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SHORT COMMUNICATION

An electrogenerative acidobasic cell utilizing biomass for the generation of electricity and molecular hydrogen

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1. Introductions

Biomass is deemed to be a renewable energy source and a source of raw materials that might be transformed to useful products by suitable chemical or electrochemical treatments. The general electrochemistry of biomass and derived materials was treated in a recent ACS monograph by Li Chum and Baizer [1]. In principle biomass can be utilized in a fuel cell to generate electricity and, in an electrogenerative cell, to afford both electricity and some useful product directly or indirectly. The possibility of obtaining electricity directly from biomass oxidation in a fuel cell was intensively studied in the 1960s [2, 3]. Efforts were then made to achieve complete oxidation of a biomass material, e.g. glucose, in biomass–oxygen cells with platinum and platinized porous carbon electrodes in aqueous solution or suspension at various pHs at temperatures ranging from 25° C to 100° C. The reaction is shown below.

$$C_2H_{12}O_6 + 6H_2O \rightarrow 6CO_2 + 24H^+ + 24e^-$$

The research was apparently discontinued because practical applications were unavailable. In our laboratory we have been concerned with the development of spontaneous (electrogenerative) electrochemical systems capable of utilizing biomass derived materials for the simultaneous generation of electricity and some useful product. For such an electrochemical system to be practical thermodynamic factors ($\Delta G < 0$) and kinetic factors (high reaction rates at the electrodes) must be favourable. In the present acidobasic cell equipped with a silver anode and a platinum cathode these requirements are well satisfied. The cell achieves spontaneous oxidation of a biomass material, e.g. glucose, in an aqueous basic medium at the silver anode. At the platinum cathode, in an acidic medium, molecular hydrogen is generated with a current density of 25 mA cm^{-2} at 60–70° C. As far as is known this is the first example of a spontaneous cell in which glucose is oxidized at the anode with the simultaneous generation of an electric current and molecular hydrogen at the cathodic product.

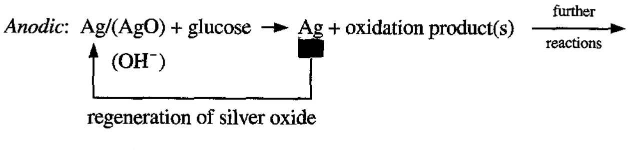
2. Experimental details

The cell was discharged under short-circuit conditions; cell voltages refer to open circuit values. The experimental cell was an ordinary H-type glass cell with the anolyte and catholyte compartments separated by a cation exchange membrane Nafion®[†]-117. This membrane is recommended for use in H_2O and HCl electrolysis and fuel cells. To each of the cell compartments, 50 ml of anolyte (20% NaOH) and catholyte (20–30% HCl or H_2SO_4) were added. After the initial cell output voltage and current were stabilized at their minimum value, the biomass material, glucose (or other biomass material), was introduced into the anolyte (basic) compartment.

The silver electrode, either a foil or a screen of 99% purity with an estimated area of 10 cm^2, was placed in the basic electrolyte containing the biomass material. A 1 cm^2 platinum plate was placed in the acidic electrolyte to function as cathode for the evolution of hydrogen. The electrodes were connected externally with a copper wire to a Fluke 77 multimeter for current and voltage measurements.

3. Discussion

The half-cell reactions are the oxidation of the biomass material, e.g. glucose, at the silver anode in the basic medium and the reduction of protons at the platinum cathode in the acidic medium. **Symbolically** these spontaneous electrochemical reactions are shown below:



Cathodic: $\underset{(H^+)Pt,\ T > 40°C}{2H^+ + 2e^- \rightarrow H_2\uparrow}$

The oxidation of glucose presumably involves heterogeneous electrocatalytic reaction steps [5–7] in which the surface oxides, not yet characterized and shown as (AgO), oxidize the glucose. The active surface oxide is spontaneously regenerated, while protons in the acidic catholyte are reduced at the

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[†] Nafion® is a registered trademark of the E.I. Du Pont de Nemours & Company.

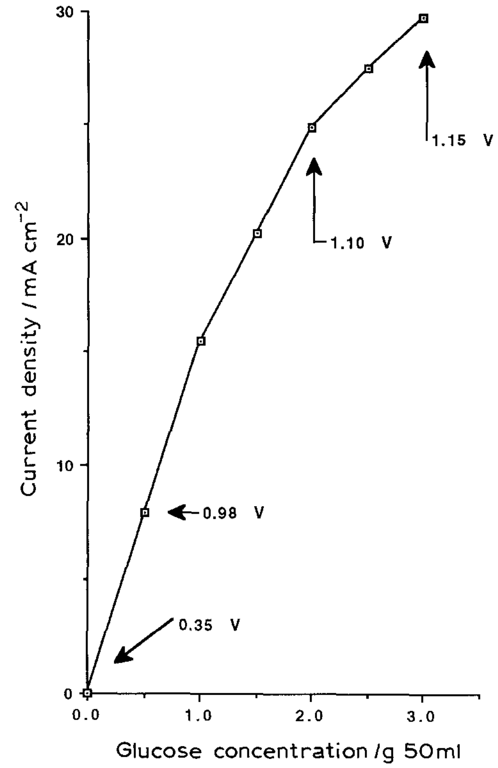

Fig. 1. Current output against amount of glucose in the anolyte, in grams per 50 ml of solution at 60° C. The solution was unstirred. Anolyte: 20% aqueous NaOH; silver anode. Catholyte: 30% aqueous HCl; platinum plate cathode.

cathode. As a result of these spontaneous electrode reactions an electric current flows in the external circuit and an ionic current, i.e. sodium ions, migrate via the Nafion membrane towards the cathode. Glucose should yield as intermediate major products, gluconic, saccharic, arabonic and formic acids [1]. If complete oxidation to CO_2 is effected 24 electrons are transferred from the anode to the cathode and 12 moles of hydrogen are liberated at the cathode in the acidic catholyte. Chemical oxidation of glucose by oxygen in the anolyte is also a possibility under the experimental conditions. There appeared to be no significant fluctuation in cell output during five days of operation at 60–70° C. Figure 1 shows the cell output at 60° C. Both the current and cell voltage increase as the amount of glucose in the anolyte increases. At glucose levels of 5–6% the cell output becomes constant. The cathodic reaction, the evolution of molecular hydrogen, becomes appreciable at temperatures above 40° C and becomes more vigorous as the temperature and acid concentration increase, as shown in Figs 2 and 3. Figure 2 demonstrates that the current, and hence the rate of hydrogen evolution, U, ($U = i/F$) is negligibly small in the absence of glucose in the anolyte. When glucose is added the cell voltage rises instantly from 0.35 to 1.10 V and the current from 0.05 mA cm^{-2} to 26 mA cm^{-2}, at 60° C (considering the area of the platinum cathode, the silver area is $\sim$ 10 cm^2). The silver terminal is always negative relative to the platinum, as would be expected if oxidation occurs at the silver in the basic electrolyte and reduction at the platinum in the acidic electrolyte. Qualitatively, similar results

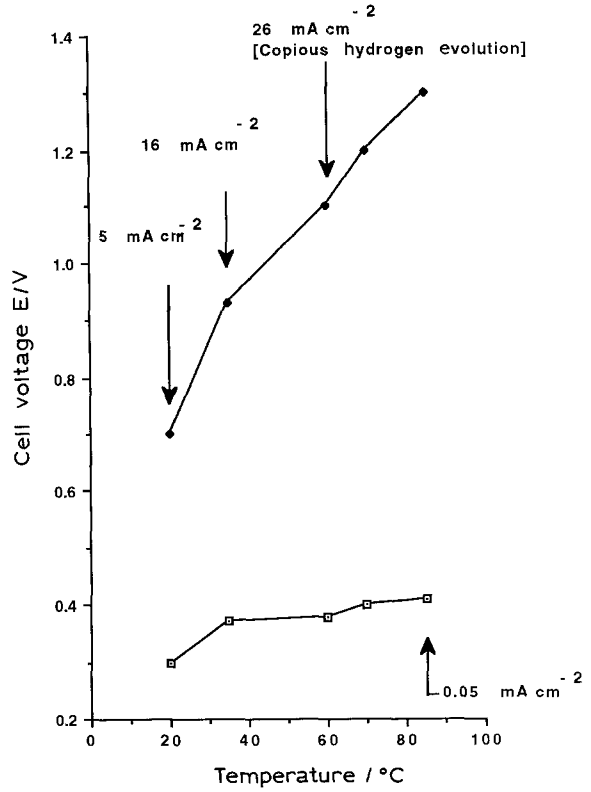

Fig. 2. Cell voltage against temperature with glucose (2 g/50 ml anolyte) and without glucose. Anolyte: 20% aqueous NaOH; silver anode. Catholyte: 30% aqueous HCl; platinum plate cathode. (◆) with glucose; (□) without glucose.

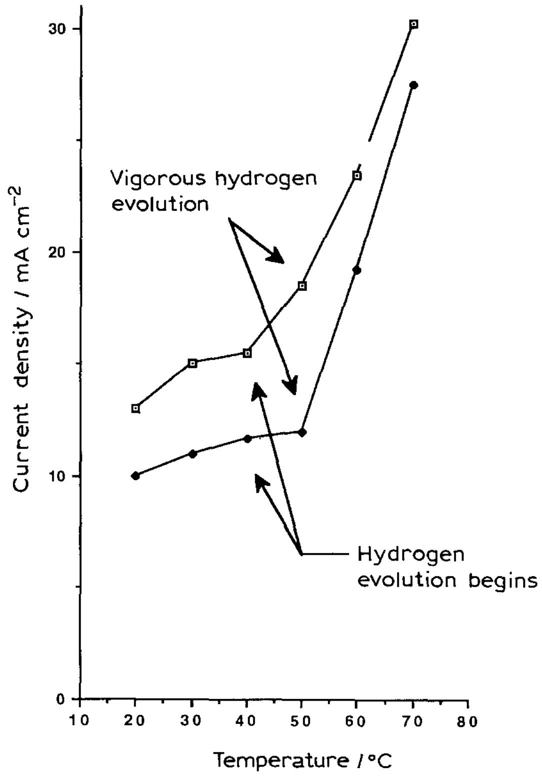

Fig. 3. Current against temperature with glucose at 2 g/50 ml of anolyte at 20% and 30% HCl. Anolyte: 20% NaOH; silver anode. Catholyte: 20% or 30% HCl; platinum plate cathode. (□) 30% HCl; (◆) 20% HCl.

were obtained with suspensions of other biomass materials, e.g. corn starch, cellulose powder, paper, overripe peach and apple pulps.

It is also of practical interest to note that if only electricity is the desired product from this acidobasic cell the addition of Fe^{+3}, NO_3^- or Ce^{4+} ions to the acidic catholyte increases the cell output but in that case no hydrogen gas is evolved. Under these conditions a current is generated even at 10° C. When the acidic catholyte contains an excess of ferric sulphate or ferric chloride and the basic anolyte an excess of glucose the cell voltage at 35° C is about 1.30 V and the current 70–80 $mA\,cm^{-2}$ but no hydrogen is evolved (apparently either because of competitive reductions at the cathode, Fe^{3+} against H^+, or chemical reduction of the Fe^{3+} ion by the nascent hydrogen produced). Under these cell conditions the measured potential of the silver electrode is −0.760 V vs SCE while that of the platinum is +0.535 V. These potential measurements were made under open circuit conditions, with the tip of the reference electrode near the surface of the electrode. Of the various electrode systems thus far tested the system silver–platinum was found to be most effective. Preliminary observations suggest that a nickel–graphite system is also a possibility. Metallic oxide electrodes as anodes with platinum or graphite as cathodes are under investigation.

4. References

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