Short communication

A study of the direct dimethyl ether fuel cell using alkaline anolyte

Kan Xu [a], Shao Jiang Lao [a], Hai Ying Qin [a], Bin Hong Liu [b], Zhou Peng Li [a],*

[a] Department of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310027, PR China
[b] Department of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, PR China

ABSTRACT

The electrooxidation behavior of dimethyl ether (DME) dissolved in acidic, neutral or alkaline anolyte has been studied. The cyclic voltammetry measurements reveal that DME in alkaline anolyte demonstrates higher electrooxidation reactivity than that in acidic or neutral anolyte. With increasing the NaOH concentration in the anolyte, the electrooxidation reactivity of DME can be further improved. Direct dimethyl ether fuel cells (DDFCs) are assembled by using Nafion membrane as the electrolyte, Pt/C as the cathode catalyst, and Pt–Ru/C as the anode catalyst. It is found that the use of alkaline anolyte can significantly improve the performance of DDFCs. A maximum power density of 60 mW cm^{-2} has been achieved when operating the DDFC at 80 °C under ambient pressure.

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1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are considered to be promising power generation devices due to their excellent performances at ambient conditions when using hydrogen as the fuel. However, low cost hydrogen production, high capacity hydrogen storage and safe hydrogen distribution are problematic for commercial applications. Many compounds with high hydrogen content such as methanol [1], hydrazine [2], borohydride [3], and dimethyl ether [4] are considered to be the potential alternative hydrogen carrier. Dimethyl ether (DME) with the formula CH_3OCH_3 is a non-toxic organic compound soluble in water. It is a clean hydrocarbon fuel with high hydrogen content of 13 wt.%. Gaseous DME can be easily pressurized into liquid under 0.6 MPa at room temperature, which is convenient for fuel storage and distribution.

DME without C–C bond is easily electrooxidized to CO_2 [5]. One mole of DME releases 12 electrons after complete electrooxidation [6]. Owing to the favorable physical properties of DME and its high theoretical energy density of 8.2 kWh kg^{-1} [7], DME as a promising fuel has attracted more and more attention. It is reported that the crossover of DME is not as severe as that of methanol [8]. Moreover, the crossover of DME shows little influence on cathode performance [5,9]. Serov and Kwak [4] have summarized the recent progress in development of direct dimethyl ether fuel cell (DDFC),

and believe that the DDFC could be a valuable direct liquid fuel cell candidate for commercialization.

However, compared with PEMFCs and direct methanol fuel cells (DMFCs), DDFCs show poor performances under ambient conditions due to the poor electrooxidation reactivity of DME [5–9]. Compared with hydrogen as the fuel for PEMFCs, more water is needed for DME electrooxidation reaction and H$^+$ migration from anode side to cathode side due to the electro-osmotic force of water according to the DME electrooxidation reaction in acid medium:

$$CH_3OCH_3 + 3H_2O \rightarrow 2CO_2 + 12H^+ + 12e^- \qquad (1)$$
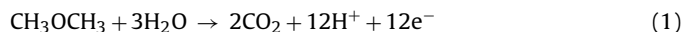
As DME can be dissolved in water with a solubility of 328 g L^{-1} (20 °C), Yu et al. [10] suggested using DME–water solution as the fuel for the DDFC. However, no significant improvement of cell performance was observed due to the poor ionic conductivity of water.

In order to improve the DME electrooxidation reactivity and the ionic conductivity of the anolyte, we studied the electrooxidation behavior of DME in acidic, neutral and alkaline solutions. The performances of DDFCs using neutral or alkaline solution as the anolyte at different temperatures were evaluated.

2. Experimental

The crystal structure of commercial Pt (40 wt.%)–Ru (20 wt.%)/C catalyst (from Shanghai Hesen Electronic Co.) was characterized by X-ray diffraction (XRD) with a Rigaku-D/MAX-2550PC diffractometer using Cu K$_\alpha$ radiation (λ = 1.5406 Å). The morphology of the catalyst was characterized by a Philips-FEI Sirion 200 field emission
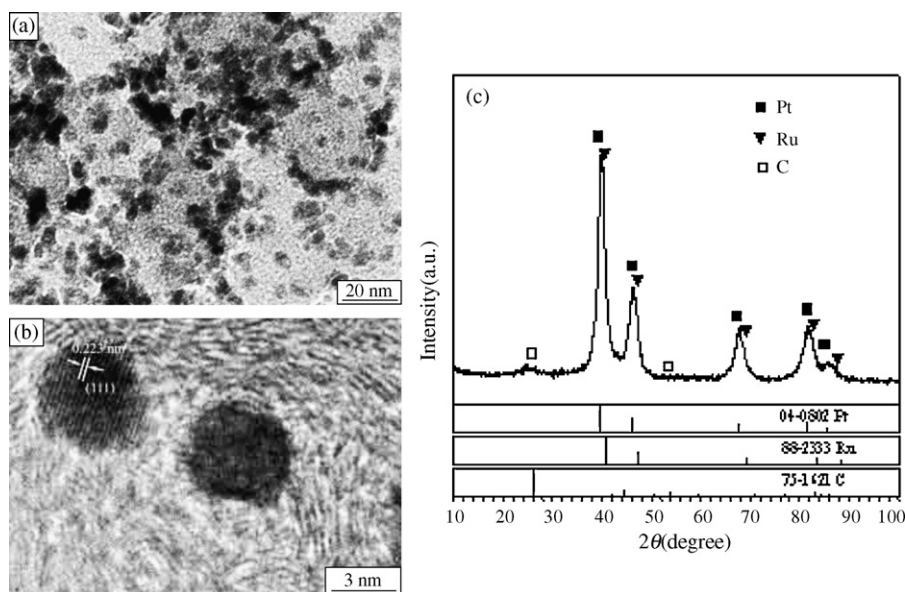
Fig. 1. The morphology (a and b) and structure (c) of Pt–Ru/C catalyst.

scanning electron microscopy (FESEM) and a JEM-2010 transmission electron microscopy (TEM).

Cyclic voltammetry (CV) measurements were performed with Zahner IM6 analyzer in a three-electrode system. Pt–Ru/C modified glass carbon (GC) electrode was used as working electrode. The electrode was prepared as follows: Pt–Ru/C powder of 0.8 mg were ultrasonically mixed with Nafion solution (5 wt.%) of 0.1 mL and anhydrous ethanol of 1.5 mL for 20 min to form homogenous ink, then 20 μL catalyst ink was pipetted onto the surface of the pretreated GC disk electrode (3 mm in diameter) and dried at room temperature. A piece of nickel foam was used as the counter electrode. A calomel electrode in saturated KCl solution (SCE) was used as the reference electrode. The tested fuels were prepared by continuously bubbling the DME in different anolyte such as Na_2SO_4, NaOH or H_2SO_4 solution. All the CV experiments were carried out at 25 °C with a scan rate of 50 mV s^{-1}. The potentials were converted to the values vs. reversible hydrogen electrode (RHE) according to the pH value of the applied anolyte:

$$E (\text{V vs. RHE}) = E(\text{V vs. SCE}) + 0.241 + 0.0591 \times \text{pH}, \quad \text{at } 25\,°\text{C} \quad (2)$$

where 0.241 is the potential of saturated calomel electrode (SCE) vs. SHE at 25 °C and 0.0591 is obtained from $2.303RT/nF$. The pH value is calculated based on the activity coefficient of the anolyte [11,12].

The cell structure and test set for performance measurements were described in our previous work [13]. Pt (40 wt.%)–Ru (20 wt.%)/C and Pt/C (5 wt.% Pt on Vulcan XC-72, from E-Tek Co.) were used as the anode and cathode catalyst, respectively. Nafion membrane N117 was used as the electrolyte. Catalyst ink was

prepared by mixing catalyst powder with anhydrous ethanol, Nafion solution (5 wt.%), and de-ionized water in the ratio of 1:3:7:3 by weight. The anode ink was pasted on a piece of nickel foam with Pt–Ru loading of 5 mg cm^{-2}. The cathode ink was pasted on a piece of hydrophobic carbon cloth with Pt loading of 0.5 mg cm^{-2}. The N117 membrane was pretreated by boiling it in 3 wt.% H_2O_2 solution and then in de-ionized water for 1 h, respectively.

The cell performances were measured at a fuel flow rate of 20 mL min^{-1} and a humidified O_2 flow rate of 10 mL min^{-1} under 40 °C, 60 °C and 80 °C, respectively. SCE was connected to anolyte with a salt bridge for polarization evaluation.

3. Results and discussion

TEM and high-resolution transmission electron microscopy (HRTEM) images of Pt–Ru/C catalyst are shown in Fig. 1. The clear interplanar spacing reveals that Pt and Ru are well alloyed to form a homogeneous phase, which is confirmed by XRD diffraction pattern as shown in Fig. 1(c). Pt–Ru alloy particles are homogeneously dispersed on surfaces of carbon particles as shown in Fig. 1(a).

In order to evaluate DME electrooxidation reactivity in acidic, neutral and alkaline anolyte under the same cation concentration, 0.5 M H_2SO_4, 0.5 M Na_2SO_4 and 1 M NaOH solutions were selected as the anolyte. As shown in Fig. 2, it can be seen that DME in alkaline anolyte demonstrates remarkable anodic current compared with that in acidic anolyte or in neutral anolyte. It reveals that DME has higher electrooxidation reactivity in alkaline anolyte than that in acidic or neutral anolyte.
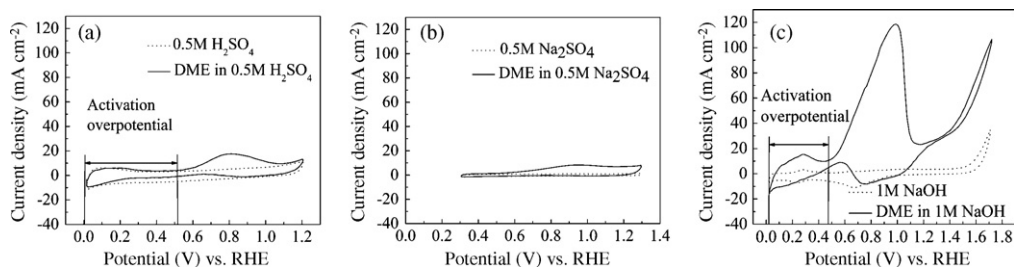

Fig. 2. CVs of DME at Pt–Ru/C/GC electrode in (a) 0.5 M H_2SO_4, (b) 0.5 M Na_2SO_4 and (c) 1 M NaOH solutions at scan rate of 50 mV s^{-1}.
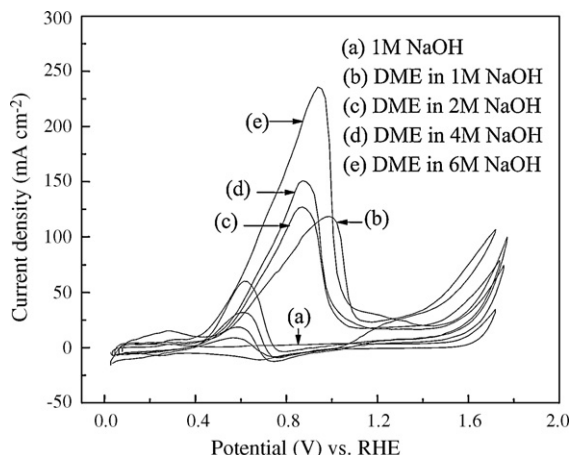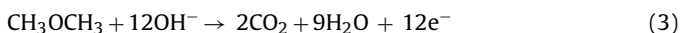
Fig. 3. Influence of NaOH concentration in anolyte on DME electrooxidation. Scan rate: $50\,mV\,s^{-1}$.

In alkaline solution, DME electrooxidation reaction can be described as:

$$CH_3OCH_3 + 12OH^- \rightarrow 2CO_2 + 9H_2O + 12e^- \qquad (3)$$

DME demonstrates lower activation overpotential in alkaline anolyte compared with the DME electrooxidation in acidic anolyte as shown in Fig. 2. Moreover, the reaction polarization of DME in alkaline anolyte is remarkably smaller than that of DME in acidic anolyte based on the slope of V–I line from the beginning of DME electrooxidation to the peak of DME electrooxidation. It is implied that OH$^-$ ion in alkaline anolyte plays an important role in improving DME electrooxidation kinetics.

Fig. 3 shows the CVs of DME in alkaline solutions with different NaOH concentrations. The electrooxidation potential of DME shifts to smaller values with increasing the NaOH concentration. It can be attributed to the fact that DME electrooxidation potential is significantly influenced by OH$^-$ concentration according to the Nernst equation based on reaction (4):

$$E = E^0 - \frac{RT}{nF}\ln\frac{[DME][OH^-]^{12}}{P_{CO_2}^2[H_2O]^9} \qquad (4)$$

DME demonstrates lower activation overpotential in anolyte with higher NaOH concentration. Furthermore, the reaction polarization of DME is decreased with increasing the NaOH concentration in anolyte regarding to the slope of V–I line from the beginning of DME electrooxidation to the peak of DME electrooxidation, which reveals that the higher NaOH concentration in anolyte is beneficial to the DME electrooxidation kinetics. It is also known that the mean activity coefficient of NaOH solution increases with increasing the NaOH concentration up to 15 M [12]. Therefore, DME electrooxidation peak current in CVs increases with increasing the NaOH concentration in the anolyte.

In order to confirm the effectiveness of using alkaline anolyte on the performance improvement, cell performances were measured by using 0.5 M Na$_2$SO$_4$ solution or 1 M NaOH solution as the anolyte in the DDFC. The cell performances and the electrode polarization behavior are shown in Fig. 4. It can be seen that not only the open circuit voltage (OCV) but also the performance are improved obviously with increasing the operation temperature. It can be attributed to the fact that higher temperatures are beneficial for improvement of not only DME electrooxidation kinetics but also oxygen electroreduction kinetics, which is similar to DMFCs and PEMFCs. Comparing Fig. 4(a) with Fig. 4(b), it can be seen that the performance of the DDFC using alkaline anolyte is higher than that of the DDFC using neutral anolyte at each operation temperatures. Fig. 4(c) gives a comparison of DME polarization behaviors in neutral or alkaline anolyte. It can be seen that not only the anode polarization but also the cathode polarization is decreased due to the fact that oxygen electroreduction is faster in alkaline media than in other media. Therefore, the use of alkaline anolyte can
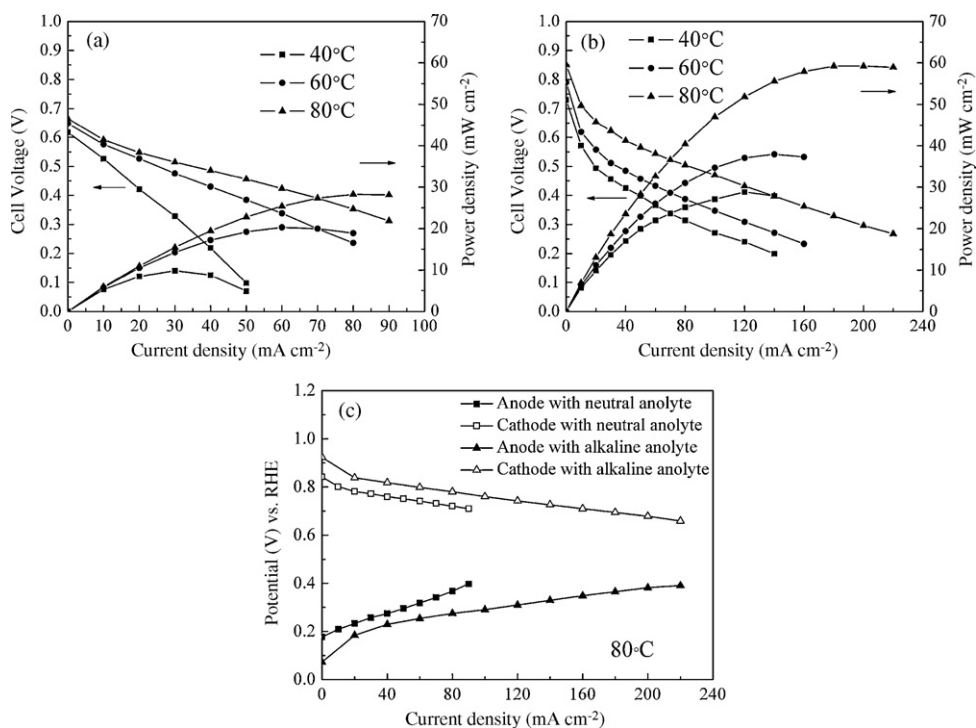

Fig. 4. Performances of the DDFC using (a) 0.5 M Na$_2$SO$_4$ solution and (b) 1 M NaOH solution as the anolyte at 40 °C, 60 °C, 80 °C respectively, and (c) corresponding electrode polarization behavior when using 0.5 M Na$_2$SO$_4$ solution or 1 M NaOH solution as the anolyte at 80 °C.

effectively improve the cell performance of the DDFC. As a result, a maximum power density of 60 mW cm^{-2} has been achieved when using 1 M NaOH solution as the anolyte and operating at 80 °C, which is an obvious performance improvement compared with the reported DDFCs at the same conditions [10,14].

4. Conclusions

DME in alkaline anolyte demonstrates higher electrooxidation reactivity than that in acidic or neutral anolyte. DME electrooxidation reactivity is improved with increasing of NaOH concentration in the anolyte up to 6 M. The use of alkaline anolyte can significantly improve the performance of the DDFC because DME has better electrooxidation reactivity and oxygen has better electroreduction reactivity in alkaline media. The DDFC using 1 M NaOH solution as the anolyte exhibits a maximum power density of 60 mW cm^{-2} at 80 °C under ambient pressure.

Acknowledgements

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