One thing should be pointed out that the UV light delayed about 3 s when it was turned on. This explains that the peaks occurred, for example, at 13 s, 33 s... instead of 10 s, 30 s... as shown by the solid line curve, which locates above the other two curves. The UV-sensitive property for electrochemically dealloyed Ag–Sn...
anode in ethylene glycol was also tested. The ON-OFF intervals are 10 s and 20 s. It was observed that there is no apparent potential change when the UV light was ON or OFF. There was only a very small shift in the potential when the UV light was ON. This is probably because the main component in the Ag–Sn anode is not so UV sensitive as the Ag anode. The chemically dealloyed Ag–Sn anode is not UV-sensitive, either.

In the H₃PO₄+ethanol solution, the UV-sensitive traits for Ag anode, electrochemically dealloyed Ag–Sn anode and chemically dealloyed Ag–Sn anode were tested. The electrochemically dealloyed Ag–Sn anode is also UV-sensitive in ethanol.

4. Conclusions

We fabricated nanoporous Ag and Ag–Sn anode catalysts. The anodic current densities were measured for porous Ag, nonporous, chemically treated and electrochemically treated Ag–Sn anodes in ethanol containing electrolytes. The highest current density achieved is 155 mA/cm² for the porous Ag anode. The electrochemically dealloyed Ag–Sn anode shows a better performance than the chemically dealloyed Ag–Sn anode in view of electrocatalysis. The porous Ag anode is UV-sensitive in ethylene glycol and ethanol. The electrochemically dealloyed Ag–Sn anode is also UV-sensitive in ethanol.

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References


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