Short communication

Towards a rechargeable alcohol biobattery

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ABSTRACT

This research focused on the transition of biofuel cell technology to rechargeable biobatteries. The bioanode compartment of the biobattery consisted of NAD-dependent alcohol dehydrogenase (ADH) immobilized into a carbon composite paste with butyl-3-methylimidazolium chloride (BMIMCl) ionic liquid serving as the electrolyte. Ferrocene was added to shuttle electrons to/from the electrode surface/current collector. The bioanode catalyzed the oxidation of ethanol to acetaldehyde in discharge mode. This bioanode was coupled to a cathode that consisted of Prussian Blue in a carbon composite paste with Nafion 212 acting as the separator between the two compartments. The biobattery can be fabricated in a charged mode with ethanol and have an open circuit potential of 0.8 V in the original state prior to charging or in the discharged mode with acetaldehyde and have an open circuit potential of 0.05 V. After charging it has an open circuit potential of 1.2 V and a maximum power density of $13.0\,\mu W\,cm^{-3}$ and a maximum current density of $35.0\,\mu A\,cm^{-3}$, respectively. The stability and efficiency of the biobattery were studied by cycling continuously at a discharging current of 0.4 mA and the results obtained showed reasonable stability over 50 cycles. This is a new type of secondary battery inspired by the metabolic processes of the living cell, which is an effective energy conversion system.

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1. Introduction

Although researchers tend to consider fuel cells and secondary (rechargeable) batteries as quite different technologies, they are both energy conversion devices. Fuel cells are electrochemical devices that convert chemical energy to electrical energy and fuel cells are considered to have high energy density, because of the ability to use high energy density fuels. Secondary batteries have a defined chemical composition and require recharging to reverse the chemistry occurring at the electrode after discharging, whereas fuel cells continuously produce electrical energy once fresh fuel is provided. Traditional fuel cells employ precious metal catalysts for the oxidation and reduction processes, whereas biofuel cells are fuel cells based on bioelectrocatalysis leveraging on microorganisms, organelles, and/or enzymes for electrocatalysis [1–3]. Biofuel cells are an attractive alternative to traditional fuel cells, because biofuel cells can be cost effective, more environmentally friendly and give the flexibility of deep oxidation of complex biofuels utilizing enzymatic cascades of metabolic pathways [4,5].

Akers et al. [6] developed an ethanol/air biofuel cell which had a high current and power density and showed that NAD+-dependant alcohol dehydrogenase bioanodes oxidize ethanol to acetaldehyde with the reduction of oxygen from air to water at a Pt cathode.

The concept behind the research described in this paper was to convert the biofuel cell technology developed by Akers et al. to a rechargeable ethanol biobattery. The main challenge for this project is to utilize a suitable cathode material that will be coupled with the NAD-dependant alcohol dehydrogenase bioanode compartment to result in a reversible system.

Extensive research has been done on Prussian Blue (PB) i.e., iron(III) hexacyanoferrate(II) with regard to its application to electrochromic displays [7–9], electrocatalysis [10,11] and ion-selective electrodes [12]. The high electrochemical reversibility and stability of PB makes it an attractive material to study for battery applications [13]. It has been shown by various researchers that Prussian Blue can be used as the cathode material for solid state secondary batteries due to its high redox potential of 0.9 V vs. SCE [8,14–16]. Neff [15] was the first to develop a secondary cell with PB. His battery electrodes were developed by electrochemically depositing PB on highly porous graphite. The major difficulty encountered in his studies was the adherence of the PB deposit on the carbon substrate; therefore there was gradual loss of PB from the electrodes after repetitive charging cycles leading to an average rate of loss 5% capacity per cycle. PB has an open structure for ion diffusion and it also has sufficient electronic conductivity [13]. Therefore in this project, we attempted to use PB in the cathode of a rechargeable ethanol biobattery that contains NAD-dependent alcohol dehydrogenase (ADH) at the bioanode, which can undergo a reversible redox process, thus the oxidation of ethanol to acetaldehyde and the subsequent reduction of acetaldehyde to ethanol in

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a paste mixture. The paste mixture was made of the ionic liquid electrolyte (BMIMCl), carbon black, and carbon fiber to increase conductivity and surface area. An electro-active species ferrocene was added to the bioanode serve as a mediator to shuttle electrons to/from the electrode surface/collector, thereby minimizing the overpotential of the system [17]. The cathode solid paste mixture was made of PB in a carbon black and carbon fiber with BMIMCl ionic liquid as electrolyte. The anode and cathode compartments were separated by Nafion® 212 membrane. The performance of the battery was characterized by both potentiostatic and galvanostatic techniques.

2. Experimental

2.1. Reagents and materials

Ethanol (Fisher), acetaldehyde (Sigma), ferrocene (Sigma), NAD$^+$ (Sigma), alcohol dehydrogenase (Sigma), potassium ferricyanide (Sigma), iron(III) chloride anhydrous(Sigma), 1-butyl-3-methylimidazolium chloride (BMIMCl/Sigma), and carbon black (Cabot) were used as purchased. Nickel mesh, Nafion NRE-212 (Sigma), graphite cloth (GC = 10/The Electrosynthesis Co. Inc.), and PVC rigid sheets were used as described in the procedure below.

2.2. Bioanode preparation

The bioanode was prepared by adding 12.5 mg of ferrocene, 12.5 mg of NAD$^+$, and ~1.5 mg of ADH into 200 μl 1-butyl-3-methylimidazolium chloride (BMIMCl) with 50 μl water and mixed in a weigh boat. After mixing well, 150 μl ethanol or acetaldehyde was added to the mixture. Then 200–300 mg of carbon black and 100 mg of carbon fiber were added, respectively and mixed well to obtain a solid paste mixture. The carbon fiber was obtained by grinding graphite cloth to fine fiber. A few drops of BMIMCl ionic liquid were added until a viscous paste was obtained.

2.3. Cathode preparation

The Prussian Blue cathode was prepared by adding about 100 mg of iron(III) chloride and 100 mg of potassium ferricyanide to about 200 μl BMIMCl ionic liquid and grinding to a mixture in a weigh boat. Then about 200–300 mg of carbon black and 100 mg of carbon fiber were added, respectively and mixed well to obtain a solid paste mixture. A few droplets of BMIMCl ionic liquid were added until a viscous paste was obtained.

2.4. Biobattery test setup

The battery was fabricated by packing and pressing both the bioanode paste mixture and the cathode paste mixture into their respective chambers of the PVC biobattery test cell. Nafion® NRE-212 PEM separates the cathode chamber from the anode chamber, as shown in Fig. 1. The chambers were made of PVC rigid sheet which had a cylindrical opening of 0.5 cm radius and a height of 1 cm. Both chambers are held together with bolts and nuts to ensure the proper seal between the cathode and anode chambers. A nickel mesh was connected to each end of the chamber to serve as a current collector and then connected to a Pine Instruments WaveNow USB potentiostat/galvanostat for electrochemical characterization of biobatteries. The potentiostat/galvanostat was interfaced to a PC computer for data collection of power density, current density and open circuit potential, as well as charging and discharging profile output generated by the biobattery employing a NAD$^+$-dependant dehydrogenase bioanode and a Prussian Blue cathode.
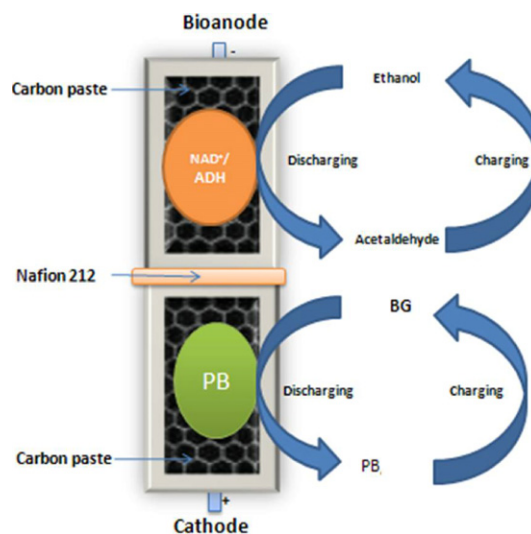

Fig. 1. Schematic of the biobattery including redox processes of the NAD-dependent alcohol dehydrogenase bioanode and the Prussian Blue cathode.

3. Results and discussion

Over the last century, we have learned a great deal about energy conversion from studying living cells and their biological machinery. Living cells consume nutrient (chemical energy) and convert it to work via metabolic pathways, such as the Kreb's cycle and glycolysis. These complex metabolic pathways are remarkably efficient and necessary for life. These metabolic pathways contain oxidoreductase enzymes to catalyze these important metabolic redox reactions. In this paper, we are utilizing one of these metabolic enzymes, alcohol dehydrogenase, for electrochemical energy conversion in a secondary (rechargeable) battery.

Ionic liquid was employed as an electrolyte in the biobattery due to its unique physicochemical properties such as high thermal stability, negligible vapor pressure, relatively high ionic conductivity and good electrochemical stability [18]. Ionic liquids have been shown to offer advantages in electrochemical studies when used as either the solvent or electrolyte or both [19]. Most common electrolytes used in batteries are either organic electrolyte or polymer electrolyte. The disadvantage with organic electrolyte is that they can be toxic, not environmentally friendly, and are not biocompatible with enzymes. On the other hand, polymeric electrolytes have interfacial problems, as compared to ionic liquids. Ionic liquids have also been employed to stabilize enzymes [20,21], which is advantageous since the lifetime of enzymes in enzymatic biofuel cells is frequently short [1].

Since ionic liquids are relatively viscous, we were concerned about mass transport limitations in our bioanode. We performed cyclic voltammetry at varying scan rates to determine if the system is transport limited. As shown in Fig. 2, there was a linear dependence of peak current to the square root of scan rate showing transport limited electrochemical performance. From this plot, the diffusion coefficient was calculated to be 3.62 ($\pm$0.76) $\times 10^{-8}$ cm^2 s^{-1}, which is a decrease in diffusion coefficient of great than an order of magnitude compared to free solution. However, this does shows that transport through the ionic liquid is still higher than through polymer electrolyte membranes (i.e., Nafion), which is important, since many bioanodes are formed by immobilizing protein in polymer electrolyte membranes [22–24].

It has been shown that biocatalytic reactions in ionic liquids exhibit higher selectivity, faster rates and enhanced enzyme stability [20]. However, most enzymes that are dissolved in pure ionic liquids show reduced catalytic activity, due to changes in their con-
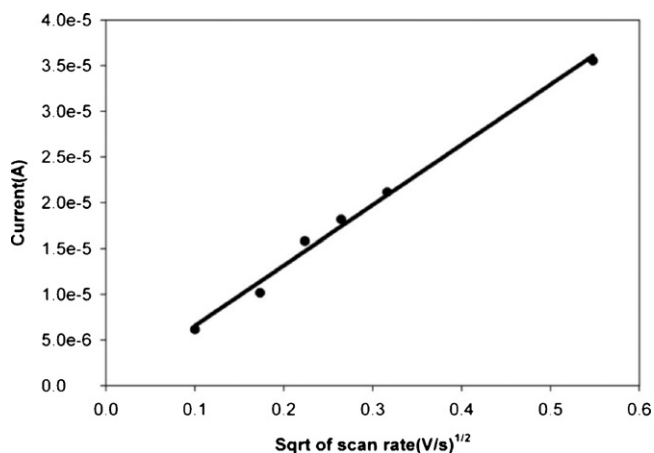
Fig. 2. Peak current of bioanode containing NAD-dependent alcohol dehydrogenase/ferrocene on a glassy carbon electrode in ionic liquid with 500 mM ethanol at various scan rates.
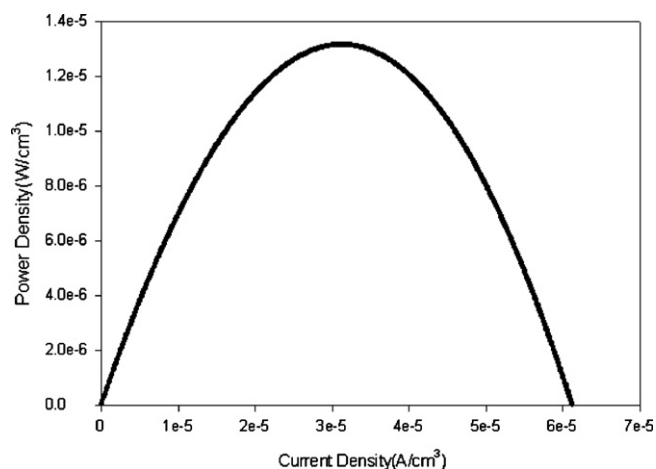

Fig. 3. Representative power curve of a biobattery containing an ethanol bioanode and a Prussian Blue cathode at room temperature.

formational state. The addition of small amount of water to the ionic liquids can overcome this drawback [20]. Shi et al. [21] studied the catalytic characteristics of alcohol dehydrogenase, using ethanol as substrate, in a medium containing BMIMCl and found out that the enzyme had higher activity when the concentration of the BMIMCl ionic liquid was below 0.15 g ml^{-1} and thermal stability was improved in the presence of low concentration of BMIMCl. Similar results were observed for this bioanode. The NAD-dependent ADH was immobilized in the ionic liquid (IL)–carbon composite material with the mediator to allow for the efficient electron transfer to the electrode/collector. When 500 mM ethanol was added to the mixture made of ferrocene and NAD-ADH in BMIMCl ionic liquid, there was a 23% increase in the peak current indicating that the ADH catalyzed the oxidation of ethanol to acetaldehyde.

Fig. 3 shows a representative power curve for the biobattery which had a maximum power density of 13.0 µW cm^{-3} and maximum current density of 35.0 µA cm^{-3}, respectively. The biobattery had an open circuit potential of 0.80 V prior to charging due to the fact that we fabricated the biobattery with ethanol instead of acetaldehyde to ensure we were in the charged state. When we fabricate the battery in discharged state with acetaldehyde, the open circuit potential prior to charging is 0.05 V. The theoretical columbic capacity and energy density was calculated based on the equivalent amount of redox species (7.63 mmol g^{-1}) in the anode. The amount of cathode material was not added into the calculation, since we had
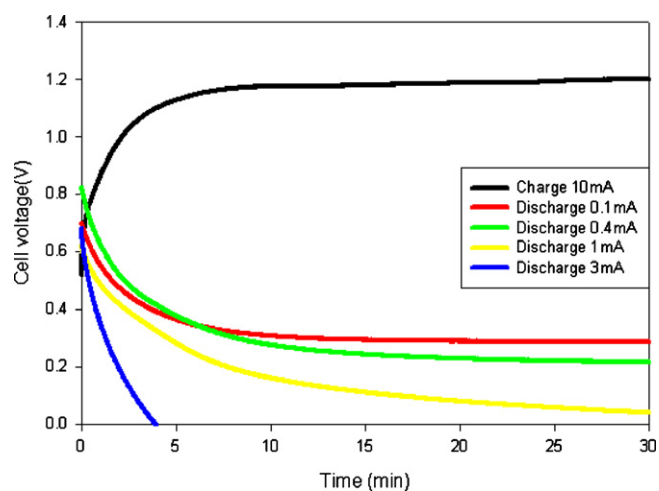

Fig. 4. Charge and discharge profile of rechargeable ethanol biobattery at low and high discharge rates.

enough cathode material to complete the reaction. The estimated charge was 1472 C g^{-1}. It has been shown by various researchers that the cyclic voltammetric behavior of Prussian Blue is accompanied by two redox couples [8,13–15]. In this cathode, the following reversible reduction reaction is occurring.

$$Fe^{III}[Fe^{III}(CN)_6]``BG'' + K^+ + e^- = KFe^{III}[Fe^{II}(CN)_6]``PB'' \tag{1}$$
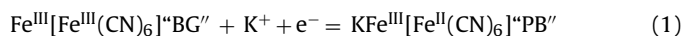
This reaction which occurs at high redox potential (0.9 V vs. SCE) involves the reduction of the starting material "Berlin Green" (BG) to Prussian Blue through one electron transfer. The electrochemistry in the anode chamber is more complex. The enzyme (alcohol dehydrogenase) is catalyzing the oxidation of ethanol to acetaldehyde while the coenzyme (biological mediator) NAD$^+$ is reduced to NADH. It is the NADH that is then oxidized at the anode. Reaction (2) below shows the enzymatic catalysis reaction and Reaction (3) shows the anodic oxidation of the coenzyme that occurs at a standard reduction potential of −0.32 V vs. NHE.

$$CH_3CH_2OH + NAD^+ = CH_3CHO + NADH + H^+ \tag{2}$$

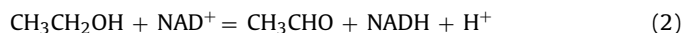$$NADH = NAD^+ + H^+ + 2e^- \tag{3}$$

Fig. 4 shows the charge/discharge profile of the battery. The battery was charged at a constant current of 10 mA for 30 min and this is more than sufficient to completely charge the battery and result in a flat potential profile at 1.2 V. When discharged at lower currents like 0.1 mA and 0.4 mA corresponding to a C-rate of 0.25 C and 1 C, the potential did not go to zero, but leveled out at a constant potential of 0.30 V and 0.22 V, respectively. At higher discharging currents of 1 mA and 3 mA corresponding to a C-rate of 2.5 C and 7.5 C, the potential of the battery decreased rapidly. This is expected because as the load increases, the discharge time suffers, because some of the battery energy is lost due to internal losses which result in the battery heating up.

The performance of the battery was investigated by charging and discharging the battery continuously for more than 50 times at a C-rate of 1 C. Fig. 5 shows the variation of percentage loss in cell voltage as a function of number of cycles. As per the graph, only 25% loss in cell voltage was observed after 50 cycles. This shows that the cell is stable and has acceptable cycleability. The results obtained so far with this type of battery are very interesting and promising, however more performance studies and optimization have to be done. This is because the cell capacity obtained (2.14 C g^{-1}) is far lower than the theoretical value (1472 C g^{-1}). We attributed this to the fact that ethanol is lost while putting the cell together and there is high internal resistance due to the design style of the cell.
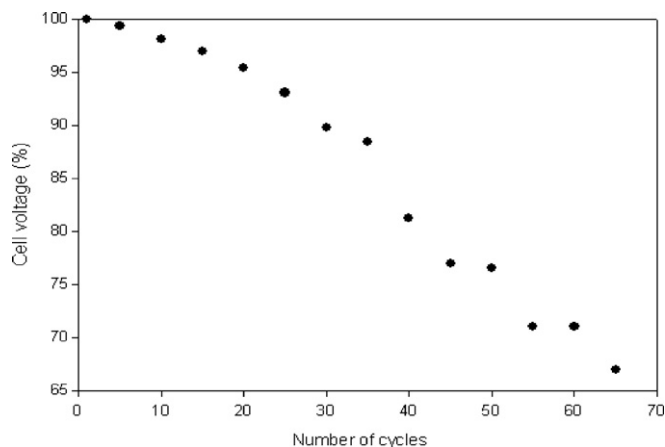
Fig. 5. Cycling performance studies of the biobattery at a discharging rate of 1 C.

4. Conclusion

An ethanol biobattery based on NAD^+-dependant alcohol dehydrogenase immobilized in a carbon composite material was developed and studied. Prussian Blue was a good cathode material when coupled with an ethanol bioanode. Rechargeable battery performance was observed. Twenty five percent of the cell voltage was lost after 50 charge/discharge cycles showing the usefulness and versatility of employing biofuel cell technology for rechargeable biobatteries.

Acknowledgements

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