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A Methanol Concentration Sensor Using Twin Membrane Electrode Assemblies for Direct Methanol Fuel Cells

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A methanol concentration sensor based on twin Nafion membrane electrode assemblies (MEAs) was constructed with anodes face to face eliminating the interference of oxygen in environment. The signal of the sensor was obtained by electro-oxidation of the methanol crossing over Nafion membranes from cathodes. During operation, carbon dioxide as a product of methanol oxidation not only was expelled from the gaps between two MEAs, but also permeated across the membranes into the cathodes, which was confirmed by GC in the outflowing stream of the sensor. Electrochemical characterization shows that the sensor has good response performance with a concentration range up to 5M and the signal increases with temperature elevating. The slightly nonlinearity of the working curves was mainly caused by electro-osmotic effect confirmed by electro-osmotic drag coefficient. Though logarithm tendency degradation with 0.9% hr^{-1} was observed from stability test, the performances in terms of high sensitivity to concentration with wide measuring range and signal recovery characteristics show that the sensor is promising for direct methanol fuel cells.

Keywords: Fuel cell, Sensor, Methanol concentration, Membrane electrode assembly (MEA)

1. INTRODUCTION

Direct methanol fuel cells (DMFCs) have received great attention as power sources ranging from transportation to portable devices because of their high energy density and comfort of operating with liquid fuel[1]. However diluted methanol is usually used to reduce methanol crossover from anode to cathode, which results in decrease of the system power density. As an ideal method, feeding direct methanol fuel cells with pure methanol can increase the system power density greatly.

Sensing methanol concentration have previously been developed by exploration of electrical, optical, sonic, magnetic or other properties[2-4], but no one seems mostly suitable for practical application in DMFCs. Electrochemical sensors operating on the potentiometric or amperometric principle are based on limiting current of methanol oxidation across a barrier layer such as Nafion membrane[5, 6].

Passive mode sensor works like a fuel cell eliminating additional power source[7-9]. But oxidant dependence and concentration saturation limit their application for high concentrations. These drawbacks can be avoided in drive mode where the concentration signal is obtained by applying a definite potential to the sensor anode. At cathode hydrogen is produced continually, serving as a dynamic hydrogen electrode (DHE). The reactions are as follows:

Anode: $CH_3OH+H_2O-6e = CO_2+6H^+$
Cathode: $6H^++6e = 3H_2$

Nafion membrane acts not only as solid electrolyte but also as a barrier layer in the cathode feeding sensor[5]. However, purging anode by inert gas continually seems to limit its application. The anode feeding sensor can measure methanol concentration in tank[10, 11] or in stream[12]. But the anode saturation needs to be alleviated when solution is more than 2M due to weak barrier effect. As a simple design, Ren et al sealed anode chamber to eliminate oxygen interference from air[9]. However the accumulation of anodic products seems to affect the performance. Composite membranes with deposited palladium was put forward by J.H.Shim et al[13] using the same principle. Too complicated art may limit its practical application.

In this work, a methanol concentration sensor was constructed using two MEAs with anodes face to face forming a half-sealed structure eliminating the interference of oxygen in environment. The performances of the sensor were characterized by electrochemical method and showed a good concentration response.

2. EXPERIMENTAL PART

2.1 Construction of the sensor

The membrane electrode assemblies (MEAs) were fabricated according to the method described in the literature[14]. Nafion®-117 (thickness: 178μm; 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 mg cm^{-2} and 2.0 mg cm^{-2} respectively.

Nafion-bonded SGL carbon papers were employed as gas diffusion layers. Figure **1** shows the schematic arrangement of the sensor. It was assembled using two MEAs (effective size: 5mm×8mm). 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. A picture of a prototype sensor is shown in Figure 2.

2.2 Measurement of methanol concentration

Hydrogen evolution and methanol oxidation occurs at cathodes and anodes respectively at the same time when a definite voltage is applied .Two cathodes of the sensor can be taken as pseudo-reference electrodes due to fast electrochemical reaction. The signal was obtained by electro-oxidizing the methanol permeating through Nafion membrane from feeding stream of cathodes. The carbon dioxide produced by the oxidation of the methanol in the anode chamber could be expelled out through the tiny openings or enter the cathode chambers across Nafion membrane.

Compared with single MEA structure[5], the two MEAs arrangement with anodes face to face eliminates the oxygen interference from air, increases the sensitivity and guarantees the performance. The hydrogen generated at the sensor cathodes would not disturb the working of fuel cell stack because it can be oxidized together with methanol.

Measurements were carried out by feeding methanol solution through the two cathode chambers in tandem. In order to maintain the sensor temperature, methanol solution flowed through a heat exchanger previously, which was bathed in hot water (deviation is ±0.2%). Methanol solution was driven by peristaltic pump at an average flow rate of 4ml min^{-1}.

CHI 760B electrochemical workstation together with supporting software (version 4.23) was used to control the potential of the anode.

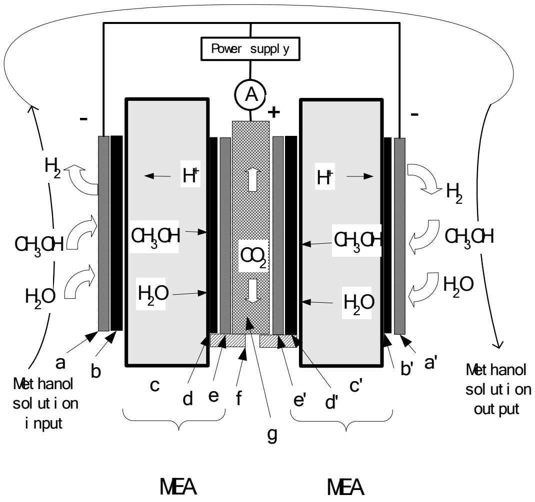

Figure 1. Schematic diagram showing sensor configuration: (a),(a'),(e),(e') gas diffusion layers ; (b),(b') catalyst layers of cathodes; (c),(c') Nafion membrane; (d),(d') catalyst layers of anodes; (f) gasket with vent and (g) meshy current collector.

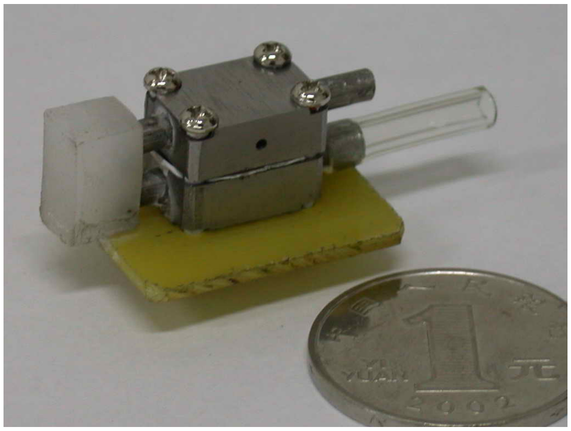

Figure 2. A photograph of the prototype sensor.

3. RESULTS AND DISCUSSION

3.1 Responses to concentration and temperature

The cyclic voltammetry (CV) results of the anode are illustrated in Figure 3 , which shows the electrochemical responses to concentration and temperature. The experiment was carried out after the methanol solution had flowed through the sensor for 5 minutes. The peak current of methanol oxidation appears in the potential region of 0.6 to 0.8V (vs. DHE) as observed in Figure 3a. The result is consistent with that of literature[18], which shows that the cathode potential is stable due to the formation of dynamic hydrogen reference electrode. The peak current of CV is proportional to methanol concentration which showed a good concentration response.

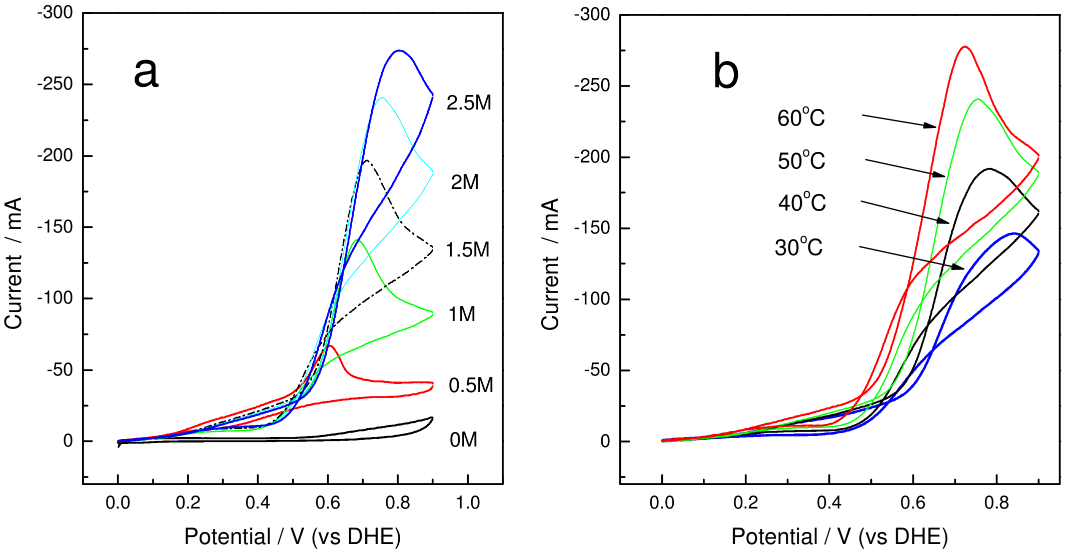

Figure 3. Cyclic voltammograms of the sensor (anode as working electrode, cathode as counter electrode and reference electrode) at a scan rate of 20mV s^{-1}. Flow rate of methanol solution, 4.2ml min^{-1} (a) effect of concentration on CV (50 ^{o}C) (b) effect of temperature on CV (2M)

The phenomenon of peak potential shift with concentration is in good agreement with Barton’s results [5]. The resistance calculated from the potential shift with corresponding current increasing is 0.96 ohm which is larger than the measured inner-resistance of 0.25 ohm. This phenomenon may be caused by electro-osmotic effect [19]. The more proton transfers from anode to cathodes following the increase of current, the more methanol is inhibited to diffuse from cathode to anode. Furthermore, the forward peaks of the CV results are obvious even concentration rises over 3M. It is believed that the intermediate poisoning species exist on the catalyst surface throughout a large concentration range[20].

Figure 3b shows the temperature effects on the performance of the sensor obtained by CV experiments with 2M methanol solution feeding through the sensor. The peak potential shifts negatively with temperature increasing, at a slope of 3.9mV K^{-1}, which is three times of onset potential shift with temperature reported by Noriaki Wakabayashi et al[21]. This may be caused by lower activation energy of methanol oxidation [22]. Furthermore, the peak current is proportional to the temperature at slope of 11mA $cm^{-2}K^{-1}$, which implies that elevating temperature could increase the response of the sensor.

The potential applied to the sensor anode can be obtained from CV results. The anode potential higher than 0.7V (vs. DHE) promotes the establishing of limiting current, however, too high potential could lead to the dissolving of Ruthenium[15]. Thus, 0.8V (vs. DHE) was chosen as anode detection potential. Without additional explaining, the operation voltage refers to 0.8V (vs. DHE) in this paper.

Figure 4 shows typical current responses of the sensor to the step change of the methanol concentration at 50°C. A baseline of current was first established when 0.5M solution was fed through the sensor after high charging current passed through. Then the feeding methanol concentration was increased by switching to different solution every ten minutes. The current increases significantly with increasing concentration between 0.5M and 2M, which indicates good response performance. The current in the plateau region shows some fluctuation with time, but the average remains relatively constant. It is believed that the fluctuation may be related to the bubbling of hydrogen out of the cathode. For the reported sensor[12], saturation phenomenon was serious when the concentration exceeds 1 M. But for this sensor the phenomenon was slight even the concentration exceeds 4M.

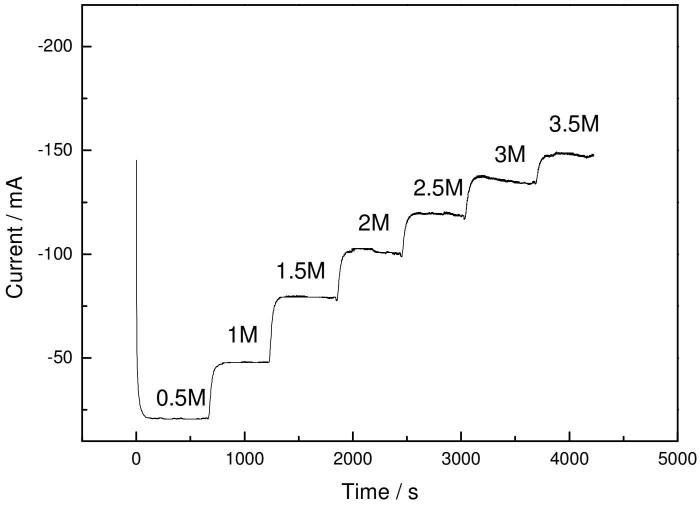

Figure 4. Sensor response current vs. elapsed time for step change of methanol concentration at 50 °C.

Figure 5 shows the working curves of the sensor at different temperatures obtained from plateau value after 10 minutes stabilization. The current increases with concentration increasing as observed from the result. However, it is likely that the saturation exists throughout the whole concentration range showing a nonlinear relation ship between current and concentration. The phenomenon becomes obvious when concentration exceed 3M. Several factors may attribute to the deviations such as the electroosmotic drag effect, the diffusion coefficient of methanol in Nafion membrane and the gas pressure of carbon dioxide [16] etc.

Considering the elecro-osmotic effect[17], the response current results in the following expression:

$$I=(mT+b)\ C\ \frac{\ln(1+6\xi x_0)}{6\xi x_0}$$

where the m is temperature coefficient, b is constant item, C is concentration, ξ is the electro-osmotic drag coefficient of protons in the membrane and x_0 is the molar fraction of methanol in the feed aqueous methanol solution.

Assuming electro-osmotic drag coefficient is only affected by concentration, the least squares fitting result was obtained (shown by solid lines in Figure 5). So the temperature coefficient (m), $3.3\text{mA}\cdot\text{cm}^{-2}\text{M}^{-1}\text{K}^{-1}$, was obtained from the working curves, which is useful for calibrating the response of the sensor. Accordingly, electro-osmotic drag coefficient was 2.1, which is consistent with reported value[18, 19]. Thus, the electro-osmosis is the main reason for the saturation phenomenon.

Furthermore, the methanol diffusion coefficient in Nafion membrane at 30 °C was found to be 9.7×10^{-6} $\text{cm}^2\cdot\text{s}^{-1}$. The result seems greater than NMR result[20]. But the calculated limiting currents, 115mA cm^{-2} and 212mA cm^{-2} respectively according to the result of 1M and 2M at 80 °C, are in good agreement with the data reported in the literature[17]. So, the limiting current is mainly controlled by Nafion membrane as a barrier layer, which attributes to the slight saturation phenomenon compared with the sensor of anode feeding[12].

The wide measuring range up to 5M and the low background current of 7 mA make the sensor more flexible to be used in DMFCs. The same measuring range sensor utilizing electrochromic properties of the aged nickel oxide film was reported by Shim et al[4], but nearly 30% background seems limited its sensitivity.

The sensitivity of sensor shown by 60mAM^{-1} at 60 °C can be obtained. Compared with planar-structure sensor[21], high sensitivity is of great use for the control of the system.

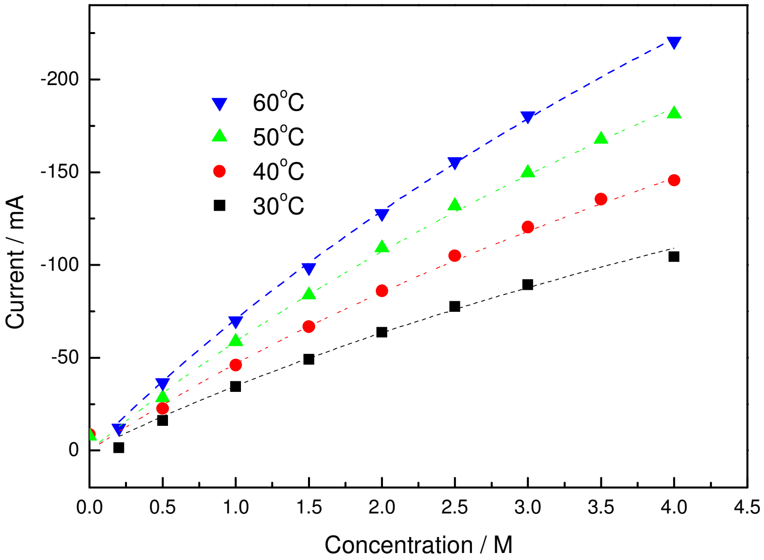

Figure 5. Sensor response current vs. methanol concentration at various temperatures. (dot: experiment result; solid line: fit result).

3.2 Product analysis

Gas chromatogram was used to analyse the composition of effluent gas from cathodes to make certain that the carbon dioxide can permeate outside not only through the gaps between two MEAs but also through Nafion membranes into the cathode stream. Though carbon dioxide can permeate across Nafion membrane as reported[9], the experimental data relating to this issue is still scarce. Figure 6 shows the gas chromatogram results of effluent gas from the sensor operated at 50 °C, 0.8V (vs.DHE). The effluent gas in the methanol stream was firstly collected by water displacement method. After separation, 100μl sample was injected into the gas chromatogram (GC14B ,PQ column, TCD detector at 180 °C; helium as carrying gas).

Figure 6a shows the GC result at 40 °C. The retention time was used to identify hydrogen, carbon dioxide, water and methanol by injecting standard substance in the GC. It can be seen that carbon dioxide exists in the effluent gas. Figure 6b shows the percentage of carbon dioxide calculated from the peak area corrected by correction factor. The result shows that percentage of carbon dioxide increases with temperature elevating. This is probably due to the increase of methanol oxidation efficiency[22]. At higher temperature such as 60 °C, the volume percentage of CO_2 is still less than 4% after correcting the dissolving part in water. Thus, carbon dioxide is mainly released from the gaps between two MEAs.

In addition, the volume of effluent gas (collected for 10 minutes) was analysed as a function of temperature (shown in Figure 7). The temperature dependency of the electrode reaction was in agreement with the CV result. Assuming the Faraday efficiency of cathodes is the ratio of the hydrogen volume obtained experimentally to the theoretical value calculated from current accordingly. The efficiency also increases with increasing temperature. The dissolved little oxygen in methanol solution, which can be electro-oxidized may attribute to this phenomenon, for the purging effect by hydrogen bubbling can be enhanced when temperature increases. Thus, higher temperature is of great advantage to the sensor.

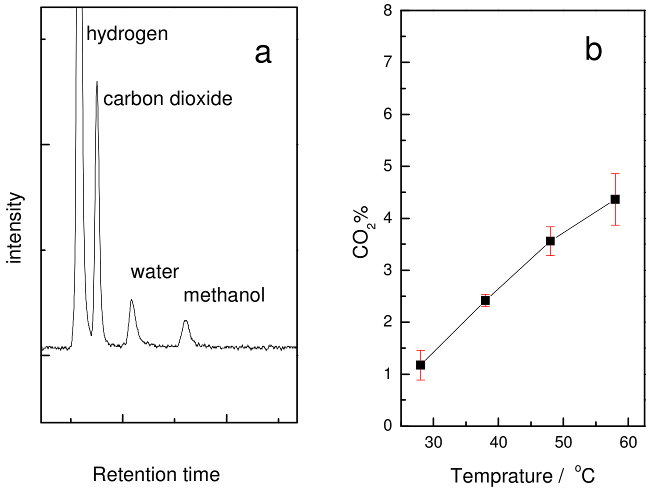

Figure 6. Gas chromatogram results of effluent gas from cathodes: (a) original GC result at 40 °C (b) volume percentage of CO_2 from cathodes of the sensor in the effluent gas.

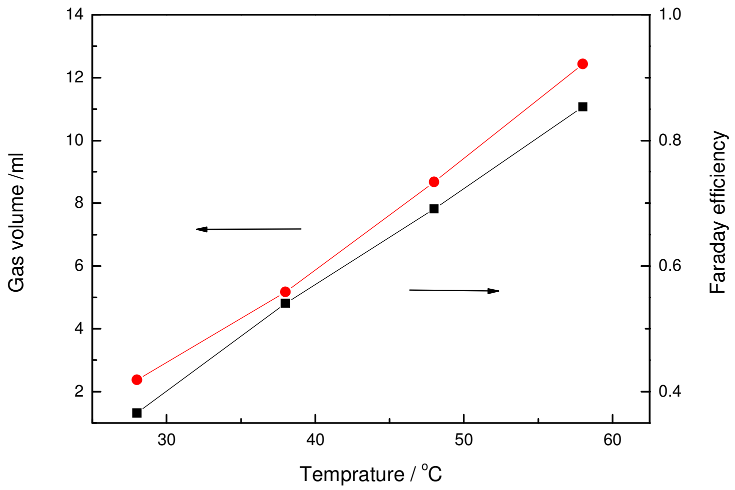

Figure 7. Volume of effluent gas collected for 10 minutes at different temperatures and the Faraday efficiency of cathodes calculated accordingly

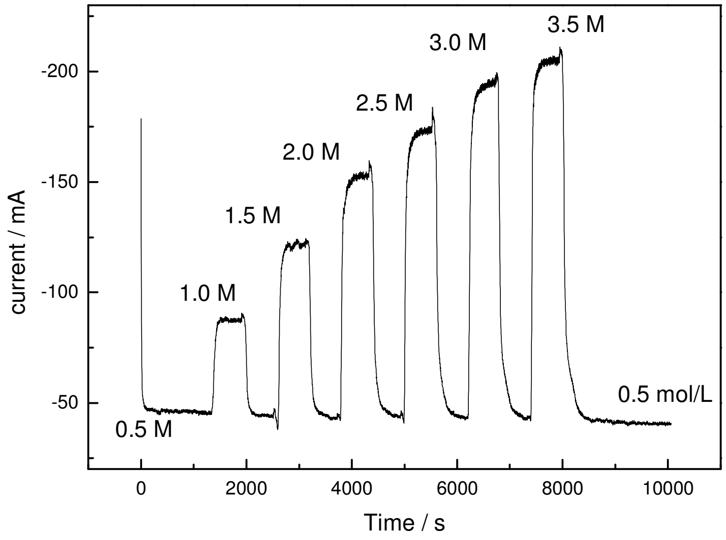

Figure 8. Stability test for the sensor by changing methanol solution between different concentration and 0.5 M every 10 min interval

3.3 Stability test

Stability is rarely reported for the sensor based on MEA, but it is crucial for the practical application. Figure 8 shows the result of stability test by concentration impacting. The sensor was operated continually at 55 °C maintained by pumping preheated methanol solution of 0.5 M through at a flow rate of 3.4 ml min^{-1}. The voltage applied between anode and cathode was maintained by 0.8 V throughout the test. The stability of the sensor was characterized by concentration impacting. Different concentration solutions were pumped through the sensor increasingly, maintained for ten minutes and then, replaced by the solution of 0.5 M. The current response at 0.5M was repeated with an extent of 98% indicating the relatively high stability in short time.

However, the long-term stability test result is not so satisfactory. Figure 9a shows the result of about 40 hours test. During the test, constant voltage (0.8V) was applied between the sensor anode and cathode throughout the test. Temperature of the sensor was maintained at 50 ^{o}C. 2M methanol solution was pumped continually at 3.4 ml min^{-1} flow rate through the sensor. The result shows that the current attenuation is obvious. For the first 3 hours, the current attenuation rate is about 6.7 % hr^{-1}. After that, the current attenuation slowed down to a rate of 0.9% hr^{-1}. The logarithm of current for the first 24 hours is shown as a function of time (Figure 9b.), the result shows that the attenuation obeys a good logarithm tendency. It is interesting that when the operation was resumed after a few seconds interval, the signal was resumed sharply with a recovery of 70%. This phenomenon also occurs in DMFC[23, 24]. The reason of the reversible attenuation is not clearly understood to date, but it is probably related to the formation of some Ru oxide[25].

This reversible recovery indicated that an intermittent operation seems promising for this sensor. Figure 10 presents the intermittent life test of the sensor integrated with circuit module for about 7 days. As observed the signal is recoverable during the last 6 days life test. However, the signal can not resume to the original level of the first day. Long time operation of the sensor can cause the catalyst surface poisonous by intermediate species [26, 27], but the unrecoverable degradation seems to be greatly inhibited by the following interval operation. In addition, no obvious degradation was observed over a shelf life of 4 months.

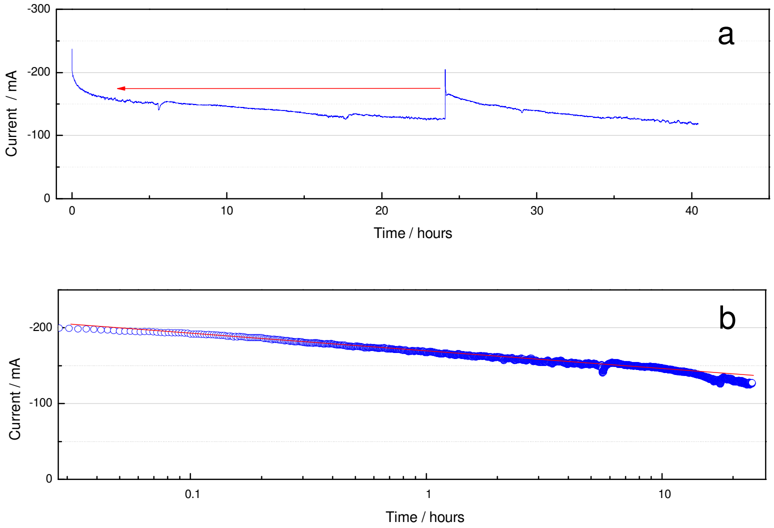

Figure 9. Stability test of the sensor (a) 40 hours test with an interrupt at 24 hours. (b) the logarithm of current vs. time for the first 24 hours result. The concentration of testing methanol: 2M, The potential applied to anode: 0.8V (vs. DHE), the flow rate of methanol solution: 3.4 ml min^{-1}, temperature maintained at 50 ^{o}C.

Further work is still necessary to investigate the degradation of the sensor especially at first several hours and to increase the stability of the sensor.

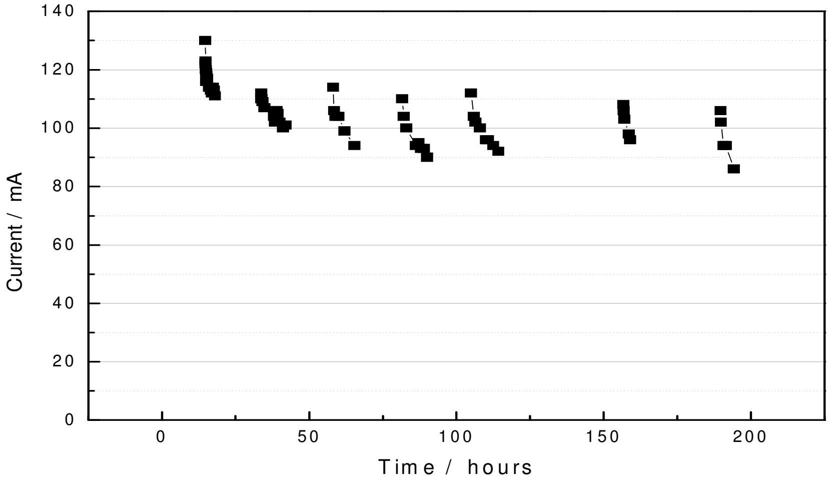

Figure 10. Life performance of the sensor in intermittent operation. The concentration of testing methanol: 1.5M; the potential applied to anode: 0.8V (vs. DHE); the flow rate of methanol solution: 3.4 ml min^{-1}, temperature maintained at 50 ^{o}C.

4. CONCLUSIONS

The two conventional MEAs using Nafion membrane were used to assemble methanol sensor. The symmetrical MEAs arrangement, with anodes face to face, eliminates the oxygen interference. Carbon dioxide reentering methanol stream across Nafion membrane was confirmed by gas chromatogram. Experimental results show that the higher temperature has significant effect on the sensor performance i.e. broadening concentration measuring range up to 5M, increasing Faraday efficiency of cathodes. The electro-osmosis in Nafion membrane is the main reason attributing to the saturation phenomenon throughout concentration range. Furthermore, the stability of the sensor was investigated. The degradation of current over long-term operation was a logarithm tendency and an intermittent operation is of great advantageous to increase its stability. The sensor is promising for DMFCs due to its high performance and simple construction.

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