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Bifunctional electrodes for an integrated water-electrolysis and hydrogen–oxygen fuel cell with a solid polymer electrolyte

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An alternative concept of an integrated water electrolysis/hydrogen–hydrogen fuel cell using metal electrocatalysts and a solid polymer electrolyte is described. Instead of operating both electrodes as hydrogen and oxygen electrodes respectively the electrodes are used as oxidation and reduction electrodes in both modes of operation. A more suitable selection of electrocatalysts and an improved cell design are possible; both can increase the efficiency of the cell considerably. New results on the electrocatalytic activity of various noble-metal containing catalysts with respect to both oxygen evolution and hydrogen oxidation in a proton exchange membrane-cell at 80 °C are reported. Kinetic data derived from Tafel plots of the oxygen evolution polarization curves agree closely with those of experiments with aqueous sulphuric acid electrodes. This agreement allows the determination of kinetic parameters for electrocatalysts difficult to prepare in solid smooth electrodes but easy to be made into porous deposits. Polarization curves of the hydrogen oxidation reaction clearly indicate a relative activity rating of the studied catalysts. In cycling tests the lifetime stability of the new bifunctional oxidation electrode was determined. Polarization data obtained under these conditions agree with those obtained in earlier experiments where electrodes were exposed to only one type of oxidation reaction. During a test of 10 cycles (30 min of electrolyser and 30 min of fuel cell mode each) no changes in the electrode potential were observed. With the conventional cell design employing a hydrogen and an oxygen electrode both catalyzed with platinum and a current density of 100 mA cm^{-2} a storage efficiency of 50% was calculated; with the alternative concept of oxidation and reduction electrodes and selected oxidation catalysts this was improved to 57%. With further improvements these efficiencies seem possible even at current densities of 500 mA cm^{-2}.

1. Introduction

Various attempts to realize an electrochemical cell operating alternatively as a water electrolyser and as a hydrogen/oxygen fuel cell have been reported in recent decades. These devices were commonly called 'reversible fuel cells'. In all the proposed systems one electrode is used solely for the oxygen reaction (oxygen evolution in the electrolysis mode, oxygen consumption in the fuel cell mode), whereas the other operates as the corresponding hydrogen electrode. A first attempt was described by Justi and Winsel [1]. Electrodes made of nickel and nickel oxide in the form of 'valve-electrodes' and an electrolyte of concentrated potassium hydroxide were used. Bone *et al.* [2] described a cell using an ion exchange membrane (IEM) as an electrolyte. Because of material problems related to the IEM and the difficult preparation of catalyst layers even at very low current densities poor efficiencies were obtained; subsequently the development was stopped. In the subsequent discussion the degree of utilisation (efficiency) is given by the ratio of the voltage of the operating fuel cell to the cell voltage during electrolysis. Findl and Klein described a 'regenerative H_2/O_2-fuel cell battery' with an alkaline electrolyte solution soaked into an asbestos separator; this limited the cell capacity [3]. At low current densities an efficiency of 50% was reported.

After a twenty year intermission further work has been reported. Kordesch *et al.* have described a cell with an alkaline electrolyte and a multilayered bifunctional oxygen electrode [4]. The electrode comprised nickel layers of fine and coarse porosity and a hydrophobic porous carbon layer. No experimental results were reported. A concept of 'reversible electrolysis and fuel cell' with a proton exchange membrane (PEM) for application in zero gravity environments was proposed by Leonida [5]. During electrolysis water is supplied to the cathode by passive wetting via a water permeable membrane. In the fuel cell mode water formed at the cathode is removed across a porous plate of titanium pressed on to the back side of

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the cathode. A small pressure difference of 0.1 atm accelerates water removal.

Because the rates of oxidation and evolution of hydrogen and (to a lesser extent) the reduction of oxygen occur with favourable kinetics at platinum, improvements of the oxygen electrode kinetics for bifunctional electrodes are crucial. Various studies pertaining to oxygen electrocatalysis at bifunctional oxygen electrodes have been published in recent years. Platinum is necessary for oxygen reduction in an acidic electrolyte solution, unfortunately it is a rather poor catalyst for oxygen evolution. Therefore other materials have been examined. Swette and Giner have studied the corrosion behaviour of several mixed oxides in alkaline electrolyte solutions, sodium-platinum oxide and lead-iridium-oxide were identified as particularly promising catalysts [6]. Ham *et al.* have investigated the influence of an increase in surface area on the electrochemical activity for lanthanum–cobalt-perovskite [7]. Yeager *et al.* presented the results of investigations of transition metal macrocycles and perovskites as materials for bifunctional oxygen electrodes [8]. For systems with alkaline electrolyte solutions ruthenium–pyrochlores and lead ruthenate were the most promising catalysts.

In fuel cells with liquid electrolytes gas diffusion electrodes are necessary for gas consuming electrode reactions. Because of their structure they are not useful for gas evolution reactions [4]. In systems with IEM gas diffusion electrodes are not necessary. In both modes of operation the catalyst is present as a thin, electronically conducting and porous layer as close to the membrane as possible [9]. As compared to cells with liquid electrolytes the use of IEM simplifies the design of an integrated cell (see following section).

This brief review indicates that attempts to develop a ‘reversible fuel cell’* have been focused on activity and stability of the oxygen electrode and on cell and electrode design.

2. Ion exchange membranes as solid electrolytes in electrochemical cells

In electrochemical cells a liquid electrolyte can be replaced by an ion exchange membrane (IEM). Since ionic conduction occurs via the fixed ions in the polymer, water has to be supplied only in order to maintain the moisturised state of the polymer. During electrolysis, in the case of a PEM, this is established by circulating purified water on the anode side; in the fuel cell mode the reactant gases are saturated with water at a temperature somewhat below the operating temperature of the cell.

Consequently the IEM serves simultaneously as a separator, an electrolyte and a catalyst/electrode support. There is no need for a circulating electrolyte solution: because of the very thin IEM ohmic losses in the cell are small. The mechanical stability of the membrane makes electrolysis under pressure possible (up to 30 bar).

In the case of electrochemical cells operating with solid polymer electrolytes, as well as the catalyst itself, the interphase (interfacial layer) established between the electrode and the polymer membrane is of central importance. The properties of this interphase are controlled by its preparation; further details pertaining to experimental procedures employed in our work and results will be reported separately [10].

3. The new concept of bifunctional electrodes

In order to solve the problems related in particular to the bifunctional oxygen electrode in the ‘reversible fuel cell’ a new concept of bifunctional electrodes was developed [11–13]. In contrast to bifunctional electrodes described so far, in this new concept oxidation and reduction reactions are assigned to the electrodes. Thus hydrogen oxidation (fuel cell mode) and oxygen evolution (electrolysis mode) proceed alternatively at one electrode, named the oxidation electrode, whereas the two remaining reactions proceed at the reduction electrode. A cell operating with these types of electrodes will be called an ‘integrated water electrolysis and hydrogen/oxygen fuel’ as opposed to the ‘reversible fuel cell’. Using the new concept it is less difficult to identify suitable electrode materials for both electrodes.

During selection of potential catalyst materials for the bifunctional electrodes in the new concept several arguments were considered. For both *reduction reactions* platinum is by far the best catalyst in acidic media. Hydrophobic graphite paper identified as the most suitable material for removal of water formed during the oxygen reduction reaction is stable during both reactions. In the conventional ‘reversible cell’ use of this paper was restricted because of its corrosion at the anodic oxygen evolution electrode potential.

The catalyst for the *oxidation electrode* can be selected based on the electrochemical activity for oxygen evolution and hydrogen oxidation. The activity of various noble metals and their oxides in contact with acidic solutions has been studied (for a detailed review see [14]). In the case of the oxygen evolution the relative activity is Ir/Ru > Ir > Rh > Pt. Because of experimental difficulties in the study of the hydrogen oxidation reaction with gas fed electrodes a respective grouping is less secure; presumably platinum is more active than the other metals listed above. A quantitative rating should be possible using a IEM-cell since electrodes in these cells need not be of the gas diffusion electrode type. Generally it is safe to assume that improvements in overall cell efficiency gained by using a better catalyst for the oxygen evolution reaction than platinum will certainly be greater than any losses caused by a slightly smaller activity of this material for the hydrogen oxidation reaction.

4. Experimental details

In all experiments a cation exchange membrane

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* This term has been used to describe an electrochemical cell as discussed in the text, obviously such a system cannot operate practically under thermodynamically reversible conditions.

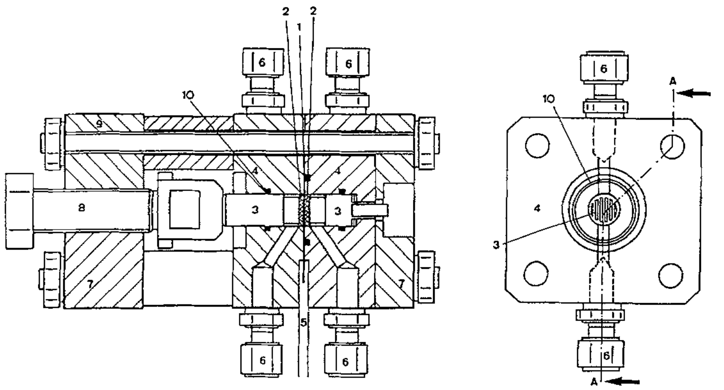

Fig. 1. Cross section of the electrochemical cell as used for experiments with the IEM cell; left: side view, right: front view. (1) membrane-electrode unit, (2) sintered titanium disc, (3) current collector (titanium), (4) cell body, (5) hole for reference electrode, (6) gas and water supplies, (7) steel plate, (8) pressure screw, (9) screw, (10) O-ring.

(CEM) Nafion® 117 was used as a solid polymer electrolyte. Basically it consisted of a perfluorinated polymer backbone with sulphonic acid groups, the equivalent weight was $1100\,\mathrm{g\,mol^{-1}}$. In its swelled state its thickness was $200\,\mu$m; in contact with 1 M sulphuric acid its specific conductivity was 0.16 to $0.18\,\Omega\,\mathrm{cm^{-2}}$. Before use the membrane was treated with semi-concentrated nitric acid, washed with distilled water and soaked for 30 min at 130 °C in an autoclave.

Catalyst-membrane units were prepared by two different methods. Platinum was deposited by chemical reduction of its anionic salt with hydrazine directly on to the membrane. All other catalysts obtained as a powder were mixed with 10% PTFE and formed into porous layers, which were pressed on to the CEM. As catalyst metal powders were used as supplied (Heraeus Feinchemikalien); metal oxides were prepared by sintering the corresponding chlorides (Heraeus Feinchemikalien) in an atmosphere of air for 2 h at 500 °C. Catalyst loading on the membrane was $5\,\mathrm{mg\,cm^{-2}}$.

A specifically designed electrochemical three-electrode cell (Fig. 1, a detailed description of the cell design has been provided elsewhere [13, 14]) with an apparent electrode surface area of $1\,\mathrm{cm^2}$ and a potentiostat (Bank POS 73) were used. Current–potential relationships were obtained under steady state potentiostatic conditions with computer-aided potential control and current recording (HP3497A data logger and HP9121 PC). Data points were measured after settling times of 200 s (with all curves containing 20 to 25 data points). Cycling measurements were done galvanostatically, electrode potentials were recorded at 60 s intervals at current densities of $100\,\mathrm{mA\,cm^{-2}}$, the mode of operation (electrolysis and fuel cell electrode reactions) was changed in 30 min intervals. iR-correction of electrode potentials was based on the results of a.c.-impedance measurements (Solartron FRA 1250A, Solartron potentiostat ECI 1286).

All measurements were performed in half cell arrangements at 80 °C, the temperature was maintained via the feed water loop.

5. Results and discussion

In order to study the feasibility of the new cell concept with bifunctional oxidation and reduction electrodes several catalyst materials were characterised with respect to their activity for the oxygen evolution and the hydrogen oxidation reaction.

5.1. *Oxygen evolution reaction*

In Fig. 2 Tafel-plots for the oxygen evolution reaction at several catalysts in an IEM-cell at 80 °C are displayed. They were obtained after the electrodes had been operated at $1000\,\mathrm{mA\,cm^{-2}}$ for five days. Over three to four decades of current density a linear relationship is observed up to $j = 1000\,\mathrm{mA\,cm^{-2}}$. A clear rating with respect to the electrochemical activity can be derived. The curves measured with iridium and its oxide as well as with rhodium and its oxide are displaced by 50 mV, respectively. Ruthenium oxide and the mixed Ru/Ir oxide show a change of Tafel slope, in the case of the mixed oxide presumably because of the presence of Ru. By extrapolating the linear portion of the plots to the thermodynamic oxygen rest potential (calculated as $E_0 = 1.195$ V/NHE under the experimental conditions) the exchange current density j_0 can be calculated. From the Tafel slope the number of electrons transferred in the rate determining step and the transfer coefficient α can be deduced. For a comparison of j_0 with literature data obtained with smooth electrodes it is desirable to correct the data obtained here with porous electrodes of a medium to high internal surface area by dividing the values of j_0 by the true electrode surface area (expressed as roughness R = true surface area/apparent area) resulting in $j_{0,c}$. All relevant data are collected in Table 1.

The electrochemically active (true) surface area of the noble metal catalysts studied in this work is difficult to determine with the exception of platinum, where hydrogen adsorption yields reliable data. The adsorption of metal ions (upd (under potential deposition)-deposition) and their subsequent analytical determination as suggested by Savinell *et al.* [15] is not applicable with an IEM-electrode unit. The only

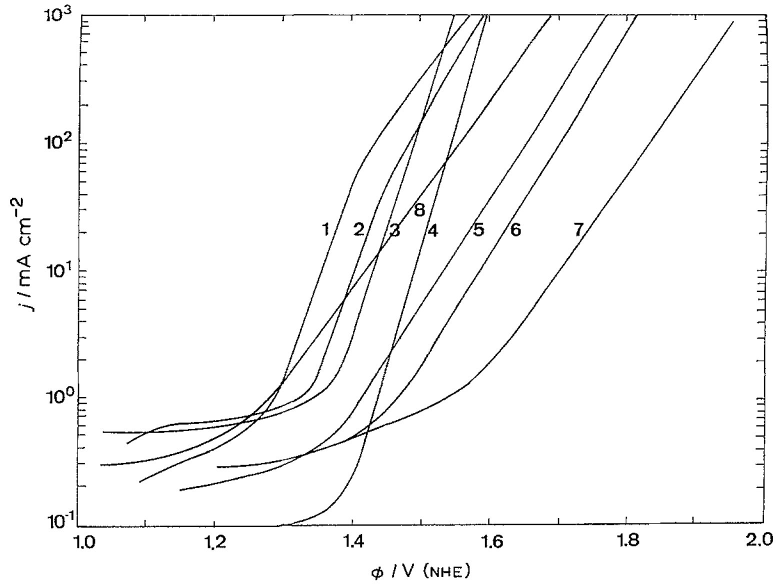

Fig. 2. Tafel plot for the oxygen evolution reaction in an IEM-cell, 80 °C, Nafion® 117 membrane, iR-corrected, (1) Ru-oxide, (2) Ir/Ru(1 : 2)-oxide, (3) Ir-oxide, (4) Ir, (5) Rh-oxide, (6) Rh, (7) Pt, (8) Rh/Ru(1 : 1)-oxide.

applicable method is the determination of the differential electrode capacitance from cyclic voltamograms recorded at various scan rates. According to Yeo *et al.* [16] CVs recorded in a potential interval of ±25 mV around the rest potential yield capacity values representing the electrochemically active surface area. Roughness data obtained this way with noble metal oxides deposited thermally on titanium range from 2000 to 20 000. These values, as well as those determined with the catalysts used in the experiments reported here, are possibly systematically too high by one to two decades. This would also explain why the corrected exchange current densities, $j_{0,c}$, as listed in Table 1 as well as reported in [16], are too small when compared with literature data obtained with smooth electrodes. Nevertheless a relative classification is justified.

With this exception, the data in Table 1, obtained with catalysts in an IEM-cell are in close agreement with literature data obtained with catalysts in contact with sulphuric acid solutions; a comparative discussion with respect to the different catalysts follows. The results also agree well with data obtained with IEM-cells and reported by Stucki and Menth for platinum and rhodium at low current densities [17] and by Millet *et al.* [18] for platinum.

In the case of platinum in an IEM-cell, as well as in a sulphuric acid electrolyte solution a one-electron process is rate determining. Presumably the reaction mechanism in both electrolytes is the same. As rate determining step the formation of a hydroxyl radical has been proposed [19] in an 'oxide pathway'. With rhodium and its oxide the kinetic data are also in agreement with results obtained with sulphuric acid solutions; this includes the difference in activity between the metal and its oxide.

In the case of iridium, because of the various possible reaction pathways and the contribution of oxide layers [20], the oxygen evolution mechanism remains unclear. Gottesfeld and Srinivasan have identified two differently active iridium oxides depending on the anodic electrode potential [21]. Kötz *et al.* have studied the mechanism of oxygen evolution at iridium electrodes using XPS; they have identified tetravalent iridium compounds [22, 23].

Based on the Tafel slope of $b = 40\,\mathrm{mV\,dec^{-1}}$ and the findings reviewed a reaction pathway similar to that discussed for platinum and rhodium, but with the electrochemical formation of a metal-oxide as the rate determining step can be proposed for an iridium electrode.

With iridium oxide prepared by thermal decomposition of iridium salts as an electrode in contact with

Table 1.

Catalyst	*Tafel slope* $b/\mathrm{mV\,dec^{-1}}$	*Transfer coefficient*	j_0 $/\mathrm{A\,cm^{-2}}$	R	$j_{0,c}$ $/\mathrm{A\,cm^{-2}}$
1 Ru-oxide	65/140	0.54/0.5	2.5×10^{-5}	2100	1.2×10^{-8}
2 Ir/Ru-oxide	56/107	0.43/0.66	8×10^{-6}	2500	3.2×10^{-9}
3 Ir-oxide	50	0.48	4×10^{-8}	7500	5×10^{-12}
4 Ir	57	0.42	8×10^{-7}	850	9.4×10^{-10}
5 Rh-oxide	120	0.59	1.5×10^{-5}	2000	7.5×10^{-9}
6 Rh	115	0.61	4.5×10^{-6}	875	5.1×10^{-9}
7 Pt	130	0.54	1.5×10^{-8}	900	1.7×10^{-11}
8 Rh/Ru-oxide	130	0.54	1.7×10^{-4}	2350	7.2×10^{-8}

a sulphuric acid solution Tafel slopes of 55–60 mV dec^{-1} have been reported [24, 25]. The Tafel slope determined from the present data, and corrected for the higher temperature is 42 mV dec^{-1} and is thus significantly lower. Trasatti has already stated the strong influence of the preparation conditions of iridium oxides upon their electrochemical activity [26]. According to his experiments the change of the temperature established during thermal decomposition of the salt from 300 °C to 550 °C leads to a decrease of the voltammetric charge within a CV between $E = 900$ and $E = 1500$ mV/NHE to 1/24 of its initial value [27]. Obviously it is difficult to deduce a reaction mechanism based on the Tafel slope alone for this catalyst.

In the literature for ruthenium oxide and iridium/ruthenium oxide Tafel slopes at room temperature and with an electrolyte of 1 M $HClO_4$ of 40–55 mV dec^{-1}, depending strongly upon the preparation conditions, have been reported [28–30]. Upon correction of the present data for temperature the resulting value of 57 mV dec^{-1} (Ru-oxide) and of 48 mV dec^{-1} (Ir/Ru-oxide) falls within this range of results. At higher current densities, with both catalysts, the slope changes to values of 140 mV dec^{-1} (Ru-oxide at 80 °C) and 107 mV dec^{-1} Ir/Ru-oxide at 80 °C). Because this may be due to a change in the reaction mechanism, as well as to an increase of the internal Ohmic resistance of the oxide layer, no specific reaction pathway can be inferred.

Data for a mixed rhodium/ruthenium-oxide as an oxygen evolution catalyst have not been reported so far. The value of the Tafel slope of 130 mV dec^{-1} (at 80 °C) cannot be interpreted as being caused by an averaging of the respective values of both oxides. Because of the high Tafel slope and the good electrochemical activity even at high current densities this mixed catalysts shows the highest exchange current density of $j_0 = 1.7 \times 10^{-4}$ A cm^{-2}. As can be seen from Fig. 2 knowledge of the exchange current density alone is not a sufficient criterion for comparing the electrochemical activity of different catalysts, certainly the Tafel slope must be considered. Nevertheless, this mixed oxide catalysts seems to be a promising catalyst for a bifunctional oxidation electrode provided that it shows a sufficient activity in the hydrogen oxidation reaction.

5.2. *Hydrogen oxidation reaction*

The *hydrogen oxidation* reaction was studied with the catalysts discussed above in order to evaluate their usability for the new cell concept. Since the hydrogen oxidation reaction proceeds with gas consumption the catalyst layers should be optimized for low transport hindrances. In the case of platinum, a platinum black/PTFE layer with very low transport overpotential up to 1000 mA cm^{-2} was developed. Unfortunately the preparation conditions developed for this material could not be applied to all other catalysts under study here. Thus the current-potential curves as collected in Fig. 3 contain significant transport limitations; Tafel plots are not applicable under these conditions. In order to establish an electrochemical activity rating the electrode potential at a current density of 1000 mA cm^{-2} was evaluated; the following order was obtained:

Pt > Rh/Ru(1 : 1)-oxide > Ir > Rh, Rh-oxide
> Ir/Ru(1 : 2)-oxide > Ru-oxide

The thermally prepared iridium oxide does not show any activity in the hydrogen oxidation reaction. This confirms earlier findings of Boodts and Trasatti, who concluded from the lack of establishment of a hydrogen rest potential an extremely small activity despite the fact that this material is quite a good catalyst for the hydrogen evolution reaction [31].

According to Fig. 3 the catalytic activity of the mixed oxide is greater than the activity of the single oxides. Assuming that the activity rating is correct this would indicate a synergistic effect.

Data on the hydrogen oxidation at ruthenium and rhodium containing catalyst are not reported in the literature, most data on this reaction so far are concerned with platinum as an electrocatalyst [32, 33]. Niedrach *et al.* have observed, that the presence of either rhodium or ruthenium greatly increases the activity of a platinum electrode towards hydrogen oxidation when carbon monoxide is present [34]. Kosak *et al.* reported, that rhodium oxide is a suitable catalyst for the hydrogen oxidation reaction, which, contrary to platinum shows only minor losses of electrode potential in the presence of up to about 30 p.p.m. of CO in the feed gas [35]. The data of this report, as obtained with pure hydrogen, are in agreement with the present data.

An improvement of the catalyst-membrane unit with respect to a better catalyst layer structure and reduced transport hindrances will provide access to further informations on the relative activity of the materials studied here and the reaction kinetics, if Tafel plots become feasible.

The close agreement between results obtained with smooth electrodes in contact with electrolyte solutions, found repeatedly and discussed here, justifies the discussion of kinetic data obtained with PEM-systems in the framework of the evaluation of conventional electrochemical cells.

5.3. *Stability of bifunctional electrodes*

In order to evaluate the stability of bifunctional electrodes, cycling tests including alternatively both modes of operation (hydrogen oxidation and oxygen evolution) were made. The electrodes were operated in each mode for 30 min at $j = 100$ mA cm^{-2}, the mode of operation was switched periodically between both reactions, ten cycles were performed. In all the results reported in the following the electrode potentials observed for both reactions did not deteriorate.

For a comparison of the new concept of a bifunctional electrode with the older one (see above) this

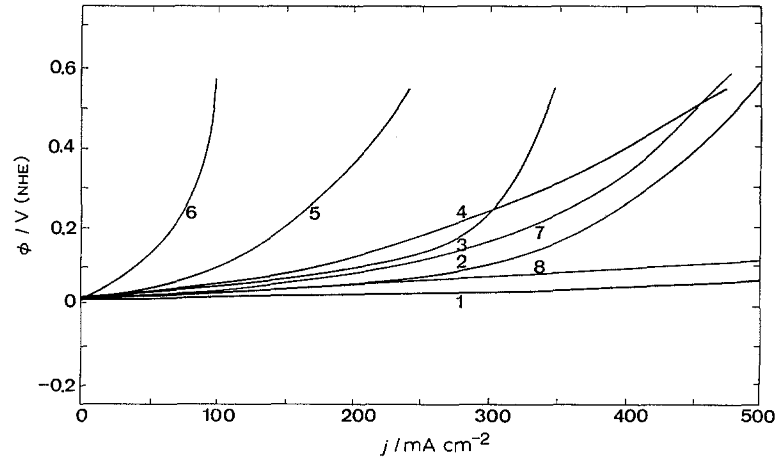

Fig. 3. Current potential curves for the hydrogen oxidation reaction at various catalysts: (1) platinum, (2) iridium, (3) rhodium-oxide, (4) rhodium, (5) iridium/rhodium(1 : 1)-oxide, (6) ruthenium-oxide, (7) rhodium/ruthenium(1 : 1)-oxide, (8) rhodium/ruthenium(1 : 1); 80 °C, 2 bar hydrogen pressure, *iR*-corrected.

cycling test was first performed with platinum electrodes for all four possible modes of operation (oxygen and hydrogen electrode, oxidation and reduction electrode). With different catalysts substituted for platinum as oxidation catalysts significantly different electrode potentials for both processes were found (see Table 2).

Taking the *iR*-corrected electrode potentials cell voltages for both the fuel cell and the electrolyser mode could be calculated. Taking into account an internal voltage loss across the IEM the ratio (fuel cell voltage)/(electrolyser voltage) and, thus, an overall efficiency can be stated; the results are collected in Table 3. The respective data for both the old and the new concept with platinum electrodes coincide. The electrode potentials for both reactions were again constant within the time frame of these experiments.

Despite the fact, that certainly transport overpotentials are included in the cell voltages a significant improvement in the efficiency from about 50 to 57% was achieved. Assuming an improved catalyst layer and further advances with respect to the electrocatalysis of the hydrogen oxidation reaction efficiencies of 60% seem possible.

When switching from the oxygen evolution to the hydrogen oxidation a break in (or 'activation') period lasting approx. 30 min is observed. Possible causes are a reduction of the oxide layer present on the catalyst during oxygen evolution or removal of the water film present during the electrolysis mode on the catalyst layer. Reduction of the oxide layer can be effected by chemical and/or electrochemical reduction. Both processes are possible and should be so fast that they cannot explain the long duration of this break in period. Removal of the water film will accelerate during current flow caused by the hydrogen oxidation and proton flow across the IEM with an accompanying 5–6 moles of water per mole of protons. In a potentiostatic experiment a corresponding increase in the anodic current with time was observed. Thus the break in period is predominantly caused by the removal of the water film. This does not pose any practical problem in actual applications, where switching between both modes will occur rarely (for a detailed description of envisaged applications of our cell see [13]).

Table 2.

Catalyst	Hydrogen oxidation	Oxygen evolution
	Electrode potential/mV	(NHE) ± 5 mV
Platinum	0.005	1.765
Rh-oxide	0.030	1.660
Iridium	0.020	1.517
Rh/Ru	0.020	1.539

5.4. *Lifetime testing*

An important criterion for further development is the long term stability of the catalysts. The oxygen evolution reaction is the most demanding process, because any catalyst degradation will be most pronounced at the very anodic electrode potentials established during oxygen evolution. Thus lifetime measurements were done at $j = 1000\,\mathrm{mA\,cm^{-2}}$ at 80 °C. Figure 4 shows the results for the metals and metal oxides studied in this work, Fig. 5 shows selected curves for the

Table 3. Cell voltages obtained with various electrode combinations during electrolysis/fuel cell operation and overall cell efficiencies

Type of electrode	Cell voltage/V		Efficiency/%
	Electrolysis	Fuel cell	
Pt-oxygen Pt-hydrogen	1.822	0.915	50.2
Pt-oxidation Pt-reduction	1.810	0.905	50.0
Rh-oxide oxidation Pt-reduction	1.705	0.880	51.6
Ir-oxidation Pt-reduction	1.562	0.890	57.0
Rh/Ru-oxidation Pt-reduction	1.584	0.890	56.2

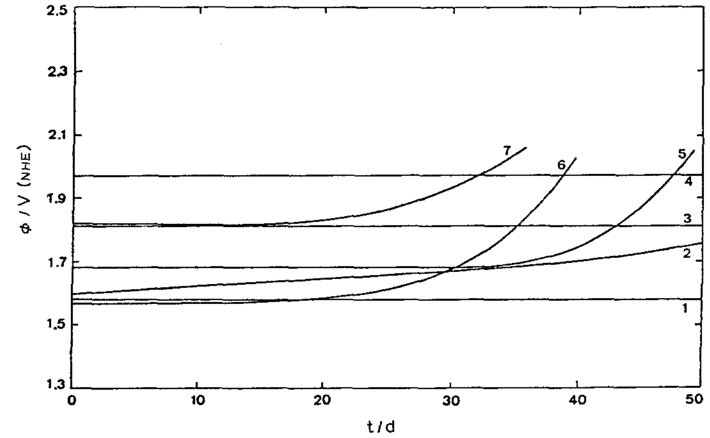

Fig. 4. Electrode potentials during oxygen evolution as a function of lifetime at 80 °C, $j = 1000\,\mathrm{mA\,cm^{-2}}$, (1) iridium, (2) iridium-oxide, (3) rhodium, (4) platinum, (5) rhodium/ruthenium(1 : 1)-oxide, (6) iridium/ruthenium(1 : 2)-oxide, (7) rhodium-oxide.

rhodium-containing catalysts. Catalysts based on metals alone show a significantly higher stability than all the metal oxides studied here; rhodium containing catalysts proved to be particularly stable.

Literature data on the long term stability of catalysts used in the oxygen evolution reaction in acidic electrolyte solution are scant. Scarpellino *et al.* have studied the corrosion behaviour of thermally stabilised ruthenium catalysts [36]. Ruthenium tempered at air and at 400–600 °C shows a smaller corrosion rate than catalysts not tempered, no further data in particular indicating electrochemical stability were available. Generally speaking a strong influence of the conditions established during preparation can be assumed. Nevertheless the use of oxides as compared to metals alone allows simple preparation of mixed catalysts. Mixed catalysts in the reduced state, and in well defined ratios, are much more difficult to prepare.

6. Applications and further developments

The applicability of any system for the storage of electric energy depends almost solely on cost considerations. Thus a reduction of the noble metal loading (generally $5\,\mathrm{mg\,cm^{-2}}$ in this work) or their substitution are highly desirable. Carbon supported platinum with a final loading of $0.5\,\mathrm{mg\,cm^{-2}}$ has been used in an IEM fuel cell [37], unfortunately the instability of carbon at oxygen evolution electrode potentials excludes this catalyst from use in bifunctional electrodes. Only a few non-noble metals or metal compounds are stable in acidic electrolytes. Tungsten carbide has been suggested as a catalyst for the hydrogen oxidation reaction [38, 39]. Although with phosphoric acid electrolytes at low current densities electrode potentials only 50 mV worse than those obtained with platinum were found the high Tafel slope implies poor electrode potentials at higher current densities. The very limited anodic stability precludes the use of WC as a bifunctional oxidation electrode. Carbon supported transition metal macrocyclic complexes have demonstrated promising activities during oxygen reduction [40, 41]; their stability during oxygen evolution is presumably very limited. Activity towards hydrogen oxidation has not been studied so far.

Acknowledgements

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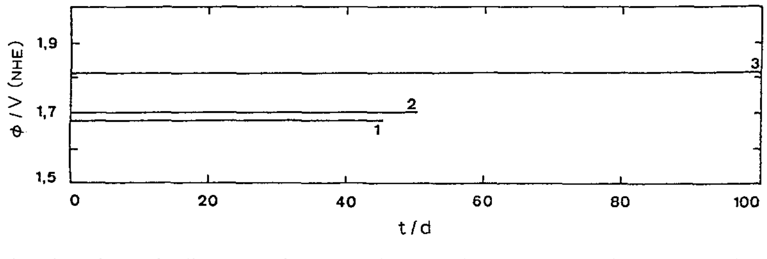

Fig. 5. Electrode potentials of various rhodium-containing catalysts during oxygen evolution as a function of lifetime at 80 °C, $j = 1000\,\mathrm{mA\,cm^{-2}}$, (1) rhodium/ruthenium(1 : 3), (2) rhodium/ruthenium(1 : 2), (3) rhodium.

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