

Chemicals and energy co-generation from direct hydrocarbons/oxygen proton exchange membrane fuel cell

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Abstract

A proton exchange membrane fuel cell for chemicals and energy co-generation was set up with hydrocarbons ethane, propane and butane as fuels, and the electrochemical performance of the cell was studied by using linear potential sweep, alternating current impedance and gas chromatography. The cell performance can be improved to a great extent by increasing the platinum load in the catalyst, by treating the membrane with phosphoric acid and by elevating temperature. The improvement of cell performance by the increase of platinum load is ascribed to the increase of reaction sites for hydrocarbon oxidation, that by phosphoric acid treatment to the increase of proton conductivity in Nafion membrane, and that by elevating temperature to the improvement in thermodynamic as well as kinetic aspects. Only a small fraction of the hydrocarbon is converted to carbon dioxide in this cell during its power generation. The current efficiency is 5% for the conversion of ethane to carbon dioxide in the ethane/oxygen fuel cell with 20% carbon-supported platinum as catalyst and phosphoric acid-treated membrane as proton exchange membrane at 0.2 V, 80 °C and ambient pressure. The reaction activity of hydrocarbons at the anode is in the order of propane, butane and ethane. The possible chemicals produced from the cell were hydrocarbons with more than six carbons, which are inactive at the anode under cell conditions.

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1. Introduction

A fuel cell system is an alternative way for energy conversion and exploitation and offers many benefits, including low or even zero emission pollutants, higher efficiency and reliability [1–3]. Several kinds of fuel cells have been developed, including proton exchange membrane fuel cell (PEMFC), phosphoric acid fuel cell (PAFC), molten carbonate fuel cell (MCFC) and solid oxide fuel cell (SOFC).

Among these fuel cells, PEMFC using hydrogen as fuel is an ideal one, because it runs at low temperature (lower than 100 °C) and there is no emission but water during its working. The developments on this fuel cell have brought the current

densities up to around 1 A cm⁻² and more [4]. However, the practical generation and storage of hydrogen remains an important technological hurdle [5]. Direct methanol fuel cell (DMFC) using proton exchange membrane has been developed to overcome this hurdle [6–8]. DMFC has a lot of advantages but still has some other disadvantages [9,10]. The activity of catalysts toward the methanol oxidation is far lower than hydrogen, and methanol can penetrate proton exchange membrane, which is poisonous to the catalysts at cathode and lowers the cell voltage. Furthermore, carbon dioxide emission from DMFC is an important problem, which can accelerate the green house effect. The same problem exists in MCFC and SOFC that utilize hydrocarbon fuels directly [11,12].

It is of interest to develop fuel cells for the conversion of hydrocarbons not to carbon dioxide but to valuable chemicals during energy generation [13–15]. This is called chem-

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icals and energy co-generation. However, solid-oxide membranes were usually used in such chemicals and energy co-generation fuel cells and the cells had to be operated under high temperature. Carbon deposition on catalysts might occur by pyrolysis from hydrocarbon under high temperature [16–18]. The purpose of this paper is to develop a chemicals and energy co-generation fuel cell by using hydrocarbons as fuels, based on proton exchange membrane and operated under mild conditions. No such kind of work has been reported up to now in literature.

2. Experimental

Fig. 1 shows the system for the control of fuel cell conditions. Hydrocarbons (ethane, propane and butane) or hydrogen and oxygen (Praxair) were supported from bottles (1) and (2), respectively, and humidified by humidifier (5). Their flows were controlled with mass flow controller (3) (URS-40, Unit Instruments), and their pressures were controlled automatically with pressure balancer controllers (4) and pressure controller (8). The temperature of the fuel cell (6) was controlled with oven (7) (Model 1305U, VWR Scientific). The exit gas was analyzed with gas chromatography (9) (Hewlett 5890, Series II), equipped with a 50/80 Porapak column.

The fuel cell consisted of a single membrane electrode assemble (MEA). Materials used for the MEA preparation included proton exchange membrane (Nafion N-117, Aldrich Chemical Company), catalysts (5–10% or 20% carbon-supported platinum, Aldrich Chemical Company), Nafion solution (5%, Aldrich Chemical company), and carbon cloth (Teflon treated, Electrochem. Inc.). Nafion membrane was

cleaned by immersing it in boiling 3% hydrogen peroxide in water for 1 h and in boiling sulphuric acid for the same time to remove organic and inorganic impurity and to ensure as full protonation of the sulphonate group as possible, and then rinsed in boiling de-ionised water for 1 h to remove any remaining acid. In the application of phosphoric acid-treated membrane, the cleaned Nafion membrane was treated by immersing in hot phosphoric acid for 4 h. The catalyst paste, made by mixing catalyst, ethanol, PTFE solution and Nafion solution, was coated on carbon cloth and then dried at 90 °C for 12 h to prepare cathode and anode. The treated membrane was sandwiched between cathode and anode, and then pressed under 150 °C and 130 atm for 5 min. The anodic and cathodic working surface has a circular shape with a diameter of 3.18 cm. The cell performances were measured with a galvanostat/potentiostat (CMS300, Gamry Instruments Inc). In the electrochemical measurement, anode was the working electrode. Cathode was the counter as well as the reference electrode.

3. Results and discussions

3.1. Basic electrochemical characteristics

Fig. 2 shows the current–potential and the current–power curves of ethane/oxygen fuel cell with 5% carbon-supported platinum as catalyst and untreated Nafion membrane as proton exchange membrane (PEM) under conditions of 90 °C and 30 psi (1 psi = 0.068 atm). It can be found that the cell can generate power although the power is low. The open circuit potential is 0.353 V. The highest power is 0.0025 mW

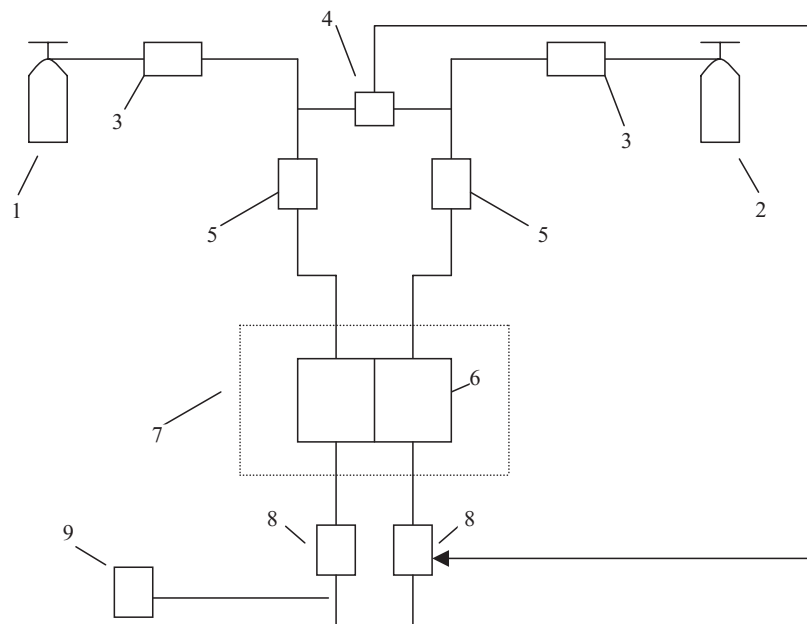


Fig. 1. The setup for the control and the performance determination of hydrocarbon/O₂ Nafion PEM fuel cell system. 1: Hydrocarbon, 2: oxygen, 3: mass flow controller, 4: pressure balancer, 5: humidifier, 6: cell, 7: oven, 8: pressure controller, 9: gas chromatograph.

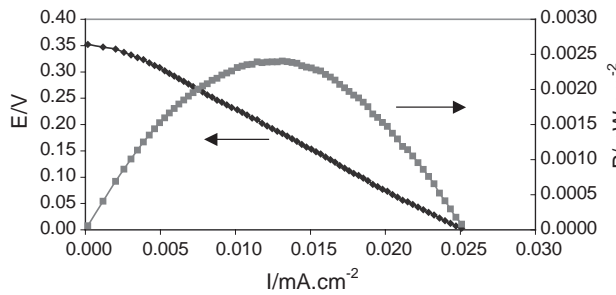


Fig. 2. Relationship of potential and power with current for ethane/oxygen fuel cell with 5% carbon-supported platinum as catalyst and untreated Nafion membrane as PEM at 90 °C and 30 psi.

and the highest current density is 0.025 mA cm⁻². Potential of the cell almost keeps the same when the current density is lower than 0.002 mA cm⁻² and then decreases linearly with increasing current density.

Fig. 3 is the electrochemical impedance spectrum of the cell at open circuit potential. It can be found that the impedance increases as the frequency from high to low and the imaginary impedance increase linearly with real impedance. This indicates that the reaction at the anode of the cell is characteristic of diffusion control. Apparently, the charge transfer step for the oxidation reaction of ethane is fast relatively compared with diffusion steps involved in the reaction, which might result from the diffusion of ethane in the catalyst and the diffusion of proton in the membrane. The ohmic resistance of the cell, obtained from the real impedance at high frequency, is 53.3 Ω cm². It is such a big ohmic resistance that results in the linear relationship of potential with current density and low current and power output. In fact, the performances of fuel cell using hydrogen as fuel, as shown in Fig. 4, is not as good as reported in literature [4]. This ohmic resistance might come from the poor electric contact between catalyst and current collector and from the poor proton conductivity of the membrane and can be reduced by improving the preparation of MEA, the fuel cell setup and the working conditions of the fuel cell. It can also be found from the inserted plot in Fig. 3 that inductive behavior appears at high frequencies. This suggests that there might be an adsorption process during the ethane oxidation at the anode.

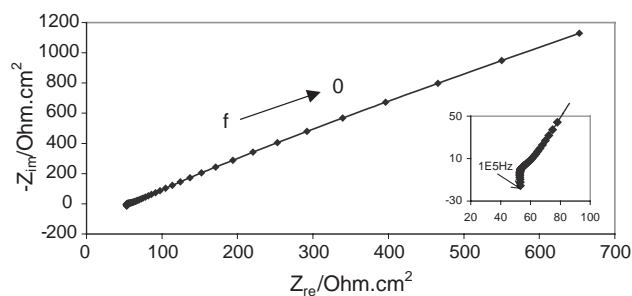


Fig. 3. Electrochemical impedance spectrum for ethane/oxygen fuel cell with 5% supported platinum as catalyst and untreated Nafion membrane as PEM at 90 °C and 30 psi, 10²-0.2 Hz.

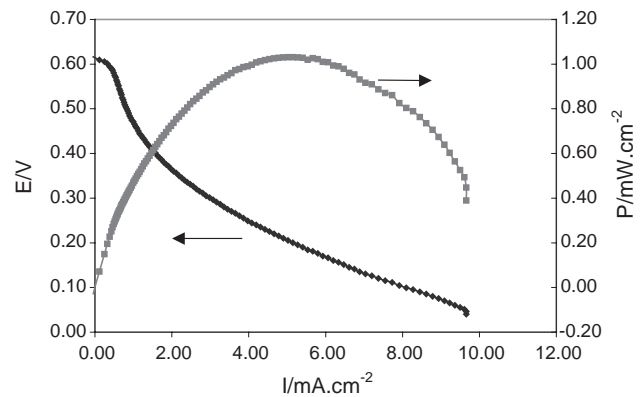


Fig. 4. Relationship of potential and power with current for hydrogen/oxygen fuel cell with 5% carbon-supported platinum as catalyst and untreated Nafion membrane as PEM at 90 °C and 30 psi.

3.2. Temperature dependence of cell performance

Fig. 5 shows the dependence of performance on temperature for the ethane/oxygen fuel cell with 5% carbon-supported platinum as catalyst and untreated Nafion membrane as PEM under 30 psi. It can be found that the electrochemical performance can be improved to a great extent by elevating temperature. The cell potential increases with elevating temperature, from 0.353 V at 90 °C to 0.531 V at 130 °C, with an average increase of 4.425 mV per degree. This indicates that the reaction activity of ethane oxidation is greatly dependent on the thermodynamics. The maximum power output of the cell are 0.0024, 0.0154 and 0.228 mW cm⁻², for 90, 110 and 130 °C respectively, with an average increase of

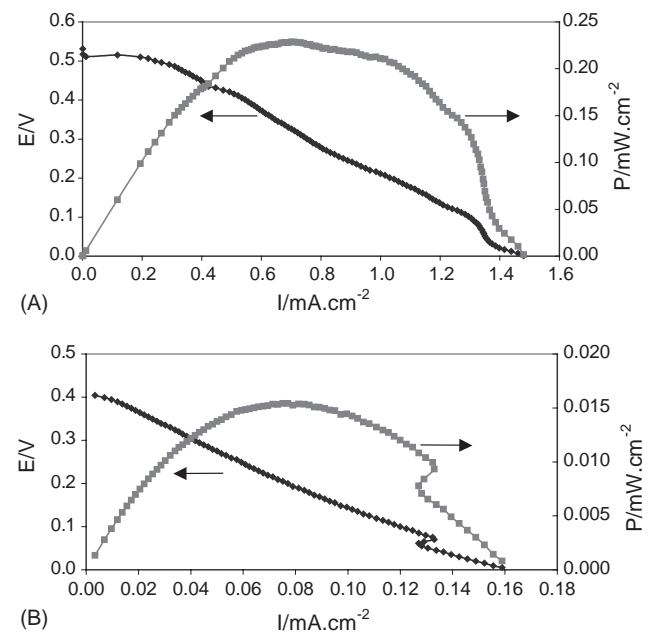


Fig. 5. Relationship of potential and power with current for ethane/oxygen fuel cell with 5% carbon-supported platinum as catalyst and untreated Nafion membrane as PEM, 30 psi, A: 130 °C and B: 110 °C.

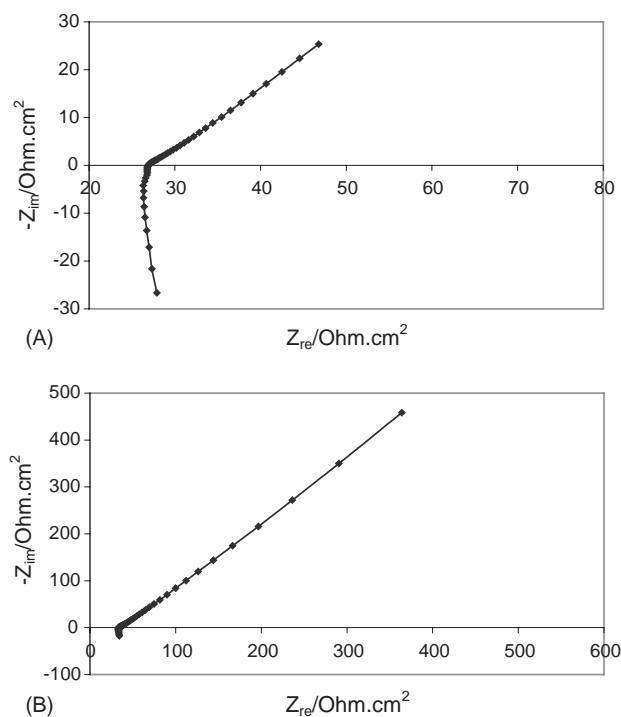


Fig. 6. Electrochemical impedance spectra for ethane/oxygen fuel cell with 5% supported platinum as catalyst and untreated Nafion membrane as PEM at 30 psi and A: 130 °C and B: 110 °C, 10^5 –0.2 Hz.

almost one decade every 20°. The maximum current output of the cell also has a great increase by elevating temperature, 0.025, 0.159 and 1.48 mA cm⁻², for 90, 110 and 130 °C, respectively. Abnormal behavior of current–potential curves at high current usually appears when the temperature is over 100 °C, as shown in Fig. 5B. This may result from water evolution on the PEM at high temperature.

Fig. 6 shows the dependence of electrochemical impedance spectrum on temperature for the cell at open circuit potential. It can be found that the impedance of the cell decreases with increasing temperature. The ohmic resistance is 53.3, 33.9 and 26.9 Ω cm², for 90, 110 and 130 °C respectively, with an average decrease of 0.66 Ω cm² per degree. The imaginary part of the impedance at 0.2 Hz decreases to a great extent with elevating temperature, 1129, 458.4 and 25.4 Ω cm², for 90, 110 and 130 °C respectively, with an average decrease of almost one decade per 20°. This indicates that the ion conductivity in membrane can be improved by elevating temperature to a great extent. The dependence of the cell performances on temperature is ascribed to the improvement of ion conductivity in the membrane as well as the improvement in thermodynamic property of ethane.

3.3. Performance dependence on catalyst load and membrane treatment by phosphoric acid

Fig. 7 shows the performance of the ethane/oxygen fuel cells with 10% or 20% carbon-supported platinum as catalyst and with treated or untreated Nafion membrane as PEM

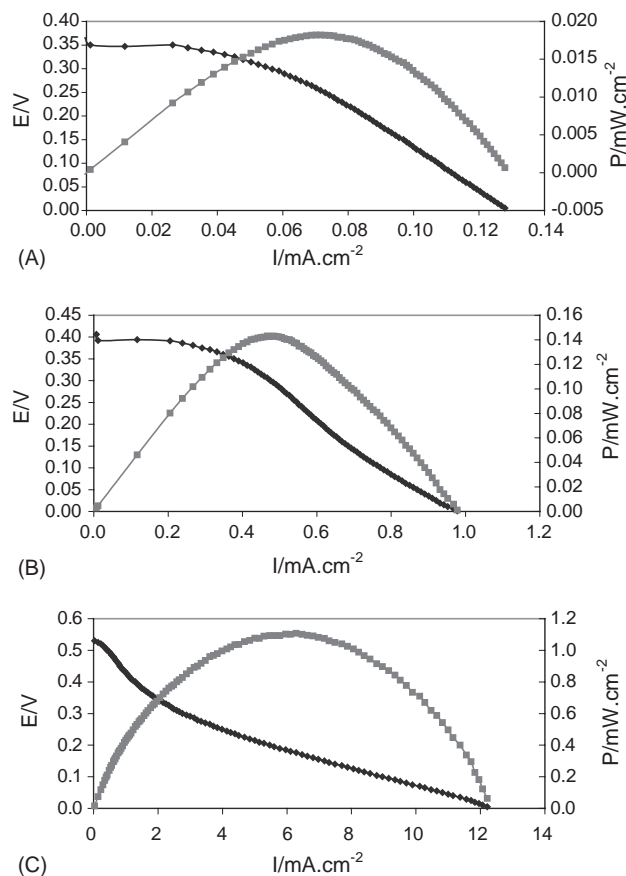


Fig. 7. Relationship of potential and power with current for ethane/oxygen fuel cells at 80 °C and ambient pressure, A: 10% Pt, untreated membrane, B: 10% Pt, treated membrane with phosphoric acid, and C: 20% Pt, treated membrane with phosphoric acid.

at 80 °C and ambient pressure. It can be found that the cell performances are influenced to a great extent by changing catalyst load and by treating Nafion membrane with phosphoric acid. The maximum power output is 0.0182 mW cm⁻² for the cell with untreated membrane (Fig. 7A) and 0.143 mW cm⁻² for the cell with treated membrane (Fig. 7B). There is an increase of almost one decade in the maximum output power by treating Nafion membrane with phosphoric acid.

Fig. 8 shows the dependence of electrochemical impedance spectrum on the PEM treated with phosphoric acid for the cell at open circuit potential. It can be found that the impedance of the cell decreases by treating the PEM with phosphoric acid. The ohmic resistance is 33.6 and 21.3 Ω cm², for untreated and treated membrane, respectively. The imaginary part of the impedance at 0.2 Hz decreases to a great extent by treating the PEM with phosphoric acid, 124.7 and 17.5 Ω cm², for untreated and treated membrane respectively, with a decrease of almost one decade by membrane treatment. This indicates that the ion conductivity in membrane can be improved also by treating PEM with phosphoric acid. The dependence of the cell performance on the membrane treatment is ascribed to the improvement of ion conductivity in the membrane.

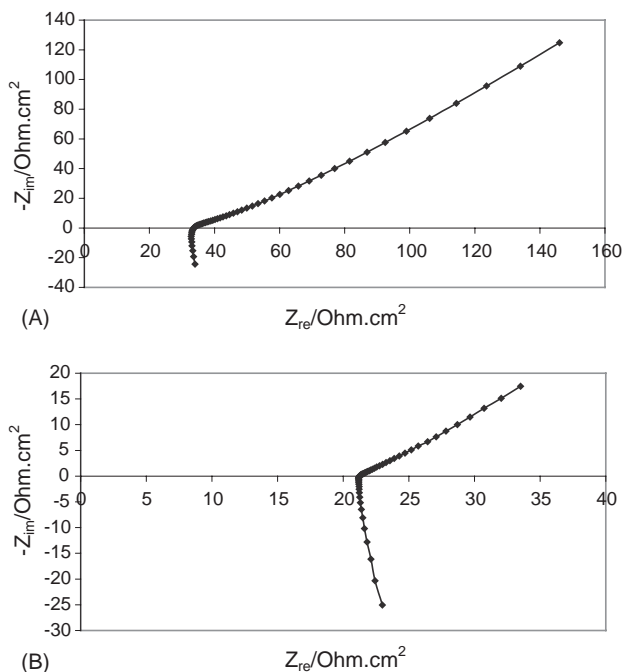


Fig. 8. Electrochemical impedance spectra for ethane/oxygen fuel cells with 10% carbon-supported platinum as catalyst at 80 °C and ambient pressure, A: untreated and B: treated membrane with phosphoric acid.

Comparing the maximum power output of the cell in Fig. 7A, which is $0.0182 \text{ mW cm}^{-2}$ under 80 °C and ambient pressure, with that of the cell in Fig. 2, which is $0.0024 \text{ mW cm}^{-2}$ under 90 °C and 30 psi, it can be found that there is a maximum power output increase of almost one decade by increasing platinum load from 5% to 10%, although the cell conditions of the former is milder than those of the latter. With the treated membrane as the PEM for ethane/oxygen fuel cell, the cell performance can also be improved by increasing the catalyst load, as shown in Fig. 7B and C. Under the same conditions, 80 °C and ambient pressure, the maximum power output of the cell with 20% carbon-supported platinum as catalyst is 1.11 mW cm^{-2} , eight times that of the cell with 10% Pt, which is 0.143 mW cm^{-2} and the maximum current output is 12.2 mA cm^{-2} for the cell with 20% Pt, 12.5 times that of the cell with 10% Pt, which is 0.98 mA cm^{-2} .

3.4. Cell performance with different hydrocarbons as fuels

Fig. 9 shows the performance of fuel cells with ethane, propane and butane as fuels, 20% carbon-supported platinum as catalyst and phosphoric acid-treated Nafion membrane as PEM at 70 °C and ambient pressure. It can be found that cell performance is influenced by the kind of hydrocarbons. The cell potential is 0.41 V for ethane, 0.57 V for propane and 0.50 V for butane, indicating that the thermodynamic activity of propane is highest, and then butane followed by ethane. There is no significant difference in the potential–current and

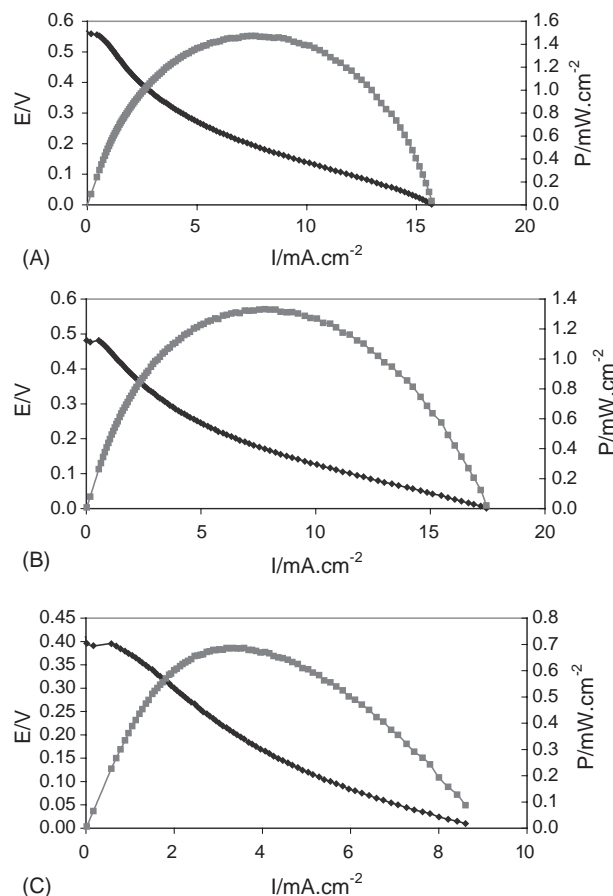


Fig. 9. Relationship of potential and power with current for fuel cells with 20% carbon-supported platinum as catalyst and phosphoric acid-treated Nafion membrane as PEM at 80 °C and ambient pressure, A: propane, B: butane and C: ethane.

power–current relationship for the cells with propane and butane as fuels. If there is, the propane has higher kinetic activity whose maximum power output is 1.47 mW cm^{-2} than butane whose maximum power output is 1.33 mW cm^{-2} . Both propane and butane have higher kinetic activity than ethane whose maximum power output is 0.69 mW cm^{-2} . Therefore, the reaction activity for hydrocarbons/oxygen fuel cells is in the order of propane, butane and ethane. It can be inferred that the reaction activity of paraffin hydrocarbons increases from C_2 to C_3 and then decreases with increasing carbon number.

3.5. Possible anodic reaction mechanism

Fig. 10 shows the on-line gas chromatography of the gas from anodic chamber of ethane/oxygen fuel cell at open circuit potential (without reaction) and at 0.2 V (under reaction). Air and ethylene besides ethane appear in the cases of reaction and no reaction. The air might come from leakage in the system and ethylene is from the fuel ethane. It can be found that only carbon dioxide is detected as the anodic product of the fuel cell. Based on content of carbon dioxide in the gas, the mass flow of ethane and the current during the measure-

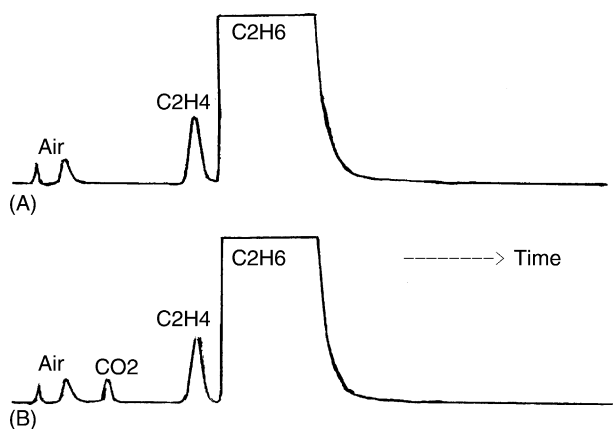
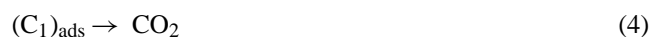
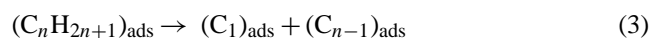
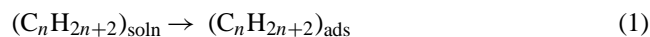


Fig. 10. On-line gas chromatography of the gas from anodic chamber of ethane/oxygen fuel cell with 20% carbon-supported platinum as catalyst and phosphoric acid-treated Nafion membrane as PEM at 80 °C and ambient pressure, A: at open circuit potential and B: at 0.2 V.

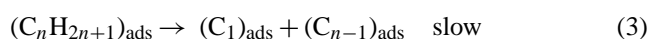
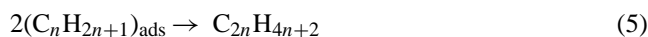
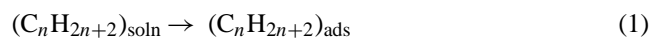
ment, the current efficiency for the transformation of ethane to carbon dioxide can be obtained. It is 5% for this fuel cell at 0.2 V. This suggests that the current efficiency of 95% is used for the transformation of ethane to valuable products.

Much work has been done on the oxidation of hydrocarbons on noble metals in aqueous solution [19–24]. It has been found that the oxidation product of hydrocarbon on noble metals in aqueous solution is carbon dioxide. The oxidation process involves adsorption of hydrocarbon on the electrocatalyst followed by the rapid formation of oxidized intermediates which are slowly oxidized into carbon dioxide. For alkane, the possible reaction mechanisms are as follows:

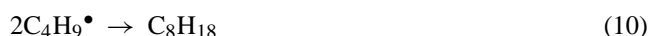
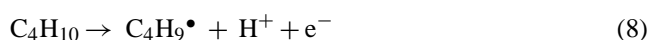
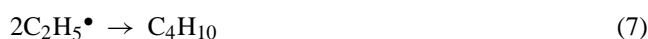
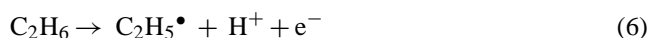


It needs oxygen-containing species for the transformation of adsorbed C_1 to carbon dioxide. Oxygen-containing species OH_{ads} can be formed from the water oxidation at the noble metals. This is why the product of hydrocarbon oxidation in aqueous solution is carbon dioxide.

The situation of the fuel cells involved in this paper is different. The fuel cells use gas as fuel and are operated at higher temperature, thus less water is available at the anodic catalyst of the fuel cells. Therefore, the reaction mechanism for hydrocarbon oxidation at the anode of the cell is different from that on the noble metals in aqueous solution. With few OH_{ads} species available due to less water existing in the system, the reaction (4) is not so easy as the reaction (3) is slow. The possible reaction mechanisms for hydrocarbon oxidation at the anode of the fuel cell are as follows:



Therefore, the possible reaction products of fuel cells with paraffin hydrocarbons are the hydrocarbons with an increased carbon number, which lacks reaction activity. As inferred in Section 3.4, the reaction activity of ethane is lower than butane and that of paraffin hydrocarbons with more than three carbons decreases with increasing carbon number. Thus, the oxidation process for ethane at the anode of ethane/oxygen fuel cell may involve:



Hexane and octane are the possible products for the oxidation of ethane in the ethane/oxygen fuel cell. Hexane is the possible product of the oxidation of propane in the propane/oxygen fuel cell and octane is the possible product of the oxidation of butane in the butane/oxygen fuel cell.

4. Conclusion

Energy and chemicals can be co-generated from a hydrocarbon/oxygen fuel cell. The amount of energy generated from the fuel cell depends on temperature, treatment of the proton exchange membrane and platinum load in the catalyst. The elevation of temperature improves the thermodynamic and kinetic activity of hydrocarbon, resulting in an average increase of over one decade in power output of the fuel cell by elevating temperature 20°. The treatment of a Nafion membrane with phosphoric acid improves the proton conductivity in the proton exchange membrane, resulting in an average increase of almost one decade in power output of the fuel cell. The power output can also be improved by increasing platinum load in the catalyst with almost one decade's increase by doubling platinum load. Most of hydrocarbon is converted to valuable chemicals during energy generation. They are hydrocarbons with more carbon atoms and less activity than the fuels.

Acknowledgements

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