

## Polyaniline Film as a Metal-free Electrocatalyst for the Anode Reaction of the Direct Ascorbic Acid Fuel Cells

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**Abstract:** A polyaniline film was prepared on the electrode surface to employ use it as an electrocatalyst for the anodic reaction of the direct ascorbic acid fuel cells. The activity was evaluated for 1) the effect of the type of dopant anion, 2) the durability of the catalytic action, and 3) the effect of the metal dispersion. The highest electrocatalytic activity was obtained with by the  $SO_4^{2-}$ -doped PANI film. The PANI film improved the durability of the catalytic action. The metal dispersion deactivated rather than activated the modified PANI film-modified electrode. The modified PANI film-modified electrode was regarded as a promising anode containing no harmful heavy metals and precious Pt.

**Keywords:** polyaniline; ascorbic acid; direct ascorbic acid fuel cell; direct methanol fuel cell; anode

### 1. INTRODUCTION

Although direct methanol fuel cell (DMFC) is a promising fuel cell, the DMFC has at least five problems to be solved for practical use: [1-5] (a) it requires precious electrocatalysts, such as Pt and Ru, for the methanol oxidation and the electrocatalytic efficiency is relatively low; (b) the active sites of the electrocatalysts are poisoned by the adsorption of reaction intermediates, such as CO; (c) the electroreduction of dissolved oxygen should be promoted; (d) high methanol crossover through the polymer membrane greatly significantly decreases the cell voltage and methanol utilization; and (e) the toxicity of methanol and by-products, such as formaldehyde and formic acid, has the risk of causing serious problems.

Our strategy for solving these problems is to employ a conductive polymer, polyaniline (PANI), as an the electrocatalyst and L-ascorbic acid as the fuel. It has already been confirmed that PANI is a promising material for alleviating problems (a), (b) and (c). The PANI film acts as a porous support on which to disperse the electrocatalysts. The dispersion can decrease the poisoning effect [6,7] as well as the amount of the precious Pt electrocatalyst [8]. In addition to the its role of as a porous support, the PANI film

itself can function as an electrocatalyst [9]. Although no electrocatalytic activity of the PANI film itself is shown for the methanol oxidation [10], the PANI film is expected to become an electrocatalyst for the oxidation of organic compounds other than methanol.

Although several kinds of alcohols other than methanol [11-13] and various organic compounds [14-17] have been attempted evaluated as the fuels, their toxicity problems still remain. The use of L-ascorbic acid as the fuel is expected to solve not only the toxicity problem, but also the crossover problem previously described as problem (d). Several successive examples have already been reported for direct L-ascorbic acid fuel cells, in which an L-ascorbic acid solution was directly supplied to the anode [18-21]. Because the PANI film functions as an electrocatalyst for the oxidation of L-ascorbic acid [22], modified PANI film-modified electrodes could become significant alternative anodes for the precious-metal-free anodes for the direct L-ascorbic acid fuel cells. In this communication, from a practical standpoint, attention was focused on the following subjects.

- 1) Effect of preparation conditions of the PANI film,
- 2) durability of the catalytic action, and
- 3) effect of the metal dispersion.

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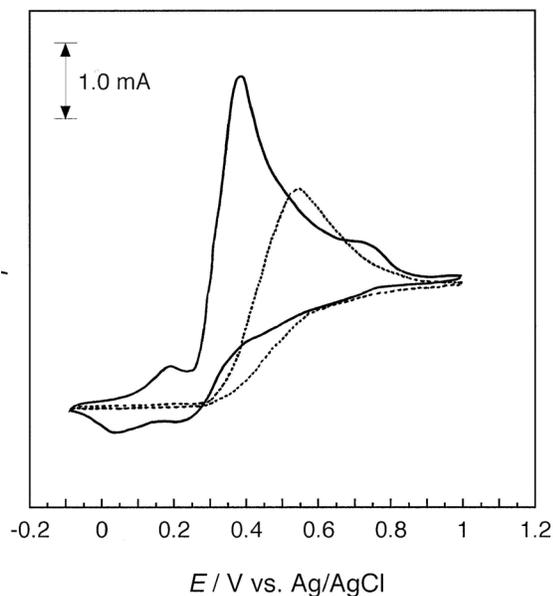


Figure 1. Cyclic voltammograms of L-ascorbic acid at  $20 \text{ mV s}^{-1}$  measured with using the modified PANI film-modified (solid line) and bare GC electrodes (dotted line).

## 2. EXPERIMENTAL

A standard three-electrode cell was employed, comprising comprised of a glassy carbon (GC) disc electrode with an electrode area of  $0.196 \text{ cm}^2$ , a commercial Ag/AgCl electrode and a Pt plate counter electrode with an electrode area of ca.  $8 \text{ cm}^2$ . The GC disk electrodes were polished with alumina powder prior to use. The electrochemical experiments were carried out using a Hokuto Denko HZ-3000 potentiostat connected to a personal computer and a Rikadenki RY-101 x-y recorder.

Aniline was reagent grade and was distilled under reduced pressure prior to use. All other chemicals were of analytical grade and used as received. The aqueous solution to measure the oxidation current of L-ascorbic acid was a  $0.25 \text{ M H}_2\text{SO}_4$  aqueous solution containing  $0.1 \text{ M L-ascorbic acid}$ . The PANI film was electrochemically deposited by repeated potential scanning ( $50 \text{ mV s}^{-1}$ ) onto glassy carbon (GC) electrodes in a  $0.5 \text{ M (1 M = 1 mol dm}^{-3}\text{) H}_2\text{SO}_4$  aqueous solution containing  $0.20 \text{ M aniline}$ . The deposited amount of the PANI film was controlled by the repeated potential scan number. Except for the experiments to examine the effect of the PANI film thickness, the repeated potential scan number was 10. If necessary, metallic particles were dispersed on the PANI film by electrodeposition from a protonic acid solution containing  $0.02 \text{ wt\%}$  of the corresponding metal ions at a constant current of  $50 \mu\text{A cm}^{-2}$ . The charge passed during the electrodeposition was  $50 \text{ mA cm}^{-2}$ .

The catalytic activities of the modified PANI-modified electrodes were mainly evaluated by linear sweep voltammetry; measurements of current-time profile (up to 30 min) and/or steady-state polarization curve were also employed to estimate the durability of the catalytic action.

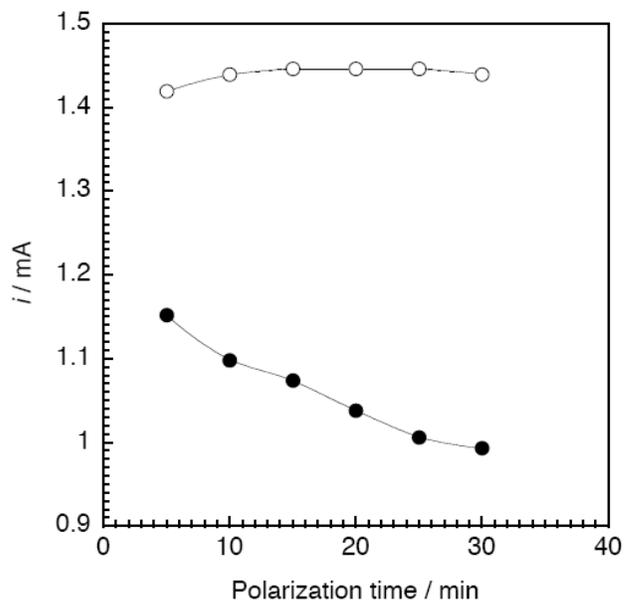


Figure 2. Time dependence of oxidation current at constant potential of  $0.4 \text{ V}$  with using the modified PANI film-modified (upper curve) and naked bare GC (lower curve) electrodes.

## 3. RESULTS AND DISCUSSION

Figure 1 shows two cyclic voltammograms of L-ascorbic acid measured with using a bare GC electrode and the modified PANI film-modified electrode. As can readily be seen in Figure 1, the oxidation current of the L-ascorbic acid obtained with using the modified PANI film-modified electrode is considerably increased compared with to that obtained with using the bare GC electrode.

To examine the durability of the catalytic action of the PANI film, L-ascorbic acid was electro-oxidized at a constant potential of  $0.4 \text{ V}$  using the modified PANI film-modified electrode and the bare GC electrode. The change in the oxidation current with time is shown in Figure 2. Although the oxidation current obtained with using a bare GC electrode gradually decreases gradually, a steady current was observed using the PANI film-modified electrode. The active sites on the GC surface are probably poisoned by the adsorption of reaction intermediates, and the current decreases with the polarization time. According to a study using electrochemically-modulated infrared reflectance spectroscopy [7], when methanol is electro-oxidized on a Pt dispersed PANI film, the PANI film adsorbs the intermediate species, such as CO, which act as poisoning species for Pt. The adsorption prevents the dispersed Pt particles from becoming deactivated. Analogously, the PANI film must absorb the unfavorable intermediates.

Measurement of the steady-state current-potential curves also revealed that the anode performance was markedly improved by the deposition of the PANI film. Figure 3 shows the steady-state current-potential curves obtained with using the modified PANI film-modified and bare GC electrodes. Both currents reach the limited limiting currents after a sharp increase. It is interesting to find note that the oxidation current begins to flow at about  $70 \text{ mV}$  less using the modified PANI film-modified electrode than that

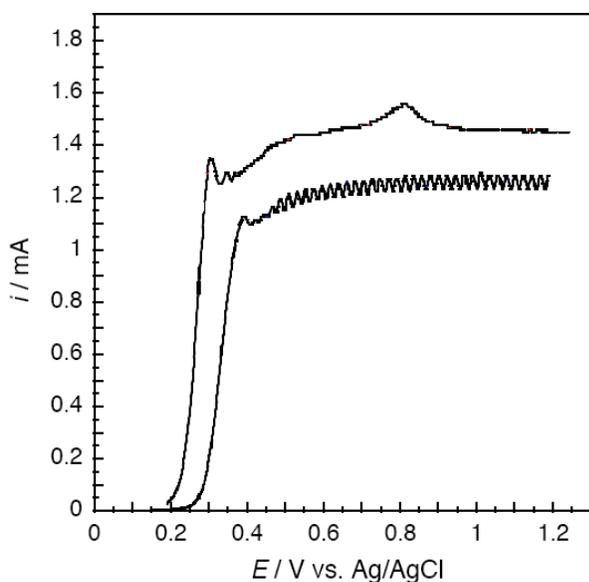


Figure 3. Steady-state current-potential curves obtained with using the modified PANI film-modified (upper curve) and bare GC (lower curve) electrodes.

using the bare GC electrode. This also means that the PANI film acts as an electrocatalyst. The surface area becomes much greater by the due to modification with of the PANI film. In addition to the effect of the surface area, however, there is another factor such as the absorption of unfavorable intermediates because there is no significant difference between the limited limiting currents.

It is well known that some electrode reactions of dissolved organic species are promoted by metal dispersion on an electrode surface. Such promotion might occur in the PANI film-modified electrode. Copper was first attempted as a representative base metal for the dispersion because the enzyme for the oxidation of L-ascorbic acid, ascorbate oxidase, is a copper containing enzyme. The voltammetric peak current of L-ascorbic acid depended on the deposited amount of Cu on the PANI film-modified electrode, and the highest value was obtained when the deposited amount was  $50 \text{ mC cm}^{-2}$ , which was charge passed during the electrodeposition of Cu. The effect of the deposition was also examined for Zn, Pt, Fe and Cr. However, the measurement of the current-time profile showed that the steady oxidation currents at those metal-dispersed PANI film-modified electrodes were smaller than those at the PANI film-modified electrode without the metal dispersion (Figure 4). The metal dispersion deactivates rather than activates the PANI film-modified electrode. In other words, the PANI film-modified electrode does not require the harmful heavy metals (Cu, Fe and Cr) and precious Pt.

In our previous study on DMFCs [8,10], it was shown that not only precious metals, such as Pt and Ru, but also several base metals, such as Sn, catalyzed the electro-oxidation of methanol. To examine whether these metals function as electrocatalysts, five metals (Pt, Cu, Zn, Fe and Cr) were electrodeposited on the modified PANI film electrode and the voltammetric peak current of L-ascorbic acid was measured using the electrodes. Unfortunately,

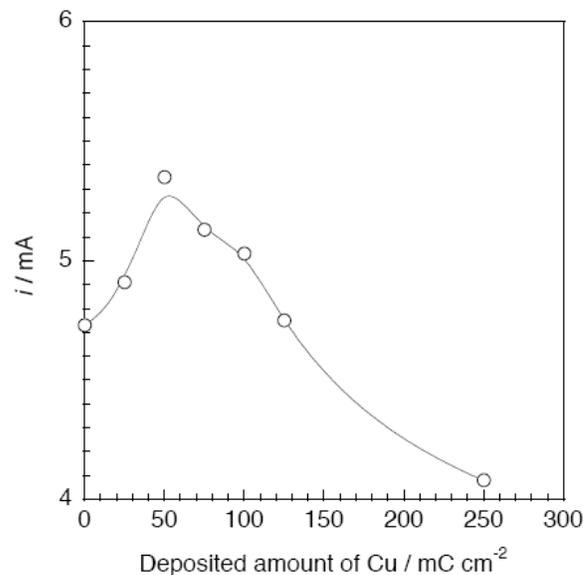


Figure 4. Effect of metal deposition on the catalytic activity of the PANI film-modified electrode evaluated by current-time profile.

however, the peak currents at these modified metal-dispersed PANI film electrodes were lower than those at the modified PANI film electrode without the metal dispersion. The metal dispersion deactivates rather than activates the modified PANI film electrode. In other words, the modified PANI film electrode does not require the harmful heavy metals (Cu, Fe and Cr) and precious Pt.

#### 4. CONCLUSIONS

These results revealed that the modified PANI film-modified electrode is quite promising for as the anode of the L-ascorbic acid fuel cell. It is highly active toward the electrooxidation of L-ascorbic acid and is free from harmful heavy metals (Cu, Fe and Cr) and precious Pt.

#### 5. ACKNOWLEDGEMENTS

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#### REFERENCES

- [1] A. M. Castro-Luna, *J. Appl. Electrochem.*, 30, 1137 (2000).
- [2] M. Goetz, H. Wendt, *J. Appl. Electrochem.*, 31, 811 (2001).
- [3] R. Dillon, S. Srinivasan, A. S. Arico, V. Antonucci, *J. Power Sources*, 127, 112 (2004).
- [4] A. S. Arico, V. Baglio, E. Modica, A. Blasi, V. Antonucci, *Electrochem. Commun.*, 6, 164 (2004).
- [5] A. Heinzl, V. M. Barragán, *J. Power Sources*, 84, 70 (1999).
- [6] H. Laborde, J. Léger, C. Lamy, F. Garnier, A. Yassar, *J. Appl. Electrochem.*, 20, 524 (1990).
- [7] H. Laborde, J. Léger, C. Lamy, *J. Appl. Electrochem.*, 24, 219

- (1994).
- [8] J. Yano, T. Shiraga, A. Kitani, J. Solid-State Electrochem., 12, 1179 (2008).
- [9] For a review, T. A. Skotheim, R. L. Elsenbaumer, J. R. Reynolds, Handbook of Conducting Polymers, Marcel Dekker, New York, U.S.A. (1998).
- [10] J. Yano, T. Shiraga, A. Kitani, J. New Mat. Electrochem. Systems, in press.
- [11] Z. Qi, M. Hollett, A. Attia, A. Kaufman, Electrochem. Solid-State Lett. 5, A129 (2002).
- [12] C. Lamy, S. Rousseau, E. M. Belgsir, C. Coutanceau, J. Léger, *Electrochim. Acta*, 49, 3901 (2004).
- [13] K. Matsuoka, Y. Iriyama, T. Abe, M. Matsuoka, Z. Ogumi, J. Power Sources, 150, 27 (2005).
- [14] K. Yamada, K. Asazawa, K. Yasuda, T. Ioroi, H. Tanaka, Y. Miyazaki, T. Kobayashi, J. Power Sources, 115, 236 (2003).
- [15] Z. P. Li, B. H. Liu, K. Arai, S. Suda, J. Electrochem. Soc., 150, A868 (2003).
- [16] S. Ha, B. Adams, R. I. Masel, J. Power Sources, 128, 119 (2004).
- [17] M. M. Mench, H. M. Chance, C. Y. Wang, J. Electrochem. Soc., 151, A144 (2004).
- [18] S. K. Mondal, R. K. Raman, A. K. Shukla, N. Munichandraiah, J. Power Sources, 145, 16 (2005).
- [19] N. Fujiwara, S. Yamazaki, Z. Siroma, T. Ioroi, K. Yasuda, Electrochem. Commun., 8, 720 (2006).
- [20] N. Fujiwara, Z. Siroma, T. Ioroi, K. Yasuda, J. Power Sources, 164, 457 (2007).
- [21] N. Fujiwara, S. Yamazaki, Z. Shiroma, T. Ioroi, K. Yasuda, N. Fujiwara, J. Power Sources, 167, 32 (2007).
- [22] I. G. Casella, M. R. Guascito, Electroanalysis, 9, 1381 (1997).