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Production of electrical energy from carbohydrates using a transition metal-catalysed liquid alkaline fuel cell

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Abstract

Biomass may be converted to energy by enzymatic hydrolysis to monomer components and fermentative conversion of those products to ethanol for use as fuel. Both glucose and xylose in aqueous solution were directly converted to electrical energy using a liquid alkaline fuel cell (AFC) at room temperature. Hydrolysis products derived from the action of cellulase and amylase on cellulose and starch, respectively, were also used as fuels in the AFC system. We suggest that this approach may provide a more direct means of accessing some of the energy available from biomass.

Introduction

In the ever-increasing search for renewable energy alternatives to fossil fuels, various approaches to derive energy from biomass have been examined. These include the enzymatic conversion of biomass to constituent monomers such as glucose and xylose and fermentative conversion of those products to ethanol (Sun & Cheng 2002, Wyman 2003). The efficiency of such an approach is hindered by the multi-stage nature of the process and the cost of recovering ethanol from the fermentation process (Sun & Cheng 2002). An alternative approach involves converting biomass-derived products (e.g. glucose) to electrical energy using fuel cell technology. This may be accomplished by converting the biomass products to hydrogen using processes such as catalytic reforming and subsequent use of that hydrogen in fuel cell systems (Cortright *et al.* 2002, Liguras *et al.* 2003). Such an approach, however, is hindered by the requirement for more efficient fuel processing and purification (Cortright *et al.* 2002). In addition, operational requirements for this approach involve the use of elevated temperatures, thereby further increasing the economic challenge. Other alternative approaches involve the use of either microbial or enzymatic biofuel cells, however, these in many cases, require the addition of redox mediators to facilitate the transfer of electrons to electrodes (Tayhas 1994).

Against the negative background of the above-mentioned approaches, transition metal-catalysed liquid alkaline fuel cells (AFCs) could potentially offer some advantages in terms of converting simple carbohydrates directly to electrical energy. These systems may be employed to directly convert entities such as ethanol to electrical energy (Larminie 1989). Pt-based catalysts can also accelerate the oxidation of glucose in alkaline environments (Popovic & Tripkovic 1992). If it could be demonstrated the carbon/Pt-based catalyst in liquid AFC systems could enhance the oxidation of simple carbohydrates, then sugars derived from the enzymatic hydrolysis of biopolymers could be employed as fuels in the suggested AFC system. Operating at ambient temperatures, such systems would permit the

direct harvesting of energy from sugars derived from the enzymatic hydrolysis of polymers and circumvent the necessity to ferment those sugars to ethanol. In addition, the economic challenge associated with the recovery of ethanol for use as a combustible fuel would be circumvented.

Here we report on the direct use of glucose and xylose as fuels in a liquid alkaline fuel cell (AFC) for the generation of electrical energy at room temperature. In addition, we demonstrate that hydrolysates derived from cellulase-catalysed and amylase-catalysed degradation of cellulose and starch, respectively, may be employed as fuels in the AFC system. We suggest that such a system may form the basis for an alternative means of deriving energy from biomass.

Materials and methods

Fuel cell configuration

The fuel cells employed in this study were obtained from Electro-Chem-Technic (UK) (Larminie 1989) and are specifically designed for small-scale studies with liquid alkaline electrolytes and fuels. They are comprised of a 65 ml fuel and electrolyte compartment that also contains a carbon-supported platinum catalyst together with a PTFE (polytetrafluoroethylene) binder that is, in turn, supported on a nickel mesh (catalyst area = 17.64 cm^2). The air cathode consists of manganese [as $KMnO_4$ at greater than or equal to 4% (wt of carbon)] on carbon with a PTFE binder and this is also supported on a nickel wire mesh (catalyst area = 13.86 cm^2) (Hoge 1990). The surface of the cathode in contact with air is coated with a gas-permeable layer of PTFE. The nickel mesh supports at both the anode and the cathode are connected to terminals on the cell.

Fuel cell operation

In these studies the electrolyte consisted of a total volume of 65 ml containing 4 M KOH as the electrolyte and the relevant quantity of glucose or xylose as the fuel. In all cases the fuel cells were operated at room temperature (15–20 °C). Fuel cells were also operated in a closed circuit mode with a 1 kΩ resistor introduced into the circuit to enable continuous monitoring of both the voltage and current output from the cells. Voltage from the cells was monitored continuously using an analogue-to-digital converter (ADC 100) unit from Picotech (UK) together with the data logging software downloaded to a PC (operating system = Windows Me). Voltage data were sampled every 15 min throughout the duration of experiments. The current was periodically monitored using a digital multimeter (Beckman Instruments Inc., USA). Using glucose as a fuel, the current (expressed in mA) was consistently 9% less than the voltage.

Enzymatic hydrolysis of cellulose and starch

Cellulose was enzymatically hydrolysed by incubating 200 mg filter paper (Whatman Grade No. 1) with 100 mg cellulase (*Trichoderma reesei*, Sigma, UK) in 10 ml (0. 1 M NaCl pH adjusted to 5) at 37 °C for 96 h. NaCl was employed to minimise the effects of buffer components on the AFC catalytic membranes. When digestion was completed, 0.1 ml samples were analysed using the DNS method for reducing sugars; the average conversion of cellulose to soluble sugars was 10%. Ten millilitre aliquots of these hydrolysates were incorporated in the AFC system containing 50 ml 4 M KOH.

Starch was hydrolysed using, α-amylase (*B. lichenoformis*, Sigma, UK) by incubating 5 mg enzyme together with 200 mg pre-boiled starch in 10 ml (0.1 M NaCl, pH 5) at 37 °C for 96 h. Following hydrolysis, 0.1 ml aliquots were analysed for reducing sugars using the DNS method and the average conversion of starch to reducing sugars was 29%. Ten millilitre aliquots of these hydrolysates were incorporated into the AFC system containing 50 ml 4 M KOH.

Results and discussion

Plant-derived carbohydrates represent a very significant reservoir of renewable energy. As mentioned above, enzymatic conversion of cellulosic materials to glucose and subsequent conversion to ethanol represents one of the strategies by which this energy reserve may be harnessed (Sun & Cheng 2002, Wyman 2003). Any means of circumventing the conversion of glucose to ethanol would be expected to contribute positively to the

overall economics of energy derivation from biomass. Since glucose oxidises slowly in alkaline media and this may be enhanced using Pt-based catalysts or Pt-based surfaces (Popovic & Tripkovic 1992), it was decided to determine whether or not a catalytic liquid alkaline fuel cell system could be employed to derive electrical energy directly from the glucose. As a result of the slow spontaneous oxidation of glucose in alkaline media, a liquid alkaline fuel cell comprising a Pt-carbon-based anode and a very efficient Mn-carbon-based cathode (Hoge 1990) was employed in these studies. In order to examine the oxidation of glucose in this system and to determine the coulombic yield, glucose was added at 100 and 200 μmol to run each cell to a fuel-exhausted state. In these experiments, a closed circuit configuration was established and a 1 kΩ resistor was placed in that circuit.

Under these conditions, the data shown in Figure 1 were obtained and they demonstrate that this system may be used to derive electrical energy from glucose. Using 200 μmol glucose, the voltage increased to 0.53 V at 3 h and the current measured at this point was 0.482 mA. After this initial peak, the voltage remained above 0.3 V (0.27 mA) for 18 h. The system continued to produce electrical energy for a further 90 h and the coulombic yield expressed as total coulombs (amperes $\times$ s) was determined to be 44 C. Using 100 μmol glucose, the voltage increased to a maximum 0.253 V at 4 h and yielded a current of 0.23 mA.

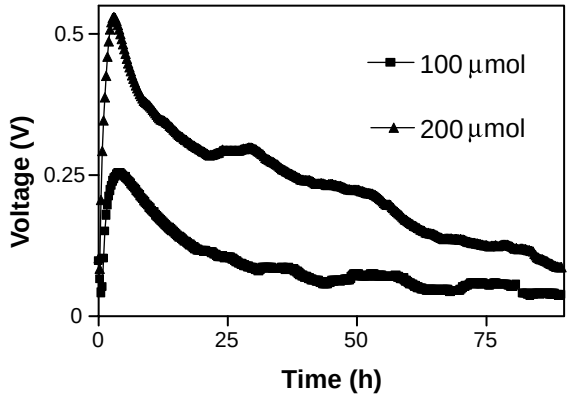

Fig. 1. Closed circuit operation of the alkaline fuel cell using 100 μmol (■) and 200 μmol (▲) glucose in 4 M KOH. The fuel cells were operated with a 1 kΩ load resistance to control the flow of electrons from the anode to the cathode.

Again the voltage decreased as glucose was depleted and the coulombic yield was determined to be 17.08 C. If glucose is employed as a fuel in biofuel cell technology then compete oxidation to CO_2 would yield 24 electrons:

$$C_6H_{12}O_6 + 6H_2O \rightarrow 6CO_2 + 24H^+ + 24e^-.$$

Since 1 mol electrons yields 96 500 C of charge, then 1 mol glucose would be expected to yield 96 500 $\times$ 24 C of charge, assuming complete oxidation to CO_2 (Tayhas *et al.* 1994). Therefore 100 μmol glucose would yield 231 C in the alkaline fuel cell if complete oxidation occurred. However, in the system described here, 17.08 C of charge was delivered during the utilisation of 100 μmol glucose. This suggests that only 2 of the 24 available electrons are being removed from the glucose molecule, since the maximum output for a 2-electron transfer would be 19.3 C. In the system employing 200 μmol glucose, the coulombic yield was 44 C and this again indicates a 2-electron transfer. Although the mechanism by which this system derives electrical energy from glucose is as yet unknown, the data suggest that glucose is being oxidised to gluconolactone +2[H] since this would involve the transfer of two electrons.

In order to examine the operation of the fuel cell with glucose concentrations that were not limiting, it was decided to employ higher quantities of glucose. In addition, since xylose is a major hydrolysis product resulting from the hydrolysis of lignocellulosic materials, we also examined the use of this monosaccharide as a fuel under similar concentrations. In these experiments, 2.8 mmol glucose and 3.3 mmol xylose were added to the system. The results shown in Figure 2 were obtained and in the both cases the voltage increased to approx. 0.9 V (0.82 mA). This, however, decreased to 0.6 V at 32 h when glucose was employed as a fuel and at 18 h when xylose was used at the fuel. Both fuel cells continued to operate for a further 300 h with the voltage remaining above 0.2 V for 200 and 280 h in the cases of xylose and glucose, respectively (results not shown). In the absence of a mechanism for fuel oxidation in this system, the reason for the decrease in voltage at earlier stages in each run are as yet unknown. However, factors such as O_2 depletion in solution and loss of catalytic centres from both the carbon-Pt and

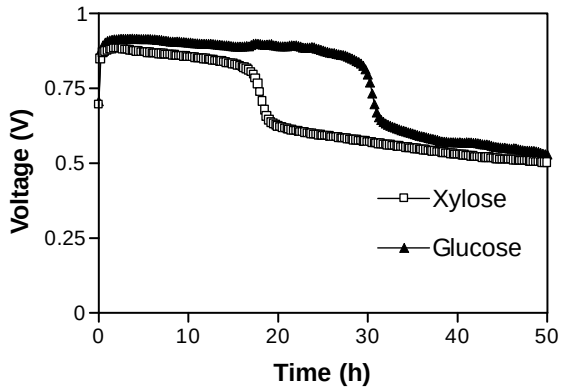

Fig. 2. Closed circuit operation of the alkaline fuel cell using 2.8 mmol glucose (▲) and 3.3 mmol xylose (□) as the fuel. A 1 kΩ to resistance was placed in the circuit.

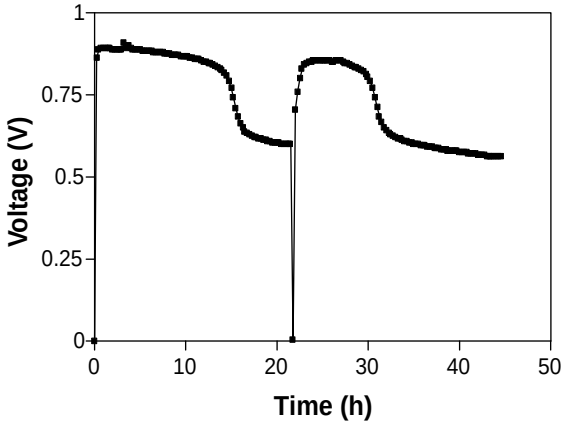

Fig. 3. Closed circuit operation of the alkaline fuel cell using glucose as the fuel. The cell was emptied and re-fed at the time indicated by the arrow. A 1 kΩ resistance was placed in the circuit during operation.

the carbon-Mn catalysts would be expected to contribute positively to such a phenomenon.

Since one of the benefits of fuel cell technology is to provide electrical energy as long as fuel is supplied to the cell, it was decided to examine the effects of re-feeding cells with xylose. In this case cells were operated until the initial voltage decrease was observed and then the system was washed, dried in air for 24 h and fuel was again added. The results (Figure 3) demonstrate that the voltage obtained following re-feeding is similar to that obtained during the first re-feed. However, the time at which this higher voltage was maintained following re-feeding, was approx. half that

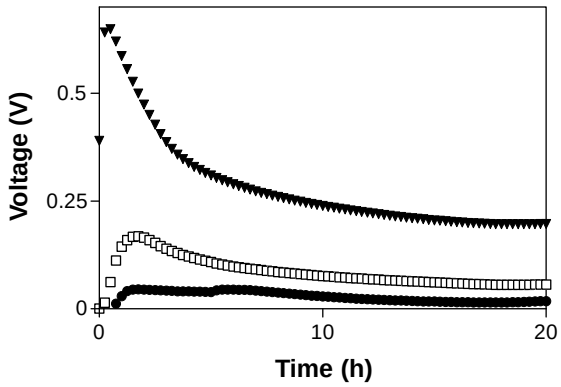

Fig. 4. Closed circuit operation of the alkaline fuel cell using hydrolysates produced by the action of celluloses fuel (▼). A 1 kΩ resistance was placed in the circuit during operation and control cells used either the enzyme (□) or undigested cellulose (■) as fuel.

observed when the cell was operated during the primary feed. Although this phenomenon may be occurring for a variety of reasons, including catalyst poisoning, preliminary results suggest the presence of both Pt and Mn in the electrolyte following prolonged operation of these cells. One possible reason for the reduced output from these cells therefore, may be a depletion of the catalytic centres from the electrodes.

For the above system to be of value in biomass-to-energy conversion systems, the AFCs would need to be capable of generating electrical energy from hydrolysates produced by the enzymatic hydrolysis of biopolymers. In this study, both cellulose and starch were employed as substrates and the hydrolysates produced following digestion with cellulase and amylase, respectively, were examined as fuels in the AFC system. When cellulose hydrolysates were employed, the data shown in Figure 4 were obtained and they demonstrate that the voltage rapidly increased to a maximum of 0.65 V. This subsequently fell to 0.2 V within 20 h. This voltage was maintained for a further 50 h (data not shown). When undigested substrate (cellulose) was added to the AFC, the voltage was comparatively negligible and when the enzyme preparation was added to the system the voltage increased to a maximum of 0.16 V and this subsequently decreased to 0.05 V at 20 h. The latter may have been due to the presence of carbohydrate-based preservatives employed in the enzyme preparation. These results indicate that the AFC system is capable of deriving electrical energy

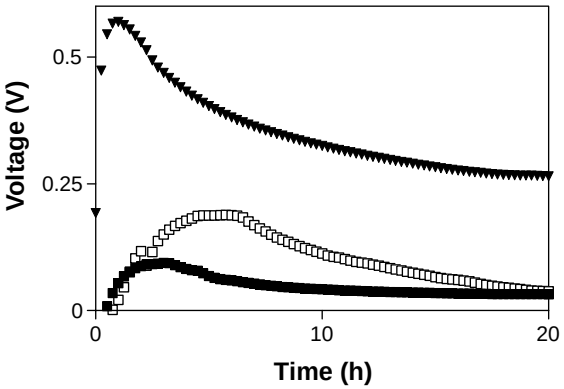

Fig. 5. Closed circuit operation of the alkaline fuel cell using hydrolysates produced following the digestion of starch by α-amylase. A 1 kΩ resistance was placed in the circuit during operation and control cells used either the enzyme (□) or undigested starch (■) as fuel.

from components in cellulose hydrolysates. Although the enzyme was shown to deliver 10% conversion of cellulose to soluble sugar, it was not possible to determine the maximum theoretical energy yield from the system since cellulase action on the substrate results in the production of glucose together with significant proportions of higher soluble oligomers.

In order to further demonstrate that enzyme-generated products from the hydrolysis of biopolymers may be employed as fuel in the AFC system, hydrolysates produced following the digestion of starch by α-amylase were used as fuel. The results (Figure 5) demonstrate that the voltage increased to a maximum of 0.55 V and this decreased to 0.26 V at 20 h. The latter voltage was maintained for 50 h (data not shown). When the enzyme and substrate were added to the AFC system as controls, the voltage increased to maxima of 0.18 and 0.08 V and falling to 0.03 and 0.04 V, respectively, at 20 h. At 20 h the AFC containing the hydrolysate remained at 0.26 V. Once again, as the products from the action of α-amylase action on starch consist of glucose together with higher soluble oligomers of glucose, and in the absence of a known mechanism of action for the oxidative events occurring in the AFC, it was not possible to determine the maximum theoretical yield of energy from this system. It is interesting to note, however, that there are similarities between the voltage profiles shown in Figures 1 and 5. Since 18 mg glucose were employed to generate the profile in Figure 1, and if the hypothesis that glucose is converted to gluconolactose is correct, then the results suggest that 18 mg glucose reducing equivalents are present in the starch lysates. Although this figure is less than that predicted by the data obtained from the DNS assay for reducing sugars, reduced energy output may be attributed to accessibility of higher soluble oligomers to the catalytic centres of the carbon-Pt catalyst. In any case, the above results demonstrate that hydrolysis products derived from the enzymatic degradation of starch may be employed as fuel in the AFC system.

In the majority of cases, biomass-to-energy conversion strategies focus on enzymatic biopolymer conversion to soluble products and subsequent use of those products in fermentative processes. The results presented here demonstrate that monosaccharides and hydrolysates derived from the enzymatic digestion of biopolymers may be used directly to produce electrical energy. Although we suggest that only a 2-electron transfer occurs during the oxidation of glucose, the output from the system appears superior to the output from previously described alternative biofuel cells (Tayhas *et al.* 1994, Pizzariello *et al.* 2002, Mano *et al.* 2003). Additionally, the problems associated with the use of a microorganisms in microbial fuel cell systems are negated. Recently, Chaudhuri & Lovely (2003) reported an elegant piece of work in which they described the operation of a mediator-less microbial fuel cell that was capable of producing electrical energy during the complete oxidation of glucose to CO_2. In that system, other monosaccharides and disaccharides could also be employed as fuel. As the authors suggest, this microbial fuel cell represents a significant step forward in the conversion of biomass-derived sugars directly to electrical energy. The authors also state that 'existing transition metal-catalysed fuel cells cannot be used to generate electric power from carbohydrates'. Although the transition metal-catalysed fuel cell described here appears to be limited in terms of oxidative efficiency, it does offer potential advantage over the system described by Chaudhuri & Lovely (2003). In converting biomass to soluble sugar derivatives, many of the enzymatic systems employed therein operate at elevated temperatures and this has stimulated the development of simultaneous saccharification and fermentation (SSF) strategies (Barron *et al.* 1995, Riordan *et al.* 1996, Krishna *et al.* 2001). In those strategies the goal has been to identify a biological

component that will convert the sugar to ethanol at operating temperatures compatible with the elevated temperatures employed during the enzymatic saccharification process. In the electrical energy-generating system described by Chaudhuri & Lovely (2003), the operating range of the biocatalyst is in the region of 25 °C and this suggests a thermal incompatibility with conventional saccharification processes (45–55 °C). Although used at room temperature in the studies described here, the operating temperature of the transition-metal catalysed fuel cell may be increased to 60 °C and well beyond that if the housing materials were adapted, thereby suggesting a thermal compatability with conventional saccharification processes.

In addition, converting glucose to electrical energy using the system described by Chaudhuri & Lovely (2003) the microorganism must exploit a proportion of the fuel as a metabolic resource. Although the transition metal-catalysed fuel cell described here appears to involve a $2e^-$ transfer, there is no metabolic requirement in the energy-generating system. Although the information was not available from Chaudhuri & Lovely (2003), derivation of the net energy product from the microbial fuel cell must take the metabolic energy requirements of the biocatalytic component into consideration. Based on our preliminary experimental observations with this transition metal-catalysed alkaline fuel cell system, and realising that significant further investigation is required, we believe that the approach described here may play a significant role in processes concerned with the conversion of biomass to electrical energy.

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