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Reduction of oxygen in an acidic methanol/oxygen (air) fuel cell: an online MS study*

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The reduction of oxygen was studied with online mass spectroscopy on 5% Pt/Norit BRX and on 20% $FePP(NO_2)_4$/RB PTFE-bonded gas diffusion electrodes. The performance of the catalysts was analysed under conditions of an acidic methanol/oxygen (air) fuel cell cathode in the presence of methanol in solution. Following the mass signal $m/e = 32$ for oxygen it can be shown that $FePP(NO_2)_4$ catalyses the oxygen reduction selectively. In contrast, on the Pt–carbon catalyst methanol is oxidized to CO_2 ($m/e = 44$) thus establishing a mixed potential and an additional consumption of methanol. Furthermore, it can be demonstrated that on a platinum-carbon electrode the methanol oxidation is catalysed in the presence of oxygen, shifting the onset potential of CO_2 production 100 mV more cathodic.

1. Introduction

In an acidic methanol/oxygen (air) fuel cell the chemical energy of the fuel methanol is directly converted into electrical energy (direct methanol fuel cell, DMFC). The possibility of constructing portable or mobile DMFC units makes this system attractive. However, up to now the development of fuel cells of technical interest has been limited by the methanol anode catalysts and also by the performance of the oxygen cathode [1, 2].

Using Pt-catalysed air diffusion electrodes as oxygen cathodes in methanol containing electrolyte, oxygen reduction and methanol oxidation take place simultaneously, resulting in a mixed cathode potential [1]. Some transition metal complexes attached to the electrode surface have been found to show a comparable performance to that using platinum for oxygen reduction. In electrolytes containing organic fuels, like methanol or formic acid, these transition metal macrocycles, like Fe-tetranitrophenylporphyrine $FePP(NO_2)_4$, catalyse oxygen reduction selectively [3–5].

For methanol oxidation in a DMFC even platinum, as catalyst material, shows rather poor activity, because the surface is poisoned by strongly adsorbed intermediates like CO_{ad} or COH_{ad} [6]. Recently, Gottesfeld *et al.* demonstrated that, for a hydrogen/oxygen fuel cell, low amounts of oxygen injected into the hydrogen feed contaminated with about 100 p.p.m. of CO could restore the activity of the Pt-carbon hydrogen anode. They proposed that this was due to the reaction of oxygen gas with the adsorbed CO_{ad} species [7].

In this paper we present a new approach to the understanding of the oxygen reduction reaction on carbon supported gas diffusion electrodes under conditions of a direct methanol fuel cell. Conventional electrochemical voltammetry was combined with an online mass spectroscopic technique (differential electrochemical mass spectroscopy, DEMS) developed in our laboratory [8, 9]. In addition to current potential diagrams gaseous and volatile species are detected during their production or consumption. In this way competing faradaic processes are highlighted and these can be separated from currents caused by the high capacitance of the large area porous gas diffusion electrodes. The advantages of the online MS method have already been reported for several electrochemical systems [9].

2. Experimental details

For analysis of volatile products a Balzers quadrupole mass spectrometer, QMG 112A, equipped with an axial beam ion source and a faraday cup ion detector was used (details are given in [9]).

A standard three-electrode arrangement was used for all experiments. The working electrode consisted of gas-diffusion electrodes made from PTFE-bonded carbon supporting the catalyst. Platinum (5% on Norit BRX) and Fe-tetranitrophenylporphyrine (20% on RB) were used as carbon supported catalysts for the investigation of the interaction oxygen–reduction and methanol-oxidation.

The platinum carbon was prepared by chemical reduction of chloroplatinic acid with potassium formate in the presence of a carbon slurry, according to the method described by Hamnett *et al.* [10].

Fe-tetranitrophenylporphyrine (Fe–$PP(NO_2)_4$) was applied to the carbon substrate by adsorption from acetone. After the evaporation of the acetone the carbon was heated to 800° C under argon for 2 h. Details

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* This paper is dedicated to Professor Brian E. Conway on the occasion of his 65th birthday, and in recognition of his outstanding contribution to electrochemistry.

are described elsewhere [5]. The carbon electrodes were bonded using PTFE (37 wt%). A PdAu–net (90 : 10) was pressed onto these carbon layers serving as a current collector.

In order to fit the gas diffusion electrodes into the cell a small disc (diameter: 0.9 cm; area: 0.64^2; superficial density: 10 mg cm^{-2}) was cut and put on a PTFE-membrane (Gore, type No. S10570; thickness: 75 μm; pore size; 0.02 μm; porosity: 50%) allowing the permeation of volatile products into the vacuum of the mass spectrometer [9]. During measurement the pressure in the ion source was typically 4×10^{-5} mbar.

For the measurement of the open circuit potential and simultaneous detection of the mass signal in $m/e = 44$ a porous platinum electrode was applied. The porous platinum electrode was made from metal lacquer prepared from metal powder (average particle size about 1–5 μm (Doduco) and lacquer (Doduco)).

A reversible hydrogen electrode (RHE) in the same solution was used and all potentials are referred to this electrode. For potential control a function generator (built in-house) and a potentiostat (Jaissle 10 000 T) were used with an xyy'-recorder (Kipp + Zonen BD91) for simultaneous recording of current and mass signal.

Prior to each experiment the gas-diffusion electrodes were cycled at 10 mV s^{-1} and 5 mV s^{-1} until a stable voltammogram was obtained (2–3 cycles at each scan rate). Then, the measurements were started with a scan rate of 1 mV s^{-1}. A new electrode was used for each experiment in order to avoid an uncontrolled loss of activity.

For preparation of electrolytes the following chemicals were used: doubly distilled water (Millipore purification); sulphuric acid (Merck, analytical grade, 98%); and methanol (Merck, analytical grade). In order to maintain a constant pressure level in the cell argon (Messer Griessheim, 99.998%) and oxygen (Messer Griessheim, 99.997%) were supplied with a flow rate of 1 dm^3 h^{-1} being adjusted by a calibrated flowmeter (Krohne).

3. Results and discussion

3.1. Galvanostatic curves

In Fig. 1 galvanostatic current/potential-curves for a 5% Pt/Norit BRX electrode in 0.5 M H_2SO_4 electrolyte with oxygen-bubbling and different methanol concentrations are shown. For each point the current density was held constant and the corresponding potential against the RHE standard was measured after 5 min. The curves were taken in a direct methanol fuel cell (DMFC) with a 5% Pt/Norit electrode serving as oxygen cathode. During the experiment the oxygen was directly purged into solution with the gas side of the cathode closed.

The curve without methanol in solution (———) is typical for good oxygen cathodes. Towards higher current densities the potential decreases linearly (due to the low oxygen solubility in solution) while the rest potential is relatively high (950 mV). For increasing methanol concentrations in solution (0.5 M: – – – –; 2 M: ······) the curves are shifted to less positive potentials. This effect also holds for the rest potentials (720 and 660 mV, respectively).

Two explanations are possible: (i) mixed potential between oxygen and methanol, and (ii) poisoning of the Pt-surface by adsorbed methanol species. Therefore online MS experiments were performed in order to determine the onset potentials of the oxygen-reduction following directly the consumption of the supplied oxygen.

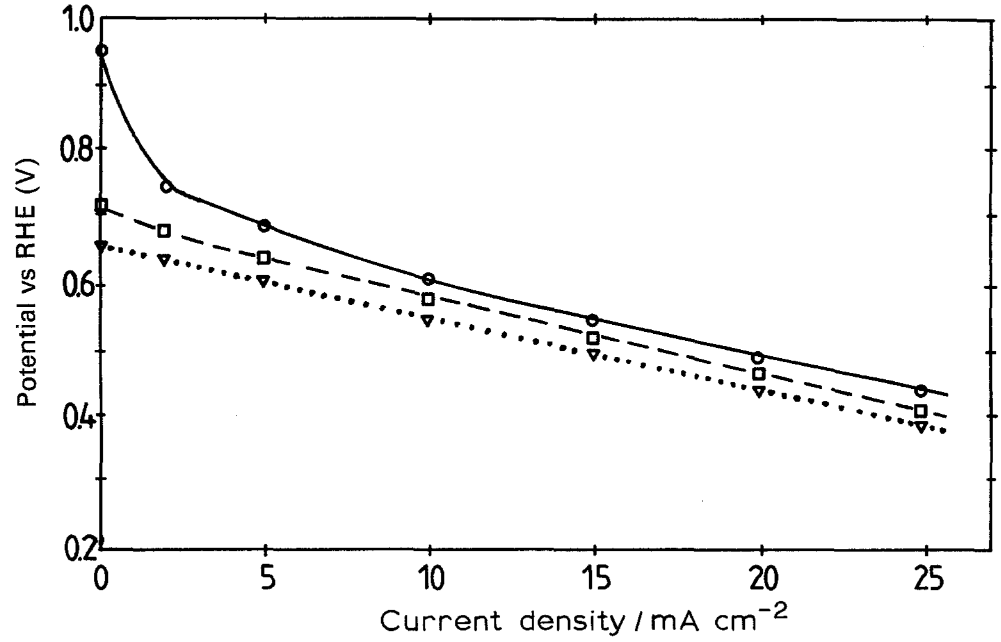

Fig. 1. Current–potential curves for a 5% Pt/Norit BRX gas diffusion electrode (18 mg cm^{-2}, 2 cm^2 geometric area) in 0.5 M H_2SO_4 with *oxygen bubbling in solution only*, gas side of the electrode closed. Key: (○) No CH_3OH, (□) 0.5 M CH_3OH and (▽) 2 M CH_3OH.

3.2. Oxygen reduction at the 5% Pt/Norit electrode

For the online MS observations the working electrode was placed at the entrance of the mass spectrometer. Therefore, the simultaneous reaction of methanol and oxygen occurred on the 'electrolyte side' of the porous working electrode.

Figure 2 shows the results of online MS experiments demonstrating the activity of a 5% Pt/Norit BRX electrode towards oxygen reduction in the presence of methanol in solution. Oxygen was bubbled with constant flow rate into the sulfuric acid electrolyte. Simulating DMFC conditions the methanol content in the cell was varied from 0.01 to 0.1 M and compared to the case of pure supporting electrolyte. For

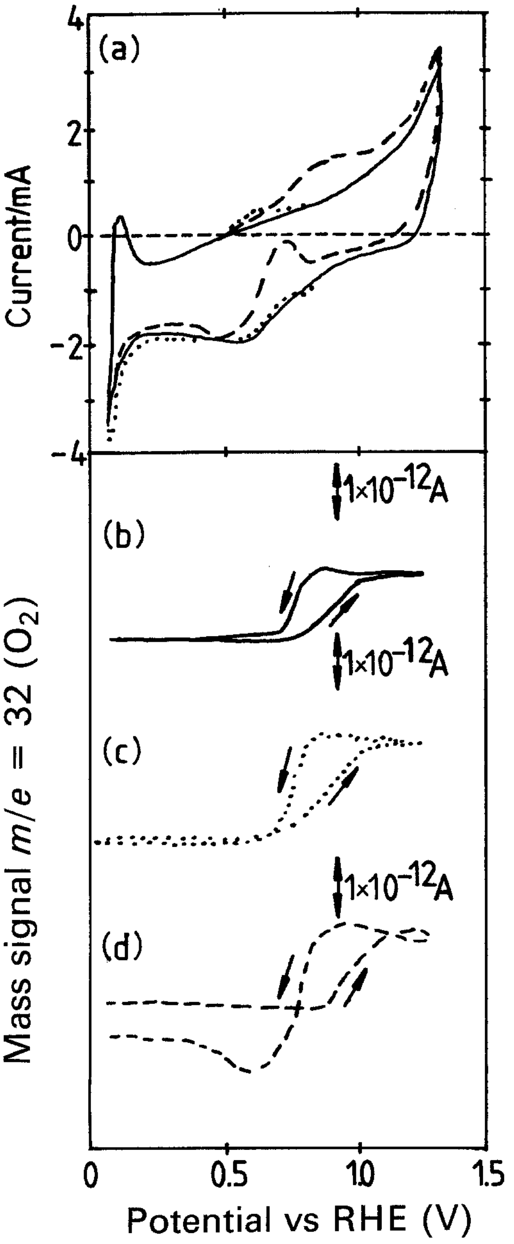

Fig. 2. Oxygen reduction at a 5% Pt/Norit BRX electrode (10 mg cm^{-2}, 0.64 cm^2 geometrical area) in 0.5 M H_2SO_4 (*oxygen bubbling in solution only*; flow rate 1 dm^3 h^{-1}); scan rate: 1 mV s^{-1}. (a) Current against potential without methanol (————), with 0.01 M CH_3OH (······) in solution and with 0.1 M CH_3OH (– – – –); (b–d) mass signal for $m/e = 32$ (O_2 *and* CH_3OH) for electrolytes without methanol (b), with 0.01 M CH_3OH (c) and with 0.1 M CH_3OH (d), respectively.

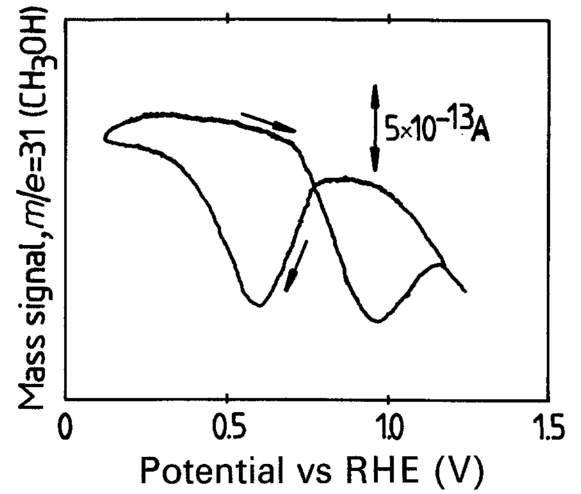

Fig. 3. Consumption of methanol ($m/e = 31$) during the oxidation of methanol at a 5% Pt/Norit BRX electrode (10 mg cm^{-2}, 0.64 cm^2 geometrical area) in a 0.5 M H_2SO_4 + 0.1 M CH_3OH solution; scan rate: 1 mV s^{-1}; *Ar-purging in solution*: 1 dm^3 h^{-1}.

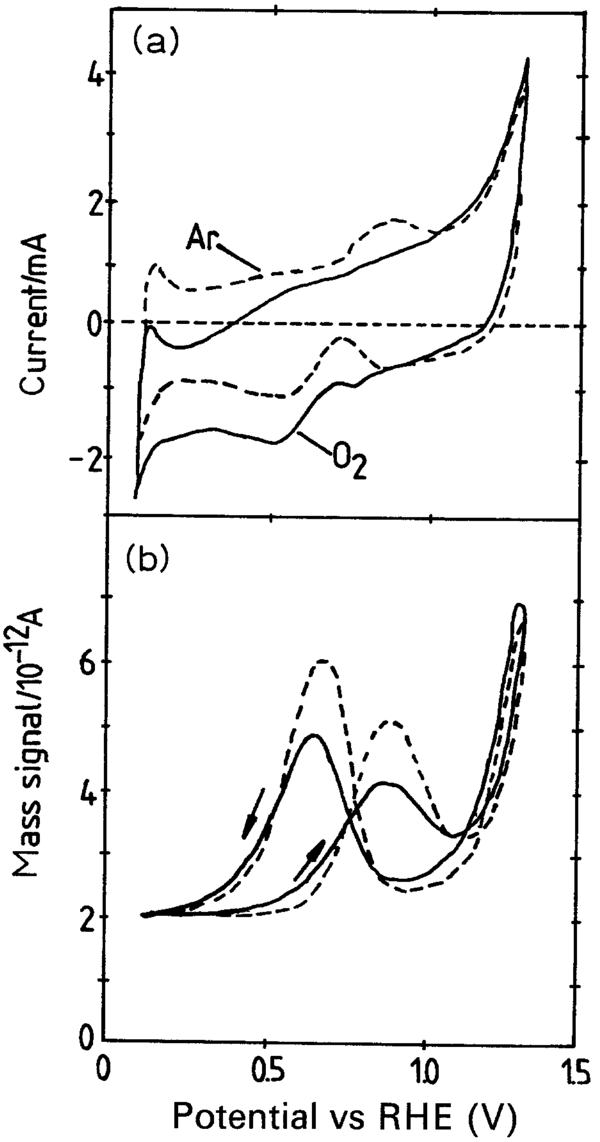

Fig. 4. *Shift in onset potential of methanol oxidation* at a 5% Pt/Norit BRX electrode (10 mg cm^{-2}, 0.64 cm^2 geometrical area) with argon purging (– – – –) and with oxygen purging (————) *in solution* (gas flow rate 1 dm^3 h^{-1}) in a 0.5 M H_2SO_4 + 0.1 M CH_3OH solution; scan rate: 1 mV s^{-1}. (a) Current against potential, (b) mass signal $m/e = 44$ (CO_2) against potential.

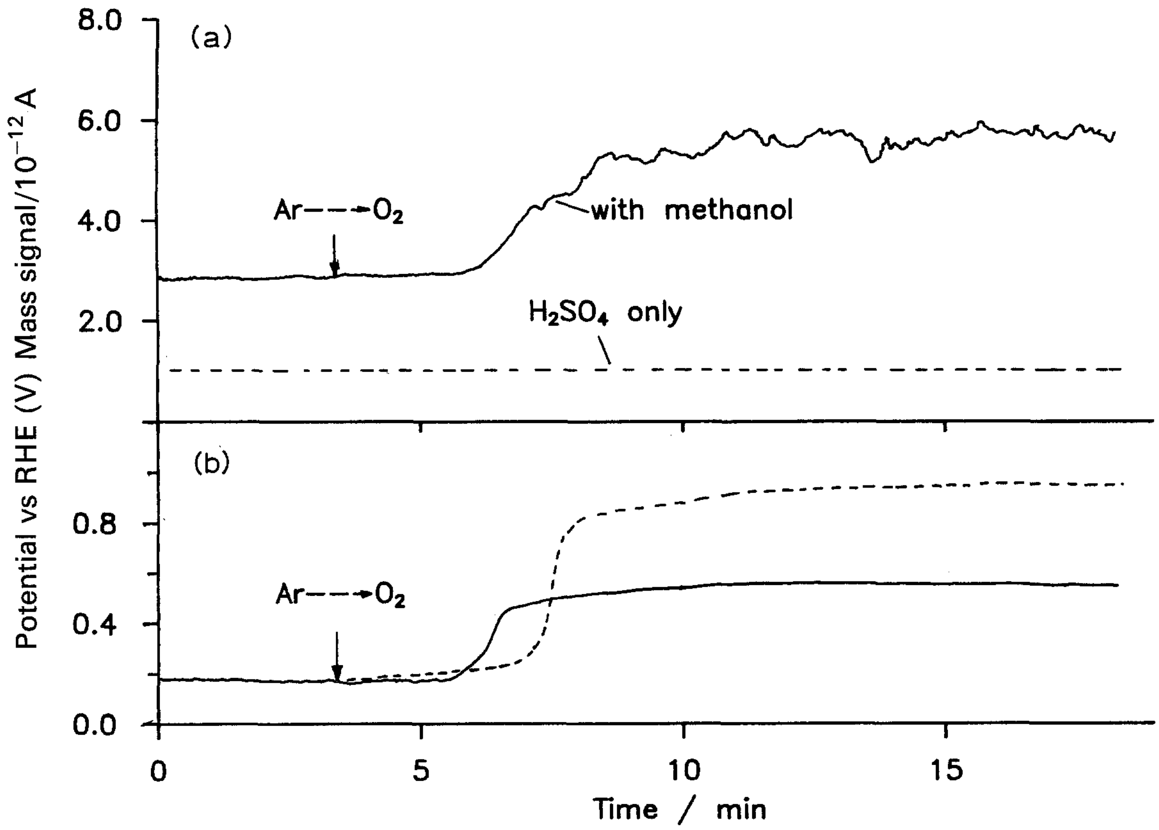

Fig. 5. *CO_2-formation at a porous platinum electrode* in 0.5 M H_2SO_4/ 0.1 M CH_3OH (———) and 0.5 M H_2SO_4 (– – – –) *at open circuit* during a change from argon purging to oxygen purging (indicated by arrow); flow rate for both gases: 1 $dm^3\,h^{-1}$. (a) Mass signal $m/e = 44$ and (b) open circuit potential against time.

the lower potential region the voltammograms of Fig. 2(a) exhibit negative current values typical of an oxygen reduction current. With addition of methanol some positive going current contributions appear between 600 and 900 mV vs RHE.

With online MS the consumption of oxygen was followed directly via the mass signal of $m/e = 32$ (molecular ion of oxygen) under the respective conditions. The resulting mass signal against potential voltammograms of Fig. 2(b)–(d) show diffusion controlled oxygen consumption. The half wave potential of 830 ± 20 mV vs RHE (cathodic scan) for oxygen reduction in pure base electrolyte does not shift within experimental error in the presence of methanol in solution. The additional features in the mass signal curve for the highest methanol concentration of 0.1 M (Fig. 2(d)) need further explanation. They are related to the consumption of methanol, implying that, in the respective potential region, the Pt/Norit electrode acts simultaneously as a methanol anode. In this case mass number $m/e = 32$ represents the molecular ion of the methanol molecule with a relative abundance of 72%. Obviously, a consumption of methanol could be better demonstrated by following the mass signal of the main methanol fragment $m/e = 31$.

3.3. Methanol consumption

The mass signal for $m/e = 31$ (main fragment of methanol) against potential is shown in Fig. 3 for a 5% Pt/Norit electrode in 0.5 M H_2SO_4 + 0.1 M CH_3OH solution during a potentiodynamic experiment. The minima in this curve correspond to the maxima in the consumption of methanol (compare Fig. 4). If the rate of methanol oxidation increases then the methanol concentration close to the electrode must decrease leading to a smaller signal in $m/e = 31$. Likewise, the methanol concentration close to the electrode starts to increase when the methanol oxidation rate has passed its maximum, see Fig. 4.

3.4. Methanol oxidation at the 5% Pt/Norit electrode

The reaction of methanol is shown in more detail in Fig. 4. A cyclic voltammogram of a 5% Pt/Norit electrode in 0.5 M H_2SO_4 + 0.1 M CH_3OH solution with Ar-purging (– – – –) and with O_2-purging (———) is presented. With oxygen-purging a reduction current can be clearly distinguished below potentials of about 750 mV vs RHE in the cyclic voltammogram.

The methanol oxidation leads to uncharacteristic local maxima in the anodic and cathodic sweeps (about 900 mV in the anodic and about 750 mV in the cathodic direction) which disappear almost completely in the currents for double layer charging and for redox-processes on the surface of the carbon support itself. Therefore cyclic voltammetry (Fig. 4(a)) is unsuited to the characterization of methanol oxidation at carbon based electrodes.

In contrast, the corresponding plots of the mass signal for $m/e = 44$ (molecular ion of CO_2) against potential in Fig. 4(b) are much more significant. The shape of the curve for Ar-purging (– – ––) is typical for CO_2-formation during methanol oxidation at platinum catalysts [2]. A comparison with the curve for O_2-purging (————) reveals that oxygen in solution shifts the onset of the methanol oxidation to more cathodic potentials by 100 mV. Between 400 and 750 mV the CO_2-formation rate is also increased in the presence of oxygen.

It can be concluded that oxygen in solution catalyses methanol oxidation at low potentials. For potentials higher than 900 mV the carbon corrosion also contributes to the overall CO_2-evolution.

Recently, Vielstich *et al.* [11] were able to separate the contributions of carbon corrosion and methanol oxidation for carbon based electrodes by using C^{13}-labelled methanol. It can be assumed that their results also apply to the present study. Furthermore, Vielstich *et al.* [11] also found that oxygen purging of a PtRu/Norit BRX electrode in methanol containing electrolyte enhances the methanol oxidation in a similar way as observed in this study.

The results outlined above show that a platinum-carbon electrode acts simultaneously as oxygen cathode and methanol anode depending on the electrode potential applied. This proves the existence of a mixed potential between oxygen and methanol on this type of electrode.

3.5. Open circuit experiments

The interesting effect of an enhanced methanol oxidation rate in the presence of oxygen is shown in Fig. 5. The change of open circuit potential (lower part) and CO_2 production (upper part) of a porous platinum electrode in methanol solution when injecting oxygen gas into the electrolyte is followed via online MS. About 2 min after the injection of oxygen, when the reacting gas has reached the electrode surface, the open circuit potential rises from about 180 mV to 500 mV. The reaction product, namely CO_2, is detected in the mass spectrometer. Porous platinum was chosen as electrode material instead of a platinum-carbon electrode in order to ensure that the CO_2 produced did not originate from carbon corrosion as discussed above. Moreover, this type of electrode adjusts more rapidly to new electrochemical parameters than does a carbon based electrode.

Gottesfeld *et al.* [7] suggested that the reactivation of a platinum-carbon methanol anode by oxygen may be caused by an oxidative removal of adsorbed CO as poisoning species. Therefore we have studied the effect of oxygen treatment on methanol adsorbates formed on porous platinum and on platinum-carbon electrodes in a flow cell [9]. No oxidative effect of oxygen on the adsorbed CO species could be detected.

3.6. Oxygen reduction at the iron porphyrin catalyst

In addition to the noble metal catalysed platinum-carbon electrode, we have studied the *activity towards oxygen reduction under DMFC conditions* for another commonly applied type of cathode material i.e. on 20% $FePP(NO_2)_4/RB$. Figure 6 shows the online MS results for oxygen consumption on this type of electrode in pure sulphuric acid electrolyte and with 0.1 M methanol in solution. Similarly to the results obtained with the Pt/Norit electrode, the voltammograms in Fig. 6(a) show negative current contributions for oxygen reduction in the lower potential region. The simultaneously recorded mass signal for $m/e = 32$ (molecular ion of oxygen) again exhibits the features of a diffusion controlled process (Fig. 6(b)). The half wave potential for oxygen reduction on 20% $FePP(NO_2)_4/RB$ is 770 ± 20 mV vs RHE (cathodic scan) and is *independent of the presence of methanol* in solution. Unlike the case of the platinum-carbon catalyst no hint of methanol consumption in the mass signal $m/e = 32$ can be detected. This was confirmed by following the mass

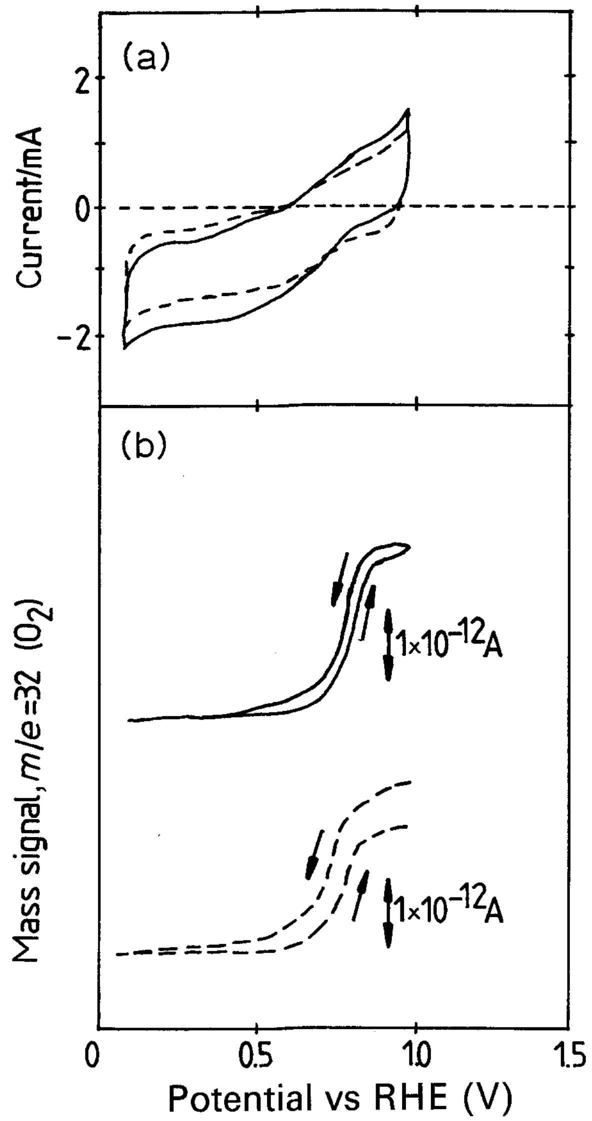

Fig. 6. Oxygen reduction at a 20% $Fe\text{–}PP(NO_2)_4/RB$ electrode (10 mg cm^{-2}, 0.64 cm^2 geometrical area) in 0.5 M H_2SO_4 (*oxygen bubbling in solution only*; flow rate: 1 dm^3 h^{-1}); scan rate 1 mV s^{-1}. (a) Current against potential without methanol (————), with 0.1 M CH_3OH (– – ––) in solution, and (b) mass signal for $m/e = 32$ (O_2 *and* CH_3OH) for electrolytes without and with methanol, respectively.

signal of the main fragment of methanol $m/e = 31$ and the possible product of methanol consumption carbon dioxide $m/e = 44$. Our results clearly demonstrate that $FePP(NO_2)_4$ catalyses the oxygen reduction reaction selectively, no mixed potential between oxygen and methanol arises.

4. Conclusions

Using online mass spectroscopy the oxygen reduction reaction was studied under conditions of a direct methanol fuel cell (DMFC). By following the mass signals $m/e = 32$ of oxygen, $m/e = 31$ of methanol and $m/e = 44$ of carbon dioxide, the two possible processes of oxygen reduction and methanol oxidation occurring at a gas diffusion cathode in methanol containing solution could be separated in an elegant way.

For the 5% Pt/Norit BRX electrode it was demonstrated that both processes occur simultaneously, leading to a mixed potential between oxygen and methanol at this type of electrode. The half wave potential of oxygen reduction remained constant, independent of the presence of methanol in solution. On the other hand, on the fuel cell anode *carbon dioxide as a product of methanol oxidation was formed* at a potential 100 mV *more cathodic in the presence of oxygen* in solution.

By contrast with the findings for the Pt-catalysed gas diffusion cathode a 20% $FePP(NO_2)_4$/RB electrode was shown to catalyse the oxygen reaction selectively.

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