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Short communication

Manganese dioxide as a cathode catalyst for a direct alcohol or sodium borohydride fuel cell with a flowing alkaline electrolyte

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Abstract

The oxygen reduction reaction at a manganese dioxide cathode in alkaline medium is studied using cyclic voltammetry and by measuring volume of oxygen consumed at the cathode. The performance of the manganese dioxide cathode is also determined in the presence of fuel and an alkali mixture with a standard Pt/Ni anode in a flowing alkaline-electrolyte fuel cell. The fuels tested are methanol, ethanol and sodium borohydride (1 M), while 3 M KOH is used as the electrolyte. The performance of the fuel cell is measured in terms of open-circuit voltage and current–potential characteristics. A single peak in the cyclic voltammogram suggests that a four-electron pathway mechanism prevails during oxygen reduction. This is substantiated by calculating the number of electrons involved per molecule of oxygen that are reacted at the MnO_2 cathode from the oxygen consumption data for different fuels. The results show that the power density of the fuel cell increases with increase in MnO_2 loading to a certain limit but then decreases with further loading. The maximum power density is obtained at 3 mg cm^{-2} of MnO_2 for each of the three different fuels.
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Keywords: Manganese dioxide; Flowing alkaline-electrolyte; Fuel cell; Methanol; Ethanol; Sodium borohydride

1. Introduction

There has been a reawakening of interest in the alkaline fuel cell [1]. Although this fuel cell suffers from a disadvantage related to the formation of carbonate in the presence of CO_2, the problem may be tackled by using a flowing alkaline-electrolyte design [2,3]. The electrolyte flowing from the fuel cell can be retreated and recycled, and will also allow heat recovery from the system. In the present investigation, the use of manganese dioxide as a cathode catalyst in flowing electrolyte design of alkaline fuel cell is systematically studied.

Noble metals such as platinum have played a key role as catalysts for the anodic and cathodic reactions in fuel cells. While they offer the advantages of high catalytic activity, high electronic conductivity and good stability, their high costs are a major concern for commercial applications [4]. It is well known that the kinetics of oxygen reduction are superior in an alkaline solution compared with those in acidic media [5]. Manganese dioxide has been found to be an alternative electrocatalyst for oxygen reduction in alkali medium. This reaction generally proceeds by either of two pathways [4], namely:

direct oxygen reduction to OH^- ions, i.e., a four-electron pathway:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad (1)$$

or an oxygen reduction to HO_2^- ions, i.e., two-electron pathway:

$$O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^- \quad (2)$$

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with subsequent reduction of peroxide ion to OH^- ions, i.e., two-electron pathway:

$$HO_2^- + H_2O + 2e^- \rightarrow 3OH^- \quad (3)$$

Eqs. (2) and (3) are collectively said to be a 2 + 2 electron mechanism [6].

Normally, manganese dioxide consists of manganese in lower valence states such as Mn(II,III), together with the dominant Mn(IV) state. Mao et al. [7], who represented it as MnO_x, studied many forms of manganese dioxide and found that γ-MnOOH is highly catalytically active compared with the other varieties, e.g., α-Mn_2O_3, Mn_3O_4, Mn_5O_8. Cyclic voltammetric investigations of different forms of MnO_x in the presence of oxygen and argon saturated in 0.1 M KOH medium showed two reduction peaks. These were assigned [7] to the 2 + 2 electron mechanism discussed above. Yang and Xu [4] synthesized non-porous, amorphous manganese dioxide by means of an aqueous redox sol–gel route oxygen and studied its activity in the presence of oxygen- or nitrogen-saturated KOH solution through cyclic voltammetry. Only one reduction peak was observed and the workers pointed out [4] that a second peak could not be obtained because of the limitation in the range of potentials that was adopted. The study also investigated the suitability of the prepared manganese dioxide as an electrocatalyst for oxygen reduction in 1 M KOH. A current density of more than 100 mA cm^{-2} was achieved by a half cell when using a catalyst loading of 0.85 mg cm^{-2}. To date, the influence of the fuel on the performance of manganese dioxide as a cathode has not been examined.

In the present study, the oxygen reduction reaction has been studied at an MnO_2 cathode by means of cyclic voltammetry in presence of KOH solution saturated with air or nitrogen gas. The MnO_2 cathode is also used in a flowing alkaline-electrolyte fuel cell and its performance is monitored with air in the cathode side and fuel (methanol, ethanol or sodium borohydride) in the anode side.

2. Experimental

2.1. Materials

A Nafion® (SE-5112, DuPont, USA) dispersion and Teflon® solutions (Dupont, USA) were used to prepare the cathode slurry and fixed it to Ni-mesh, respectively. Manganese(IV) oxide (Merck-Schuchardt, Germany) was used as the electrocatalyst for cathode. The mean particle size of the manganese dioxide was 17 μm, as determined by a particle-size analyzer (CILAS 120). Potassium hydroxide pallets (Qualigen fine chemicals, India) were used for the preparation of electrolyte. Carbon-paper (Lydall 486C-1, USA) was employed as the cathode substrate to support the electrocatalyst. A perforated nickel sheet of 0.4 mm thickness served as the current-collector. A Pt/Ni anode (1.2 mg cm^{-2} Pt loading, Electro-Chem-Technic, UK) acted as the standard electrode throughout the study.

2.2. Electrode preparation

Manganese dioxide was first dispersed ultrasonically in the required quantity of Nafion® solution for 30 min to obtain a cathodic slurry. The cathodic slurry was spread on the carbon-paper in the form of continuous wet film, and then dried in an oven for 30 min at 80 °C. The catalyzed carbon-paper was pressed on to the nickel mesh with the Teflon dispersion as a binder. The other surface of the nickel mesh was covered with carbon paper, pressed at 60 kg cm^{-2} and 120 °C for 10 min, and then sintered at 250 °C for 2 h. Finally, a Teflon film was pressed on the uncatalyzed side of the carbon paper to form the cathode electrode. The Teflon-coated side of the electrode was exposed to the air-side in alkaline fuel cell, and thereby prevented leakage of electrolyte to the air-side and allowed oxygen to permeate. The morphology of the cathode was examined by scanning electron microscopy.

2.3. Experimental set-up and procedure

2.3.1. Cyclic voltammetry

The reduction of oxygen from air was studied in a simple three-electrode cell that contained a platinum counter-electrode, an Ag/AgCl/saturated KCl reference electrode and the MnO_2 cathode as a working electrode. The electrolyte was 3 M KOH solution. Cyclic voltammograms were conducted with a PGSTAT 30, Autolab potentiostat. The experiments were performed in either nitrogen- or air-saturated electrolyte over the potential range −0.8 to 0.0 V at a scan rate of 5 mV s^{-1}.

2.3.2. Fuel cell experiments

The manganese dioxide cathode was tested against a standard anode in flowing alkaline-electrolyte fuel cell. A schematic diagram of the fuel cell is shown in Fig. 1. A hollow cylinder containing the cathode attached to one side was placed inside a beaker. The standard anode, Pt/Ni (Electro-Chem-Technic, UK), was placed at the bottom of the beaker. The space between anode and cathode was filled with the mixture of electrolyte (3 M KOH) and fuel (1 M). The solution was continuously agitated with a magnetic stirrer, which was located on the perforated anode shield. The fresh fuel and electrolyte mixture was continuously supplied and withdrawn from the cell at 1 ml min^{-1}, and was maintained up to a certain level such that one side of the cathode was in contact with fuel while the other side was exposed to air. The oxygen present in the air acted as the oxidant and the fuel was methanol, ethanol or sodium borohydride. The performance of the cathode was evaluated in terms of open-circuit voltage, short-circuit current and current–voltage (*I–V*) characteristics. The oxygen consumption at the cathode was measured by a gas-displacement method to provide information on the reaction mechanism.

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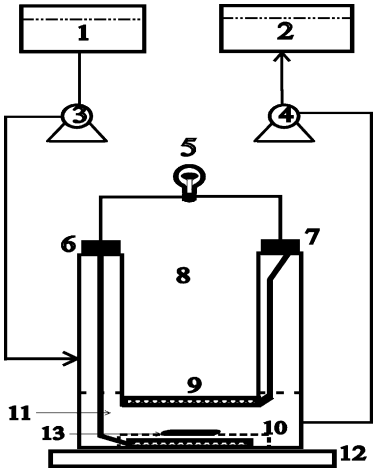

Fig. 1. Schematic diagram of flowing alkaline-electrolyte fuel cell: (1) fuel–electrolyte mixture storage; (2) exhausted-fuel–electrolyte mixture storage; (3, 4) peristaltic pumps; (5) load; (6) anode terminal; (7) cathode terminal; (8) air; (9) cathode electrode; (10) anode electrode; (11) fuel and electrolyte mixture; (12) magnetic stirrer; (13) anode shield.

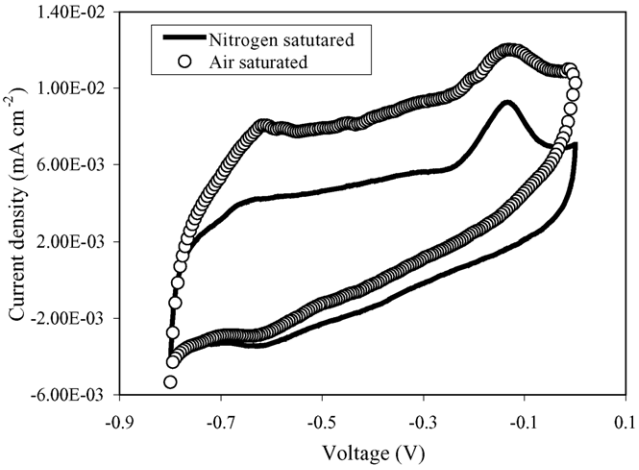

Fig. 3. Cyclic voltammetric curves for MnO_2 cathode (3 mg cm^{-2}) in 3 M KOH saturated with air or nitrogen gas. Scan rate = 5 mV s^{-1}.

3. Results and discussion

3.1. Electrode morphology

A scanning electron micrograph of the MnO_2 cathode is presented in Fig. 2. The electrode is composed of fine particles of MnO_2, relatively larger particles of carbon, pores (black spots) and rod-like carbon fibres. The compressed carbon particles in the form of a sheet are also visible.

3.2. Cyclic voltammetry

Cyclic voltammograms for the MnO_2 cathode in nitrogen- or air-saturated electrolyte are shown in Fig. 3. The current peak observed at −0.175 V corresponds to the oxygen reduction reaction. The single reduction potential peak supports the four-electron pathway mechanism (Eq. (1)). The cyclic voltammograms were repeated 40 times for a wide range of potential sweeps. The reduction peak clearly indicates that the manganese dioxide is electroactive. A higher peak current is observed for the oxygen-saturated than for the nitrogen-saturated alkaline medium. This suggests that the presence

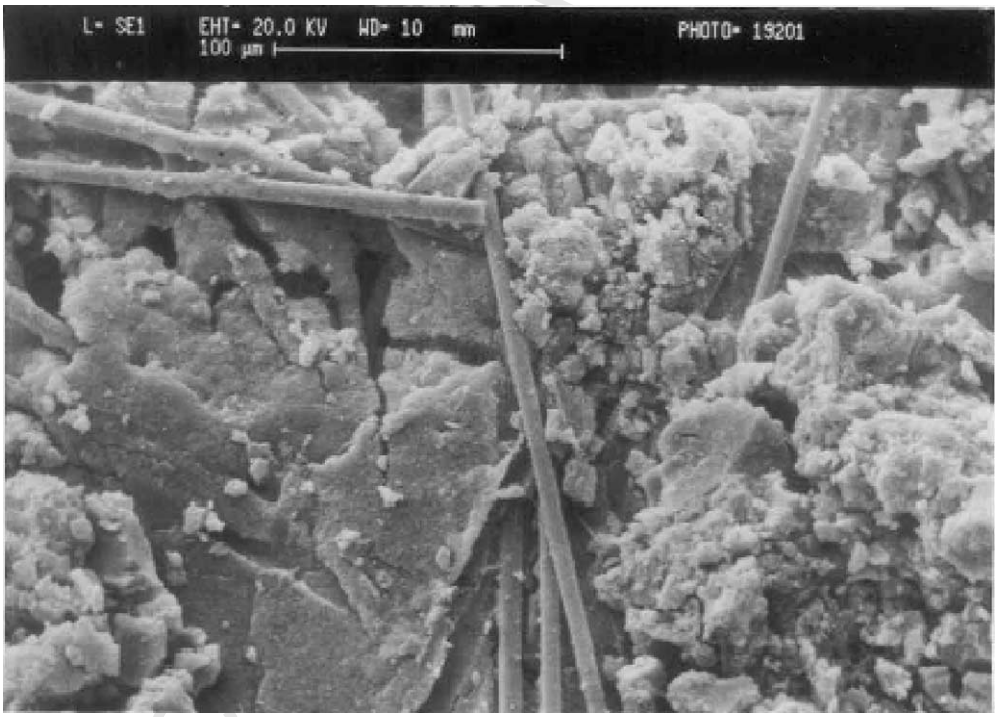

Fig. 2. Scanning electron micrograph of catalyzed cathode with 3 mg cm^{-2} manganese dioxide.

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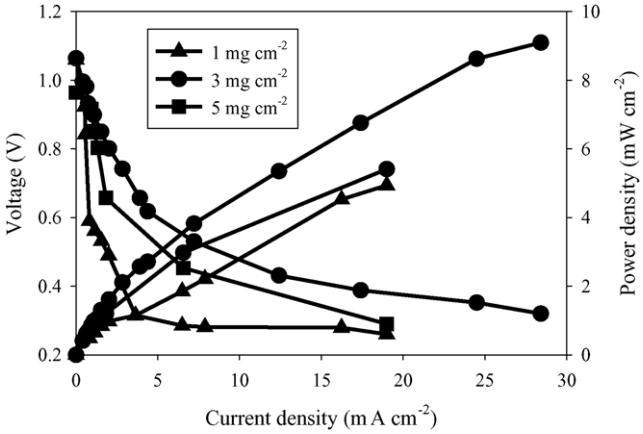

Fig. 4. Voltage–current curves for flowing alkaline-electrolyte (3 M KOH) direct methanol (1 M) fuel cell with different loadings of manganese dioxide as cathode catalyst.

of air increases the cathodic current and expands the voltammetric curve. The other peaks at −0.58 and −0.61 V may indicate redox cycling of manganese species.

3.3. Polarization curve

Current–voltage curves are presented in Figs. 4–6 for three different fuels and with different loadings of manganese dioxide as the cathode catalyst. With methanol as the fuel (Fig. 4), the cell performance increases with increase in catalyst loading up to a certain MnO_2 loading, but then decreases. This may be due to a decrease in the number of active site per unit mass with increase in catalyst loading as a result of decreases in porosity when accommodating large amounts of catalyst in the same volume. The performance in the presence of 3 M KOH + 1 M ethanol and 3 M KOH + 1 M sodium borohydride is shown in Figs. 5 and 6, respectively. The trends of the plots are similar to those obtained for methanol. To be specific, the performance of the fuel cell increases with increase in MnO_2 loading at the cathode from 1 to 3 mg cm^{-2} and then decreases with further increase in catalyst loading. From Figs. 4 and 5, it is seen that the performance of ethanol is better than methanol. In case of ethanol (Fig. 5), the maximum power density obtained is 14.6 mW cm^{-2} at 34 mA cm^{-2}, whereas for methanol (Fig. 4), it is 9.2 mW cm^{-2} at 28.5 mA cm^{-2}. A maximum power density of 19 mW cm^{-2} is obtained at 39 mA cm^{-2} for sodium borohydride, as shown in Fig. 6.

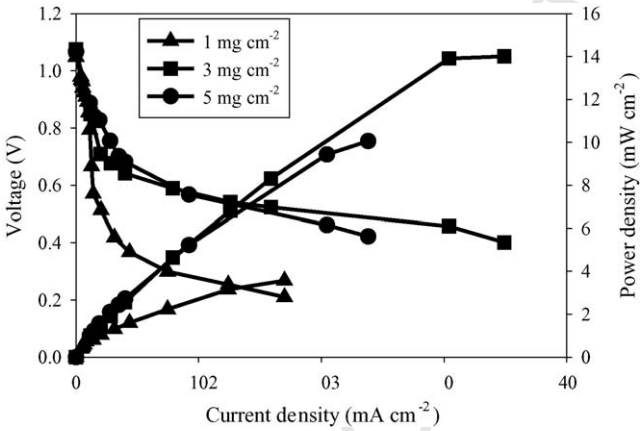

Fig. 5. Voltage–current curves for flowing alkaline electrolyte (3 M KOH) direct ethanol (1 M) fuel cell with different loadings of manganese dioxide as cathode catalyst.

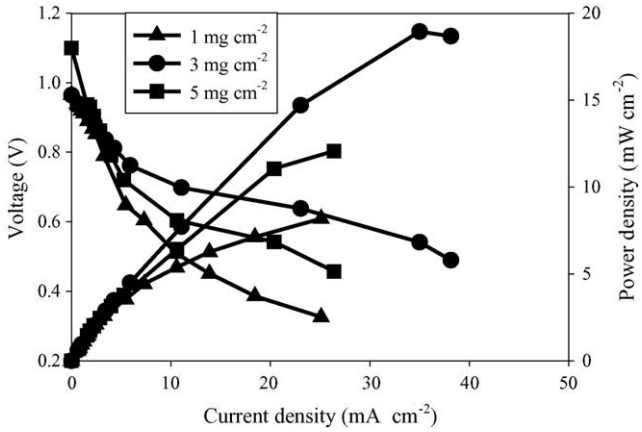

Fig. 6. Voltage–current curves for flowing alkaline electrolyte (3 M KOH) direct sodium borohydride (1 M) fuel cell with different loadings of manganese dioxide as cathode catalyst.

Table 1
Oxygen consumption at cathode for different fuels

Fuel	Average current (mA)	Oxygen consumed (ml h^{-1})	Calculated electrons reacted per oxygen molecule
Methanol	31.8	6.3	4.63
Ethanol	39.46	8.6	4.26
Sodium borohydride	43.25	15	4.54

3.4. Oxygen consumption

Oxygen consumption at the cathode in the flowing alkaline-electrolyte fuel cell was measured by gas-displacement method and the electrons per molecule of oxygen reacted were calculated. The number of electrons is the same as that theoretically estimated, i.e., four electrons (Eq. (1)). The typical calculated values of electrons involved in the cathode reaction for different fuels are given in Table 1. This confirms that oxygen reduction at the MnO_2 cathode follows the four-electron mechanism and is the same for the different fuels (methanol, ethanol, $NaBH_4$) tested.

4. Conclusions

Cyclic voltammetry and oxygen consumption experiments reveal that oxygen reduction at the MnO_2 cathode follows a four-electron mechanism. In a flowing-alkaline elec-

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trolyte fuel cell, the maximum power density is obtained with 3 mg cm^{-2} of MnO_2 at cathode for three different fuels, e.g., methanol, ethanol and $NaBH_4$. The power density decreases with further increase in MnO_2 loading at the cathode. The maximum power density for methanol obtained is 14.6 mW cm^{-2} at 34 mA cm^{-2} and that for ethanol is 9.2 mW cm^{-2} at 28.5 mA cm^{-2}. Sodium borohydride produces a power density of 19 mW cm^{-2} at 39 mA cm^{-2}.

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