



Composite electrocatalysts for anodic methanol and methanol-reformate oxidation[†]

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Abstract

Binary anode electrocatalyst formulations were prepared by adsorption of phthalocyanine and tetraphenylporphyrin complexes of different transition metals on a commercial carbon supported platinum catalyst. Only after pyrolyzing the complexes at 700 °C under nitrogen were catalysts of some activity obtained. A binary Pt/Ni electrocatalyst prepared by this procedure exhibits considerable anodic catalytic activity in the acidic environment of the Nafion[®] electrolyte for reformate and direct methanol oxidation for more than 400 h without deterioration. Ternary electrocatalyst formulations Pt/Ru/W = 1/1/y were produced according to the Bönemann method. The Pt/Ru/W catalyst of 1/1/1.5 (mol/mol/mol) composition is optimal. Compared to the Pt/Ru catalyst, it enhances the performance of reformate (H₂ + 150 ppm CO) fuel cells by 50% and of direct methanol fuel cells (steam/methanol vapour = 50:1 mol/mol) by 80%. Attached to a GC electrode by a thin Nafion[®] film, the catalysts were also tested for methanol oxidation in aqueous methanol solutions in half cells by slow potential stepping. This procedure is useful for fast initial screening.

1. Introduction

For electrotraction the direct methanol fuel cell seems to be superior to reformate-fuelled PEMFCs from a systems point of view, as it requires little additional equipment compared to the extensive gas process technology for methanol reforming and reformate gas conditioning in indirect methanol fuel cell systems [1]. On the other hand, anodic methanol oxidation at platinum and platinum alloy catalysts is a self-poisoning reaction which blocks the active electrocatalyst surface by strongly adsorbed reaction intermediates such as CO, much stronger than dilute carbon monoxide present in purified reformate gas. Methanol crossover further reduces the efficiency of the cell due to poisoning of the cathode catalyst [2] and only relatively poor mass-specific power densities are obtained with DMFCs compared to cells operated on H₂ or reformate. Therefore it is necessary to place more emphasis on electrocatalyst research and to develop catalyst formulations which, with a reduced platinum loading, attain a significantly higher power density than current catalysts [3].

The working hypothesis is the generally accepted and well substantiated idea that any additional component

of the catalyst system should enhance the kinetics by chemically oxidizing adsorbed CO as do ruthenium oxides in the binary Pt/Ru catalyst, (Stimming et al. [4]). Therefore cocatalysts should exhibit one or several redox systems with redox potentials close to that of hydrogen (or CO or methanol). Most transition metals and many of their complexes have this property [5]. Iron, cobalt and nickel, being cheap, are of particular interest. For the Pt/Ni system cocatalytic activity for oxidation of CO in contaminated hydrogen has been reported [6]. Nickel is claimed to be stable in 85% H₃PO₄ at 100 °C for the time of the experiment, which however lasted only 3 hrs. In an investigation using similar catalysts with macrocycles of Fe, Co, Ni, Sn and Ru, but without any heat treatment higher than 130 °C, Bett et al. [7] found no enhancement of methanol oxidation, except in the case of the tin complex, which slightly increased the activity of platinum. It is the aim of this paper to reinvestigate these types of complex as cocatalysts for anodic reformate and methanol oxidation. Binary catalysts are obtained from active carbon supported platinum by adsorbing macrocycle complexes of different transition metals, in particular Mn, Rh, Co and Ni. Pyrolysis of the adsorbed complexes under an inert atmosphere is performed to improve the catalytic activity.

By systematically changing the Pt/W ratio of ternary Pt/Ru/W (1/1/y) catalysts the optimal composition will be determined. All catalysts are electrochemically characterized in two steps: (a) preliminary stepping

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voltammetry at glassy carbon electrodes in aqueous methanol, and (b) long term performance tests for between 400 and 500 h in 25 cm² cells operated on simulated reformat gas and steam–methanol vapour.

2. Catalyst systems

2.1. Binary electrocatalysts obtained from active carbon supported platinum and macrocycle transition metal complexes and their pyrolysis products

Porphyrin and phthalocyanine complexes are supposed to act as cocatalysts for methanol oxidation on platinum because they exhibit many redox steps and adsorbed macrocycles are expected to possess lateral mobility on the catalyst support, the surface diffusion of the redox species possibly enhancing the chemical oxidation of CO adsorbed on platinum.

From investigations with transition metal macrocycles as oxygen reduction catalysts it is known that after pyrolysis the metal is still present on the surface in a state of higher valency, stabilized by residues of the pyrolysed ring [8, 9]. This effect might also improve the catalytic action of platinum in methanol and CO oxidation. Investigations concerning the catalytic activity of transition metal macrocycles for anodic reactions are relatively few. For carbon-supported iridium and rhodiumtetraphenylporphyrin (IrTPP and RhTPP) catalytic activity for the anodic oxidation of pure CO was reported [9–11], but these were results for the supported complex without platinum. In the case of nickel phthalocyanine-tetrasulfonic acid and cobaltphthalocyanine (NiPCTSA and CoPC) we found some cocatalytic activity in preliminary experiments [12]. Upon pyrolysis of the complexes the catalytic activity increased. To clarify whether pyrolysis products of macrocycles are necessary for the cocatalytic activity of Ni and with the additional aim of confirming our previous preliminary measurements, a Pt/Ni catalyst was synthesized by the Bönemann method and compared with the pyrolysed Pt/Ni catalyst.

2.2. Ternary catalyst formulations

The Bönemann method is suitable for synthesizing nanodisperse, colloidal binary and ternary noble or non-noble transition metal alloys [13, 14]. Catalysts are prepared by adsorbing the colloids from these solutions on carbon black. For W a cocatalytic activity for anodic CO and methanol oxidation at Pt has repeatedly been confirmed, [15–17], and it was shown by the present authors that the cocatalytic effect of tungsten is also operative when it is added to the Pt/Ru (1/1) catalyst [3]. Tungsten was the most effective catalyst among W, Mo, Sn and others but the optimal composition of the ternary Pt/Ru/W formulation is unknown. In a series of experiments the tungsten content is varied systematically, leaving the Pt/Ru ratio at the established optimum of 1/1.

3. Experimental details

3.1. Catalyst synthesis

The procedure to prepare the carbon-supported binary and ternary catalysts according to Bönemann and the production of MEAs is described in detail in [3]. Vulcan XC-72 is used as the support for all catalysts, which always had a noble metal loading of 20 wt %.

The nickel complex of phthalocyanine-tetrasulfonic acid, NiPCTSA, cobaltphthalocyanine, CoPC, manganese phthalocyanine-chloride, MnPC-Cl, and tetrasulfonated rhodium tetraphenylporphyrin, RhTPP-S, were used as cocatalysts. RhTPP-S was prepared by S. Hofmann, (Institute of Inorganic Chemistry, Darmstadt University of Technology) by an in-house method. The other complexes were purchased from Aldrich. The electrocatalysts were prepared by suspending a commercially supplied carbon supported Pt-catalyst (20% on Vulcan XC-72) in a solution of the respective macrocycle complex in a suitable solvent at 80 °C followed by total evaporation of the solvent. Heating the catalyst in N₂ atmosphere to 700 °C for 1 h pyrolysed the macrocyclic compound. The molar ratio of macrocycle to Pt was always 1/4 in these electrocatalysts, as it was impossible to adsorb higher amounts of the complex with reproducible loading.

3.2. Preparation of catalysed GC-electrodes and of MEAs

3.2.1. Formation of electrocatalyst films on glassy carbon electrodes

Electrochemical characterization of electrocatalysts in aqueous, methanol-containing electrolytes at elevated temperatures demands electrodes with electrocatalyst embedded in recast ionomer films. From our experience, this is only achieved by the method of Gloaguen et al. [19, 21], which includes heat treatment of the electrode at temperatures sufficiently high, 160 °C in this case. High boiling triethylphosphate (TEP, b.p. 215 °C) as the cosolvent prevents decomposition of Nafion[®]. Annealing without TEP at only about 130 °C results in an ionomer which is subject to excessive swelling in a hot aqueous methanol electrolyte and leads to rapid destruction of the film.

To produce the catalyst-covered glassy-carbon (GC) electrodes a catalyst ink was prepared containing 2.3 vol % of 1% Nafion[®] solution (in 1/1 water–methanol, prepared in-house), 0.5 vol % triethylphosphate (TEP), 30 vol % water, 67 vol % ethanol and the respective amount of catalyst to yield 2 mg ml⁻¹ of noble metal. An appropriate volume of ink to achieve a noble metal loading of 34 μg cm⁻² was pipetted onto the polished (1 μm diamond suspension) surface of a cylindrical GC electrode (Sigri Inc., Meitingen, Germany; dia. 7 mm). It was dried at room temperature and then heated to 160 °C in a N₂ atmosphere for 1 min.

3.2.2. MEA production

MEAs were manufactured by spraying an ink containing catalyst, Nafion[®] solution, glycerol, water and tetrabutylammonium hydroxide directly onto the heated Na⁺-loaded membrane using a hand spray method developed by Gottesfeld and improved at our laboratory as previously described [22], [3]. MEA electrodes were approximately 15 μm thick and were formed by a spray technique (air brush) of five to six successive layers. The MEAs had an active area of 25 cm² and a noble metal loading of 0.4 mg cm⁻² at the anode. The cathode catalyst was always a commercially available 20 wt % platinum on carbon catalyst obtained from E-TEK and was also applied with a load of 0.4 mg noble metal per cm². The MEAs were mounted in commercially available graphite blocks (Electrochem Inc., Woburn, MA) together with hydrophobized carbon paper (Toray, TGPH-090 from E-TEK Inc., Natick, MA) as the gas diffusion layer.

3.3. Electrochemical characterization of the catalysts

3.3.1. Half cell measurements by potential stepping

It has been shown by other authors that steady state measurements at solid electrodes in methanol are impossible because the electrocatalyst deteriorates too fast. But potential stepping can be used, at least for initial screening [18–20]. A glass cell with a PTFE lid which contained electrode holders, gas inlet, gas outlet with reflux condenser, reference electrode (reversible hydrogen in the same electrolyte, RHE), counter electrode and a temperature control device, was used for these experiments. The electrodes were immersed in the N₂-purged base electrolyte (1 M H₂SO₄) at 70 °C and were kept at 75 mV vs RHE for 20 min. Methanol was then added to make up a 1 molar methanol solution. After 3 min, the start potential of 300 mV vs RHE was adjusted and the first current reading was performed after 15 min. Subsequently the potential was raised in 50 mV steps up to 650 mV vs RHE always with a holding time of 15 min.

3.3.2. Longterm operation of single fuel cells

For operation on hydrogen and H₂/CO-mixtures, the anode gas was humidified at 85 °C and dry oxygen was used as the cathode feed. The cell temperature was 75 °C during these experiments. For DMFC operation, 1 ml min⁻¹ of a 1 M aqueous methanol solution was totally evaporated and fed into the anode compartment of the cell. The cathode gas was dry oxygen. The cells were operated at ambient pressure at 95 °C. After an initial accommodation period of two weeks (340 h), the MEAs were always operated for between 400 and 500 h, sometimes even for six weeks (1000 h). Three MEAs had been prepared and investigated for each catalyst formulation in order to check the reproducibility. Current readings of these different specimens were reproducible within plus or minus 5% and catalyst deterioration between 400 and 500 h of operation was almost undetectable.

Current voltage curves were recorded galvanostatically holding each current for 5 min before reading the cell voltage. The current voltage curves were repeated at least three times after 24 h intervals. Between the measurements the cells were operated at half of their short-circuit current. All efforts to establish a reliable and longterm stable reference electrode for in-cell measurements failed. Therefore no reference was used. Operating on pure hydrogen all cells had the same current voltage characteristics. Therefore it was assumed that the cathode activity was identical for all cells and thus the observed cell voltage differences in operation on H₂/CO on the one hand and on methanol on the other hand were due to differences in the electrocatalytic activity of the different anode catalyst formulations. However, crossdiffusion of methanol (not that of the 150 ppm CO in reformat fired cells) also seriously impairs the catalytic activity at the cathode, although in a reproducible way. Therefore the cell voltage data of methanol and reformat supplied cells cannot be compared directly.

4. Results

4.1. Nanomorphology of polymetallic catalysts

The morphological characterization of the polymetallic catalysts was performed by C. Roth, B. Krause, G. Mische and H. Fuess at the Department of Materials Sciences, Darmstadt University of Technology. The morphological characterization of Pt/Ru/W catalysts prepared by the Bönemann method are discussed in a separate paper [22]. The catalyst particle size ranges from 1.8 to 2.5 nm. In a Pt/Ru/W (1/1/1) catalyst EDX and chemical analysis confirm the gross stoichiometry defined by the preparation method. XPS reveals that almost all the tungsten is not in the metallic, but in the hexavalent state. Neither crystalline tungsten trioxide nor hydrated tungsten trioxide [24] can be detected by X-ray diffraction and these compounds do not form a well defined crystalline phase but are present in some kind of X-ray amorphous state. It is not clear whether the reductive process in the Bönemann procedure was incomplete or whether reoxidation of the less noble catalyst components by air took place. However, in the case of tungsten other authors also report that the Bönemann method does not produce tungsten metal [25]. The Bönemann procedure is obviously not as effective as anticipated in achieving the formation of well defined highly dispersed binary and ternary alloys by codeposition of different metals. In particular, some segregation of non-noble and noble metals can occur.

4.2. Electrochemical measurements

4.2.1. Deterioration of catalyst layers on catalysed glassy carbon electrodes

A catalyst utilization close to 100%, as determined by cyclic voltammetry in sulfuric acid solution, and long

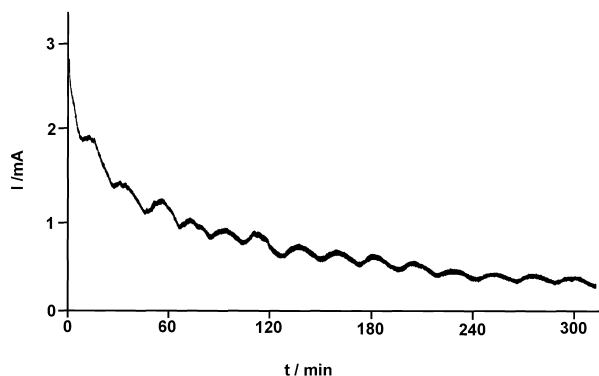


Fig. 1. Current transient measured at a glassy carbon electrode coated with catalyst/Nafion® with a loading of $13 \mu\text{g}$ ($34 \mu\text{g cm}^{-2}$) noble metal at 450 mV vs RHE in aqueous 1 M methanol/1 M H_2SO_4 at 70 °C.

term stability for anodic oxidation of dissolved hydrogen were confirmed. In methanol solution a relatively fast current decrease was observed within 1 to 2 h (Figure 1). (The current oscillations modulating this curve were reproducible, but have not yet been explained). The problem can be tackled by using potential-stepping. This at least allows a comparison of the results obtained for different catalysts and has been repeatedly applied for similar electrodes [18–20, 26] and by other authors, too.

4.2.2. Stepped potential measurements at catalysed glassy carbon electrodes

The complexes of Mn, Rh, Co and Ni with phthalocyanines and porphyrins enhance the catalytic activity of methanol oxidation only marginally, if at all. Pyrolysis enhances their cocatalytic effect remarkably. Current–voltage curves compare the activities of Pt and four pyrolysed Pt/macrocycle–Me catalysts in Figure 2 with Mn, Co, Rh and Ni as transition metal components. Mn

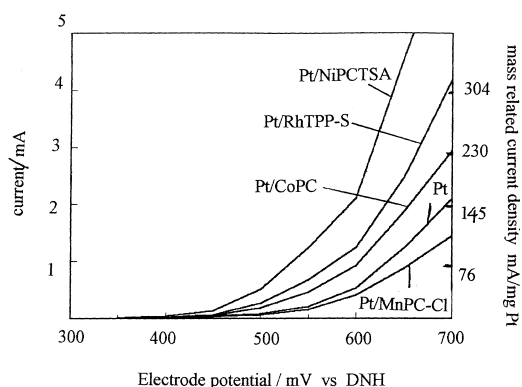


Fig. 2. Voltammograms of anodic methanol oxidation (aqueous 1 M methanol/1 M H_2SO_4 at 70 °C) measured by the stepped potential method with catalyst coated GC electrodes. All binary catalysts were prepared from commercial Pt on carbon by adsorption of the respective transition metal complexes. The complexes are pyrolysed in N_2 at 700 °C. Platinum loading amounts to $34 \mu\text{g cm}^{-2}$. Complex forming agent: (PC) phthalocyanine, (PCTSA) phthalocyanine-tetra-sulfonic acid, (TPP-S) tetrasulfonated tetraphenylporphyrin.

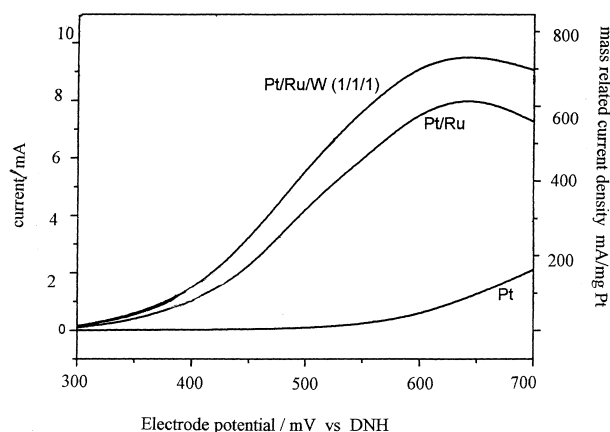


Fig. 3. Voltammograms of anodic methanol oxidation measured by the stepped potential method with catalyst coated GC electrodes. Ternary Pt/Ru/W (1/1/1) and binary Pt/Ru (1/1) catalyst are prepared by the Bönemann method. Noble metal loading (Pt + Ru) amounts to $34 \mu\text{g cm}^{-2}$ -aqueous 1 M methanol/1 M H_2SO_4 at 70 °C.

attenuates the activity of Pt. Catalysts containing Rh and Co are slightly more active and, when they contain the pyrolysed nickel complex of PCTSA, are remarkably more active than the platinum catalyst. This is not only demonstrated by the height of measured anodic currents at, say 500 mV, but is also confirmed by the ‘ignition potentials’ for methanol oxidation derived from slow first scan voltammetry.

It can therefore be stated that nickel in pyrolysed Pt/Me catalysts could make a good cocatalyst, whereas cobalt and rhodium are cocatalytically active but are certainly not very promising candidates.

Figure 3 shows stepping voltammograms of Pt/Ru and Pt/Ru/W (1/1/1), obtained by Bönemann reductive precipitation. This result confirms our previously published data [3] obtained by in-cell measurements and underlines the statement that, as a cocatalyst for anodic methanol oxidation, tungsten is able to enhance not only the effective catalytic activity of platinum but also that of the binary Pt/Ru catalyst.

4.3. Fuel cell experiments

4.3.1. Binary catalysts from pyrolysed Pt/macrocycle metal complexes

Figure 4 depicts the current voltage curves for methanol oxidation obtained by longterm in-cell measurement with binary Pt/Me catalysts obtained by pyrolysis of the respective transition metal complexes. Current–voltage curves for Pt and the binary Pt/Ni catalyst, prepared according to the Bönemanns procedure, are also plotted. The most important finding is the remarkable effect of nickel as a cocatalyst, in particular with pyrolysed nickel macrocycle complexes.

4.3.2. Optimizing the composition of ternary Pt/Ru/W (1/1/X) catalyst formulations

Figure 5 compares (as a summary of the results of recent work [3]) the current voltage curves for anodic

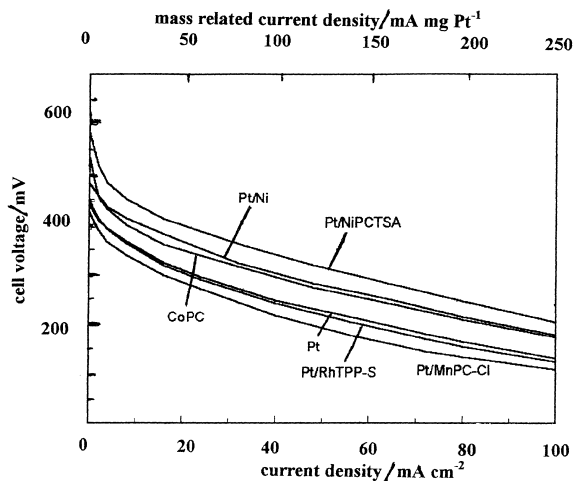


Fig. 4. Current–voltage curves of methanol fuel cells operated at 95 °C with a Pt/Ni catalyst (prepared according to the Bönemann method) and Pt/pyrolysed transition metal macrocycle catalysts. Complex forming agent: (PC) phthalocyanine, (PCTSA) phthalocyanine-tetrasulfonic acid, (TPP-S) tetrasulfonated tetraphenylporphin; all macrocycles pyrolysed at 700 °C in N₂. Platinum loading amounts to 0.4 mg cm⁻².

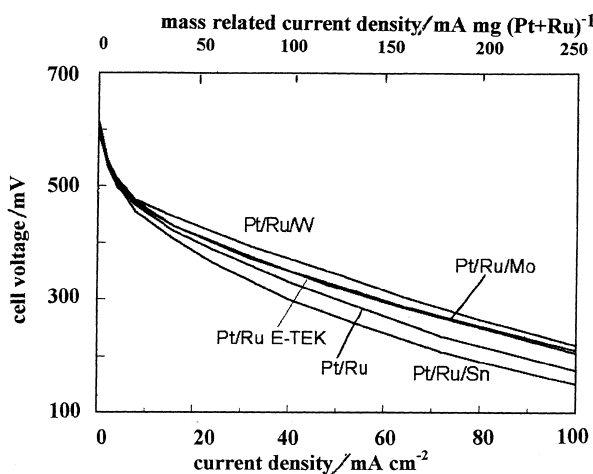


Fig. 5. Current–voltage curves of methanol fuel cells at 95 °C with ternary Pt/Ru/Me electrocatalysts (Me = W, Mo and Sn [3]) prepared according to the Bönemann method); Pt + Ru loading: 0.4 mg cm⁻². Plot shows also current–voltage curve for best commercially available binary Pt/Ru catalyst (E-TEK) which matches that of the Pt/Mo catalyst.

methanol oxidation with three different ternary Pt/Ru/Me formulations (Me = Sn, Mo and W) and compares them with the binary Pt/Ru electrocatalyst prepared according to the Bönemann procedure. Clearly Mo and W improve the catalytic activity of the binary Pt/Ru(1/1) catalyst but tungsten is more effective than molybdenum.

Figures 6 and 7 compare the current voltage curves of fuel cells with four different Pt/Ru/W electrocatalyst formulations prepared by the Bönemann method. The cells are operated on hydrogen containing 150 ppm of

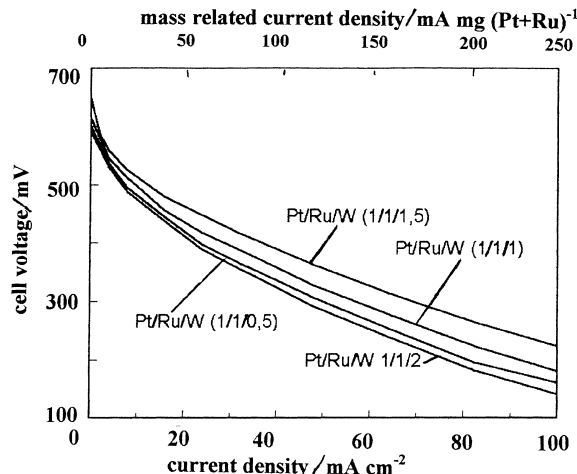


Fig. 6. Current–voltage curves of methanol fuel cells at 95 °C with ternary Pt/Ru/W electrocatalysts of systematically varied composition prepared according to the Bönemann method. Pt + Ru loading 0.4 mg cm⁻².

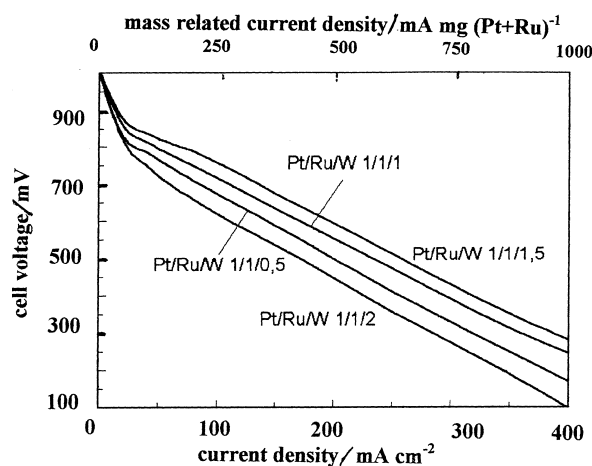


Fig. 7. Current–voltage curves of reformate fuel cells at 70 °C with ternary Pt/Ru/W electrocatalysts of systematically varied composition prepared according to the Bönemann method. Pt + Ru loading: 0.4 mg cm⁻².

CO (simulated reformate) (Figure 7) and on methanol (Figure 6), respectively. The Pt/Ru ratio is always 1 but the W/Pt ratio in the catalyst changes from 0.5 to 1 to 1.5 and 2.

It is obvious that at a ratio of 1.5 an optimum for both fuels is obtained. Figure 8 evaluates this effect by plotting the current densities of the respective compositions normalized with respect to those of the binary Pt/Ru catalyst, versus the ratio W/Pt. With simulated reformate the cell voltage is set at 600 mV, with methanol to 400 mV. With simulated reformate the improvement versus the binary Pt/Ru catalyst amounts to approximately 50% and with methanol it is 80%. But the current density in reformate cells at 600 mV cell voltage is higher than in methanol cells at a cell voltage of 400 mV by a factor of about 5.

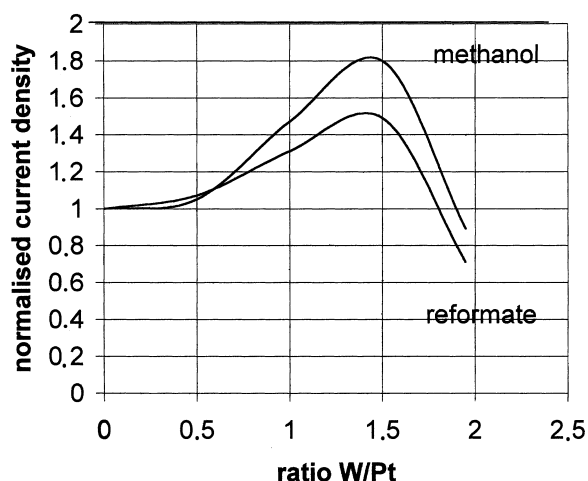
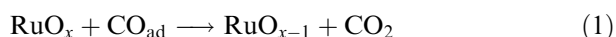


Fig. 8. Current-densities of methanol and reformat fuel cells with ternary Pt/Ru/W electrocatalysts normalised with respect to those of the binary Pt/Ru (1/1) catalyst against W/Pt ratio; Pt + Ru loading 0.4 mg cm^{-2} ; methanol cells operated at 95°C with 400 mV cell voltage, reformat cells operated at 70°C with 600 mV cell voltage.

5. Discussion

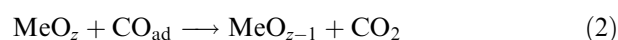
This investigation demonstrates the fact that results from short-term experiments of composite electrocatalysts on immersed GC electrodes are only of limited value. Initial current densities in these experiments are usually higher by a factor of at least 2 than those obtained by long-term cell experiments. However, the steady state condition is never obtained on immersed single electrodes and the transient currents decrease within hours to values which are much lower than steady state data obtained in fuel cells. The reason for this discrepancy is not yet clear. The present work is mainly explorative and gives little opportunity and background for well founded mechanistic discussions. The theoretical background of methanol oxidation catalysis is still meagre and the molecular kinetics of electrocatalysis on more involved catalyst formulations is not well understood. Only with regard to platinum and Pt/Ru do we know enough to understand the catalytic effect.

From the work of Stimming and coworkers we know that the cocatalytic activity of ruthenium in Pt/Ru is due to its oxidation to ruthenium surface oxides which chemically oxidize adsorbed carbon monoxide according to Equation 1 [27]. CO_{ads} has a relatively high surface diffusivity on platinum and can, therefore, easily diffuse to ruthenium oxide patches on a platinum surface [4]:

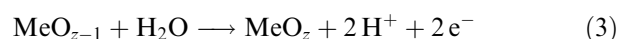


Rolison et al. [24] showed that in commercially available Pt/Ru blacks the noble metals are not entirely in the zerovalent state but some fraction of Pt is present as PtO_x , whereas most of the Ru is apparently present as hydrated ruthenium oxide RuO_xH_y . They claim that this species is the active cocatalyst. Roth and Fuess found, in catalysts prepared by the Bönemann method, that part of the Ru, as well as less noble components such as W,

are in an oxidized state, [22]. Therefore it has to be accepted that in the ternary catalysts there exist at least three different phases: metallic Pt/Ru alloy, ruthenium oxide and tungsten oxides. In principle the same mechanism of cocatalysis could be expected for WO_y as in the case of RuO_x , where it has been established that the cocatalytic effect of the non-noble metal oxides originates from oxide-containing surface groups formed at higher anodic potential. If a significant amount of the metal oxides is not in contact with the platinum particles (which is not known, but possible) adsorbed carbon monoxide would possibly be oxidized, not only at the two-phase boundary between metal oxide and platinum, but might also spill over via the active carbon support to the oxide phase where it is oxidized according to Equation 2:



The higher valent metal oxide would be regenerated by anodic oxidation according to Equation 3:



The concept of spill-over is difficult as carbon monoxide is only weakly adsorbed on carbon and, therefore, CO-spillover from platinum to the catalyst support should be thermodynamically hampered. Yet, Auer et al. [28] reported good activity of a bimetallic catalyst consisting of separate Pt and Ru particles on a carbon support. The activity of this catalyst can be understood using the above assumption, while it cannot easily be explained by the conventional understanding of the bimetallic mechanism in Pt/Ru cocatalysis, which is assumed to be due to the action of alloyed particles and their mosaic surface.

Nickel is stable in the Nafion[®] electrolyte of membrane fuel cells and a very interesting cocatalyst, as it is cheaper and can be chemically handled much more easily than the heavy transition metals W or Mo. If applied to Pt catalysts in 0.25 molar ratio by pyrolysis of adsorbed complexes of polynuclear compounds, its cocatalytic effect is roughly half that of W in binary Pt/W (1/1) formulations prepared by the Bönemann method. Much more work is necessary to find the optimal composition, the corresponding nanostructure of this binary catalyst and to find out definitively, whether this binary Pt/Ni catalyst is sufficiently stable in the long term.

The optimal ratio of the tungsten content in the ternary catalyst Pt/Ru/W, determined empirically using the Bönemann procedure, must not be taken as the last word on the subject, as it very likely holds only for the Bönemann procedure. The location of the tungsten species on the catalyst or its support has not yet been identified, neither by TEM nor by XRD [22]. We understand that too much of the cocatalyst deactivates platinum. Too much tungsten oxide would cover and block the most important part of the catalyst system,

that is, the platinum. This metal is indispensable as the prime mover, as it chemisorbs methanol and is responsible for CH splitting.

A more quantitative explanation for the cocatalytic activity of tungsten in the ternary catalyst cannot be given unless further clarification of the exact morphology, including the segregation, dispersity and chemical nature of the tungsten species, is achieved.

With respect to the ternary Pt/Ru/W catalyst the optimal ratios of platinum to the second and third metal still have to be determined. Still the Pt/Ru molar ratio, which was kept constant at 1/1 during this investigation, should be varied in order to improve the catalyst performance further. This is time-consuming and difficult unless more efficient catalyst testing procedures are developed allowing for combinatorial methods.

In this paper we have attempted to demonstrate the usefulness of a not yet generally accepted methodological approach of combining nanomorphological [22] with long term electrode kinetic measurements, which in our opinion is as essential for electrocatalyst development as for the development of heterogeneous catalysts for gas phase reactions. The data from this investigation, though interesting from a practical point of view, need further investigation and also clarification by more fundamentally oriented work.

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