



Investigation of methanol crossover and single electrode performance during PEMDMFC operation

A study using a solid polymer electrolyte membrane fuel cell system

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Abstract

Direct Methanol Fuel Cells (DMFC) employing Polymer Electrolyte Membrane (PEM) electrolytes have recently gained considerable interest because they are attractive candidates for vehicular applications. A manifold of potential sources of performance losses exists for these systems, a very serious one being methanol crossover across the membrane electrolyte. This work is focused on the dependence of crossover on reaction conditions, such as temperature and methanol concentration. Anode performances are also evaluated. Results are given for the establishment of single electrode potentials during cell heat-up and of single electrode performances during operation under various conditions. Additionally, a cyclic voltammetry technique is presented, which allows the evaluation of methanol crossover in a fuel cell under operating conditions. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

Considerable efforts have recently been made in the field of Direct Methanol Fuel Cell (DMFC) electrocatalysis [1–9]. Systems considerations for whole fuel cell units become necessary with the advent of a certain advanced stage in fuel cell electrocatalysis, as in general, poor catalytic activities are not solely responsible for limited fuel cell performances, of which a recent compilation is given in Ref. [10]. Material issues certainly need revived efforts [11], and gas flow distribution is also of importance. One of the major chemical problems is fuel crossover in the DMFC and its impact on cathode operation and system efficiency. This has already been focused on [1–3,5–8], but needed further characterization concerning its dependence on reaction conditions. Work of this type was recently carried out by means of fuel cell to Mass Spectrometer coupling [12]. In contrast, results obtained in this work represent a classical approach to fuel cell reaction engineering. As Polymer Electrolyte Membrane (PEM)

systems are currently the most promising ones for vehicular and stationary applications, our efforts have been devoted to their study. Different relations for successful PEMDMFC operation, such as dependence of anode and cathode performance on fuel concentration could be obtained using a rather simple experimental set-up [1].

2. Experimental

2.1. Electrode preparation

Gas diffusion electrode preparation and manufacture of membrane electrode assemblies (MEAs) employing the hot-pressing technique have already been described in great detail [1]. With the exception of E-TEK 20% Pt on Vulcan ELAT electrodes with a loading of 1.1 mg Pt/cm², which served as cathodes through the first part of this work, all other electrodes were of our own manufacture, i.e., chemically deposited 29% PtRu on Norit BRX was used as anode catalyst in the first part, and 60% PtRu on Ketjenblack was used in the second. The cathode used in the second part consisted of 20% Pt on active carbon

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(Heraeus). The atomic ratio between Pt and Ru was always close to 1:1. The anode noble metal loadings were 2.3 mg/cm² and 5 mg/cm². All electrodes were of squaric shape and of 6.25 cm² active electrode area.

2.1.1. Catalyst morphology

The catalysts employed represent a large variety of BET surfaces of the carbon supports. The properties of the supports are listed in Table 1.

For the anode catalysts, two different supports and deposition methods were employed: (i) 29% PtRu (1:1) on NORIT BRX was chemically deposited from chloride precursors using the formate reduction method [13] and, (ii) 60% PtRu (1:1) on Ketjenblack was chemically deposited using the sulphito colloid method [14]. The catalysts were characterized using transmission electron microscopy (TEM). TEM images of the anode catalysts are shown in Figs. 1 and 2. For a discussion see Section 3.2.3.

Two well-established materials were employed for the cathodes: (i) Pt on active carbon of unknown manufacture (Heraeus), which had already been introduced by Holze and Vielstich [15] and, (ii) Pt on Vulcan XC 72 R, which was used as part of ready-made ELAT-electrodes (E-TEK). For a TEM image see the front page of the 1996 E-TEK catalogue. A TEM image of the Heraeus catalyst is provided in Fig. 3.

2.2. Cyclic voltammetry under technical conditions

The investigations done in this work were carried out using a laboratory scale in-house built test fuel cell representing pre-stack technology. It was equipped with a Dynamic Hydrogen Electrode (DHE, [1]), allowing the registration of cyclic voltammograms in a DMFC under operating conditions. Details about this fuel cell test station have recently been given elsewhere [1,2]. The DHE was located

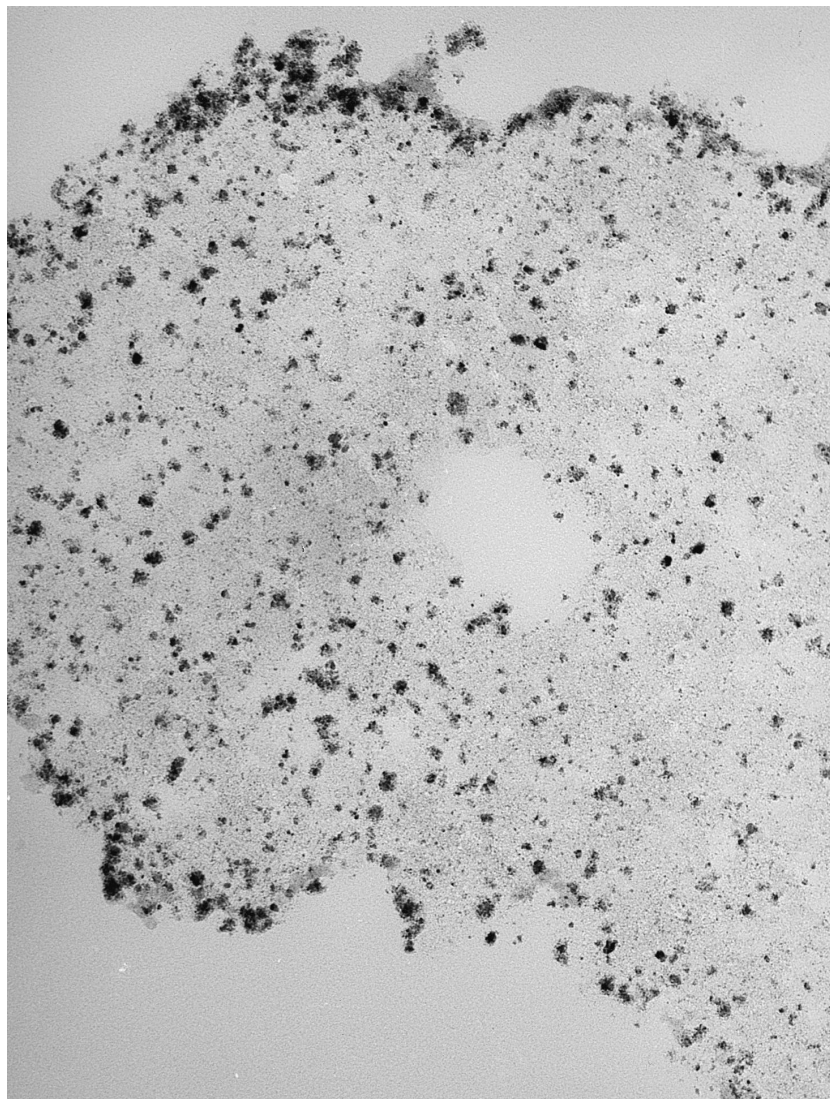


Fig. 1. TEM micrograph (200 000:1, Hitachi H-500-H) of the 29% PtRu (1:1) on NORIT BRX anode catalyst.

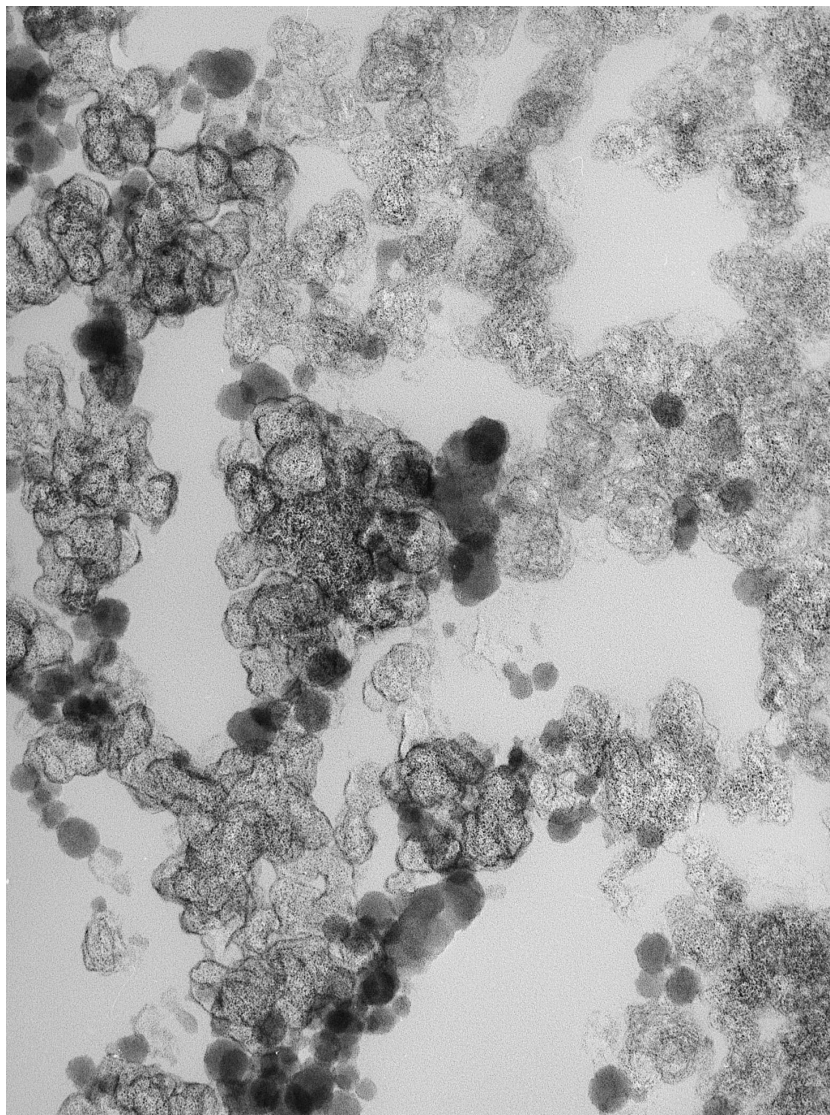


Fig. 2. TEM micrograph (200 000:1, Hitachi H-500-H) of the 60% PtRu (1:1) on Ketjenblack anode catalyst.

at the anode side of the MEA. The cell could be heated by means of resistive strap heaters obtained from Horst, Germany. Gaseous fuels were supplied using a filter-press-type gas humidification unit from Giner, operating on either circulated water and hydrogen gas or a circulated 20% methanol in water solution at 100°C. Argon (Messer Griesheim) was used to blow the methanol/water vapour into the cell. Stoichiometric operation on fuel vapour could not be adjusted. The only adjustment criterium was stable cell operation. The cell and humidifier temperatures were controlled by means of a TEMPAT temperature control unit equipped with 'Pt 100' (Sensycon) temperature sensors. Gas flows could be roughly controlled by flow-meters. Oxygen humidification was performed in the same way as given in Section 2.3.

Our 3-electrode set-up is in fact advantageous to the 2-electrode concept used by Srinivasan et al. [16] for cyclic voltammetry, because the counter electrode can deliver

high currents without being in danger of destruction and access to the investigation of both anodic and cathodic faradaic reactions is thus given. Furthermore, the influence of the anode feed upon the cathodic reaction could be studied. The potentiostatic circuit consisted of a Jaissle 10000 T heavy duty potentiostat, an in-house built function generator and a 'xyy' pen recorder.

2.3. PEMDMFC operation

The above described fuel cell, which was equipped with a Nafion™ 117 membrane electrode assembly (MEA), was connected to a fuel vaporiser, consisting of a PTFE tube, a controllable tube heater, an ice-cooled 200 ml fuel reservoir and an adjustable piston pump for fuel circulation. For a schematic drawing see Fig. 4. Different methanol contents in the anode feed were achieved by filling the reservoir with different mixtures of methanol and water so

that a fuel mixture was injected in the range of 1 to 50% by volume. The circulation speed was adjusted in such a way that cell operation was stable using the lowest methanol concentration.

The cathode compartment was fed with pure oxygen which was humidified by passing the gas through a bottle filled with distilled water. The humidification bottle was left at room temperature. The DHE reference electrode was then charged with hydrogen at ca. 20 mA during 30 min. Afterwards, the cell was slowly heated to 100°C by means of a resistive strap heater and the single electrode potential readings were followed. The membrane electrode assembly was allowed to equilibrate with fuel vapour and humidified oxygen at this temperature. Single electrode potential and cell voltage were determined as described in Ref. [1]. An in-house built power supply served as galvanostatic current drain.

3. Results and discussion

3.1. Voltammetric illustration of the effect of methanol crossover on technical cathodes

Recent improvements in the design of the technical PEMDMFC prototype gave access to in-situ data for methanol crossover investigations.

A membrane electrode assembly (MEA) consisting of a PtRu on carbon anode, an E-TEK ELAT Pt on carbon cathode of 6.25 cm² geometric area each and a Nafion™ 117 membrane was manufactured by hot-pressing [1]. This MEA was mounted between the cell's graphite plates, equilibrated with the respective humidified gaseous fuel and pure oxygen at 70°C and was then connected to the heavy duty potentiostat. The cathode was used as a working electrode in a 3-electrode voltammetric circuit. The

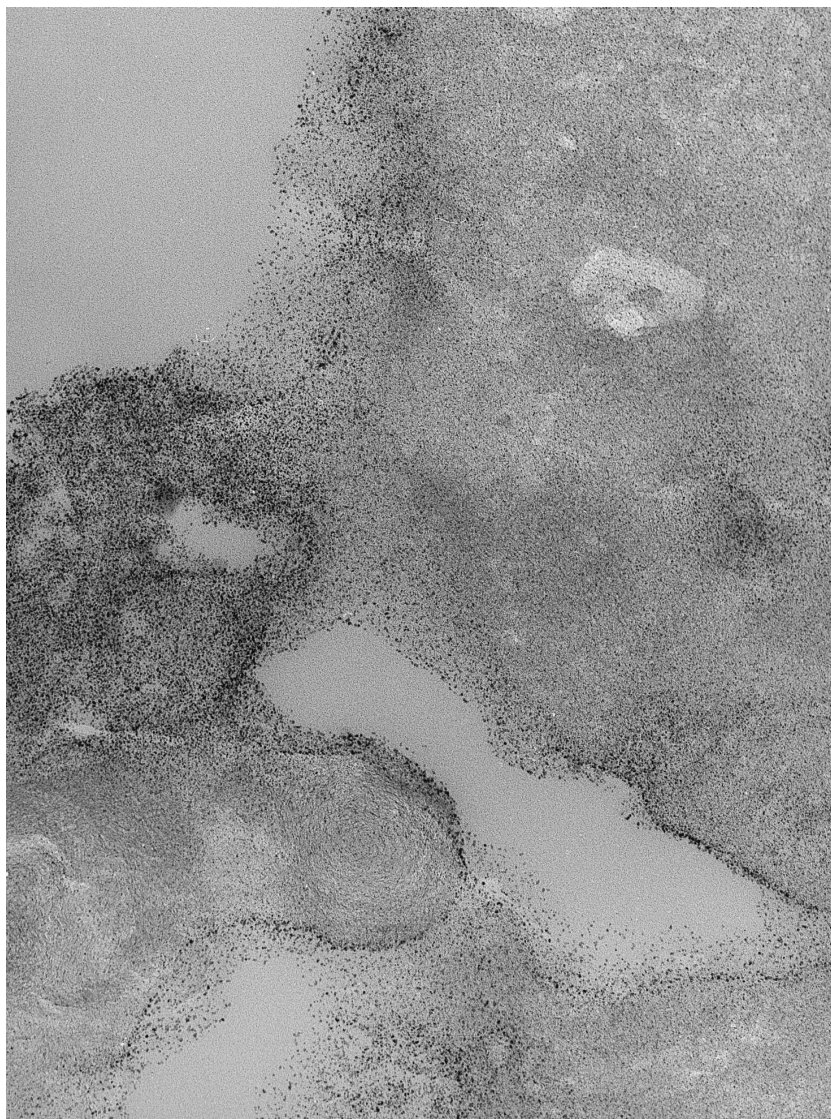


Fig. 3. TEM micrograph (200 000:1, Hitachi H-500-H) of the Heraeus 20% Pt on active carbon cathode catalyst.

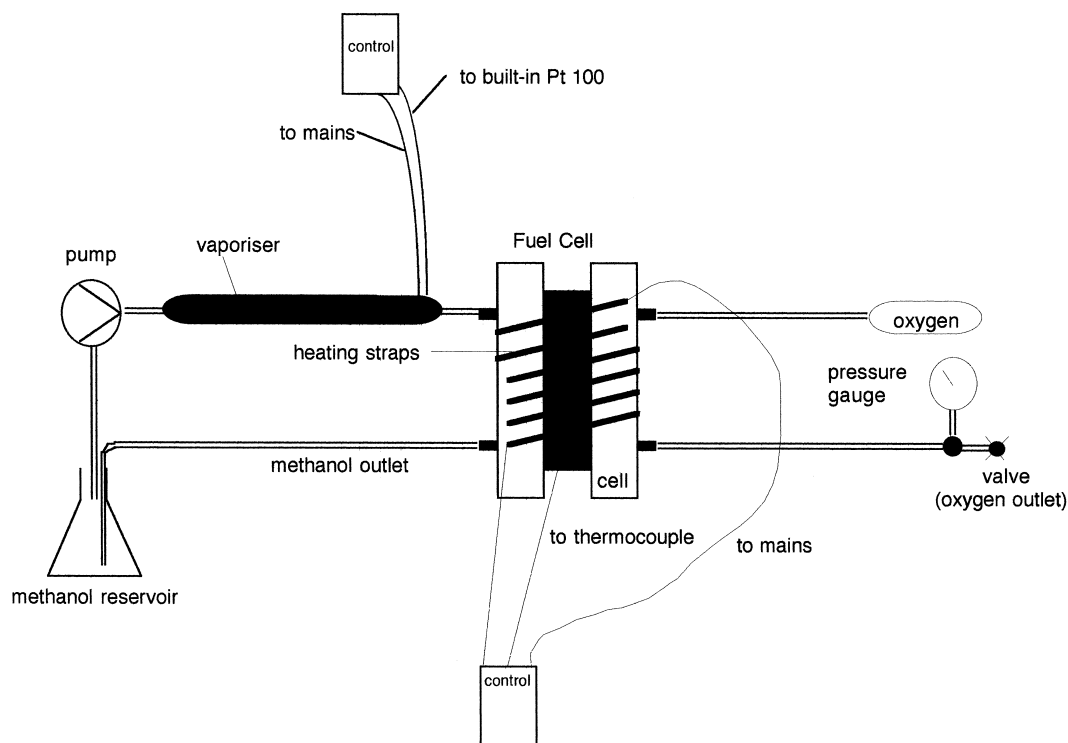


Fig. 4. Schematic description of the vapour-fed direct methanol fuel cell test station.

fuel cell was first fed with hydrogen as anode fuel and pure oxygen at the cathode side. The gas flows were roughly adapted to the highest current densities to be expected during a voltammetric scan. The circuit was then switched to potentiostatic control and a cathodic scan from 1050 mV to 450 mV vs. DHE and the subsequent anodic scan were recorded at 10 mV/s. The same procedure was employed when using methanol as fuel (Fig. 5).

It is interesting to see that (i) a rough estimation of the amount of methanol crossover can be obtained through an evaluation of the anodic section of the voltammograms. A value of 50 mA/cm² (corresponding to $1.6 \cdot 10^{-5}$ mol/s) can be found assuming that every methanol molecule crossing the membrane electrolyte gets oxidised at the cathode and that; (ii) the cathode's depolarisation amounts more or less to 100 mV, which is the same value as previously determined via stationary curves [1]; (iii) the above crossover data agree well with estimations presented by International Fuel Cells [6].

3.2. Whole-cell study of the dependence of single electrode potentials on methanol concentration during DMFC heat-up and operation

Results given in this section are an extension of the work described in Ref. [1]. The newly-constructed vaporising unit was employed here in order to allow the adjustment of different feed concentrations.

3.2.1. Observation of anode and cathode rest potentials under various conditions

A membrane electrode assembly (MEA) was fabricated in a similar way as previously described in [1], but using PtRu 60% on Ketjenblack manufactured by Prof. Hamnett's group at Newcastle University as anode catalyst, and Heraeus 20% Pt on active carbon as cathode material. The fabrication process provided a MEA loaded with 5 mg/cm² PtRu for the anode and 1.7 mg/cm² Pt for the cathode.

The establishment of anode and cathode open circuit potentials during cell heat-up as a function of methanol concentration and temperature was assumed to be a first fingerprint for the catalytic activity of the electrodes. Results for circulated solutions of 2% methanol and 10% methanol in water are shown in Figs. 6 and 7. Circulation speed was equal to the minimum speed necessary for stable fuel cell operation with 2% methanol. The curves basically show the same trends towards establishment of lower methanol potentials at high temperatures. On the other hand, the cathode *open circuit* potentials depicted in Figs. 6 and 7 differ by ca. 50 mV, indicating once more that methanol crossover is significantly lower at low methanol concentrations in the anode feed. The methanol potentials do not seem to be significantly affected by a variation of methanol concentration as further variations between 1% and 50% yielded anode potentials in the same range. It has to be noted, however, that stable cell operation under load was by no means possible using 1% methanol in water as gaseous anode feed because fuel

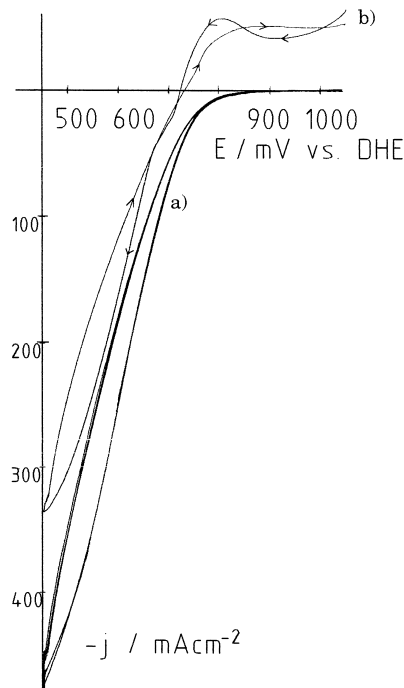


Fig. 5. Cyclic voltammograms obtained at 70°C using '3-electrode fuel cell cyclic voltammetry' and a Nafion™ 117-bonded E-TEK gas diffusion electrode. (a) Oxygen reduction in the presence of hydrogen in the anode compartment, (b) oxygen reduction in the presence of methanol in the anode compartment. Scan rate: 10 mV/s. Pure oxygen, no overpressure.

depletion caused the anode potential to rise unacceptably, even at high pumping speeds.

Another feature is quite remarkable in these experiments: following a decrease between 50 and 92°C, a slight increase of the oxygen open circuit potential can be observed for both methanol concentrations (2% and 10%) above ca. 92°C. We believe that methanol crossover is

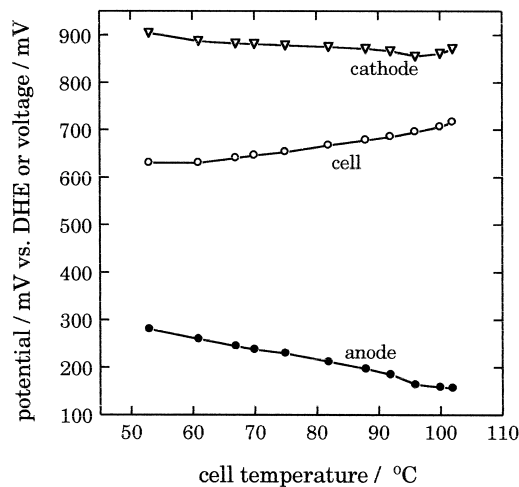


Fig. 6. Plots of open circuit cathode potential, anode potential and cell voltage as a function of temperature. Measured values were observed during cell heat-up using 2% by vol. methanol in water in the anode compartment and pure oxygen as cathode feed. Cathodic overpressure: 1.6 bars.

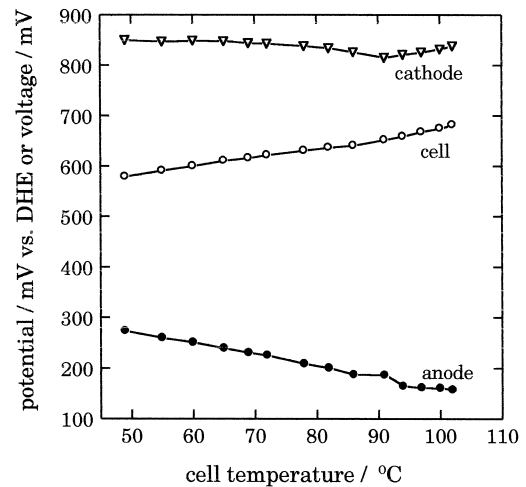


Fig. 7. Plots of open circuit cathode potential, anode potential and cell voltage as a function of temperature. Measured values were observed during cell heat-up using 10% by vol. methanol in water in the anode compartment and pure oxygen as cathode feed. Cathodic overpressure: 1.6 bars.

lowered above this temperature because the transport of water across the membrane is preferred in the presence of gaseous methanol.

3.2.2. Full cell testing and single electrode performance analysis

Full cell testing was performed using various methanol concentrations in water. Fig. 8 shows a plot of data obtained during operation on 10% methanolic solution at 100°C. Analysis of the plot reveals that the cathode profile is superimposed by a small (and constant) amount of methanol crossover, but the overall oxygen reduction slope is dominated by an inevitable iR -drop. This is due to the fact that the DHE was located in opposition to the cathode

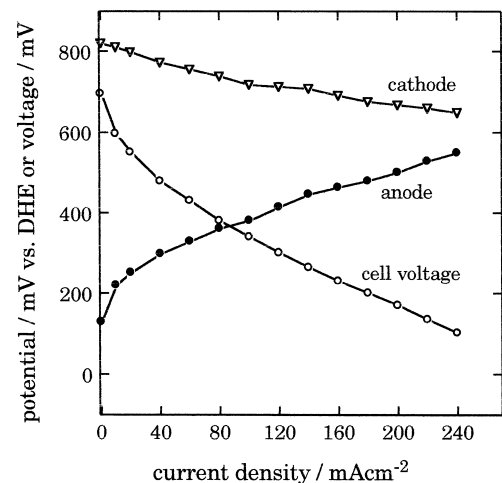


Fig. 8. Plots of anode potential, cathode potential and cell voltage vs. current density measured during operation of the PEMDMFC on 10% by vol. methanol in water and pure oxygen at 100°C. Cathodic overpressure: 1.6 bars.

so that the whole membrane resistance behaviour is superimposed on the cathode characteristics. The electrolyte resistance was not determined at operating temperature. It is observed here that a concentration of 10% methanol in the vapour feed and operation at 100°C is very beneficial in obtaining a good cathode performance, although methanol crossover is still present.

3.2.3. Fuel cell operation at constant current

Further conclusions will be drawn from a comparison of cell performances observed as a function of methanol concentration at a constant current density of 100 mA/cm². These results are given in Fig. 9. Surprisingly, the highest cell voltage was obtained using a 50 vol.% methanol in water feed corresponding to a molar ratio of 1.5/1 water/methanol (such as IFC used in Ref. [6]), although anode potential and voltage values became affected by fluctuations at higher methanol concentrations, possibly because of temporary anode flooding. We are of the opinion that despite the above-stated molar ratio the active sites experience a water depletion caused by water-drag across the membrane plus water consumption during methanol oxidation. This feed composition therefore represents the limit of methanol content to be used with the experimental configuration employed here.

A very stable DMFC operation was achieved with 10% methanol in water. The most important finding of this section is that oxygen electrode depolarisation at 100 mA/cm² does *not* follow the trend found for open circuit cathode potentials, as there is no decrease in cathode performance when increasing the methanol concentration from 10 to 50% by volume. It is therefore apparent, that fuel crossing the membrane is catalytically oxidized at Pt sites which are not ionically in contact with the electrochemical reaction zone, whereas the electrochemically accessible area is utilized almost exclusively for the cathode

reactions. Similar conclusions were drawn in application-oriented papers [6,7] and a study employing impedance spectroscopy [17], where the authors found that methanol was causing only a minor Pt site-blocking effect besides establishing a mixed potential.

For 50% methanol, cathode depolarisation does not significantly increase but the anode potential is only 335 mV (*not* iR-corrected) at 100 mA/cm². A similar benign influence of the methanol concentration on anode performance was recently reported [4,8].

It has to be noted that these anode potentials obtained at 100°C using 60% noble metals deposited on Ketjenblack by the sulphito-complex method [5,14] do not significantly differ from anode potentials obtained at 70°C [1] with 29% PtRu on Norit BRX (see Section 2.1) using the alkaline formate reduction method [13]. The reason for this is not quite clear, but we assume that a poor utilization of the noble metals in the anodes could cause a nivellating effect. TEM images shown in Figs. 1 and 2 reveal that the 60% noble metal on carbon catalyst contains many zones of colloidal morphology with primary crystallites in the 3 nm range, whereas the 29% noble metal on carbon material shows well-defined crystallites with particle diameters down to 4 nm. Therefore, the morphologies have to be called totally different. A thorough physical characterization of anode catalysts was carried out in Ref. [18], where the question of alloy formation was also addressed. This question should be considered in DMFC investigations, but was left for future work concerning the catalysts employed here. It could be expected that a large excess of water in the anode feed could give rise to water 'blanketing' such as can be found for nitrogen with air cathodes. However, we do not doubt that appropriate adjustment of porosity and hydrophobicity of the gas diffusion electrodes to the respective water content of the fuel gas feed could allow the achievement of an optimum performance.

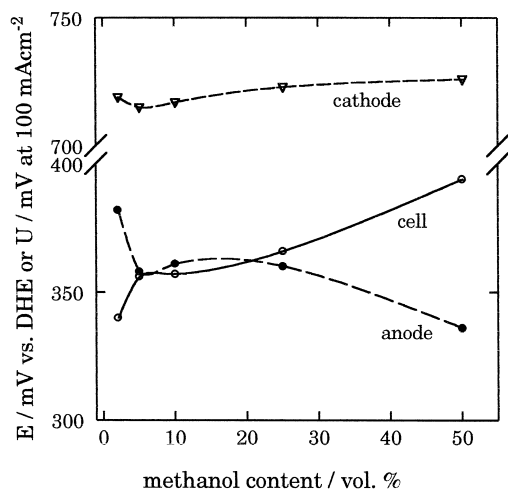


Fig. 9. Plots of anode potential, cathode potential and cell voltage vs. methanol concentration in the anode compartment measured during operation of the PEMDMFC at a constant current density of 100 mA/cm² at 100°C. Cathodic overpressure: 1.6 bars (pure oxygen).

4. Conclusions

It is shown that 3-electrode fuel cell cyclic voltammetry is a powerful means to check cathode features under operating conditions.

Stationary voltage vs. current density curves obtained using the 3-electrode circuit can be used to study the relation between anode performance and methanol crossover. Open circuit measurements show that cathode depolarization is lower at temperatures around 100°C. According to our findings, the goal of a maximum cell voltage or power density should be reached employing methanol feed concentrations slightly below 50% by volume. In addition, it was found that the performance of an operating cathode is not severely affected by an increase of the methanol concentration in the anode compartment. Potential-lowering methanol crossover is already present at low concentrations and an increase in methanol permeation

preferably leads to fuel losses via direct chemical oxidation. Questions about fuel utilization and methanol oxidation product distribution under these conditions have to be dealt with in order to optimize the overall system performance.

Good performance data have been obtained employing 29% PtRu on Norit BRX thus giving a total noble metal loading of only 2.3 mg/cm² or 1.6 mg Pt/cm². A catalyst composition of a molar ratio of 1:1 for PtRu is recommendable for PEMDMFCs operating near 100°C. Further efforts have to be made to find the system's optimum in every respect, such as maximum power density at maximum fuel utilization. We believe that the DMFC will not consist of a conventional membrane but of newly developed, for instance layered [19,20] types.

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