Methanol oxidation at carbon supported Pt and Pt–Ru electrodes: an on line MS study using technical electrodes

S. WASMUS, W. VIELSTICH

Institute für Physikalische Chemie der Universität Bonn, Wegelerstraße 12, D-5300 Bonn 1, Germany

Methanol oxidation at technical carbon based electrodes in 0.05 M H_2SO_4 has been investigated by cyclic voltammetry using online MS under the conditions of an acid methanol fuel cell (DMFC). 5% Pt on Norit BRX and 30% Pt/Ru (40/60) on Norit BRX were used as catalysts. It is shown that methanol oxidation at technical electrodes can be characterized by a combination of cyclic voltammetry and mass spectroscopy. The onset potentials and potential dependences of the methanol oxidation rate can be determined directly by monitoring the formation of CO_2. Onset potentials of 0.5 V and 0.25 V/RHE have been measured for Pt and Pt–Ru catalysts, respectively. The onset of methanol oxidation can be shifted to even more cathodic potentials (0.2 V) if the Pt–Ru electrode reduces oxygen simultaneously. Carbon monoxide gas was also purged into the methanol containing electroyte during measurement in order to investigate the catalyst performance under more adverse conditions. C^{13}-labelled methanol was used to distinguish between CO_2 formed from methanol ($m/e = 45$) and CO-oxidation ($m/e = 44$). Without CO the use of C^{13}-labelled methanol enabled a distinction between methanol oxidation and carbon corrosion. The methanol oxidation at the platinum catalyst is severely inhibited by the presence of CO, shifting its onset to 0.65 V/RHE. In contrast the performance of the Pt–Ru electrode is not seriously affected under these conditions. It is concluded that Pt–Ru is an excellent catalyst for a methanol anode in an acid methanol fuel cell (DMFC).

1. Introduction

An acid methanol fuel cell (DMFC) is an extremely attractive power source for mobile systems. In contrast to combustion engines, fuel cells have no emissions of toxic compounds like CO, NO_x, CH_x or carcenogenic soots. Due to their high efficiencies (40–60%) in comparison to combustion engines (20–30%) it may also be expected that the amount of carbon dioxide emitted is dramatically reduced.

Apart from being an active contribution to the protection of the environment this type of fuel cell has numerous other advantages. Liquid methanol is easy to handle avoiding the complexity of the storage of gases. The continuous supply of the fuel removes the necessity of frequent recharging, which is required by most secondary battery systems under development for application in electrotraction.

Despite these advantages the catalysis of methanol oxidation remains problematic due to the formation of poisoning species at the electrode. A discussion of methanol oxidation is presented in a review by Iwasita [1]. In particular, platinum catalysts tend to form strongly adsorbed species which are thought to be CO_{ad} or related adsorbates like COH_{ad} [2]. At low potentials these species cause poisoning of the platinum electrode. Nevertheless, platinum is a good catalyst for the adsorption of methanol which is a necessary step in its oxidation to carbon dioxide. Thus,

a catalyst must be found which is able to adsorb methanol as well as platinum but which can also oxidize the poisoning species at much lower potentials. Consequently, the search for a suitable catalyst system was directed towards platinum alloys. Almost 30 years ago Koch [3] suggested the alloying of Pt with less noble metals like Pb, Sn, Tl or others because it was hoped that these foreign metals might form surface oxides at lower potentials than platinum thus being able to oxidize the poisoning species at more cathodic potentials. Frumkin et al. [4], reported, as early as 1965, that a Pt–Ru alloy has a beneficial effect on methanol oxidation.

Recently, methanol oxidation at Pt–Ru electrodes has been investigated using modern electrochemical methods. Iwasita et al. [5] employed a FTIR method concluding that CO_{ad} is less strongly bonded to a Pt–Ru electrode and that CO_{ad} is removed at much lower potentials than in the case of pure platinum. The authors attribute the latter effect to the fact that Ru forms adsorbed OH at lower potentials.

Hamnett and Kennedy [6] studied methanol oxidation at bimetallic carbon supported anodes using steady state polarization curves. These authors characterized the chemical state of the catalysts by XPS. It was found that Pt–Ru, Pt–Os and Pt–Ir promote the methanol oxidation in comparison to Pt with Pt–Ru giving the best results. In contrast, Pt–Au and Pt–Pd serve as inhibitors. With XPS measure-

ments, it was found that Ru, Os and Ir form stable oxides.

Gottesfeld et al. [7] presented a new approach to eliminate the electrode poisoning by supplying oxygen to the H_2/CO-mixture of a gas diffusion anode.

Vielstich et al. [8] have demonstrated that oxygen purging of a 5% Pt on Norit electrode shifts the onset of methanol oxidation to more cathodic potentials by 100 mV using a combination of online MS and cyclic voltammetry.

The high capacitive and redox currents of the carbon support itself do not allow the exclusive application of potentiodynamic techniques for the investigation of methanol oxidation at technical electrodes. The currents caused by this process are almost completely obscured. Online MS enabled a more direct study of methanol oxidation by monitoring the formation of CO_2. It can be shown that only at comparatively high anodic potentials (> 0.9 V/RHE) does the carbon corrosion contribute significantly to the overall CO_2 formation. By using C^{13}-labelled methanol, it is also possible to separate the carbon corrosion from methanol oxidation. The application of C^{13}-labelled methanol offers the additional advantage of separating the CO_2 product from a simultaneous oxidation of methanol and CO. Online MS [9] is a powerful tool for studying methanol oxidation at technical electrodes.

2. Experimental details

For analysis of volatile products a Balzer's quadrupole mass spectrometer QMG 112A equipped with an axial beam ion source and a Faraday cup ion detector has been used (details are given in [10]).

A standard three electrode arrangement was used in all experiments. The working electrode consisted of electrodes made from PTFE-bonded carbon supporting the catalyst. Platinum (5% on Norit BRX) and platinum–ruthenium (40/60; 30% on Norit BRX) were used as carbon supported catalysts for the investigation of the methanol oxidation.

The platinum and platinum–ruthenium carbon was prepared by chemical reduction of chloroplatinic acid and ruthenium (III) chloride with potassium formate in the presence of the carbon slurry, according to a method described by Hamnett et al. [11]. PTFE (37%) was used to bond the carbon electrodes. A Pd–Au-net (90 : 10) was pressed on to 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 cm^2; area weight: 6 and 10 mg cm^{-2}) was cut and pressed on to 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, 10]. During measurement the pressure in the ion source was typically 4×10^{-5} mbar.

A reversible hydrogen electrode (RHE) in the same solution was used as a reference electrode. All potentials in the present study 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 technical electrodes were cycled with 10 mV s^{-1} and 5 mV s^{-1} until a stable voltammogram was obtained (2–3 cycles at each scan rate). Afterwards, 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 uncontrolled loss of activity.

In the preparation of electrolytes the following chemicals were used: doubly distilled water (Millipore water purification system); sulphuric acid (Merck, analytical grade, 98%); methanol (Merck, analytical grade); and C^{13}-labelled methanol (Aldrich, 99 at % C^{13}). Argon (Messer Griessheim, 99.998%) and carbon monoxide (Messer Griessheim, 99.997%) were supplied to the electrochemical cell at a pressure of 1 atm.

For some experiments, it was necessary to supply argon or oxygen (Messer Griessheim, 99.997%) with a constant flow rate of 1 dm^3 h^{-1} controlled by using a calibrated flowmeter (Krohne).

3. Results and discussion

In Fig. 1 methanol oxidation at a carbon supported Pt-catalyst (5% Pt on Norit BRX) in 0.05 M H_2SO_4/ 0.1 M $C^{13}H_3OH$ with Ar-bubbling (dashed curves) and CO-bubbling (continuous curves) is shown. The current against potential curves, Fig. 1(a), do not reveal any significant effect of methanol oxidation due to the high capacitive and redox currents of the carbon support itself. It can therefore be concluded that cyclic voltammetry alone is not well suited to the study of electrochemical processes at technical carbon supported electrodes.

In contrast, the plots of the mass signals against potential show much more detail. Additionally the use of C^{13}-methanol enables the discrimination of methanol oxidation and CO_2-formation due to carbon corrosion. Therefore the curve for $m/e = 45$, Fig. 1(b), shows exclusively the contribution of C^{13}-methanol oxidation while $m/e = 44$, Fig. 1(c), is characteristic for the carbon corrosion in the absence of CO. In the presence of CO, of course, carbon corrosion and CO-oxidation overlap in this mass signal.

Methanol oxidation at the carbon supported Pt-catalyst shows the same behaviour as on smooth or porous platinum electrodes [1] having an onset potential of 0.5 V/RHE in the anodic scan (see Fig. 1(b), dashed curve).

Additionally, CO_2 is formed from the carbon electrode above 0.9 V/RHE (see Fig. 1(c), dashed curve). This corrosion behaviour is also observed in the absence of methanol. A control experiment in supporting electrolyte with a Pt/carbon electrode previously extracted five times with acetone and afterwards dried in vacuum for 48 h, showed no difference concerning the corrosion behaviour. Possible contaminations, which are able to be oxidized to CO_2,
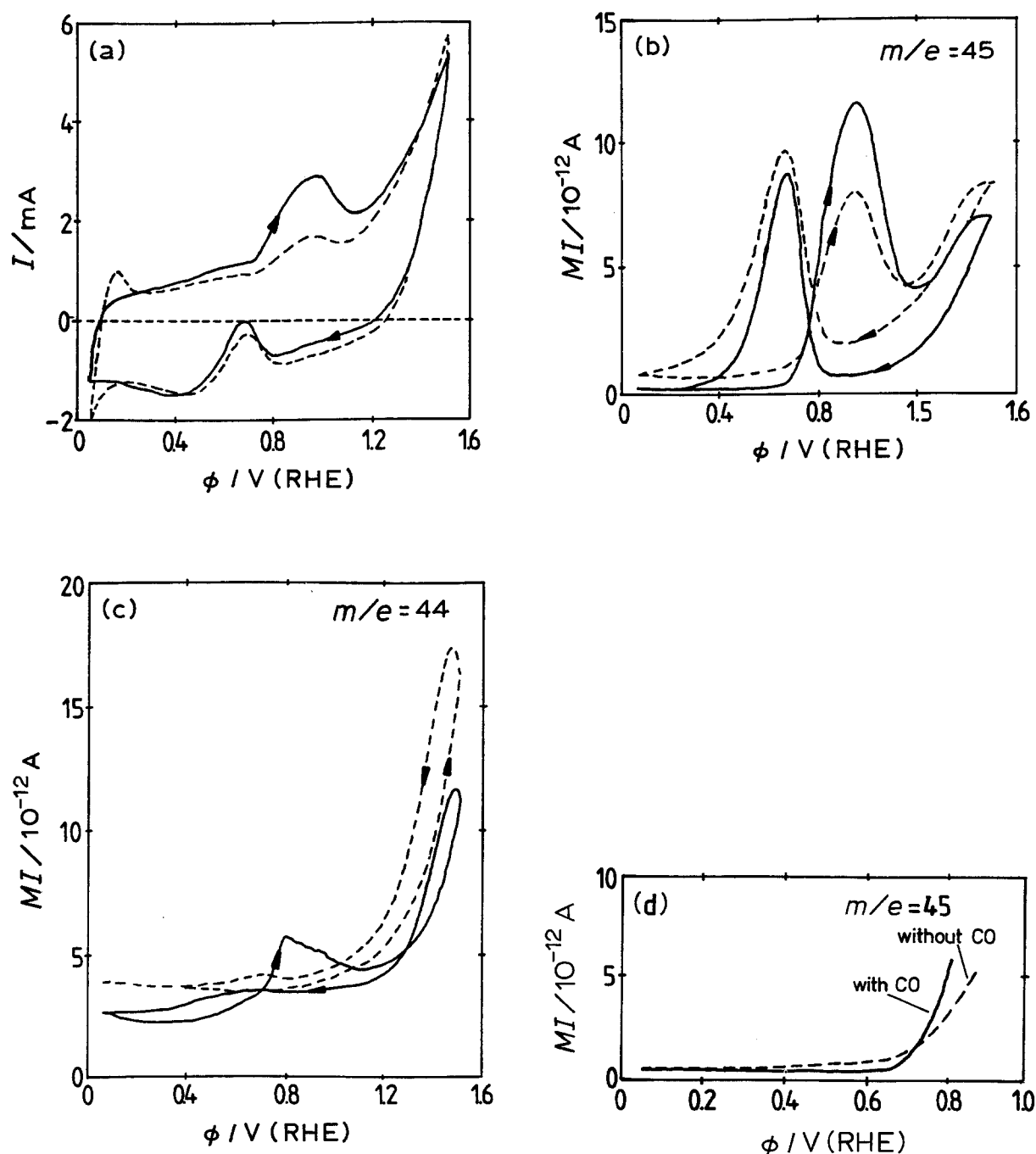
Fig. 1. CO_2-formation at a 5% Pt/Norit BRX electrode ($10\,\mathrm{mg\,cm^{-2}}$, $0.64\,\mathrm{cm^2}$) in $0.05\,\mathrm{M}$ $H_2SO_4/0.1\,\mathrm{M}$ $C^{13}H_3OH$-electrolyte during potentiodynamic methanol oxidation with Ar-purging (dashed line) and CO-purging (continuous line) in solution; scan rate: $1\,\mathrm{mV\,s^{-1}}$. (a) Current against potential; (b) mass signal $m/e = 45$ against potential; (c) mass signal $m/e = 44$ against potential; and (d) expanded version of Fig. 1(b) in order to demonstrate the inhibition of methanol oxidation in the presence of CO more clearly (anodic scan shown only).

were removed by the extraction procedure indicating that the carbon support itself is oxidized to CO_2 at sufficiently anodic potentials. It seems unlikely that PTFE, used to bond the electrode, can be oxidized to CO_2 due to the extremely high stability of the CF-bond. The corrosion behaviour of carbon electrodes also depends strongly on the type of carbon used with the onset potentials ranging from 0.9 to 1.4 V/RHE [12].

It is commonly accepted that CO_{ad} is an intermediate in methanol oxidation [1]. Therefore a good catalyst for methanol should also be effective for the oxidation of CO meaning that methanol oxidation in the presence of CO should not be strongly influenced.

For a more thorough test of the catalyst, experiments with methanol and CO in solution were conducted. In the presence of CO (1 atm) methanol oxidation at the Pt-catalyst is strongly inhibited, shifting the onset of CO_2-formation caused by methanol oxidation from 0.5 V (dashed lines. Fig. 1(b) and (d)) to 0.65 V/RHE (continuous lines). In Fig. 1(c), the continuous curve displays the CO_2-formation during CO-oxidation and carbon corrosion, both measured via $m/e = 44$ as mentioned above. The same potential dependence of $m/e = 44$ is observed without methanol in solution but with CO-purging.

All results clearly demonstrate that platinum is a bad catalyst for a methanol anode. Especially at low

potentials, where a methanol anode should operate at the highest possible efficiency, platinum shows a strong poisoning effect.

In contrast to Pt, Pt–Ru offers a dramatically improved catalyst performance towards methanol oxidation as evidenced by Fig. 2. With respect to the catalyst stability the anodic potential limit was restricted to 1.0 V/RHE.

Again the current voltammograms (a) do not show many details. In Fig. 2(b), the dashed curve demonstrates that the methanol oxidation at the carbon supported Pt–Ru catalyst (30% Pt–Ru (40/60) on Norit BRX) starts at a potential of 0.25 V/RHE. In the potential range chosen no significant carbon corrosion occurs, as shown in Fig. 2(c), (dashed curve).

With CO in solution, methanol oxidation is not very strongly affected (see Fig. 2(b), continuous curve). In the continuous curve of Fig. 2(c), the CO-oxidation at the Pt–Ru catalyst is shown. The same behaviour is also obtained without methanol in solution but with CO-purging. It can be seen that CO is oxidized at 0.35 V/RHE, which is a significant improvement over platinum (compare to Fig. 1(c), continuous curve). In conclusion, Pt–Ru is much better suited for application as a catalyst in a DMFC than platinum.

Recently, Gottesfeld et al. [7] and Vielstich et al. [8] have shown that the addition of oxygen improves the performance of platinum catalysts towards the oxidation of carbon monoxide and methanol. Therefore, an experiment was performed using a PtRu/carbon electrode in order to check if its already excellent catalytic performance could be further improved by purging with oxygen.

In Fig. 3 the results of this experiment are shown. As in the case of the Pt/carbon [8], reduction currents in the cyclic voltammogram can be observed with oxygen bubbling (compare continuous and dashed curved in Fig. 3(a)). The application of C^{13}-labelled methanol is not useful under the condition of this experiment because in the potential range investigated no significant carbon corrosion occurs.

A simultaneous oxygen reduction at the PtRu/ carbon electrode enhances the methanol oxidation shifting the onset from 0.25 to 0.2 V/RHE (compare continuous and dashed curved in Fig. 3(b)). This fact could not have been concluded from the cyclic voltammogram alone (Fig. 3(a)).

The results from the present study support the assumption that the supply of oxygen containing species (i.e. surface oxides, adsorbed water, oxygen radicals) at low electrode potentials is the most critical factor influencing the catalysis of methanol oxidation. Pt–Ru is known to form stable surface oxides at comparatively low electrode potentials [5, 7] thus contributing to much easier removal of the poisoning species formed during methanol oxidation.

4. Conclusions

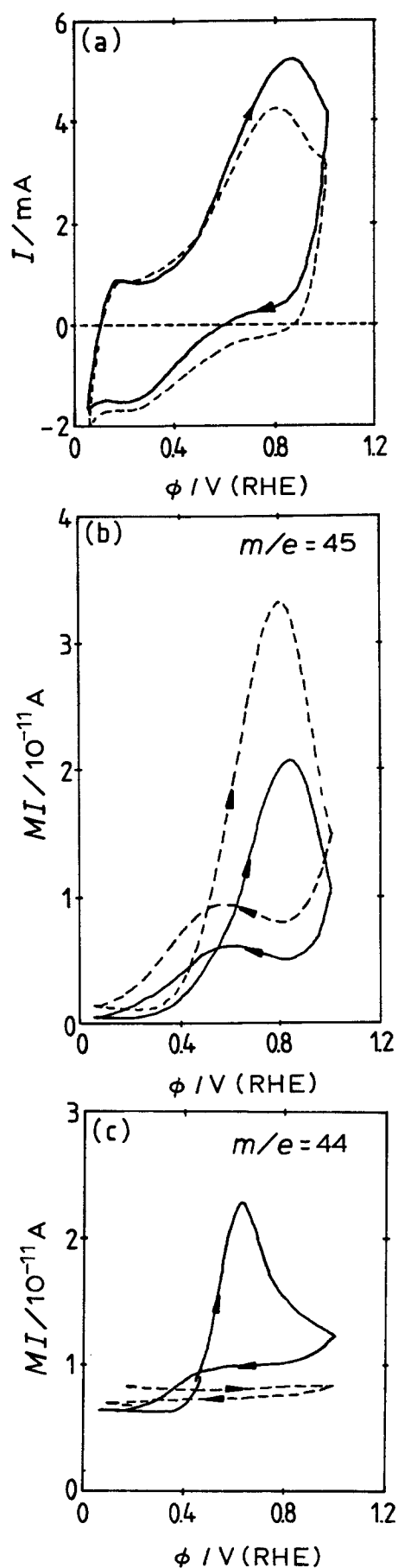It has been shown that the combination of cyclic volammetry and online MS is a very suitable method

Fig. 2. CO_2-formation at a 30% Pt/Ru (40/60) on Norit BRX electrode (6 mg cm^{-2}, 0.64 cm^2) in 0.05 M H_2SO_4/0.1 M $C^{13}H_3$OH-electrolyte during potentiodynamic methanol oxidation with Ar-purging (dashed line) and CO-purging (continuous line) in solution; scan rate: 1 mV s^{-1}. (a) Current against potential; (b) mass signal $m/e = 45$ against potential; (c) mass signal $m/e = 44$ against potential.
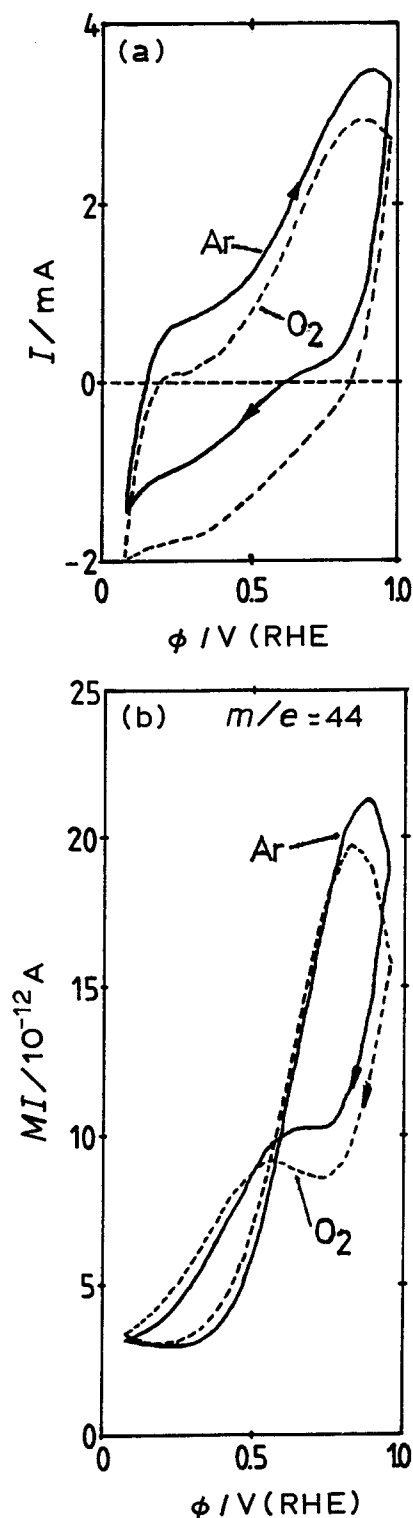
Fig. 3. CO_2-formation at a 30% Pt/Ru (40/60) on Norit BRX electrode ($10 \, \text{mg cm}^{-2}$, $0.64 \, \text{cm}^2$) in $0.05 \, \text{M} \, H_2SO_4/0.1 \, \text{M} \, CH_3OH$-electrolyte during potentiodynamic methanol oxidation with Ar-purging (continuous line) and O_2-purging (dashed line) in solution; (flow rate: $1 \, \text{dm}^3 \, \text{h}^{-1}$); scan rate: $1 \, \text{mV s}^{-1}$. (a) Current against potential and (b) mass signal $m/e = 44$ against potential.

to study the oxidation of methanol at highly porous technical carbon-based electrodes, especially when using C^{13}-labelled methanol.

Pt (5% on Norit BRX) and PtRu (40/60, 30% on Norit BRX) have been employed as electrocatalysts. From these catalysts Pt–Ru showed the better performance, the onset potential of methanol oxidation being shifted to a more cathodic value of 0.25 V in comparison to pure platinum (0.5 V/RHE). Methanol oxidation at the Pt–Ru catalyst in the presence of CO in solution is only slightly poisoned as compared to the case without CO.

It is possible to enhance the already excellent catalytic properties of Pt–Ru by purging oxygen into the solution, which shifts the onset of methanol oxidation from 0.25 to 0.2 V/RHE.

Acknowledgement

References

[1]   T. Iwasita, in 'Advances in Electrochemical Science and Engineering', Vol. 1, (edited by C. Tobias and H. Gerischer), VCH Weinheim (1990) p. 127.

[2]   T. Iwasita and F. C. Nart, J. Electroanal. Chem. 317 (1991) 291.

[3]   D. F. A. Koch, Australian Patent No. 46 123 (1964).

[4]   O. A. Petry, B. I. Podlovchenko, A. N. Frumkin and H. Lal, J. Electroanal. Chem. 10 (1965) 253.

[5]   T. Iwasita, F. C. Nart and W. Vielstich, Ber. Bunsenges. Phys. Chem. 94 (1990) 1030.

[6]   A. Hamnett and B. J. Kennedy, Electrochim. Acta 33 (1988) 1613.

[7]   S. Gottesfeld and J. Pafford, J. Electrochem. Soc. 135 (1988) 2651.

[8]   B. Bittins-Cattaneo, S. Wasmus, B. Lopez-Mishima and W. Vielstich, J. Appl. Electrochem., in press.

[9]   O. Wolter, C. Giordano, J. Heitbaum and W. Vielstich, Proc. Symp. Electrocatalysis, The Electrochemical Society, Pennington, NJ, (1982) p. 235.

[10] B. Bittins-Cattaneo, E. Cattaneo, P. Königshoven and W. Vielstich, in 'Electroanalytical Chemistry', Vol. 17 (edited by A. J. Bard), Marcel Dekker, New York (1991) p. 181.

[11] J. B. Goodenough, A. Hamnett, B. J. Kennedy, R. Manoharan, S. A. Weeks, Electrochim. Acta 35 (1990) 199.

[12] S. Wasmus, PhD Thesis, Bonn University (1992).