Short communication

Selective membrane electrode assemblies for bipolar plate-free mixed-reactant fuel cells

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Abstract

Membrane electrode assemblies (MEAs) with PtRu/C and Pt/C as both sides electrocatalysts have been fabricated and used in a mixed-reactant alkaline fuel cell without bipolar plate. It has been found that the reactant selectivity of the electrocatalyst is tunable by changing the electrode hydrophobicity. The measurement on a three-cell stack with MEAs using a more hydrophobic PtRu/C electrode and a more hydrophilic Pt/C electrode in an ethanol/oxygen mixed solution shows that the PtRu/C electrode serves as a cathode and Pt/C electrode performs as an anode. The steady-state power density of 31 mW cm^{-2} is achieved in an ethanol solution by continuously bubbling oxygen at ambient temperature and atmosphere pressure.
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1. Introduction

It is traditionally essential that the fuel and oxidant are separated to prevent the parasitic chemical reaction at the electrodes in conventional proton exchange membrane fuel cells (PEM-FCs). The bipolar plate provides the channels for fuel and oxidant as one of the functions. But the bipolar plate may block part of the active area of the electrode and account for up to 80% of the volume of the cell stack and one third of the materials cost [1]. It is desirable to develop more compact and cheaper fuel cells, especially for portable applications. The fuel cell without bipolar plate is a big gift because the volume and weight of the stack will decrease sharply. Priestnall et al. [1], Long et al. [2] and Shen et al. [3] reviewed the development of the compact mixed-reactant (CMR) fuel cells. The compact mixed-reactant technology relies on the selectivity of the anode and cathode electrocatalysts that allows the oxidation and reduction reactions to perform in a common electrolyte without the interference [1,4–8]. FeTMPP/C, CoTMPP/C, FeCoTMPP/C,

RuSe/C [7], RuSeMo/C [4], MnO$_2$–PTFE on Ni mesh [1], Ag and Au [9], AgNi [10] have been used as selective cathode electrocatalysts for O$_2$ reduction. Previous work showed that the tungsten carbide promoted electrocatalyst used for oxygen reduction is tolerant to alcohols that could be a potential candidate for the mixed-reactant fuel cells [11–13]. It is also possible eliminating the bipolar plate by using a porous membrane electrode assemblies and passing the fuel–oxidant mixture through a stack of porous cells [1,6]. A strip-cell structure has been reported to further reduce the volume of the fuel cells [4].

On the other hand, Ferrigno et al. reported a membrane-less vanadium redox fuel cell using laminar flow [14]. Their design is based on a liquid flowing at low Reynolds number (Re) to eliminate the convective mixing of fuels. Two separate streams of oxidizing and reducing flow parallel to one another through the channel without the aid of membrane to separate these streams (only diffusive exchange occurs across the interface between them). It shows that only at the situation where the fuel and oxidant can be supplied quasi-separately the non-selective Au/C electrode behaves selective for corresponding reactions.

Here, we report the selectivity of the electrocatalysts resulted by changing the hydrophobic properties of the electrodes. A flow

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Table 1
The composition of the half cell electrodes

Number	PTFE treated carbon paper (wt.% PTFE)	Carbon layer	Catalyst layer
1#	10	15 wt.% Nafion® 1.0 mg cm^{-2} C	Pt/C 36 wt.% Nafion® 2.08 mg cm^{-2}
2#	10	20 wt% PTFE 1.0 mg cm^{-2} C	Pt/C 36 wt.% Nafion® 2.1 mg cm^{-2}
3#	30	20 wt.% PTFE 1.0 mg cm^{-2} C	Pt/C 15 wt.% PTFE 2.0 mg cm^{-2}
4#	30	20 wt.% PTFE 1.0 mg cm^{-2} C	PtRu/C 15 wt.% PTFE 1.8 mg cm^{-2}
5#	20	20 wt.% PTFE 1.0 mg cm^{-2} C	PtRu/C 30 wt.% Nafion® 2.0 mg cm^{-2}

through three-cell stack was assembled based on this concept using traditional PtRu/C and Pt/C electrocatalysts.

2. Experimental

The electrode was prepared using the procedure as follows. Carbon paper (280 μm, Toray Industries Inc., Japan) was used as current collector. The diffusion layer on the carbon paper was composed of 1.0 mg cm^{-2} carbon powder (Vulcan XC-72R, Cabot Corp., USA). The active area of a typical electrode was 0.785 cm^2 containing a 2.0 mg cm^{-2} Pt (50 wt.% Pt/C, Johnson Matthey) and 2.0 mg cm^{-2} PtRu (60 wt.% PtRu/C, atom ratio of Pt:Ru = 1:1, Johnson Matthey). The carbon and the electrocatalysts were sprayed on the PTFE treated carbon paper. The detailed composition of the electrode is shown in Table 1. A Ni-MH battery separator (BS095015, Coin Nanotech Innovations Co. Ltd., China) was used as a separator. The separator is a polypropylene membrane at the thickness of 0.15 mm and the porosity of the membrane is about 66%. It contains sub-denier fibers and has been treated for permanent wetting ability. The brim of the separator was brushed by adhesive such as KE445 (Beijing Tietop Technology Ltd.) to avoid the leakage of liquid. Three cells were directly assembled together without the use of the bipolar plate. Fig. 1 shows the schematic diagram of a three-cell stack and schematic diagram of the experimental set-up. A solution of 0.5 mol dm^{-3} ethanol and 2 mol dm^{-3} KOH was fed at 10 ml min^{-1} along with bubbling oxygen gas at 1.01 min^{-1}. The mixed-reactant (ethanol and oxygen) was pumped through the porous electrodes

of the fuel cell stack. An IM6e electrochemical workstation (ZAHNER-Elektrik, Germany) was used to record the data.

3. Results and discussion

In a mixed-reactant fuel cell, oxygen or air is dissolved in aqueous solution containing fuel (e.g. ethanol). Our original idea was to quasi-separate the gaseous oxygen and liquid fuel by designing the electrode with different hydrophobicity. The hydrophobic electrode favors the access of the gaseous oxygen and the hydrophilic electrode favors the contact with liquid fuel. The hydrophobicity of the electrode is adjusted by changing the amount of polytetrafluoroethylene (PTFE) and Nafion® in the components (carbon paper, carbon powder sub-layer, electrocatalyst layer). The more the amount of PTFE in the component the more hydrophobic of the component is. The components and compositions used for fabricating membrane electrode assemblies (MEAs) are listed in Table 1. The electrode was series in ascending hydrophobic properties as 1# < 2# ~ 5# < 3# ~ 4#. 4# and 5# electrodes were prepared by using PtRu/C electrocatalyst and 1# ~ 3# electrodes were prepared by using Pt/C electrocatalyst. The MEAs were numbered as shown in Table 2. It is obvious that the hydrophobicities of the anode and cathode in MEAs were different due to the different content of PTFE and Nafion® at each side. The compositions of the 3# and 4# electrodes were almost the same except that the electrocatalysts were Pt/C and PtRu/C, respectively. It can image that a MEA1 fabricated by 3# and 4# electrodes possesses almost the same hydrophobicity on both sides. The hydrophobic degree of the MEAs is MEA1 < MEA2 < MEA3 based on PtRu/C electrode 4# and MEA1 < MEA4 based on Pt/C electrode 3#. The open circuit voltage (OCV) of each MEA was measured in two solu-
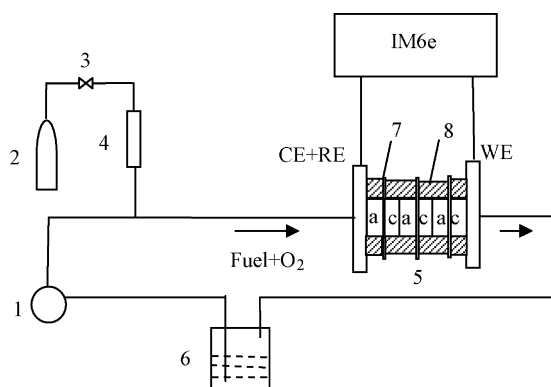

Fig. 1. Schematic design of a three-cell mixed-reactant fuel cell and schematic diagram of the experimental set-up. 1, liquid pump; 2, O$_2$ cylinder; 3, valve; 4, flow meter; 5, fuel cell stack (three cells); 6, ethanol storage tank; 7, separator and 8, seals.

Table 2
Comparison of the OCV of different MEAs

MEA	OCV[a]	OCV[b]
MEA1 (4#–3#)	0.8 V	−0.12 V
MEA2 (4#–2#)	1.2 V	0.2 V
MEA3 (4#–1#)	1.9 V	0.55 V
MEA4 (5#–3#)	0.7 V[*]	−0.32 V

[a] Conditions: O$_2$ 1.01 min^{-1} at atmosphere pressure; 0.5 mol dm^{-3} ethanol + 2 mol dm^{-3} KOH 10 ml min^{-1}.

[b] Conditions: O$_2$ saturated 0.5 mol dm^{-3} ethanol + 2 mol dm^{-3} KOH 10 ml min^{-1}.

[*] Conditions: O$_2$ 2.01 min^{-1}; 0.5 mol dm^{-3} ethanol + 2 mol dm^{-3} KOH 10 ml min^{-1}.

tions. One was a solution of $0.5\,mol\,dm^{-3}$ ethanol + $2\,mol\,dm^{-3}$ KOH by bubbling O_2 at $1.01\,min^{-1}$ at atmosphere pressure. The solution was injected into the cell at $10\,ml\,min^{-1}$. The second one was a solution of $0.5\,mol\,dm^{-3}$ ethanol + $2\,mol\,dm^{-3}$ KOH saturated with O_2. The solution was also injected into the cell at $10\,ml\,min^{-1}$. The data are summarized in Table 2. Generally, the OCV was denoted as positive to indicate that PtRu/C electrode acts as cathode for O_2 reduction reaction. In this case, PtRu/C electrode shows a higher potential than that of Pt/C electrode. A negative OCV means that PtRu/C electrode acts as anode. The OCV of MEA1 showed a small negative value when fed an O_2 saturated ethanol solution. However, the OCV changed to positive value when O_2 bubbled during the ethanol feeding process. In that case, the PtRu/C electrode acts as a cathode. With the increase in the difference of hydrophobicities of the two electrodes, the OCVs of the MEAs became positive and increased in both reactant feeding conditions, indicating that PtRu/C acts as cathode at all the cases. The OCV increased from 0.8 to 1.9 V when $1.01\,min^{-1}$ O_2 flowed through the porous electrode with the increase in the difference of the hydrophobicities between two electrodes (from MEA1 to MEA3). In the case of O_2 saturated solution, the OCV also increased accordingly from -0.12 to 0.55 V from MEA1 to MEA3. The OCV of the O_2 saturated solution was much lower than that at O_2 flow through condition. It suggests that O_2 is richer on the surface of the electrocatalyst at O_2 flow through condition which lessen the effect of the mixed-reactants and results in higher OCV. The hydrophobic property decreased when electrode 4# was used instead of electrode 5#, resulting in an increase in the difference of hydrophobicity of two electrodes for MEA4 compared to MEA1. By using Pt/C as electrocatalyst in electrode 3# and PtRu/C as electrocatalyst in less hydrophobic electrode 4# (the electrocatalyst layer is hydrophilic), the OCV of MEA4 in the O_2 saturated solution was more negative than that of MEA1 as expected, showing that Pt/C acted as O_2 reduction electrocatalyst. But the OCV was still positive when O_2 flows through the MEAs, indicating that PtRu/C still acted as cathode electrocatalyst. It may deduce that PtRu/C is prone to O_2 reduction reaction relative to Pt/C when feeds the cell with mixed fuel and oxidant in alkaline media.

The performance of O_2 reduction reaction on Pt/C and PtRu/C were tested in O_2 saturated $2\,mol\,dm^{-3}$ KOH with or without $0.5\,mol\,dm^{-3}$ ethanol. The results are shown in Fig. 2. Fig. 2a shows the linear sweep curves of oxygen reduction on Pt/C and PtRu/C electrocatalysts in $2\,mol\,dm^{-3}$ KOH solution. The onset potentials of Pt/C and PtRu/C are about -12 and $0\,mV$ (versus Hg/HgO), respectively. However, in the presence of $0.5\,mol\,dm^{-3}$ ethanol, the onset potential of Pt/C changed to be more negative value of $-84\,mV$ while the onset potential of PtRu/C only slightly changed to $-8\,mV$. On the other hand, the reaction on Pt/C electrode transferred to the ethanol oxidation and caused the huge oxidation current when the potential sweep goes to more negative value than $-0.15\,V$. The results indicate that the combination of such a more hydrophilic Pt/C electrode and a more hydrophobic PtRu/C electrode to fabricate a MEA, the PtRu/C electrode will perform as a cathode in a direct ethanol fuel cell.
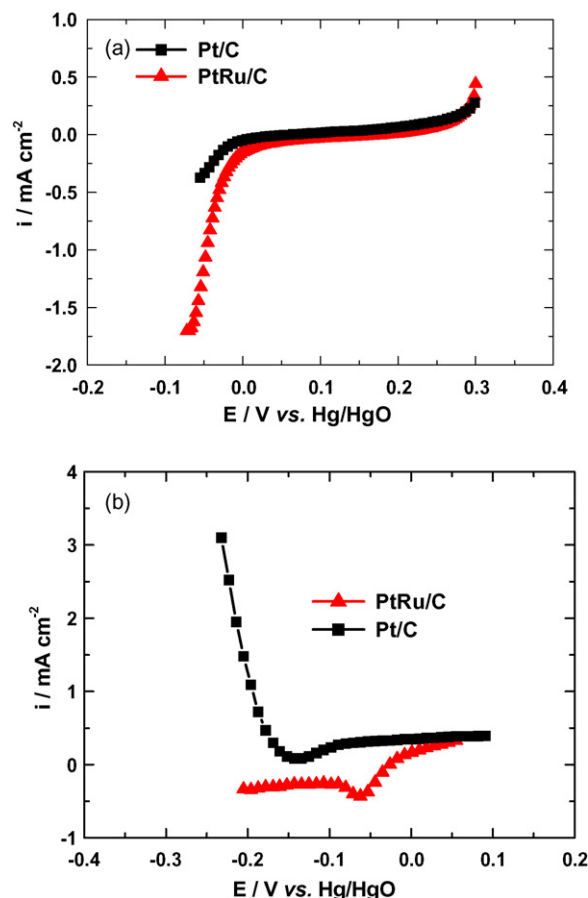

Fig. 2. (a) Linear sweep curves of oxygen reduction on Pt/C and PtRu/C electrocatalysts in $2\,mol\,dm^{-3}$ KOH. Scan rate: $2\,mV\,s^{-1}$. (b) Linear sweep curves of oxygen reduction on Pt/C and PtRu/C electrocatalysts in $0.5\,mol\,dm^{-3}$ ethanol + $2\,mol\,dm^{-3}$ KOH. Scan rate: $2\,mV\,s^{-1}$.

The performance of the three-cell stacks with different MEAs is shown in Fig. 3. The voltage was the total voltage of a three-cell assembly. The stacks gave the reasonable power densities in a mixed-reactant mode at the cell temper-
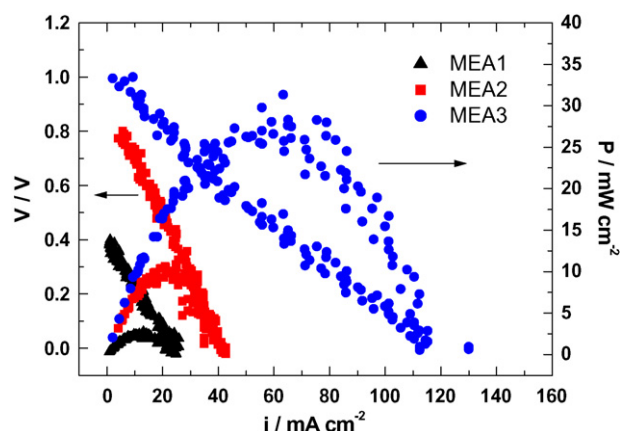

Fig. 3. The performance of the mixed-reactant fuel cell (three-cell stack) with different MEAs. Conditions: O_2 $1.01\,min^{-1}$ at atmosphere pressure, $0.5\,mol\,dm^{-3}$ ethanol + $2\,mol\,dm^{-3}$ KOH $101\,min^{-1}$, T_{cell}: $26\,°C$. Scan rate: $10\,mV\,s^{-1}$. MEA1: cathode 4# and anode 3#; MEA2: cathode 4# and anode 2# and MEA3: cathode 4# and anode 1#.

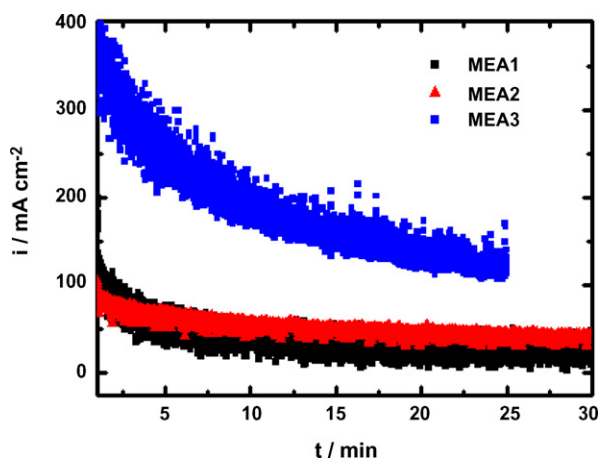Fig. 4. The stability of the mixed-reactant fuel cell (three-cell stack) discharged at 100 mV. Conditions: O_2 1.0 l min^{-1} at atmosphere pressure, 0.5 mol dm^{-3} ethanol + 2 mol dm^{-3} KOH 10 l min^{-1}. T_{cell}: 26 °C. MEA1: cathode 4# and anode 3#; MEA2: cathode 4# and anode 2#; MEA3: cathode 4# and anode 1#.

ature of 26 °C. The better performance was observed for the MEAs with larger difference in the hydrophobic degree of two electrodes (MEA1 < MEA2 < MEA3). It was found that the initial current density was 231.8 mA cm^{-2} at 0.607 V (i.e. 140.7 mW cm^{-2}) for MEA3. However, the steady-state output of the power density was reduced to 31 mW cm^{-2}. The highest power densities of MEA3, MEA2 and MEA1 are 31 mW cm^{-2} at 0.495 V, 10.3 mW cm^{-2} at 0.358 V and 1.95 mW cm^{-2} at 0.308 V, respectively. It demonstrates from the polarization curves in Fig. 3 that the fuel cell stack fabricated by the present method can be operated in the absence of the bipolar plates. Fig. 4 shows the current response curves of the different stacks at a constant voltage. The steady-state discharge was achieved after less than 30 min. The performance is promising compared to the result reported by Scott et al. for a mixed-reactant DMFC using Nafion® as solid electrolyte at 90 °C [7]. Fig. 5 compares the performance of a three-cell stack with MEA3 fed by a solution of O_2 saturated 0.5 mol dm^{-3} ethanol and 2 mol dm^{-3}
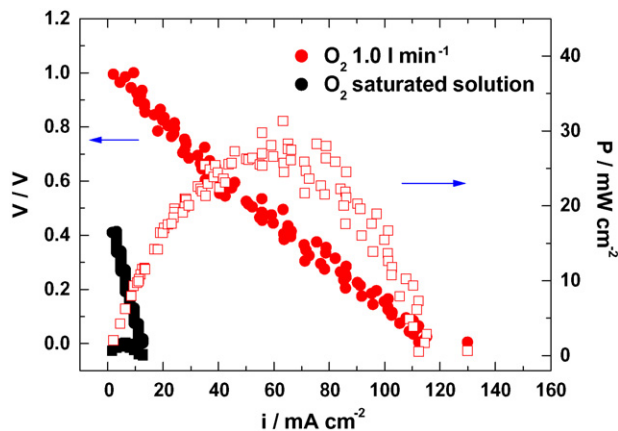
KOH at 10 ml min^{-1}, or fed a solution of 0.5 mol dm^{-3} ethanol and 2 mol dm^{-3} KOH along with the O_2 bubbling at 1.0 l min^{-1}. In the case of continuously bubbling O_2, a much better performance was observed than that in O_2 saturated solution.

It is well known that PtRu/C and Pt/C are non-selective electrocatalysts for traditional direct alcohol fuel cells. But, hydrophobic PtRu/C is prone to O_2 access and for further reduction as shown in Fig. 2b in O_2 saturated ethanol alkaline solution. The selectivity of the electrode shown in this study is an unexpected discovery but it is true since we have carefully repeated the experiment. The proper explanation is difficult at this stage. However, it is clear that the hydrophobicity of the electrode plays an important role for the selective access of the gaseous O_2 and liquid alcohol. The more hydrophobic electrode favors the gaseous oxygen to access for further reduction and the electrode acts as a cathode. If more selective electrocatalyst [11–13] is used, it is expected that the performance will be better than that of PtRu/C and Pt/C electrocatalysts.

4. Conclusions

A membrane electrode assembly fabricated by using a hydrophobic PtRu/C electrode and a hydrophilic Pt/C electrode in an ethanol/oxygen mixed solution shows reactant selectivity for both electrodes. The hydrophobic electrode favors gaseous oxidant to diffuse to the surface of the electrode and the electrode serves as a cathode, while the hydrophilic electrode favors liquid fuel to access the surface of the electrode and the electrode performs as an anode. A three-cell stack gave steady-state power density of 31 mW cm^{-2} in an ethanol solution and bubbling oxygen continuously during the operation at ambient temperature and atmosphere pressure. This study demonstrates that the reactant selectivity of the electrocatalyst could be tunable by just adjusting the electrode hydrophobicity.

Fig. 5. The performance of the mixed-reactant fuel cell (three-cell stack) with MEA3. Conditions: □, O_2 1.0 l min^{-1} at atmosphere pressure; ■, O_2 saturated solution; 0.5 mol dm^{-3} ethanol + 2 mol dm^{-3} KOH 10 l min^{-1}. T_{cell}: 26 °C.

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