

# A methanol concentration sensor using twin membrane electrode assemblies operated in pulsed mode for DMFC

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Received 16 June 2006; received in revised form 20 July 2006; accepted 20 July 2006

Available online 12 September 2006

## Abstract

A methanol concentration sensor based on twin Nafion membrane electrode assemblies (MEAs) was constructed and characterized by electrochemical methods. Pulsed amperometric detection (PAD) method, using a low frequency (67 mHz) potential waveform of  $E_{\text{red}}$  (cathodic activation potential) =  $-0.2$  V,  $E_{\text{pre-oxd}}$  (anodic pre-oxidation potential) =  $+0.60$  V and  $E_{\text{det}}$  (detection potential) =  $+0.80$  V versus DHE with the same pulse width of 5 s was applied to the sensor to enhance its performance. The response in pulsed mode had better linearity over a wider concentration range than that in potentiostatic mode. Furthermore, using this PAD method, the stability of the sensor was enhanced significantly with a slightly linear degradation rate of  $2.9$  mA h<sup>-1</sup> during long-time test. The performances of the sensor in terms of linearity, low anodic saturation and high stability show its potential application for direct methanol fuel cells.

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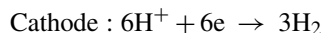
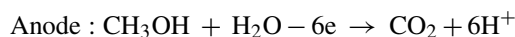
**Keywords:** Direct methanol fuel cell; Sensor; Methanol concentration; Membrane electrode assembly (MEA); Pulsed amperometric detection

## 1. Introduction

Direct methanol fuel cells (DMFCs) are receiving much attention as power sources ranging from transportation to portable devices because of their high energy density and comfort of operating with a liquid fuel [1]. However diluted methanol, usually less than 2 M, is used to reduce methanol crossover from anode to cathode, which results in the decrease of system power density significantly. Hundred percent methanol feeding to anode of direct methanol fuel cells is crucial to their practical application, in order to increase power density of the systems.

Methods of monitoring methanol concentration have previously been developed by exploration of electrical, optical, sonic, magnetic or other properties [2–4]. Electrochemical sensors operating on amperometric principle are based on the limiting current of methanol oxidation across one barrier layer such as the Nafion membrane [5,6]. Passive mode sensors, like fuel cells, do not need additional power source [7,8], however, oxidant depen-

dence and concentration saturation limit their application for measuring high concentrations. These drawbacks can be avoided in drive mode in which a definite potential is applied to the sensor anode to oxidize methanol. Hydrogen is produced continually at cathode which is used as dynamic hydrogen electrode (DHE). The reactions are as follows:



Nafion membrane acts not only as solid electrolyte but also as one barrier layer in the sensor of cathode feeding mode [5]. However, purging anode by inert gas continually limits its application. The sensor of anode feeding mode can measure methanol concentration in tank [9,10] or in stream [11]. But the anodic saturation due to weak barrier effect is also serious when concentration exceeds 2 M. As a simple design, Ren and Gottesfeld sealed anode chamber to eliminate oxygen interference from air [12]. But the stability is rarely reported. Heretofore, the methanol concentration sensor using more reasonable structure is in urgent need.

In the present work, a methanol concentration sensor was constructed by two identical MEAs with anodes face to face. Two

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cathodes of the sensor are taken as pseudo-reference electrodes due to their fast electrochemical reaction. Methanol permeates through Nafion membrane from cathodes in the feeding stream to anodes. Carbon dioxide produced by the oxidation of the methanol in the anode chamber can be expelled outside through tiny openings or enter the cathode chambers by permeating through the Nafion membrane. Compared with single MEA structure, the unique arrangement avoids the interference of oxygen from environment, increases the sensitivity and, what is more important, the two combined cells can provide two current signals at the same time to guarantee the performance of the sensor.

Nevertheless, the methanol concentration sensor based on MEA seem to have saturation phenomenon over several molar concentration when it was operated in potentiostatic mode [5,11]. The main reason attributing to this phenomenon may be the electro-osmotic effect on the methanol diffusion over Nafion membrane and sluggish oxidation of methanol due to poisonous intermediate products. In addition, the electrochemical sensors based on MEA have issues with stability. Though the factors have been focus on the membrane and catalysts [13], the methods of promoting its stability were rarely reported.

In the present work, pulsed amperometric detection (PAD) method was employed to this sensor to alleviate the anodic saturation and improve the stability. It is well known that PAD technique have been extensively utilized in detecting carbohydrates in anion-exchange chromatography to enhance its sensitivity and long-time stability [14,15]. PAD works by applying a repeating potential versus time waveform (normally a triple-potential waveform) [16] to the working electrode in a flowthrough detector cell. The first portion of the waveform is the detection potential  $E_{det}$  at which analyte oxidation current is measured. The detection portion is followed by steps to anodic oxidation potentials ( $E_{oxd}$ ) and cathodic activation potential ( $E_{red}$ ). The

purpose of these steps is to clean the electrode and maintain a catalytically active surface. So, a repeating triple-potential waveform was applied to the anode of the sensor and the experimental results show that the performance in pulsed mode is superior to that in potentiostatic mode.

## 2. Experimental

### 2.1. Construction of the sensor

The MEAs were fabricated according to the method described in the literature [17]. Nafion<sup>®</sup>-117 (purchased from Du Pont) was employed as solid electrolyte. PtRu black and Pt black (purchased from Johnson Matthey Inc.) were used as anode and cathode catalysts with metal loadings of 4.7 and 2.0 mg cm<sup>-2</sup> respectively. Nafion-bonded SGL carbon paper was employed as gas diffusion layer. The sensor was assembled with two MEAs (5 mm × 8 mm) as shown in Fig. 1. A SS316L mesh current collector was sandwiched by these two MEAs with anodes face to face. There were tiny vents opening into anode chamber between gaskets impacted by double MEAs.

### 2.2. Measurement of methanol concentration

Measurements were carried out by feeding methanol solution through the two cathode chambers in tandem. In order to maintain the sensor temperature, methanol solution flow though a heat exchanger previously, which is bathed in hot water (deviation is  $\pm 0.2$  °C). Methanol solution was driven by peristaltic pump at an average flow rate of 4.2 ml min<sup>-1</sup> or 2.6 ml min<sup>-1</sup>.

CHI 760B electrochemical workstation (Austin, Texas) together with supporting software (Version 4.23) was used to control the potential. Cyclic voltammetry was measured at a scan rate of 20 mV s<sup>-1</sup> in the range from 0 to 0.9 V. The poten-

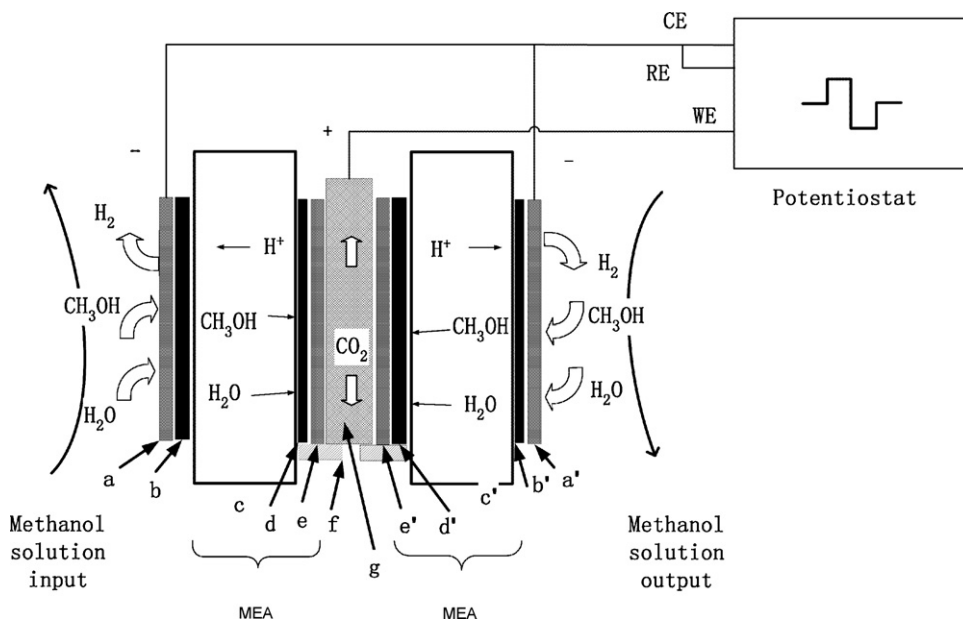


Fig. 1. Schematic diagram showing sensor configuration: (a, a', e, e') gas diffusion layers; (b, b') catalyst layers of cathodes; (c, c') Nafion membrane; (d, d') catalyst layers of anodes; (f) gasket with vent and (g) meshy collector of current.

tial wave-form applied in pulsed mode was generated by setting suitable parameters in “Muti-Potential Steps” technique.

### 3. Results and discussion

#### 3.1. Characterization by CV experiments

Cyclic voltammetry (CV) experiments were carried out to investigate the responses to concentrations. Prior to the experiments, the methanol solution had flowed through the sensor for 5 min. The last results of five cycle experiments are shown in Fig. 2. In the positive-going sweep, methanol oxidation commences at about 0.5 V giving a peak in the potential region of 0.6–0.8 V (versus DHE), which is consistent with that of literature [18]. This shows that the cathode potential is stable due to the formation of dynamic hydrogen reference electrode. Though the anode potential higher than 0.7 V (versus DHE) promotes the establishing of limiting current, too high potential could lead to the dissolving of ruthenium [19]. So, the range of potential that can be applied to the sensor anode, 0.7–0.9 V, was obtained from CV results.

The peak current of CV is proportional to methanol concentration, which shows a good concentration response. The resistance calculated from the potential shifting with corresponding current increasing is  $0.96 \Omega$  which is larger than the measured inner-resistance of  $0.25 \Omega$ . This phenomenon may be caused by electro-osmotic effect, because the more proton transfers from anode to cathode following the increase of current, the more methanol is inhibited to diffuse from cathode to anode [5,20]. Furthermore, the forward peaks of the CV results are obvious even the methanol concentration rise over 3 M. It is believed that the intermediate poisoning species exist on the catalyst surface throughout a large concentration range [21].

#### 3.2. Operation in potentiostatic mode

Fig. 3 shows the working curves of the sensor at different temperatures operated in potentiostatic mode (0.8 V versus

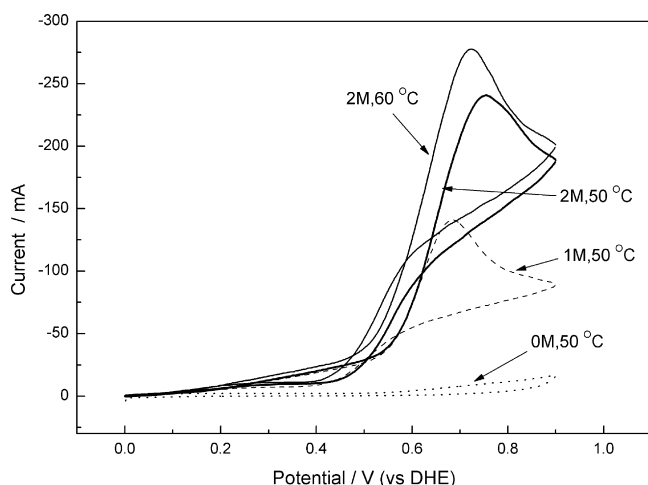


Fig. 2. Cyclic voltammograms of the sensor anode at a scan rate of  $20 \text{ mV s}^{-1}$ . Flow rate of methanol solution:  $4.2 \text{ ml min}^{-1}$ .

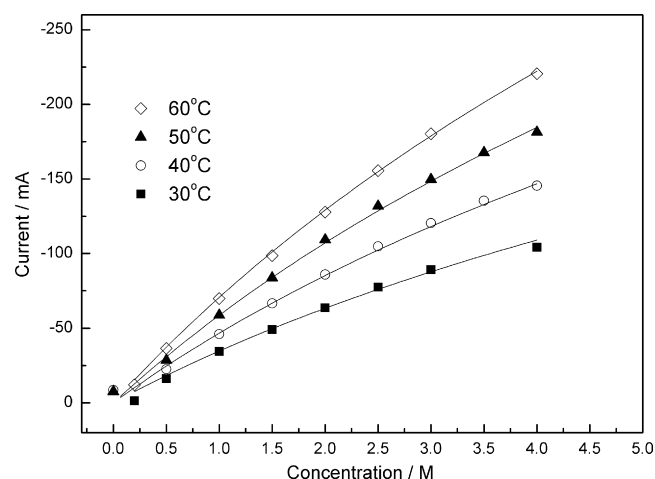


Fig. 3. Response current of the sensor operated in potentiostatic mode vs. methanol concentration at various temperatures (dot: experimental result; solid line: fitting result).

DHE). The result was obtained from the plateau value of current versus time after 10-min stabilization. It is obvious that the current increases as concentration increases at definite temperature. However non-linearity exists in the whole concentration range and no obvious saturation concentration is observed. Several factors were ascribed to the deviations such as the electroosmotic drag especially at higher current density and low methanol oxidation rate [5].

It is observed that elevating temperature greatly increases the sensitivity of the sensor. High temperature promotes the electro-oxidation of methanol [22]. CV results, the higher peak current of  $60^\circ\text{C}$  appears ahead of  $50^\circ\text{C}$  (shown in Fig. 2), also gives good agreement. The sensitivity of  $43.8 \text{ mA M}^{-1}$  at  $50^\circ\text{C}$  was obtained and the temperature coefficient of  $1.33 \text{ mA M}^{-1} \text{ K}^{-1}$  can be obtained by least squares fitting the data of the working curves after electro-osmotic correction [23].

Electro-osmotic drag coefficient of 2.1 can also be obtained from the fitting result. It is consistent with reported value for Nafion membrane [24,25]. In addition, for the methanol concentration of 1 and 2 M at  $80^\circ\text{C}$ , the calculated limiting currents are 115 and  $212 \text{ mA cm}^{-2}$  respectively. They agree well with the methanol-permeating rate across Nafion membrane [23]. Thus, the methanol diffusion is mainly controlled by Nafion membrane as barrier layer which attributes to the stable performance and high concentration measuring range.

The response time of the sensor was determined by switching methanol solution from 0 to 1 M at different temperatures. The response time decrease from 34 s at  $30^\circ\text{C}$  to 18 s at  $60^\circ\text{C}$ . The increased diffusion coefficient of Nafion membrane could attribute the enhanced response when temperature increases [20]. But the response time of the sensor was not improved by twin MEA structure.

#### 3.3. Operation in pulsed mode

In order to alleviate the anodic saturation and improve the stability, a triple-potential waveform was applied to this sensor. The cathodic potential  $E_{\text{red}}$  with reversed polarity was to

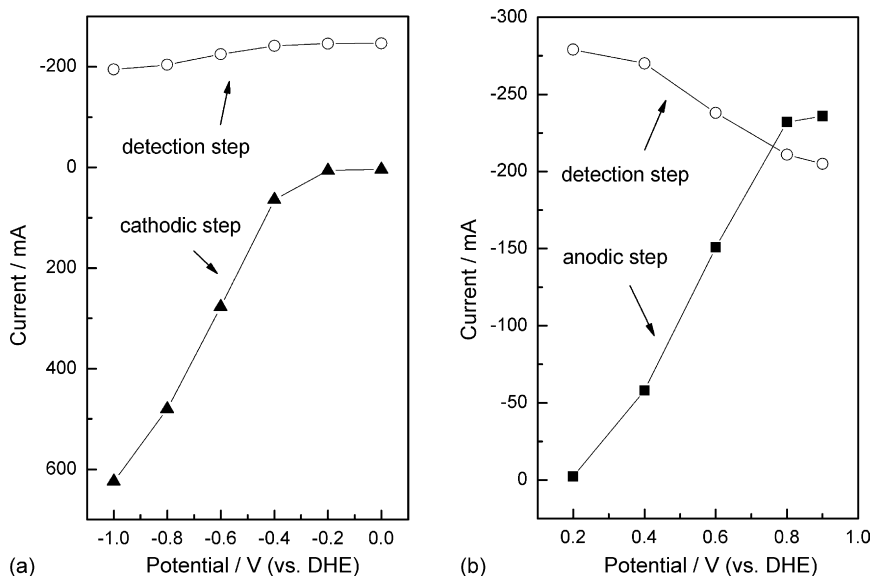


Fig. 4. Effect of the  $E_{\text{red}}$  (a) and  $E_{\text{pre-oxd}}$  (b) applied in the pulsed amperometric detection mode to the sensor anode on the amperometric response. The methanol solution is 2 M methanol at a flow rate of  $2.6 \text{ ml min}^{-1}$ .

alleviate the electro-osmotic effect and the anodic pre-oxidation potential  $E_{\text{pre-oxd}}$  was to regenerate the active electrode surface of nanosized PtRu catalyst. The detection potential  $E_{\text{det}}$  was specified at 0.8 V that have been determined in potentiostatic mode.

The cathodic step of the waveform ( $E_{\text{red}}$ ) is to make the electrode reactive and is believed to alleviate the electroosmotic effect caused by long-term operation. Fig. 4(a) shows the optimizing result for  $E_{\text{red}}$  when 2 M methanol flows through the sensor at  $50^\circ\text{C}$ . The current of detection step and the current of cathodic step are shown as a function of  $E_{\text{red}}$ . The result shows that reduction at the electrode occurs when  $E_{\text{red}}$  is more negative than  $-0.2 \text{ V}$  (versus DHE) and the current of proton reduction increases significantly with increasing the negative value. But the current of detection step decreases slightly due to reducing the transient current through regenerating the electrode surface. Considering both of the situations,  $-0.2 \text{ V}$  (versus DHE) was chosen as  $E_{\text{red}}$ . Though the value is not negative enough to meet the positive detection potential, the changed polarity had reversed the electrochemical reaction at both sides and would alleviate the electro-osmotic effect. In addition, the over-oxidized catalyst layer caused by long-term anodic potential could be regenerated together with proton reduction [26]. The regeneration of the catalyst activity can make the electrode remain in good state.

As is known, anodic potential  $E_{\text{pre-oxd}}$  is to maintain a catalytically active surface by cleaning the absorbed species [16]. More positive potential is ideal for conventional Pt or Au electrode. However the potential more positive than 0.8 V (versus DHE) risks the dissolving of the ruthenium in anode. Fig. 4(b) shows the optimizing result for  $E_{\text{pre-oxd}}$  when 2 M methanol flows through the sensor at  $50^\circ\text{C}$ . The currents of detection step and anodic step are shown as a function of  $E_{\text{pre-oxd}}$  using a constant  $E_{\text{red}}$  value of  $-0.2 \text{ V}$ . It was illustrated that the current of anodic step increases obviously with  $E_{\text{pre-oxd}}$  increasing. But

the detection current decreases with the increasing of  $E_{\text{pre-oxd}}$ . It was widely reported that the absorption of intermediate species, such as CO is still obvious at PtRu electrode, which strongly depends on the electrode potential [27,28]. Oxidation of CO at the potential lower than 0.6 V (versus DHE) was verified by CO-stripping experiments [29]. So in this work 0.6 V (versus DHE) was chosen as  $E_{\text{pre-oxd}}$  to assist the oxidation of methanol without serious absorption of poisons and maximally reserve the activity of PtRu catalyst.

Distinguished from conventional planar electrode, the MEA is porous structure with large interface area of three phases. When potential step is applied to the electrode, large charging current is unavoidable at the beginning of steps, so low frequency is necessary to avoid the charging effect. From experiment results we observed that the charging current will not disappear until the process prolongs for 1 or 2 s. These characteristics limit the high frequency application. Luckily, the low frequency will not retard the response because methanol diffusion across Nafion membrane limits the response time to some dozens of seconds for the sensor based on MEA. So 10–500 mHz low frequency waveform can be used. In the present work, 67 mHz low frequency (5 s for every step) was used.

Fig. 5 shows the PAD result for this sensor when the methanol concentration was step changed from 0 to 1.5 M using the unique triple potential waveforms at  $50^\circ\text{C}$ . With methanol concentration increasing, the response current (outlined by detection points, shown by "a" in the graph) increases. The result of PAD agrees well with the result of potentiostatic mode (shown by "b" in the graph). The response current of 1 M methanol solution was enlarged in the inset part. As observed two anodic current pulses (anodic step followed by the detection step) with one cathodic current pulse appear repeatedly. It is evident that the large charging current about 200 mA appears at the beginning of every step. The capacitance effect was significantly enhanced at MEA comparing with conventional planar electrode. Furthermore, the

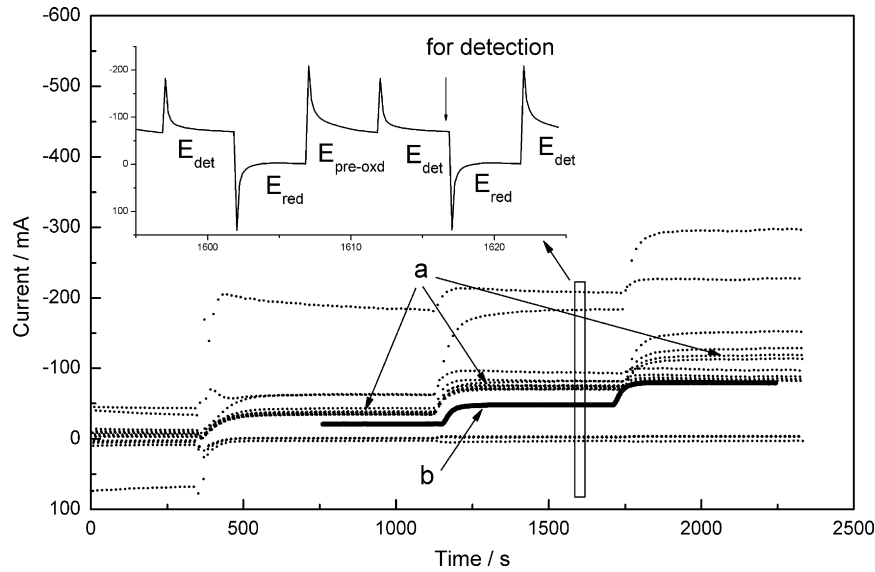


Fig. 5. Sensor response current vs. elapsed time for step change of methanol concentration from 0 to 1.5 M operated in pulsed mode in comparison with potentiostatic mode (solid line) at 50 °C. (The inlet is the partially enlargement of pulsed result.)

detection current obtained in PAD is higher than that obtained in potentiostatic mode for defined methanol concentration. This is the consequence of the unstable concentration distribution in the electrode when pulsed potential is applied to the membrane electrode. The transient stripping current of methanol oxidation obviously attributes to this phenomenon. In addition, the relatively small potential change between  $E_{pre-oxd}$  and  $E_{det}$  leads to decreasing charging current with a certain extent.

Fig. 6 shows two periods of the signal for methanol solution with 0, 1, 2 and 3 M in pulsed mode. As observed the amperometric response increases significantly with increasing concentration. The current at the end of detection step is proportional to concentration. It is interesting that not only the detection current but also the shape of curve change with concentration. At the initial part of detection step, the charging current decreases with increasing concentration and a dull peak appears

when the concentration exceeds 3 M. As is known, the absorption of methanol at the surface of PtRu catalyst can change the interfacial capacitance greatly. The increased oxidation current may overwhelm the charging current if methanol concentration increases. This may attribute to the shape changing with concentration. The tolerance of high current for current measuring device seems beneficial from the sluggish increase of charging current especially at high concentration.

The current at the end of detection step was chosen to be the amperometric response to minimize the charging effect. Fig. 7 shows the working curves of the sensor at different temperatures obtained in pulse mode. The sensitivity was increased in pulse mode. As for 50 °C the sensitivity of  $73.2 \text{ mA M}^{-1}$  is about twice as high as that of potentiostatic mode. It is evident that a cluster of curves of the current versus concentration is different from the potentiostatic result [5]. The increase in amplitude with ele-

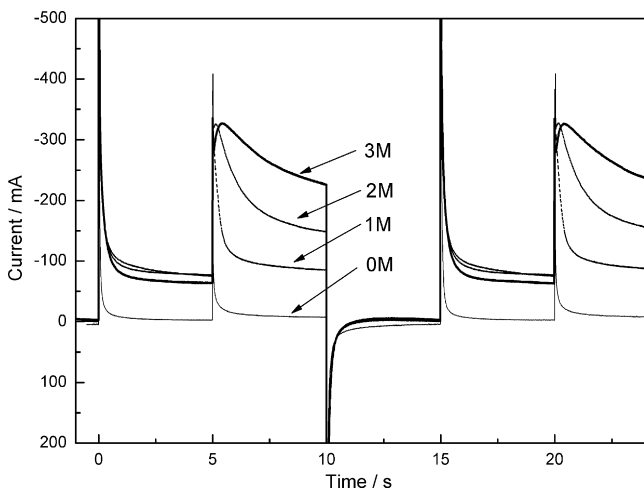


Fig. 6. Two periods of PAD response for methanol concentration (0; 1; 2; 3 M) at 50 °C.

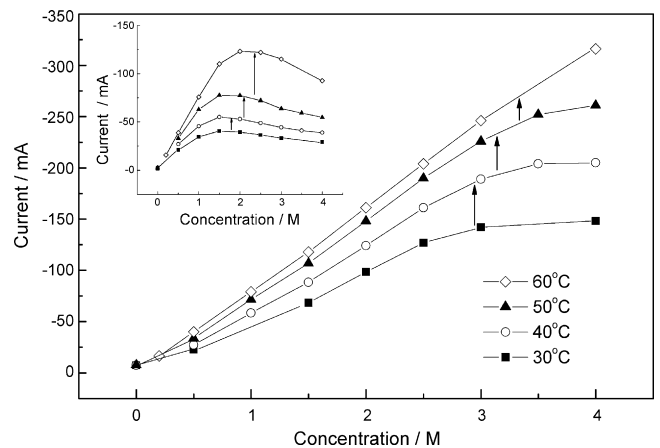


Fig. 7. Response current of the sensor operated in pulsed mode (sampled at the end of  $E_{det}$ ) vs. methanol concentration at various temperatures. (The inlet graph: current sampled at the end of  $E_{pre-oxd}$  (0.6 V) vs. methanol concentration at different temperatures).

vating temperature is not well-proportioned comparing with the result of potentiostatic mode. It is obvious that the linear relationship between current and concentration was greatly enhanced when temperature increased and the linear range was expanded from 2.5 M at 30 °C to more than 4 M at 60 °C. As observed, the upper limit of the linear range can be taken as saturation concentration. When temperature increases to about 60 °C, the saturation concentration can exceed 4 M. However, the working curves in potentiostatic mode (shown in Fig. 3) shows the uniform non-linearity in the whole concentration range even at high temperature. It is reasonable that at more positive potentials, methanol oxidation is mainly via  $\text{CO}_{\text{ad}}$  and the rate of oxidation is largely limited by the oxidation rate of CO [30]. Thus, during long-term potentiostatic operation, the intermediate species such as CO can accumulate at the electrode, thus lower the activity of electrode. In pulsed mode, the effect can be alleviated by the pre-oxidation steps. In order to show this effect, the current at the end of pre-oxidation step was illustrated as a function of concentration (shown in the inset graph in Fig. 7). A set of bell shaped curves at different temperatures was observed. The oxidation rate of poisoning species at PtRu electrode surface can be accelerated when methanol concentration increases over several molars [21], which can be confirmed by the decrease of pre-oxidation current in anodic steps. So, the effect of cleaning poisoning species was revealed by the maximal current.

Furthermore, on increasing temperature, the amplitude of pre-oxidation current (shown by arrows) increases obviously with increasing temperature. The increasing of amplitude seems to compensate for the decreasing in detection step. In order to analyze the relationship of compensation, the addition of detection current and pre-oxidation current is shown in Fig. 8. Under the same condition, the current is about 70% larger than in potentiostatic mode which is the consequence of transient potential pulse. The concentration dependence with a non-linear trend and temperature dependence with a linear trend agree with working curves of potentiostatic mode. Thus, the pre-oxidation step can calibrate the bias and alleviate the saturation by partially oxidizes the poison material accumulated during detection steps. This calibration effect was enhanced by increasing temperature and the linearity range was expanded as a result.

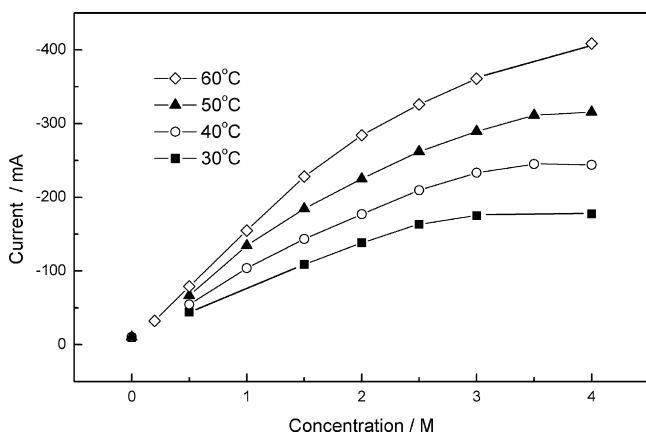


Fig. 8. The addition result of detection current and pre-oxidation current vs. concentration at different temperatures in pulsed mode.

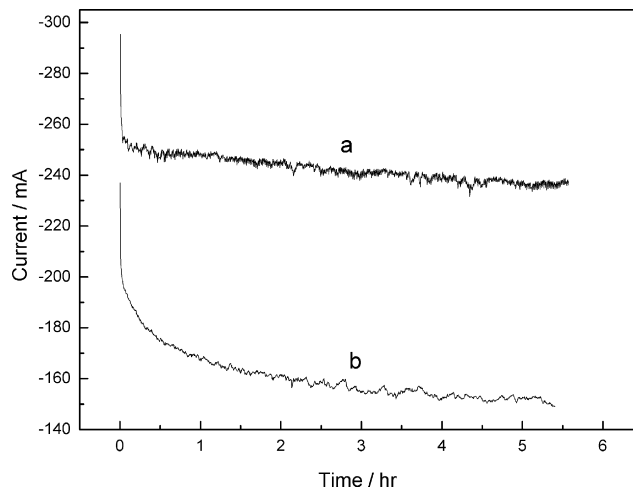


Fig. 9. The stability test of sensor at 50 °C in pulsed mode (a) and in potentiostatic mode (b). Methanol solution: 2 M at flow rate of 2.6 ml min<sup>-1</sup>.

### 3.4. Stability test

Fig. 9 shows the stability test result of the sensor in pulsed mode. For comparison, the result in potentiostatic mode is also shown in this figure. The current value comes only from the detection steps. As can be observed from the result, the current is relatively higher than that in potentiostat mode due to characteristic of transient measuring. The high currents are observed at the beginning of tests in two modes. However, the stability in pulse mode is distinguished from the potentiostatic mode. The current in potentiostatic mode decreases exponentially with time at a degradation rate of 30 mA h<sup>-1</sup> for the first hour. However, the current in pulsed mode is stable during about 6-h test with a slightly linear degradation rate of 2.9 mA h<sup>-1</sup>. This is the result of regenerating catalyst active surface by cathodic pulse and anodic pulse repeatedly. So it is highly advantageous to operate the sensor in pulsed mode.

## 4. Conclusions

The twin-MEA-assembled sensor operated in pulsed mode shows good performance in the methanol concentration range of 0–4 M. The linear relationship between current and concentration is greatly enhanced in PAD mode especially at high temperature. Moreover, the long-term operation test shows that the sensor operated in pulsed mode is more stable than potentiostatic mode. Both the electroosmotic phenomenon and the anodic saturation phenomenon occurred in potentiostatic mode can be alleviated by employing the low frequency triple potential wave-form in the pulsed mode. The simple constructed sensor operated in pulsed mode is promising for the determination of methanol concentration at the levels expected in DMFCs.

### Acknowledgements

This work was financially supported by Innovation Foundation of Chinese Academy of Sciences (K2003D2), National Natural Science Foundation of China (Grant No. 20173060),

Hi-Tech Research and Development Program of China (2003AA517040) and Knowledge Innovation Program of the Chinese Academy of Sciences (KG CX2-SW-310).

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