Biofuel Power Cells Using Conducting Polymer Catalyst

Sadahito UTO, Mao NISHIKAWA and Keiichi KANETO*
Department of Biomedical Engineering,
Faculty of Engineering,
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Abstract

Biofuel cells were fabricated using a conducting polymer, poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT*PSS) for the anode catalyst. Ni mesh and CuNi plated polymer cloth (tape) were employed as the anode current collector. The cathode catalyst was Pt-black with a current collector composed of carbon sheet/stainless steel. The cells were direct and passive types using a polymer electrolyte of Nafion®, and fueled with ascorbic acid (vitamin C) or citric acid. Cell performances in terms of voltage and maximum output power were compared among various anode materials (catalyst and current collector). The open circuit voltage, 0.64 V and the maximum power, 1.9 mW/cm² were obtained in the cell having PEDOT*PSS anode catalysts coated on CuNi tape for 0.5 M ascorbic acid. However, in 0.4M citric acid, the open circuit voltage, 0.70 V and the maximum power density, 2.2 mW/cm² were obtained in the cell with the same anode materials. These values were higher than those of the typical 0.52 V and 1.04 mW/cm² in the reference cell of Pt-black/Pt-black as anode/cathode catalysts for a 0.5M ascorbic acid fuel. The results show that PEDOT*PSS exhibited excellent anode catalytic activity combined with CuNi tape. The mechanisms of high power generation are discussed for the synergy effect of PEDOT*PSS and CuNi.

Keyword; Biofuel cell, conducting polymer, PEDOT*PSS, catalyst, ascorbic acid, citric acid, output power
1. Introduction

Recently, fuel cells are interested and studied intensively for a potential candidate of sustainable energy sources to conserve the global environment. There are several types of fuel cells depending on purposes, namely, size of output power, electrolyte and fuels\(^1\). Fuels are hydrogen, natural gas (methane) and bio-materials. The most efficient fuel is based on hydrogen; therefore, natural gas is usually converted to hydrogen by a method of steam methane reforming. The biomaterials are, for example, glucose, alcohol and organic acid, which have been (photo-) synthesized by plants. They are easy to obtain as daily foods. Fuel cells using these bio-materials are called as biofuel cells and a direct type without reforming the fuels. Biofuel cells using glucose and alcohols have been developed to commercial products\(^2,3\) from portable to vehicle sizes. Organic acids like ascorbic acid (AsA: vitamin C)\(^4,5\) and citric acid (CitA), which are major contents of a lemon, are also interested and candidates for biofuels, since they are abundantly obtained from fruits, and the side-products are nonpoisonous\(^6\). Especially, CitA is an attractive biomaterial, since CitA is the key compound in the citric acid cycle to synthesize energy source of adenosine triphosphate (ATP) in living cells.

Catalyst is the key component in fuel cells, since the catalyst significantly enhances the rate of chemical reaction and increase the conversion efficiency from chemical energy into electrical energy. Rare metals like Pt, Pd and Ru are commonly employed for high performance fuel cells, because they are almighty as catalysts. Therefore, the cell performance obtained using rare metal catalysts can be the referential standard cell. For instance, the power density of 7 mW/cm\(^2\) was reported based on Pd catalyst in 0.5 M AsA biofuel\(^4,5\). The Pd catalyst showed the highest performance among variety of rare metal catalysts. However, cells with carbon black catalysts like Vulcan XC72 and Ketjenblack EC were found to exhibit higher power\(^4,5\) ranging 12-15 mW/cm\(^2\). This figure was twice power of the cell using Pd catalyst. These cells were the active type, namely, the cells were tested in the condition that AsA and humid oxygen gas were circulated by flow rates of 4 mL/min and 100 mL/min, respectively\(^5\). The high catalytic activity of carbon blacks was associated with the enormous surface area of the carbon black. These facts indicate that rare metals are not always optimized catalyst, and the activity depends on the kind of fuels.

We have been studying the catalytic activity of conducting polymers in biofuel cells, in order to replace rare metals to cheap catalytic materials\(^1,6\). Conducting polymers have also been studied for mediators of biosensors and/or fuel cells\(^7,8\). The mediators immobilize catalyst (enzyme) on the electrode surface, and support the charge transfer from catalyst to electrode. However, there have been few reports, which mentioned the catalytic activity of conducting polymers in biofuel cells. Our cell was the passive type, namely, the fuel and oxygen were supplied by mass diffusion\(^6\). The cell was composed of biofuel/anode catalyst/polymer electrolyte/cathode catalyst/air. Nafion® was employed for the polymer electrolyte as proton transfer membrane\(^6\). AsA was used for the biofuel. We found that conducting polymers, poly(3,4-ethylenedioxy thiophene) polystyrene sulfonate (PEDOT*PSS) exhibits excellent anode catalytic activity in AsA biofuel cell. The performance was almost comparable or better than the cells using Pt catalyst\(^6\). Furthermore, polyaniline (PANI) and polypyrrole (PPy) were also found to exhibit a little anode and cathode catalytic activity\(^6\).

This paper reports an interesting finding that the output power was largely enhanced for AsA biofuel cell by combining PEDOT*PSS with Ni-mesh or CuNi-tape. The mechanism of power enhancement in these cells is discussed. The study of CitA as biofuels was motivated by the fact that a lemon juice fuel cell demonstrated enormous output power\(^9\) than that of AsA. In fact lemon juice contains about 5-8 % CitA.

2. Fabrication of Biofuel Cell

Figure 1 shows a fundamental structure of biofuel cell\(^1,6\), which was composed of fuel/current collector/ diffusion layer (mediator)/anode catalyst/polymer electrolyte/cathode catalyst/diffusion layer (mediator)/ current collector/air.

![Fig.1. Fundamental structure of a biofuel cell.](image)

The anode catalyst oxidizes biofuel directly and generates proton (H\(^+\)) and electron (e\(^-\)) as shown by scheme (1) for example of AsA.

\[
\text{AsA} \rightarrow \text{Dehydro-AsA} + 2\text{H}^+ + 2\text{e}^- \quad (1)
\]
The current collector receives electrons from catalyst via diffusion layer (mediator) and leads electrons to the external circuit. The protons migrate through a polymer electrolyte (proton transfer membrane) to cathode. Electrons move through the load at the external circuit to cathode. Thus at the cathode the protons and electrons reduce oxygen to water, as shown by the scheme (2). Eventually, current flows from the cathode to anode, supplying electric power to the load.

\[
\frac{1}{2} O_2 + 2H^+ + 2e^- \rightarrow H_2O
\]  

The detailed structure of fabricated biofuel cell\(^1\) is shown in Fig. 2. The frame of cell was made of polymethyl methacrylate (PMMA) with 4.0 x 4.0 cm² x 0.5 cm and tank of 1.0 x 1.0 cm² x 0.5 cm. Current collectors were laminated with double layer of anti-corrosive stainless steel (SUS 316L) and carbon sheet (C-sheet). The C-sheet played the role of mediator and/or diffusion layer to make good contact with catalysts. In the present biofuel cell, Ni-mesh or CuNi conducting tape was used as anode material with conducting polymer, as shown in Fig.2.

Nafion\(^\circledR\) (N117) was used as the polymer electrolyte. The core laminate shown in Fig.2 was composed of the polymer electrolyte, which was sandwiched with anode catalytic material, cathode catalyst of Pt-black and C-sheets. Pt-black was pasted on the Nafion\(^\circledR\) film by approximately 1 mg/cm². The core laminate was pressed at the stress of approximately 1 MPA and at 130 °C. Pt black (Pt-B) of High Spec. 1000 was purchased from Johnson Matthey Fuel Cells. CuNi plated polyethylene cloth (E05R2010) with the surface resistance, 0.05 Ω/□ was obtained from Seiwa Electric MFG Ltd. The carbon sheet of TGP-H-060 was Electrically conductive (TGP-H-060) was obtained from Chemix Co., Ltd. A double sided tape (3M Scotch SRT-15) was used to seal between the fuel tank, SUS collector and the polymer electrolyte. L-ascorbic acid and citric acid as biofuels were obtained from Sigma-Aldrich.

Aqueous emulsion of PEDOT:PSS was presented by Prof. Okuzaki, Yamanashi University with courtesy. PEDOT:PSS was mixed with 5 Vol% of dimethyl sulfoxide (DMSO), then coated on CuNi tape and Ni mesh followed by heating at approximately 150 °C to obtain the insoluble solid film.

Figure 3 shows the photograph and microscope pictures of the PEDOT*PSS coated on CuNi tape. The weight of PEDOT*PSS coated on both sides of CuNi tape was typically 1-2 mg/cm². CuNi tape was woven with polyester fibers of 10 μm in diameter as shown by bear surface of CuNi tape in Fig.3 (b). Figure 3 (a), (c) and (d) show the area of PEDOT*PSS, which adhered well on CuNi tape. The CuNi tape coated with PEDOT*PSS was cut into 1x1cm² and used as the anode catalytic materials shown in Fig.2.

3. Experimental Procedures and Analysis

Output characteristics of biofuel cells were obtained by the same method as reported in our previous papers\(^1\). Figure 4 shows a typical time response of the cell voltage (\(E_{cell} (V)\)), current (mA/cm²), power (mW/cm²), potentials of anode (\(E_{fuel} (V)\)) and cathode (\(E_{air} (V)\)) against the Ag reference electrode. Notes at the top of Fig.4 indicate the structure of cell. 0.5 M AsA was used as the biofuel, CuNi tape and PEDOT*PSS were used for the anode catalytic materials. The \(E_{cell} (V)\) at \(t = 0\) (or \(R = \infty\)) corresponds to the electromotive force, \(E_0\). The stepwise change of these curves was caused by switching the load resistances. The plateaus of current and power curves as well as \(E_{cell}, E_{fuel}\) and \(E_{air}\) indicated that the response of cell was a few seconds.
Fig. 4. Typical responses of cell parameters upon switching of load resistances $\infty \rightarrow 10 \, \Omega$.

Curves in Fig. 5 show the typical output characteristics of the biofuel cell deduced from Fig. 4 as the function of current. Potentials of $E_{\text{fuel}}$ and $E_{\text{air}}$ are also shown to evaluate the chemical activities of anode and cathode materials. According to the analysis of power vs. current curves reported in our previous papers, the maximum power ($P_{\text{max}}$) was obtained to be 1.9 mW/cm$^2$ at the current 7.2 mA/cm$^2$, where the cell voltage ($E_{\text{max}}$) was 0.3V. For the evaluation of cell performances, $E_{0\text{cell}}$, $P_{\text{max}}$ and $E_{\text{max}}$ were adopted. It is noted that $E_{\text{cell}}$ largely decreased with increasing current, showing the similar behaviour to $E_{\text{air}}$, but to $E_{\text{fuel}}$ being little change. The fact indicates that the cell voltage was mainly controlled by reaction activity at the cathode. That is, the cell performance could be improved by optimizing the cathode assembly.

4. Results and Discussion

Table 1 shows the cell performances using various anode materials. The cell performance of $\odot$ Pt-B employed for anode and cathode catalysts is also shown as the referential standard cell. To make these performances visual, the bar graphs are also shown in Fig. 6. It is interesting to note that higher output power were obtained in the anode materials of combination of PEDOT*PSS with $\odot$ Ni-mesh or $\odot$ CuNi tape for AsA and $\odot$ CitA fuels. It is worthwhile to note that $\odot$ PEDOT*PSS alone demonstrated the catalytic activity to AsA, even a half of the performance of $\odot$ Pt-B.

![Fig.5. Output characteristics of 0.5M AsA fuel cell using anode materials of CuNi and PEDOT*PSS.](image)

**Table 1. Performances of biofuel cells with various anode catalytic materials and biofuels of AsA or CitA.**

<table>
<thead>
<tr>
<th>Fuel/Anode Materials</th>
<th>$E_0$ (V)</th>
<th>$P_{\text{max}}$ (mW/cm$^2$)</th>
<th>$E_{\text{max}}$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5M AsA/Pt-B (1mg/cm$^2$)</td>
<td>0.45</td>
<td>1.04</td>
<td>0.20</td>
</tr>
<tr>
<td>0.5M AsA/Ni-(100)mesh</td>
<td>0.82</td>
<td>0.48</td>
<td>0.39</td>
</tr>
<tr>
<td>0.5M AsA/Ni-mesh/PEDOT*PSS(dip)</td>
<td>0.95</td>
<td>1.35</td>
<td>0.39</td>
</tr>
<tr>
<td>0.5M AsA/PEDOT*PSS(film alone)</td>
<td>0.52</td>
<td>0.53</td>
<td>0.47</td>
</tr>
<tr>
<td>0.5M AsA/CuNi/PEDOT*PSS(both side)</td>
<td>0.64</td>
<td>1.9</td>
<td>0.42</td>
</tr>
<tr>
<td>0.5M AsA/CuNi (alone)</td>
<td>0.80</td>
<td>0.16</td>
<td>0.28</td>
</tr>
<tr>
<td>0.4MCitA/CuNi/PEDOT*PSS(both side)</td>
<td>0.70</td>
<td>2.2</td>
<td>0.29</td>
</tr>
<tr>
<td>0.4MCitA/CuNi (alone)</td>
<td>0.72</td>
<td>0.38</td>
<td>0.41</td>
</tr>
</tbody>
</table>

It was surprising that $\odot$ CitA exhibited largest cell performance for anode material of PEDOT*PSS coated CuNi tape. That is, the $P_{\text{max}}$ was twice of $\odot$ AsA fuel/Pt-B catalyst. We were also aware of the power generation in $\odot$ Ni-mesh, $\odot$ CuNi tape for AsA and $\odot$ CuNi tape for CitA as shown in Fig. 6. For CitA fuel, however, it was found that anode catalytic materials of Pt-B and PEDOT*PSS scarcely generated any output power (the results are not shown in Table 1). The mechanisms for these results are discussed later.

![Fig.6. Cell performances using AsA and CitA biofuels and various anode materials deduced from Table 1.](image)
CitA being pH1.99 at around 20 °C, indicating that they are acid.

It is interesting to note that Ni mesh and CuNi tape showed higher $E_0$ than Pt-B and PEDOT*PSS as seen in Fig.6. Furthermore, they generated electric power from AsA and CitA, though the $P_{\text{max}}$ were a half or less than that of Pt-B. This fact reminds us a lemon battery, in which the mechanism is based on the Volta battery, Zn/lemon/Cu, associated with the ionization tendency of $\text{Zn}^+ > \text{Ni}^+ > \text{H}^+ > \text{Cu}^+$. Namely, in the lemon battery, the ionization or dissolution of Zn into $\text{Zn}^+$ generates electrons at the anode, as shown by scheme (3).

$$\text{Zn} \rightarrow \text{Zn}^+ + e^- \quad (3)$$

This ionization occurs simultaneously with reduction of $\text{H}^+$ in the fuel acid with $e^-$ at Cu cathode generating hydrogen, as shown by scheme (4).

$$2\text{H}^+ + 2e^- \rightarrow \text{H}_2 \quad (4)$$

The reaction may continue until proton or Zn is consumed.

In the present study of Ni mesh and CuNi tape at the anode, the similar ionization of Ni might take place as shown by the scheme (5) due to the acidity of AsA and CitA.

$$\text{Ni} \rightarrow \text{Ni}^+ + e^- \quad (5)$$

The same number of $\text{H}^+$ from AsA or CitA to $\text{Ni}^+$ might migrate via the polymer electrolyte to reduce oxygen at the cathode by the reaction of scheme (2). This reaction was supported with the observation of etching of CuNi tape.

Figure 7 shows photographs of etching in CuNi tape covered partially with PEDOT*PSS immersed in AsA (a) and CitA (b) for 70 h. It was observed that CuNi tape was etched in several hours. On the other hand, PEDOT*PSS protected etching of CuNi from acids.

In AsA biofuel cell, the oxidation of AsA into dehydro-ASA (1) was superimposed to (5) and enhanced the anode reaction, resulting in the high power generation. On the other hand, CitA biofuel cell may not oxidize by itself, even with help of catalytic Pt-B and PEDOT*PSS as mentioned previously. Namely, for example the oxidation of carboxyl group into alcohol and CO$_2$ might not take place. However, it is interesting to see the result that the combination of CuNi tape and PEDOT*PSS resulted in the highest electric power generation. The obtained high power performance in cells and was also associated with the large surface area of CuNi tape, low contact resistance and matching of chemical potentials between CuNi and PEDOT*PSS.

Figure 8 shows the current decay of a cell discharged with 1.0 kΩ. The anode was PEDOT*PSS coated on C-sheet same structure to in Table1. The fuel tank was filled with 0.5M AsA, corresponding 2.5 x $10^{-4}$ mol, which might deliver electronic charges of 48.0C according to scheme (1). The electronic charge obtained by integration of current by the time until 50 h was 44.1C. The experimentally obtained charge coincided well with the calculated one. The bump observed at 20-30 h was due to air condition of the room at 24°C from 18 °C in day time. The result confirmed the catalytic activity of PEDOT*PSS to AsA until consumption of the biofuel.

5. Summary

Anode catalytic activity of conducting polymers, PEDOT*PSS in AsA and CitA biofuel cells has been studied in comparison with the performance of Pt-B catalyst. The cells with catalysts of PEDOT*PSS coated CuNi tape demonstrated the high output power, being twice of Pt-B in AsA biofuel. We proposed the synergy effect in combination of PEDOT*PSS with Ni enhanced the catalytic activity. The role of Ni has been discussed taking ionization of Ni in the acidity of fuels. However the detailed role of PEDOT*PSS is not clear at the present state, and will be studied in future, as well as lemon fuel cells.
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