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Research Letter

Direct urea fuel cells based on CuNi-plated polymer cloth as a anode catalyst

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Abstract

Direct urea fuel cells were fabricated using CuNi-plated polymer cloth for anode catalyst and current collector, and Pt-black for cathode catalyst. The output power was significantly enhanced by coating the CuNi cloth with a conducting polymer, poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT*PSS). The open circuit voltage, 0.80 V and the maximum output power, 3.0 mW/cm^2 were obtained for the fuel of 0.5 M urea water solution under ambient conditions. Improvement over the cell structure demonstrated to lighten a light emitting diode.

Introduction

Urea, which is major component, has been attracted interests for direct and/or microbial fuel cells as a ultimate sustainable and renewable biomass energy source.[1–7] The usefulness of urea was pointed out by Lan and Tao[1] in terms of the volumetric energy density, being about 1.6 times larger than the liquid H_2. The issue in direct urea fuel cells is anode catalysts. Pt and rare metals are active to most of biofuels such as glucose and alcohol, however, they are inactive to oxidize urea at the anode.

We have studied conducting polymers such as polypyrrole (PPy), polyaniline (PANi), and poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT*PSS) to explore potentiality in biosensors[8] and biofuel cells.[9,10] PPy was found to be an excellent mediator to immobilize enzyme of urease to detect urea.[8] PANi and PEDOT*PSS exhibited catalytic activity for biomaterials of ascorbic acid and citric acid.[9,10]

Recently, Ni and Co compounds[1,2,5] have been found to be effective catalysts for urea and urine. Direct urea fuel cells[1] with the structure of nano-sized Ni particle for anode and MnO_2 for cathode catalysts with anion exchange polymer membrane demonstrated 14.2 mW/cm^2 at the maximum power density. Ingenuity upon anion transport membrane and cathode catalyst enhanced the performance to 26.5 mW/cm^2 at 300°C.[2] The highest output power reported recently was 33.8 mW/cm^2 using anode catalyst, Co_3O_4NiO and cathode catalyst, $Co_3O_4MnO_2$ on carbon cloth fibers.[5]

We fabricated direct urea fuel cells using CuNi-plated polymer cloth, which played the role of anode catalyst and current collector.[7] CuNi cloth was woven with fine polyester fibers, therefore, resulting in substantially enormous surface area. It was found that the catalytic activity of the CuNi cloth was significantly enhanced by coating with the conducting polymer PEDOT*PSS. The maximum output power was obtained to be 1.88 mW/m^2. This value was not larger than those of the reported values.[1,2,5] However, the CuNi cloth and the membrane are commercially available, and the cells were operated at ambient temperature without circulation of fuel and air.

In this communication, it is mentioned that the performance of direct urea fuel cells is enhancement by the improvement of cell structure and materials. Fabrication of stacked cells to demonstrate lightening a light emitting diode (LED) is also reported.

Fabrication of cells

The cell structure shown in Fig. 1(a) is the core laminate,[7,9,10] being piled with CuNi cloth (anode)/PEDOT*PSS/cation exchange membrane (CEM)/Pt-black(Pt-B)/carbon paint/CuNi cloth (cathode). The anode is a fuel electrode, and cathode is an air (oxygen) electrode. Pt-B (High Spec. 1000) was purchased from Johnson Matthey Fuel Cells and used as a cathode catalyst. Nafion® (N117) was used as the CEM with the thickness of 188 μm.

CuNi-plated polyester cloth was obtained from SEIWA Electric Mfg. Co., Ltd. The photograph of surface morphology is shown in Fig. 1(b), consisting of woven fibers with the diameter of 10 μm. The large surface area is effective at enhancing the catalytic activity. The CuNi cloth was prepared by electroless Cu plating with the thickness of approximately 1–2 μm, followed by electrodeposition of Ni by the thickness of 0.1∼0.3 μm. The surface resistivity was 0.05 Ω/□. Modification of piling materials was also tested to confirm the functional effect of materials. For instance, carbon sheet (C-sheet), TGP-H-060 from Chemix Co., Ltd. was used instead of carbon paint. A stainless steel mesh (SUS316 #200; anticorrosive electrode) was also employed as the replacement of CuNi cloth for the current collector.

The Pt-B was spread on the CEM with approximately 2 mg/cm^2 for the active area of 1 × 1 cm^2. Carbon paint (Aquadag,

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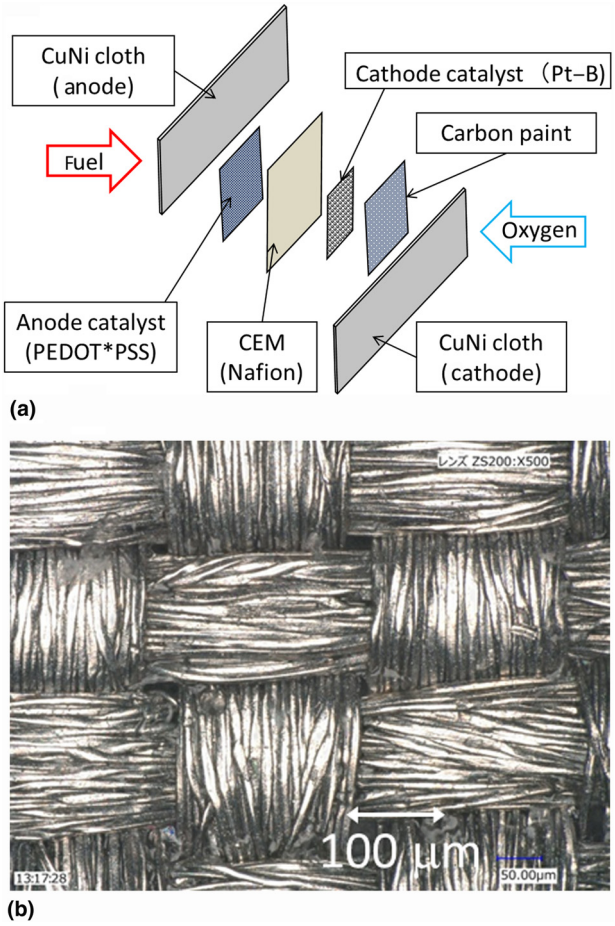


Figure 1. (a) Structure of core laminates in direct urea biofuel cells. (b) Photographs of CuNi-plated polyester cloth.

Acheson) was coated on the back side of CuNi cloth (cathode) to make good contact with Pt-B. Ni also was plated on C-sheet by the typical condition of 2 mA/cm^2 for 1 h as the anode catalyst. Water emulsion of PEDOT*PSS was painted on CuNi cloth and Ni-coated C-sheet by typically 2–3 mg/cm^2. The concentration of urea was 0.5 M water solution, and the volume of fuel tank was 0.24 cm^3. The urea of extra pure reagent (purity >99.0%) was purchased from Nakarai Tesque and used without further purification. The cells were tested under ambient conditions of approximately 22°C and humidity of 40%–60%. The experimental setup and characterization of fuel cells were described in our previous papers.[7,9,10]

Results and discussion

Figure 2 shows typical output characteristics (polarization curves) in a direct urea fuel cell for the cell configuration, #B in Table 1. The cell voltage, E_{cell} (V); electric power, P (mW/cm^2); potentials at fuel electrode, E_{fuel} (V); and air electrode, E_{air} (V) against a reference electrode of Ag^+/Ag^0 are shown as a function of the current density, i (mA/cm^2). E_{cell} is given by $E_{air} - E_{fuel}$, and $P = E_{cell} \times i$.

The E_{cell} dropped steeply at the beginning of current increase as shown in Fig. 2, which was usually observed and due to the decrease of E_{fuel} and E_{air}, namely, polarization at electrode surfaces. Cell performances in various cell structures (core laminates) are summarized in Table I, where E_0 is the electromotive force (open circuit voltage), P_{max} is the maximum power density, E_{max} and I_{max} are the E_{cell} and current density at the maximum power, respectively. To visualize the cell performance bar graphs in various core laminates are depicted in Fig. 3.

The P versus i curve represents a parabolic curve[9,10]; $P = -ri^2 + Ei$, where r is the internal resistance and E is the cell potential, respectively. Best fitting of P versus i to the experimental curve for the cell, #B gave $E = 0.43$ V and $r = 18\ \Omega/cm^2$. These values are approximately consistent with the values of E_0 and $r = E_{max}/I_{max}$, as shown by #B in Table I. The typical maximum current, which is basically twice that of I_{max}, was about 20 mA/cm^2.

The cell type #A indicates that CuNi cloth alone catalyzed urea at an appreciable level and served as the current collector. It is interesting to note that coating the CuNi cloth with PEDOT*PSS enhanced remarkably the catalytic activity by ten times as shown by #B in comparison with #A in Fig. 3. The results of #A and #C demonstrated that CuNi cloth was superior to Ni mesh, because of large surface area in CuNi cloth. Comparison of #A and #D indicated that plating of Ni on the C-sheet gave better performance than that of CuNi cloth, probably suggesting that C-sheet could be more porous than the CuNi cloth or some other reasons. It should be noted that using C-sheet and SUS mesh for the cathode current collector resulted in better performance in power and cell voltage than those of carbon paint and CuNi cloth, as shown in Fig. 3. The results were associated with that leakage and/or crossover of urea through CEM fell off the cathode activity at the CuNi cloth current collector. Hence, the cell #E demonstrated the best performance.

It was observed that a cell with C-sheet alone for the anode material showed $E_0 = 0.4$ V and $P_{max} = 0.5\ \mu W/cm^2$, and that with PEDOT*PSS coated C-sheet exhibited $E_0 = 0.3$ V and $P_{max} = 8\ \mu W/cm^2$, indicating that these materials were not effective for anode catalyst. Long-term immersion of CuNi cloth in 0.5 M urea did not result in corrosion or degradation of CuNi for a month, indicating CuNi cloth is stable in urea. The results mentioned above indicate that Ni plays the major role of the catalyst in urea fuel cells and combination with PEDOT*PSS enhances the catalytic activity for urea.[7] The detailed role of PEDOT*PSS is not known, however, may be due to the polymeric structure of conjugated π electrons, which could be fitted to oxidized biofuels energetically and spatially. And also loose packing of polymer structure should allow penetration of urea molecules inside the film.

The anode reaction should be complicated, however, we proposed a possible reaction by the overall reaction (1) with four electron transfer[7]:

$$CO(NH_2)_2 + 4O_2 \rightarrow CO_2 + 2HNO_3 + H_2O. \quad (1)$$

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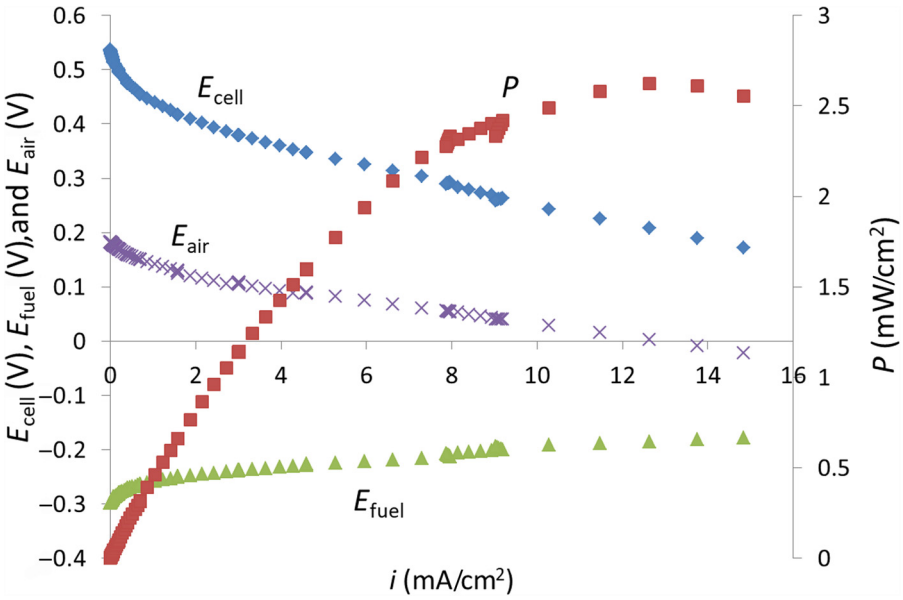


Figure 2. Typical polarization curve in a direct urea fuel cell (#B) obtained for 0.5 M urea and CuNi cloth coated with PEDOT*PSS.

Table I. Summary of cell performances of E_0, P_{max}, E_{max}, and I_{max} in various core laminates of direct urea fuel cells

Core laminates	Cell type #	E_0 (V)	P_{max} (mW/cm^2)	E_{max} (V)	I_{max} (mA/cm^2)
CuNi cloth(alone)/CEM^Pt-B/carbon paint^CuNi cloth	A	0.66	0.29	0.19	1.53
CuNi cloth^PEDOT*PSS/CEM^Pt-B/carbon paint^CuNi cloth	B	0.54	2.62	0.21	12.5
Ni mesh (#200)/CEM^Pt-B/C-sheet^SUS mesh (#150)	C	0.68	0.03	0.33	0.091
Ni-plated C-sheet/CEM^Pt-B/C-sheet/SUS mesh (#150)	D	0.79	0.82	0.32	2.6
Ni-plated C-sheet^PEDOT*PSS/CEM^Pt-B/C-sheet/SUS mesh (#150)	E	0.80	3.0	0.33	9.1

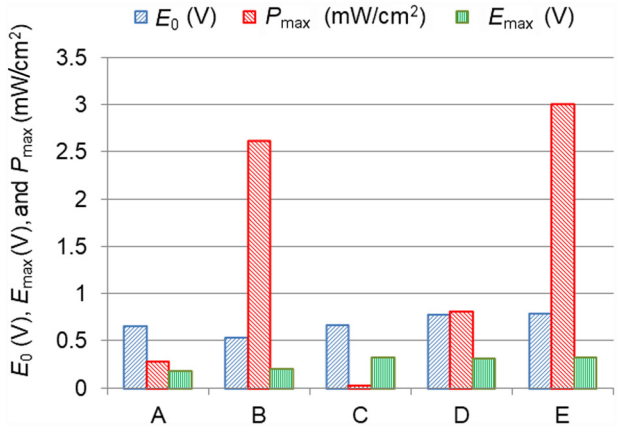


Figure 3. Comparison of cell performances in various core laminates.

The production of nitric acid (HNO_3) was associated with the observation that long-term operation resulted in etching of Ni on CuNi cloth but not Cu. Alternatively, however, ionization of Ni due to the oxidative force through the cathode reaction may not be excluded. The cell potential[7] was estimated from reaction (1) to be 0.86 V, which was slightly larger but nearly coincided with the observed E_0 in #D and #E in Table I. E_0 should depend on the redox mechanisms of fuel and catalyst activity, as well as crossover of fuel and oxygen through membrane. Moreover, there should be the other intermediate products such as nitrogen oxides NO_x, NH_3, and so on besides (1). Furthermore, the possibility of Ni ionization and consumption is not entirely excluded. The purity of fuel may be also another important issue for practical use of urine fuel cells. We do not discuss the details at the present stage until the analysis of reaction products in the fuel solution. These will be done in a future study.

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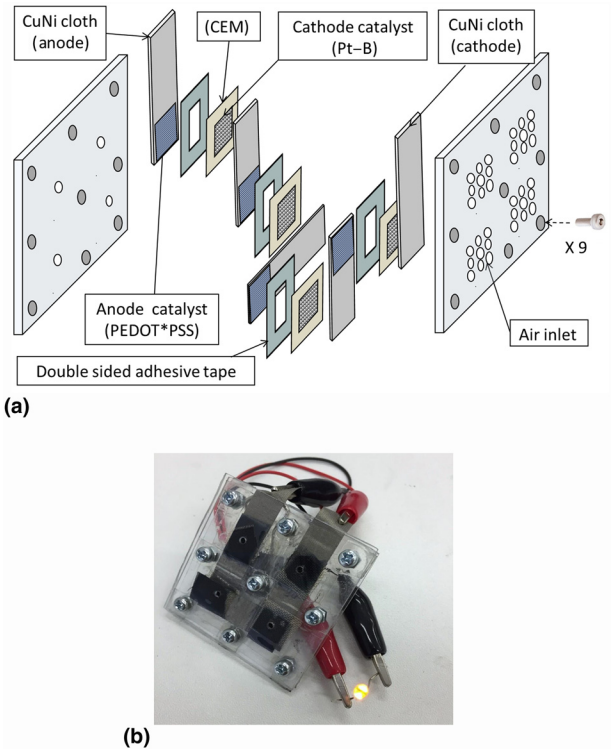


Figure 4. (a) Assembly of stacking four cells to lighten an LED. (b) Demonstration of lightening of an orange LED.

Figure 4(a) shows schematic drawing of stacking four cells (type #B) to elevate the output voltage (approximately 2.2 V) for lightening LED. The voltage to turn on an orange LED requires more than 2 V and the current of larger than 0.1 mA. The voltage depends on the color of LEDs. The lightening of an orange LED is demonstrated in Fig. 4(b). The LED lasted lightening for about 3 h with 0.05 cm^3 of 0.5 M urea water solution.

Summary

Direct urea fuel cells were fabricated using CuNi-plated polymer cloth as the anode catalyst, which served also as current collectors. The cell performance was remarkably enhanced by coating CuNi cloth with the conducting polymer of PEDOT*PSS. The cell was further improved by using Ni-plated C-sheet and PEDOT*PSS. A possible scheme of the reaction in direct urea fuel cells was proposed and the mechanism of catalyst was discussed. Further studies on the detailed mechanism of catalytic reaction by CuNi, the role of conducting polymers, and stability of cells will be continued.

Acknowledgments

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