JOURNAL OF APPLIED ELECTROCHEMISTRY **23** (1993) 322–331

Characterization of membrane-electrode assemblies for solid polymer electrolyte water electrolysis

P. MILLET

SOPHITECH, 6 rue Henri Poincaré, 91120 Palaiseau, France

T. ALLEAU

Laboratoire d'Applications Spéciales de la Physique, Centre d'Etudes Nucléaires de Grenoble, 38041 Grenoble Cedex, France

R. DURAND

Centre de Recherche en Electrochimie Minérale et Génie des Procédés, BP 75, 38402 Saint-Martin d'Hères Cedex, France

Received 4 November 1991; revised 3 June 1992

The development of medium size SPE® (Solid Polymer Electrolyte) water electrolysers requires satisfactory membrane-electrode assemblies. Pt–Nafion®–Pt, Pt–Ir–Nafion®–Pt and Pt–Ru–Nafion®–Pt composites have been tested for such applications. Anodic overvoltage, cathodic overvoltage and ohmic drop across the SPE® have been measured in the temperature range of 20 to 80° C and in the current density range 0 to 1 A cm^{-2}. Kinetic parameters for the oxygen and hydrogen evolution reactions have been measured and compared to values obtained in aqueous acid solutions. Electrode structure has been investigated, before and after 2 500 h of continuous electrolysis at 1 A cm^{-2}, by scanning electron microscopy, in order to check electrode stability at high current density. The effect of membrane surface etching on the roughness factors of the electrodes has also been investigated. Life tests performed on bare membranes and SPE composites at various operating pressures are presented and discussed. Results on the poisoning effect of nickel ions added to the feed water of the cells are reported.

1. Introduction

Water splitting by electrolysis using the so-called SPE® (Solid Polymer Electrolyte) technology is of considerable interest for on-board production of pure oxygen in submarines and for energy storage purposes in spacecraft. For such applications, the main advantages of this technique over the classical alkaline water electrolysis are, firstly, greater safety, since no caustic electrolyte is circulated, the membrane prevents gas mixing and supports high differential pressure. Secondly, there is greater reliability since less corrosion problems are encountered, and thirdly, cells are more compact so that the possibility of operating cells efficiently up to several A cm^{-2} with typical cell thicknesses of a few millimetre is afforded.

Perfluorosulphonic acid polymer membranes (such as Dupont de Nemours Nafion® products) are generally chosen as the solid electrolyte because of their chemical inertness and low electrical resistance [1]. Noble metal based electrocatalysts have to be used to avoid corrosion of the electrodes in contact with the highly acid electrolyte [2, 3].

Several methods have been proposed in the literature for the preparation of SPE®–electrocatalyst composites. The work on SPE® electrolysis performed over several years at General Electric Company (USA) provides a large body of information about this technique [4–7]. In two previous papers [8, 9], we presented a procedure for the preparation of efficient SPE® composites. Tiny particles of electrocatalyst were precipitated simultaneously inside and outside the membrane. The main characteristic of the membrane-electrode assemblies thus obtained was that the electrodes strongly interpenetrated with the SPE® and remained tightly linked to the membrane surfaces. In this paper, we investigate the possibility of using such SPE® composites as electrochemical cells in medium sized water electrolysers.

Results obtained with iridium and ruthenium based anodes are discussed with regard to long time stability and electrochemical property enhancement. Kinetic parameters for the oxygen and hydrogen evolution reactions deduced from Tafel plots have been compared to results obtained in aqueous acid solution in order to gain information on mass transport phenomena and electrode kinetics.

SEM micrographs of a platinum anode were taken before and after 2 500 h of continuous electrolysis at 1 A cm^{-2} in order to check its adhesion to the SPE. Membrane surface etching has been performed by gas plasma treatment before electrode plating. Its effect on the roughness factor of the electrodes has been measured and is discussed.

0021-891X

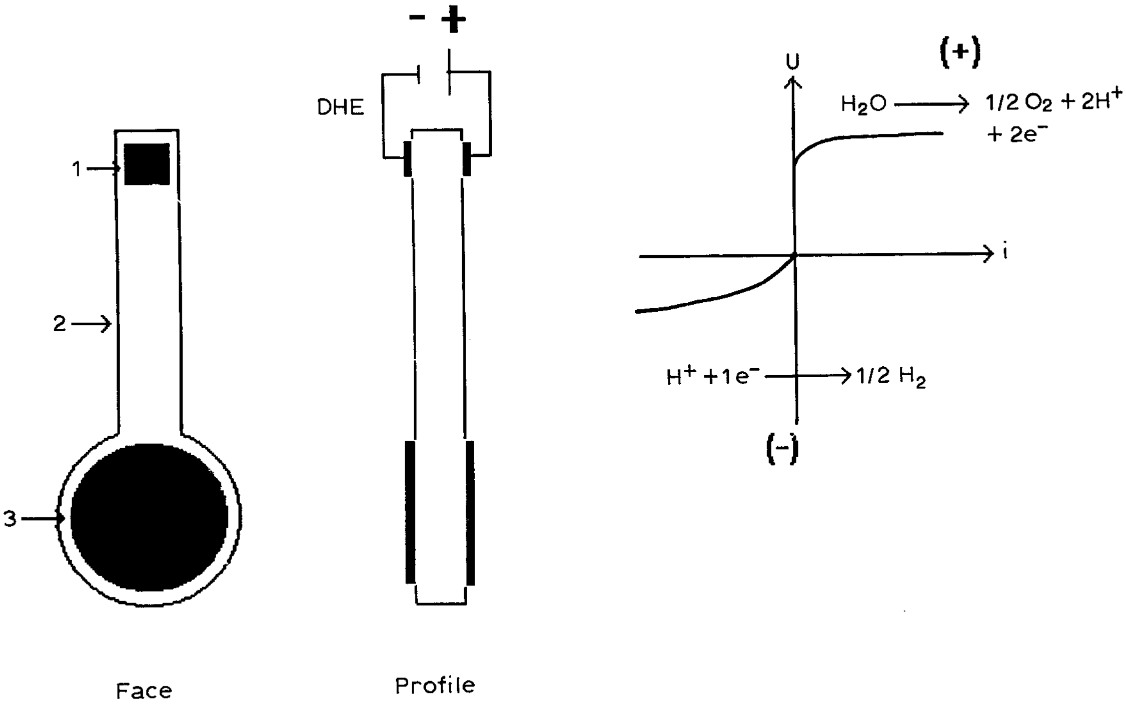

Fig. 1. Schematic diagram of a dynamic hydrogen electrode (DHE): 1-reference electrode; 2-membrane strip; 3-SPE® composite.

The influence of high operating pressure on the stability and performances of SPE® composites has also been investigated. Finally, results concerning the poisoning effect of nickel ions added to the feed water of the cells are also reported.

2. Experimental details

2.1. *Materials*

Nafion® 117 perfluorosulphonic membranes (Dupont de Nemours) were chosen as the solid polymer electrolyte. $[Pt(NH_3)_4]Cl_2 \cdot H_2O$, K_2IrCl_6 and $RuCl_3 \cdot H_2O$ (Johnson Matthey) were used to prepare the plating solutions. The reducing agent was sodium borohydride (Merck). Pure water (resistivity of 18 MΩ cm at 20° C) was used for the preparation of the plating solutions and for the electrochemical characterizations.

2.2. *Preparation of the membrane-electrodes assemblies*

The procedure used for the preparation of the Pt/Nafion® 117/Pt, Pt–Ir/Nafion® 117/Pt and Pt–Ru/Nafion® 117/Pt composites has been described elsewhere [8, 9]. The membranes (geometrical areas of 2.3 cm^2) were cut with a strip at the top of which was placed the reference electrode as shown in Fig. 1 [10, 11].

For half-cell measurements, a dynamic hydrogen electrode (DHE) coupled with an oxygen anode was used. A constant current of a few hundred microampères was imposed across the cell and the cathode was used as the DHE. It was found that the length of the strip should be of at least 2 cm to obtain stable results. The anodic and cathodic overvoltages were obtained as follows. It was assumed that the electrode potentials measured against the reference electrode were the sum of either the anodic or the cathodic overpotential and half the ohmic drop across the SPE®. Therefore, raw data were corrected by subtracting half the ohmic drop across the solid polymer electrolyte.

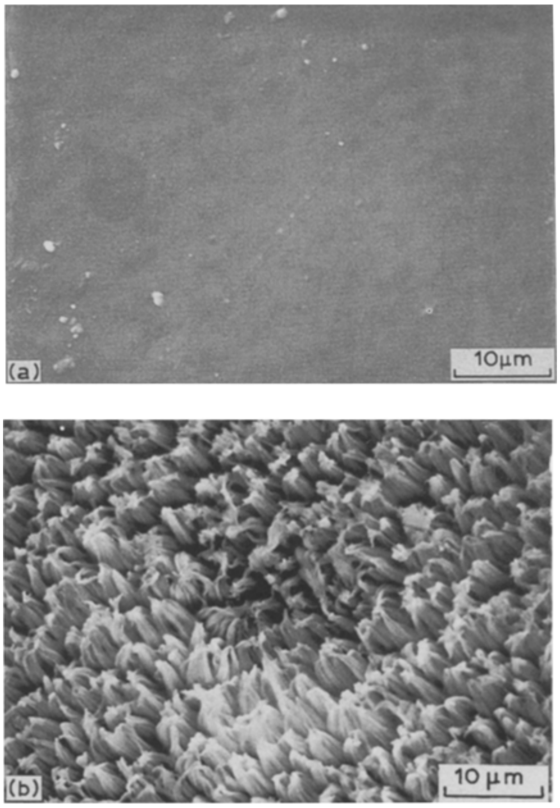

Fig. 2. SEM micrograph of the surface of a Nafion® membrane (a) before and (b) after the etching process.

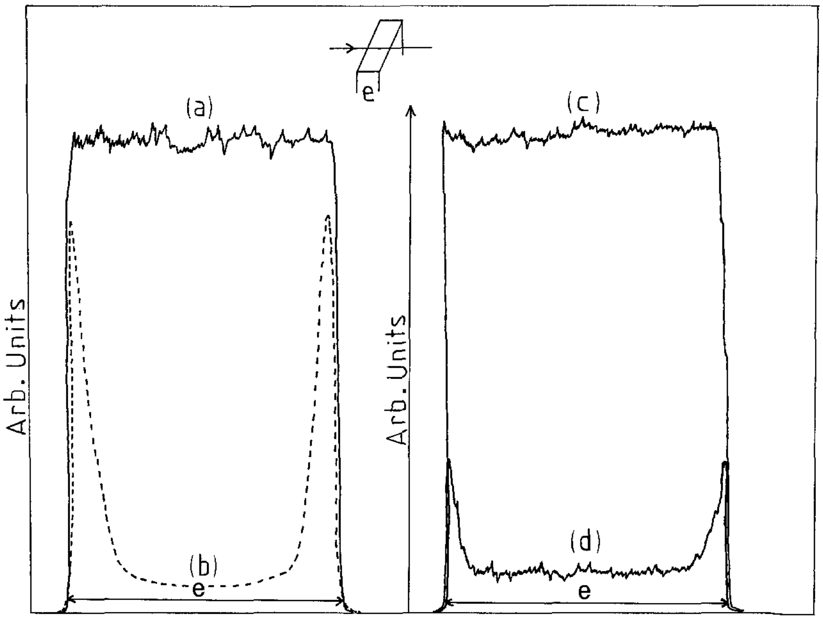

Fig. 3. Electron microprobe concentration profiles across the membrane thickness (*e*) in arbitrary scale. (a) Ruthenium exchanged Nafion® membrane (sample soaked 2 h in 10^{-2} M $RuCl_3 \cdot xH_2O$); (b) ruthenium exchanged Nafion® membrane treated with $NaBH_4$ 3 g dm^{-3}; (c) iridium exchanged Nafion® membrane (sample soaked 30 min at room temperature in 7.3 mM $[Ir(H_2O)_6]^{3+}$); (d) iridium exchanged Nafion® membrane (sample soaked 24 h at 80°C in 0.1 M K_2IrCl_6).

2.3. *Membrane surface abrasion*

In order to measure the influence of membrane surface etching on electrochemical performances, some membrane surfaces were roughened by gas plasma treatment before electrode deposition. Those membranes were treated for 5 min with oxygen (residual pressure of 0.01 torr) activated by a radiofrequency discharge (Fig. 2).

2.4. *Samples characterization*

The SPE® composites were immersed in a thermostatted bath and the electrochemical measurements were performed using a PAR 273 potentiostat. Membrane conductivities were deduced from a.c. measurements; impedance diagrams were recorded using a 1250 Solartron. Micrographs of the surface of the electrode were obtained using a Jeol JSM 35 C scanning electron microscope.

Concentration profiles across the membrane thickness were obtained with a Camebax electron microprobe analyser. Noble metal loadings were determined gravimetrically after vacuum drying of the samples.

2.5. *High pressure tests*

High pressure tests were performed in a pressure vessel made from bulk nickel (from 1 to 70 bar and 20 to 80° C). The pressurizing gas was nitrogen. The samples were immersed in pure water in a beaker to avoid contamination.

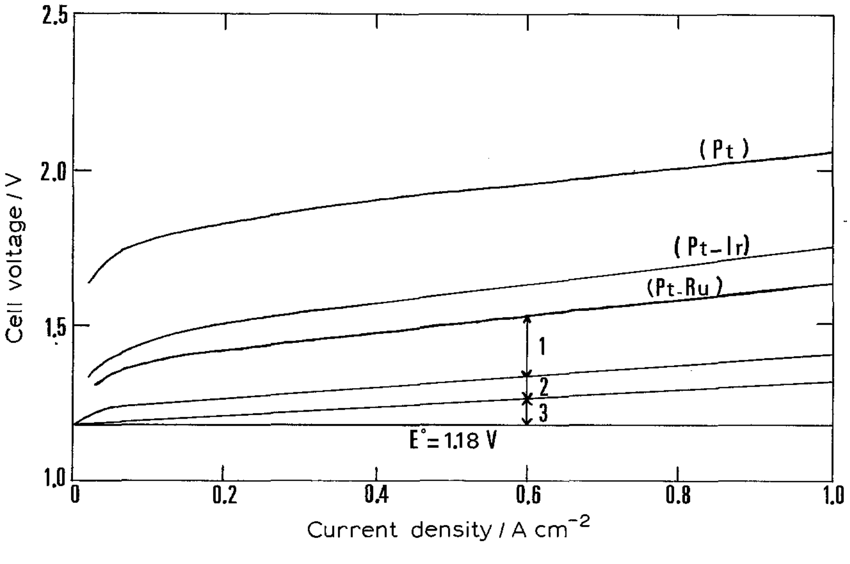

Fig. 4. Constituents of the cell voltage at 80° C. Comparison of Pt, Pt–Ir and Pt–Ru as anodic catalysts; (1) anodic overvoltage; (2) cathodic overvoltage; (3) ohmic drop across the SPE®.

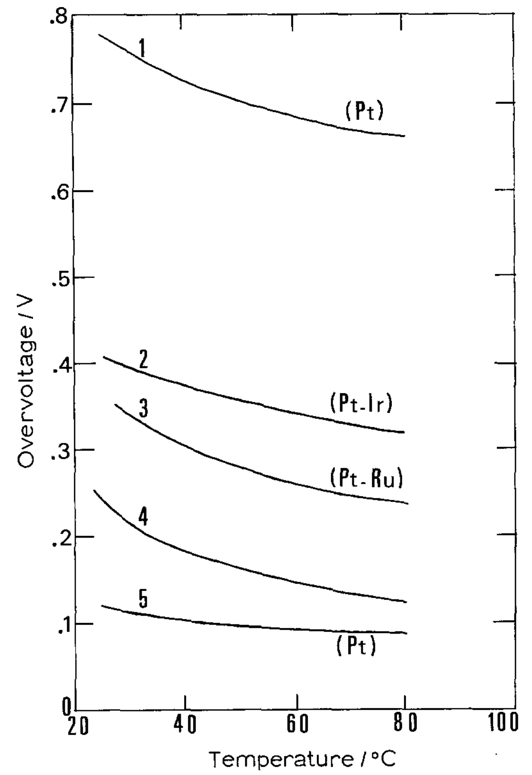

Fig. 5. Influence of temperature on overvoltages and ohmic drop at 1 A cm^{-2}. (1, 2, 3) anodic overvoltages; (4) ohmic drop across the SPE®; (5) cathodic overvoltage.

3. Results and discussion

3.1. *Iridium and ruthenium based composites*

Ruthenium and iridium based anodes are interesting in that they allow a large reduction in the anodic overvoltage. Efforts are still being made to obtain more efficient and more stable electrode compositions. Ruthenium oxide based electrodes are also interesting for SPE® brine electrolysis.

3.1.1. Ruthenium. Ruthenium can be easily incorporated into Nafion® membranes. This is achieved simply by soaking the membrane at room temperature in an aqueous solution of ruthenium trichloride.

Figure 3(a) shows a ruthenium concentration profile across the membrane thickness obtained by electron microprobe analysis. The membrane was soaked for 2 h in a 10^{-2} M $RuCl_3 \cdot xH_2O$ aqueous solution.

Once incorporated, ruthenium cations can be precipitated either to the oxide form (using a KOH solution) or to the metallic state (using a reducing solution such as aqueous $NaBH_4$) (Fig. 3(b)). In both cases, it is possible to obtain localized microprecipitates near the membrane surfaces as in the case of platinum [8], with typical ruthenium loadings varying from 0.3 to 1.5 mg cm^{-2}, depending upon the number of successive cycles of loading-precipitation.

For the oxygen evolution reaction, hydrated ruthenium oxide $RuO_2 \cdot xH_2O$ exhibits poor electrocatalytic properties, probably because of its low electronic conductivity. Better electrocatalytic properties and stability can be expected after a heat treatment, but at a temperature (above 150° C) incompatible with the membrane thermal stability [12]. In contrast, metallic ruthenium, either chemically or electrochemically reduced as previously indicated in [8], exhibits much more interesting performance (see Section 3.1.3) but is rapidly corroded [13]. A certain amount of metallic ruthenium dissolves under oxygen evolution and is found in the bulk membrane in the form of isolated clusters [9].

One interesting route for stabilizing ruthenium would be the in-situ formation of Pt–Ru alloys (platinum and ruthenium have similar crystalline structure). Results obtained so far (coprecipitation followed *in situ* by EXAFS in dispersive mode) indicate that platinum and ruthenium are reduced separately [14].

3.1.2. Iridium. Iridium can be incorporated into Nafion® membranes directly from the commercially available anionic form $[IrCl_6]^{2-}$, but the amount incorporated remains low, even after several hours of soaking at 80° C (Fig. 3(d)). Cationic iridium species can be obtained as described in [15]. At pH less than 3, $[Ir(H_2O)_6]^{3+}$ predominates and can be easily ion-exchanged (Fig. 3(c)).

Chemical reduction to the metallic state using $NaBH_4$ was found inadequate (the kinetics were very low and it was difficult to obtain localized precipitates) and we adopted an electrochemical route in which iridium was reduced onto the platinum electrode even below the membrane surface (see [9]).

3.1.3. Half-cell characterization. Using a DHE coupled with an oxygen anode (see experimental section) as reference electrode, it is possible to measure separately each term of the cell voltage at different current densities (Fig. 4). Cells having Pt, Pt–Ir and

Table 1. Tafel parameters for oxygen and hydrogen evolution reactions. Pt and Pt–Ir electrodes coated on to a Nafion® membrane

Electrode	$\frac{\delta \text{ anodic}}{\delta \log i}$ /mV	Measured i_0^a /A cm^{-2} (geometrical area)	$\frac{\delta \text{ cathodic}}{\delta \log i}$ /mV	Measured i_0^c /A cm^{-2} (geometrical area)
Pt				
25° C	110	1×10^{-7}	125	0.17
80° C	130	2×10^{-5}	105	0.14
Pt–Ir				
25° C	110	2×10^{-4}	–	–
80° C	130	6×10^{-3}	–	–

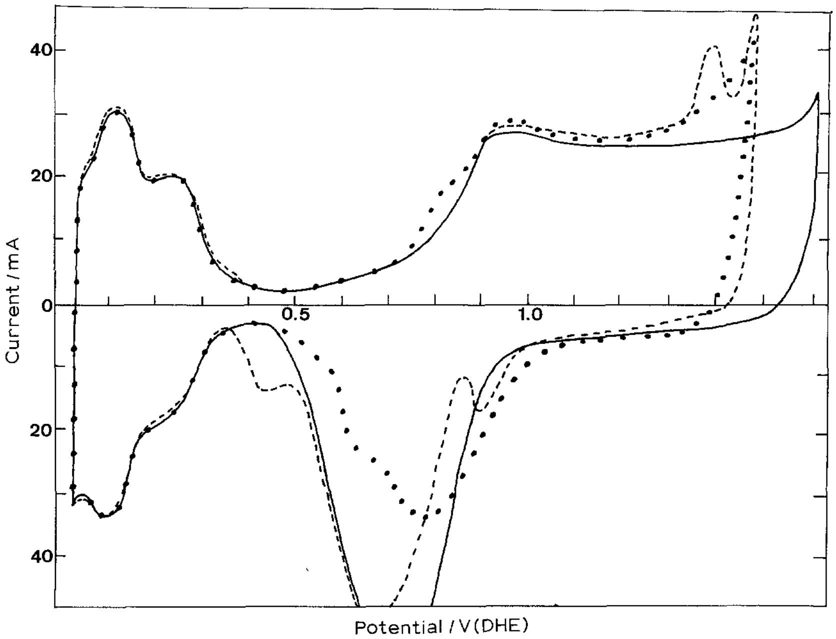

Fig. 6. Cyclic voltammograms of a 2.3 cm^2 SPE® composite; (a) (——) platinum electrode, Nafion® in H$^+$ form; (b) (- - -) platinum electrode, $[Ir(H_2O)_6]^{3+}$ exchanged Nafion® membrane; (c) (···) platinum + Ir^0 electrode, Nafion® in H$^+$ form. Sweep rate: 10 mV s^{-1}.

Pt–Ru anodes and Pt cathodes were tested. For Pt–Ru anodes, electrochemical performances could not be maintained for more than a few minutes at 1 A cm^{-2}. Rapidly, the anodic overvoltage increased while with Pt and Pt–Ir anodes, stable results were obtained.

The influence of temperature on the various terms of the cell voltage were determined likewise (Fig. 5). From those measurements, we have deduced kinetic parameters for oxygen and hydrogen evolution reactions (Table 1). Correction made for the roughness factor of the electrodes, values of the exchange current density, i_0, and the Tafel slope (as well as their temperature dependence) are similar to those obtained in aqueous acid solution on polished electrodes [16, 17]. This suggests that all the electroactive sites detected on the cyclic voltammograms, even those embedded below the membrane surface, are active and not penalized by hydrogen or oxygen diffusion.

Figure 6 shows the cyclic voltammograms recorded on (a) a platinum electrode in a SPE® composite (membrane in H$^+$ form), (b) the same electrode after $[Ir(H_2O)_6]^{3+}$ incorporation and (c) the same electrode

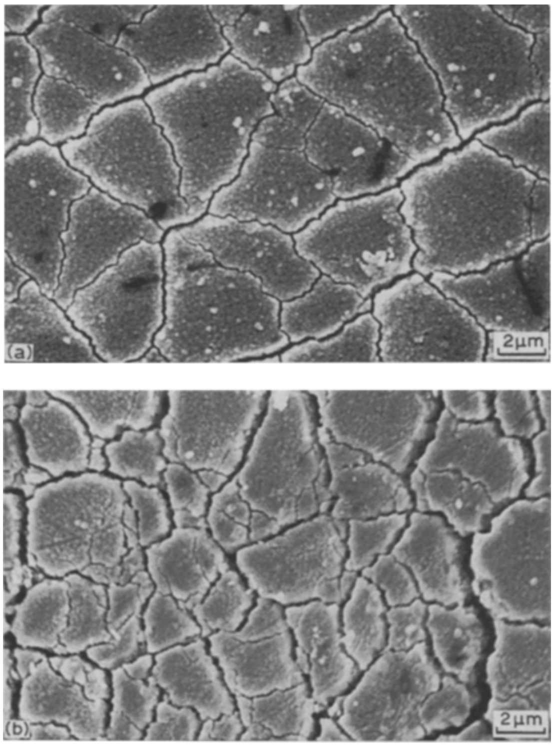

Fig. 7. SEM micrographs of a Nafion® coated platinum electrode (SPE® composite) before (a) and after (b) 2 500 h of continuous electrolysis at 1 A cm^{-2}. View of the anodic side.

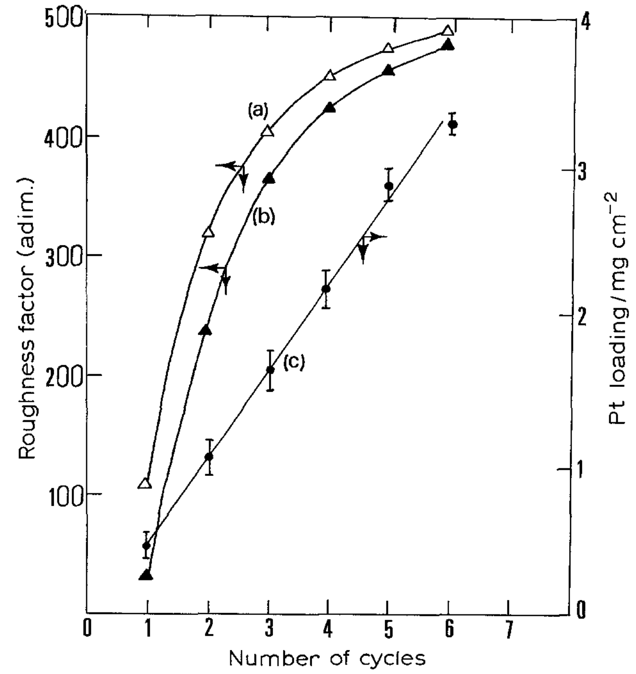

Fig. 8. Variation of the roughness factor of a Nafion® coated platinum electrode (SPE composite) with the number of cycles of loading-precipitation. (a) Etched and (b) unetched membrane. (c) Platinum loading against the number of cycles.

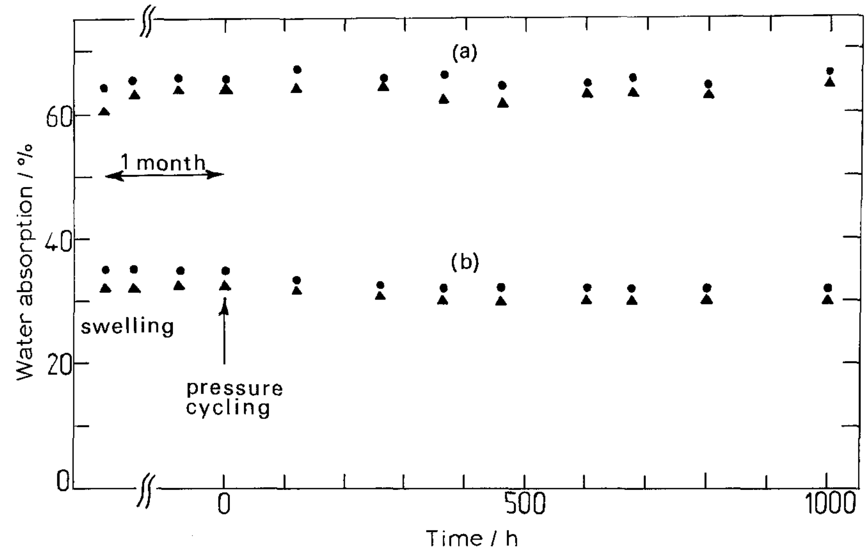

Fig. 9. (a) Volume and (b) weight variations for two samples (bare Nafion® membranes) over 1 000 h of pressure cycling. Percentage expressed relative to the dry membrane. (●) Sample 1; (▲) sample 2.

after electro-reduction of iridium salts (membrane back to the H^+ form). A loading of about 0.2 mg Ir cm^{-2} was obtained. Curve 6(c) is similar to those recorded on bare iridium electrodes in aqueous acid solutions [18].

STEM analysis revealed that platinum is not homogeneously covered by iridium [9]. But even with a low iridium coverage ratio, a clear improvement in the kinetics of oxygen evolution is seen.

3.2. *Long time performances*

Pt/Nafion®/Pt samples from 2 to 150 cm^2 were tested under continuous electrolysis conditions at different current densities (from 0.5 to 1 A cm^{-2}), up to 15 000 h. No change in cell voltage could be observed during the tests. This suggests that no deterioration of the electrodes occurred, even at high current density.

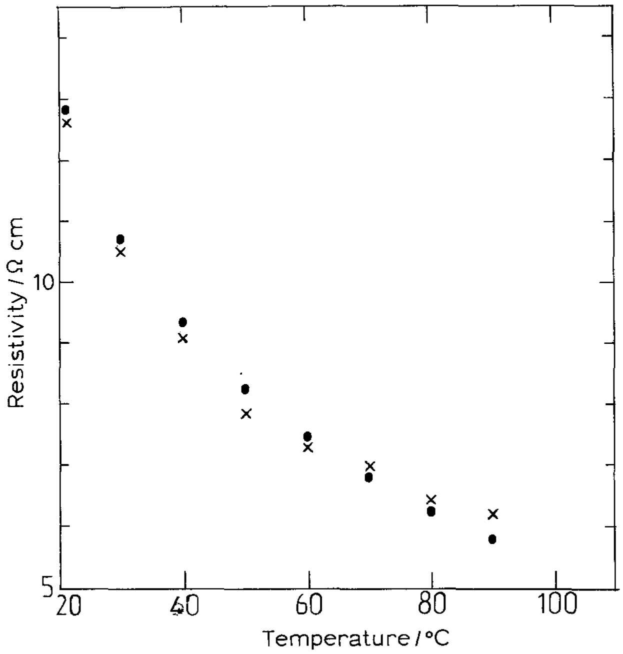

Fig. 10. Electrical resistivity of a Nafion® membrane (H^+ form) as a function of temperature, before (●) and after (x) 1 000 h of pressure cycling, at 70 bars and 80° C.

In Fig. 7, the two SEM micrographs show the surface of a platinum anode before (a) and after (b) 2 500 h at 1 A cm^{-2}. Cracks are already present before electrolysis (Fig. 7(a)), which are not artefacts of preparation for the analysis. They probably formed during electrode plating (reduction of platinum salts occurs under hydrogen bubbling, hydrogen being produced by the decomposition of $NaBH_4$).

After 2 500 h of continuous electrolysis (Fig. 7(b)), the cracks are more numerous and somewhat wider, but no part of the electrode peeled off. This indicates that the platinum electrodes remain strongly bonded to the SPE® during electrolysis and confirms the interest of the plating procedure used for the preparation of the composites. It may be concluded that during electrolysis, gas evolution occurs preferentially through the cracks and that the electrodes do not work homogeneously: their porosity is not sufficient to allow gas departure.

Concerning Pt–Ir/Nafion®/Pt composites, similar results were obtained but after several thousand hours of continuous electrolysis, losses in cell performance were observed.

3.3. *Membrane etching*

Abrasion of membrane surface has already been mentioned in the literature as an interesting way of increasing the active area of the electrodes as well as improving their adhesion to the membranes [19, 20]. In order to quantify this assumption, we etched Nafion® 117 membranes prior to metal plating (Section 2) and measured the roughness factor of the platinum electrodes with the number of cycles of loading precipitation. The determination of the active area of the platinum electrodes was based on the integration of the charge of the hydrogen adsorption region

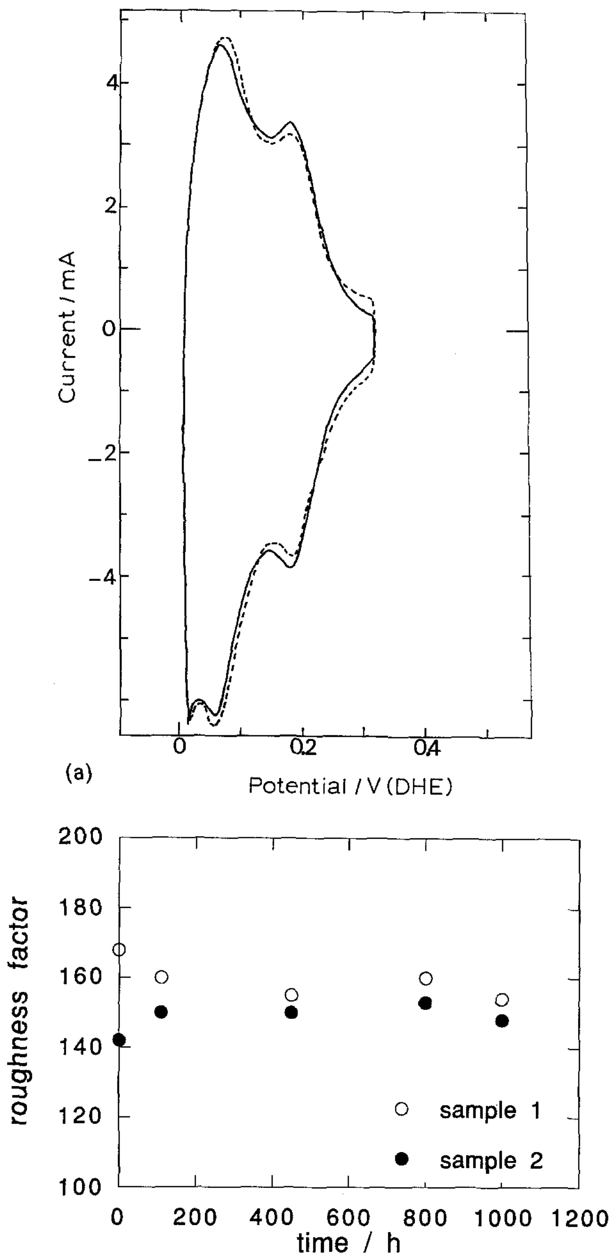

Fig. 11. Effect of pressure cycling on the roughness factor of a Nafion® coated platinum electrode. (a) Cyclic voltammograms recorded before (——) and after (– – –) the pressure cycles; (b) measured roughness factors at different times of the experiment (two samples were tested, ○ sample 1, ● sample 2).

of the steady state cyclic voltammogram after subtracting the double-layer charge. The conversion factor of 210 μC cm^{-2} of platinum was used.

The difference between etched and unetched membranes remains low and becomes even lower after several cycles of loading precipitation (Fig. 8). In fact, membrane surface etching results in the reduction of membrane thickness and, as a consequence, in lower mechanical strength, higher gas diffusion and lower faradaic yield (not measured here).

3.4. *Effect of operating pressure*

For certain applications, oxygen and/or hydrogen storage capabilities should be added to the electrolyser. For example in submarines, the hydrogen produced during electrolysis should be stored and not released to sea. In spacecraft, the use of regenerable fuel cell systems requires H_2/O_2 storage tanks [21]. To avoid the main drawbacks associated with the use of compressors (noise, pollution, weight, power and space requirements), it may be interesting to operate the electrolyser well above atmospheric pressure. It is therefore important to test the effect of high operating pressure on the SPE® composites as well as the effect of large changes in pressure.

In a preliminary set of experiments, we attempted to measure the influence of successive cycles of pressurization–depressurization on the physical and electrochemical properties of bare Nafion® membranes and platinum based SPE® composites. The idea was to check if variations in the dimensions of the membrane, and therefore changes in its properties, could be associated with higher operating pressure or repetitive changes in operating pressure.

Several bare Nafion® membranes and several platinum-based SPE® composites were introduced into a pressure vessel. At 80° C, successive pressure cycles (from 1 to 70 bar for 1 000 h) were applied to these samples. From time to time, they were cooled down to atmospheric pressure and temperature. Volume, weight (Fig. 9) and ionic conductivity in H^+ form (Fig. 10) variations were measured on bare samples while roughness factors of platinum electrodes were measured as previously indicated on platinum based composites (Fig. 11).

In a second set of experiments, the current voltage plots at 80° C and under various operating pressures (from 1 to 70 bars) were measured directly within the pressure vessel. Results obtained are shown in Fig. 12.

From these measurements, it appears that both the physical and electrochemical properties of Nafion® membranes and platinum based SPE® composites are constant over several hundred hours of operation at high pressure. This suggests that the degree of swelling of the membrane remains unchanged. In fact, the main effect of higher operating pressure may be on lower gas purity and faradaic yield (not measured here).

3.5. *Sensitivity to poisoning*

Metallic platinum is often used as cathodic material in SPE® water electrolysis because of its high activity toward hydrogen evolution [16], and because only noble metals can be placed in contact with the highly acid environment of Nafion® membranes. This higher catalytic activity, however, is not selective and platinum is also highly sensitive to poisoning by 'under potential deposition' (UPD) of monolayers of other metals such as copper [22], lead [23] etc. Once the platinum surface is covered by such monolayers, hydrogen discharge takes place on the new surface and the cathodic overvoltage increases drastically.

In SPE® water electrolysis, UPD of non-noble metals on platinum can affect the cell performances [24], and ruthenium dioxide obtained by thermal decomposition of chloride ruthenium salts [25] has

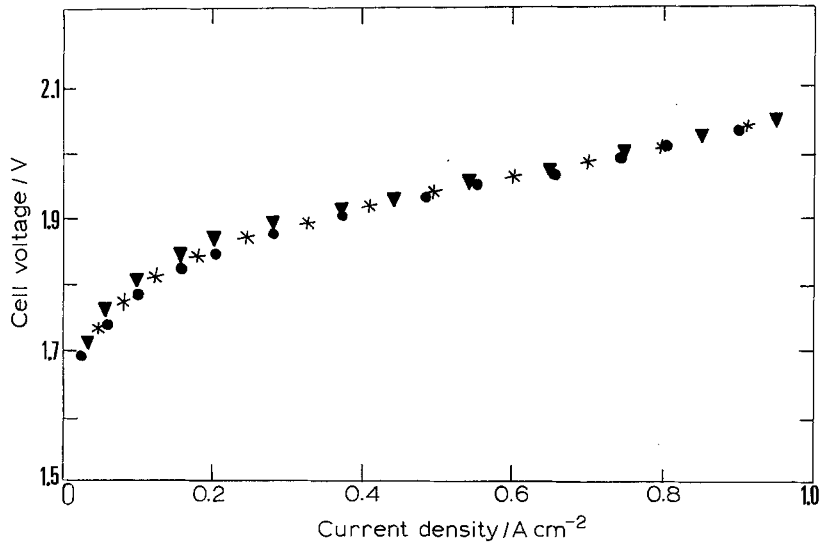

Fig. 12. Effect of operating pressure at 80° C on the cell voltage against current density relation for a 5.3 cm^2 Pt–Nafion®–Pt composite. (●) P atm, (∗) 30 bar and (▼) 70 bar.

already been proposed as an alternative cathodic material.

We consider here the effect of nickel ions on the performance of SPE® cells. From a practical point of view, nickel in the feed water comes from steel piping dissolution in the highly de-ionised water circulated in the cell-stack.

Figure 13 shows the $i(t)$ response of a SPE® cell at two different controlled cell potentials. In the first case, $U = 2.35$ V. Introduction of 5 cm^3 of 10^{-2} M $NiSO_4$ in the feed water results in a strong decrease in current density, while in the second case ($U = 2.05$ V), no change occurs.

The change in membrane conductivity is not the only reason for such a current variation as shown in Fig. 14. Figure 14(a) shows the quasi-steady state $i(U)$ cell response when the membrane is in H^+ form. Now if, prior to the recording, the membrane is equilibrated with $NiSO_4$, flat plateaux appear; their position depends upon the nickel concentration within the membrane (Fig. 14(b–d)).

Half cell recording shows that the plateaux appear on the cathodic side of the cell (Fig. 15). The phenomenon is reversible, and once nickel ions are

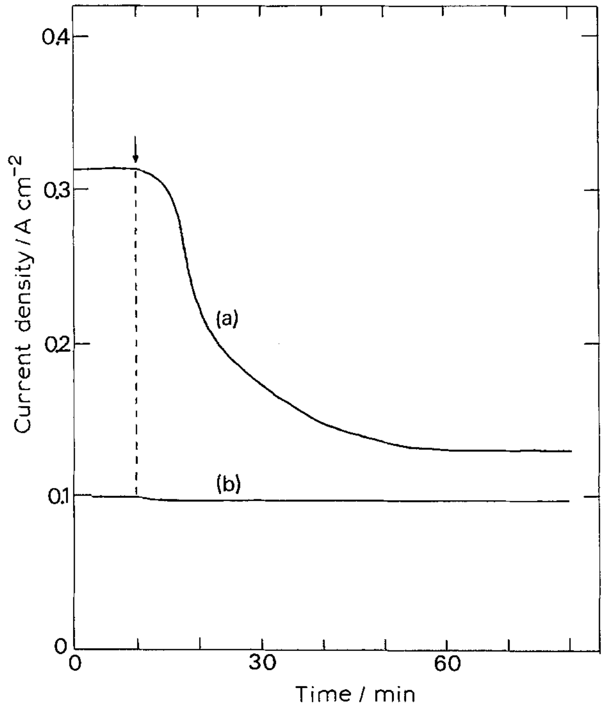

Fig. 13. $i(t)$ response of a 5.3 cm^2 Pt/Nafion®/Pt SPE® cell after introduction of 5 cm^3 of 10^{-2} M $NiSO_4$ in the feed water. Imposed voltage: (a) 2.35 V and (b) 2.05 V.

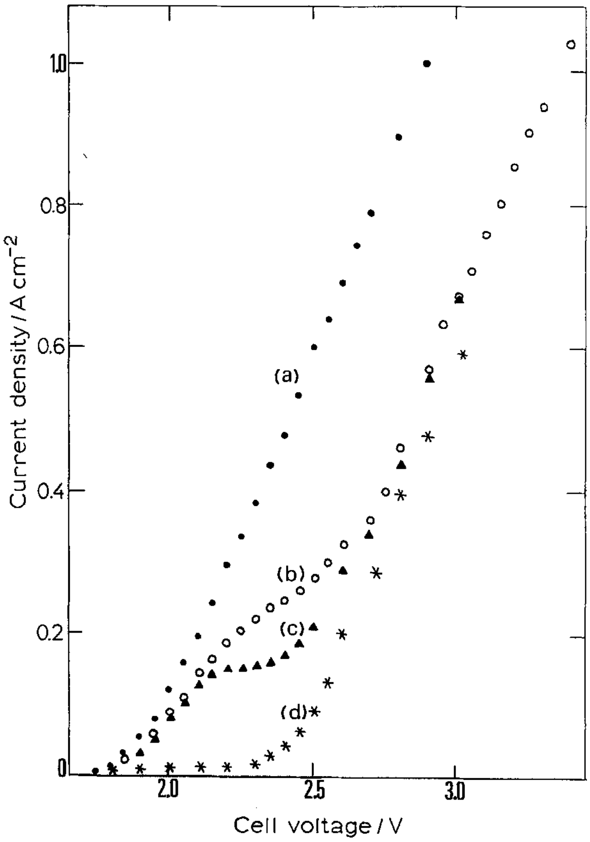

Fig. 14. $i(U)$ response of a 5.3 cm^2 Pt/Nafion®/Pt SPE® cell after membrane equilibration with (b) 10^{-3}, (c) 10^{-2} and (d) 10^{-1} M $NiSO_4$ solution. (a) Membrane in H^+ form. Scan rate: 1 mV s^{-1}.

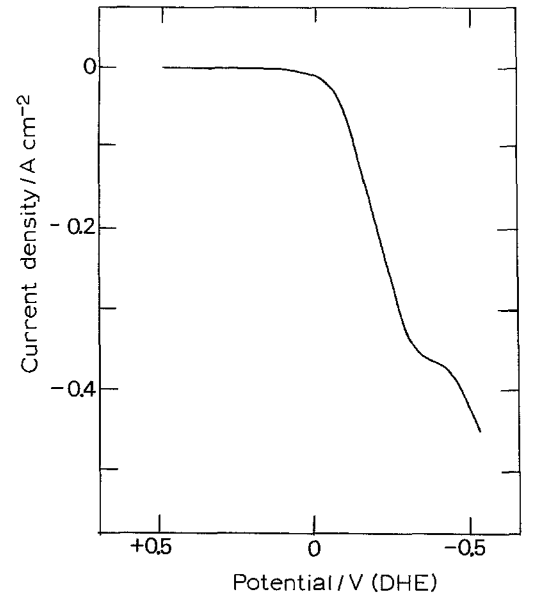

Fig. 15. Cathodic overvoltage–current density plot for a Nafion® coated platinum electrode. The membrane is equilibrated with 10^{-2} M $NiSO_4$. No iR correction is made.

removed and the membrane is back to the H^+ form, curve (a) is obtained.

Those plateaux are not caused by nickel UPD as shown in Fig. 16. In fact, bulk nickel deposition should be considered to explain their formation. The lower the $NiSO_4$ concentration in the membrane, the lower is the potential of bulk nickel deposition. As the current density increases, the cathodic potential decreases because of the hydrogen evolution overpotential. Bulk nickel deposition then occurs and proton discharge takes place on nickel with a much higher overvoltage than on bare platinum.

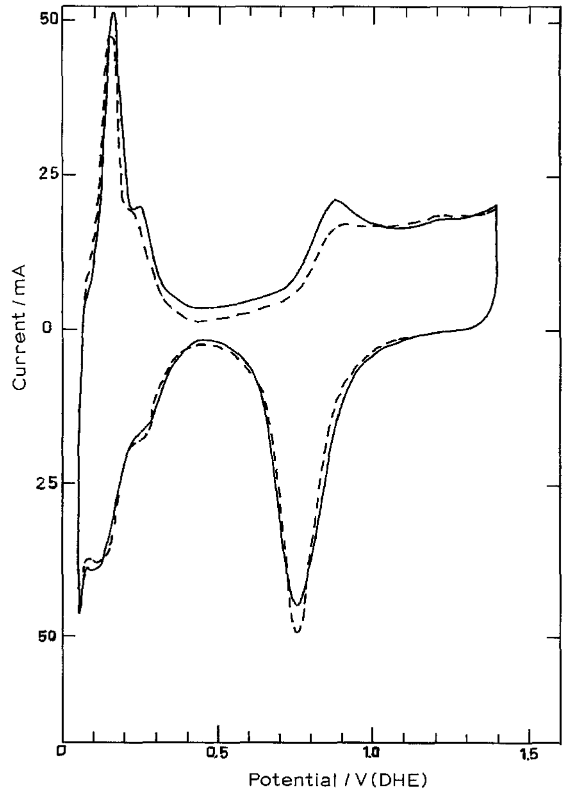

Fig. 16. Cyclic voltammograms of a 5.3 cm^2 Nafion® coated platinum electrode before (——) and after (– – –) equilibration with 10^{-2} M $NiSO_4$. Sweep rate: 10 mV s^{-1}.

4. Conclusions

Various types of membrane-electrode assemblies have been characterized for solid polymer electrolyte water electrolysis applications. Platinum based composites can be prepared with stable and reproducible electrochemical properties and are currently used in our laboratory for the testing of medium size water electrolysers. With a typical cell voltage of 2.1 V at 1 A cm^{-2}, it has been shown [26] that heat problems can be handled in a simple way. Better electrochemical performances can be obtained using Pt–Ir or Pt–Ru anodes but stability problems encountered with such electrodes must be solved before they can be used.

Membrane surface etching before electrode plating was found useless. The gain in electrode roughness factor is not very significant while drawbacks associated with thinner membranes are severe.

The effect on SPE® composites of high operating pressures, as well as successive cycles of rapid pressurization–depressurization, was found negligible during the 1 000 h of the experiments. This suggests that high operating pressure water electrolysers can be designed.

Concerning the influence of nickel ions on the performance of SPE cells, it has been confirmed that the purity of the feed water should be checked very carefully to avoid large increases in cell voltage. Because of the low hydrogen overpotential, cathodic protection of the piping is not achieved, even if the circuitry is connected to the negative pole of the power supply. Online deionizers may be considered though their use generally imposes lower rating pressure.

References

[1] R. S. Yeo, *J. Electrochem. Soc.* 3 (1983) 533.
[2] W. A. Titterington and J. F. Austin, 'Ext. Abstr.', ECS Fall Meeting, New York (1974) p. 576.
[3] P. W. T. Lu and S. Srinivasan, *J. Appl. Electrochem.* **9** (1979) 269.
[4] L. J. Nuttall, Proceedings of the 1st World Hydrogen Energy Conference (WHEC). Miami Beach, Florida (1976) p. 6B-21.
[5] L. J. Nuttall and J. H. Russel, Proceedings of the 2nd WHEC. Zurich, Switzerland, **1** (1978) p. 391.
[6] 'Solid Polymer Electrolyte Water Electrolysis Technology Development for Large Scale Hydrogen Production', General Electric Coy, DOE report no. DOE/ET/26 202-1 (1981).
[7] A. B. La Conti, E. N. Balko, T. G. Coker and A. G. Fragala, Proceedings of the Symposium on Ion Exchange and Interfacial Properties. The Electrochemical Society, Pennington, NJ (1981) p. 318.
[8] P. Millet, R. Durand and M. Pinéri, *J. Appl. Electrochem.* **19** (1989) 162.
[9] *Idem, Int. J. Hydrogen Energy* **15**(4) (1990) 245.
[10] S. Stucki and A. Menth, Proceedings of the Symposium on Industrial Water Electrolysis. ECS series (1978) p. 180.
[11] J. McBreen, *J. Electrochem. Soc.* **132** (1985) 1112.
[12] A. Michas, Ph.D. Thesis, Grenoble, France (1986).
[13] J. L. Weineiger and R. R. Russel, *J. Electrochem. Soc.* **125** (1978) 1482.
[14] P. Millet and R. Durand, unpublished results.
[15] P. Beutler and H. Gamsjager, *J. Chem. Soc. Chem. Common.* (1976) 554.

[16] A. Damjanovic, A. Dey and J. O'M. Bockris, *J. Electrochem. Soc.* **113** (1966) 739.

[17] J. O'M. Bockris and A. K. N. Reddy, 'Modern Electrochemistry', Plenum-Rosetta Ed., **2** (1977) 1238.

[18] J. M. Otten and W. Visscher, *J. Electroanal. Chem.* **55** (1974) 1.

[19] H. Takenaka, E. Torikai, Y. Kawami and N. Wakabayashi, *Int. J. Hydrogen Energy* **7** (1982) 397.

[20] R. J. Lawrence and L. D. Wood, *U.S. Patent 4 272 353* 9 June (1981).

[21] P. Millet, T. Alleau, P. Mathonnet, M. Pinéri and R. Durand, Proceedings of the ESA Symposium on Power Sources in Space. Madrid (1989).

[22] B. J. Bowles, *Electrochim. Acta* **15** (1970) 589.

[23] F. El Omar and R. Durand, *J. Electroanal. Chem.* **17** (1987) 343.

[24] E. R. Kotz and S. Stucki, *J. Appl. Electrochem.* **17** (1987) 1190.

[25] R. Adams and R. L. Shriner, *J. Amer. Chem. Soc.* **45** (1923) 2171.

[26] P. Millet, *Electrochim. Acta* **36**(2) (1991) 263.