New solid polymer electrolyte composites for water electrolysis

P. MILLET, M. PINERI

Centre d'Etudes Nucléaires de Grenoble, 38041 Grenoble Cedex, France

R. DURAND

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

A new procedure for the preparation of SPE–electrocatalyst composites has been developed. In this procedure, noble metal cationic species are chemically reduced within a solid polymer electrolyte. The metallic particles are not homogeneously distributed across the SPE thickness but predominate near its surfaces. The structure and the distribution of the precipitates along the membrane thickness have been investigated by scanning electron microprobe analysis and transmission electron microscopy. Application to SPE water electrolysis has been performed using Nafion membranes and platinum-group electrocatalysts. The SPE–electrocatalyst composites prepared according to this new procedure present good electrochemical properties, low catalyst loadings, long-time stability and high energetic efficiencies.

1. Introduction

Solid polymer electrolyte (SPE) water electrolysis has demonstrated its advantages over the more conventional alkaline water electrolysis [1–5], thanks to the introduction of the Nafion membranes. These materials, which have excellent chemical and mechanical stability, together with high ionic conductivity and good gas impermeability, allow the realization of compact and energetically efficient cells.

The most important drawbacks of this technique which limit its application for large-scale hydrogen production are economic factors. The investment cost remains high, due to the price of the Nafion membranes as well as to the price of the electrocatalysts used. These electrocatalysts are generally platinum-group metals because of the strong acidity of the Nafion membranes which would cause the corrosion of other metals. Some attempts have been made to find a viable alternative to the Nafion products without success to date [6], in spite of earlier encouraging results [7].

The two other solutions for keeping capital costs within economic bounds are to decrease catalyst loadings and to increase current densities. Typical noble metal loadings of a few $mg\,cm^{-2}$ and typical current densities of several $A\,cm^{-2}$ are currently obtained. Because of these somewhat severe conditions of operation (the electrodes have to support high mechanical tension during gas evolution), much attention must be devoted to the structure of the electrodes, not only to reduce the noble metal loadings, but also to strengthen the bonding of the electrodes onto the SPE [8–10].

Over many years, several methods for the preparation of SPE–electrocatalyst composites have been proposed. The pioneering work of the US firm General Electric Company has led to a development program for large-scale hydrogen generators based on the coating, under heat and/or pressure, of a mixture of a catalyst powder and a binder (such as Teflon) on each side of the SPE [11–16]. Japanese workers have proposed an electroless method for the deposition of noble metals on each face of the SPE under wetting conditions based on the diffusion through the membrane of a reducing agent which reacts with an anionic salt of the metal to be plated [3, 17]. The Swiss firm Brown Boveri Company is also very active in this field and has marketed its Membrel process [18, 19].

In this paper we present a new simple procedure for the preparation of SPE–electrocatalyst (Pt- and Ir-based) composites which are characterized by low noble metal loadings, excellent electrochemical properties and strong adhesion of the electrodes onto the membrane [20]. This preparation is based on the phenomenon of localized precipitation of micro-particulates in perfluorinated ion-exchange membranes, a phenomenon which was first reported in one of our earlier papers for hydrated ruthenium oxide particles [21].
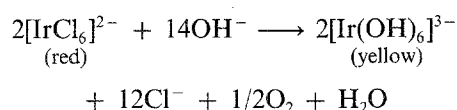
2. Experimental details

2.1. Materials

Perfluorosulfonic acid polymer membranes (Dupont de Nemours Nafion products) were used as the SPE. Nafion 117 (equivalent weight 1100 and dry thickness

0.178 mm) was chosen because of its commercial availability. Before electrode deposition, a two-step standard procedure of cleaning was followed for every sample: (1) immersion for 30 min in a boiling HNO_3–H_2O (1:1 vol.) solution to remove impurities; (2) immersion for 1 h in boiling deionized water, to introduce a reproducible amount of water into each sample.

$[Pt(NH_3)_4]Cl_2 \cdot H_2O$ and K_2IrCl_6 (Johnson Matthey) were used as precursor salts for metallic Pt and Ir precipitation. $NaBH_4$ from Merck was used as reducing agent. Solutions of cationic iridium compounds were prepared according to the following procedure [22].

A given amount of K_2IrCl_6 was dissolved in a 0.1 M NaOH solution (stoichiometry: $7OH^-/1Ir$) and left at room temeprature for 24 h. The following reaction took place:

$$2[IrCl_6]^{2-} + 14OH^- \longrightarrow 2[Ir(OH)_6]^{3-}$$
$$\text{(red)} \qquad\qquad \text{(yellow)}$$
$$+ 12Cl^- + 1/2O_2 + H_2O$$

Then the pH was lowered to ca 8 by dropwise addition of a 0.1 M $HClO_4$ solution. A white precipitate of iridium hydroxide developed according to:

$$[Ir(OH)_6]^{3-} + 3H^+ \longrightarrow [Ir(OH)_3(H_2O)_3]$$
$$\text{(white precipitate)}$$

The white precipitate was separated from the solution in a centrifuge, washed with water and dissolved in a 0.1 M $HClO_4$ solution at pH 3 to obtain a purple solution of a mixture of iridium cationic compounds ($[Ir(OH)_2(H_2O)_4]^+$, $[Ir(OH)(H_2O_5]^{2+}$, etc.). The final step of purification mentioned in [22] was not performed, and the purple solution was used directly for iridium deposition.

2.2. Sample characterization

The samples were embedded in resin and cut with a MT 500 Sorvall ultramicrotome. The thin sections of a few hundred Å thus obtained were used to investigate the interpenetration of the electrodes and the SPE with a Jeol EM 100 CX II transmission electron microscope, while the remaining part was used to investigate the distribution of the precipitates across the sample thickness with a Camebax electron microprobe analyser. The noble metal loadings were determined gravimetically.

Pure water (resistivity of 18 Mohm cm at 20° C) was used for the preparation of the solutions and for the electrochemical experiments.

3. Results and discussion

3.1. Chemical precipitation of metallic platinum in Nafion membranes

When a Nafion membrane (H^+ form) is soaked in a $Pt(NH_3)_4Cl_2$ aqueous solution, hydrogen ions are replaced by platinum ions (Fig. 1a). When this
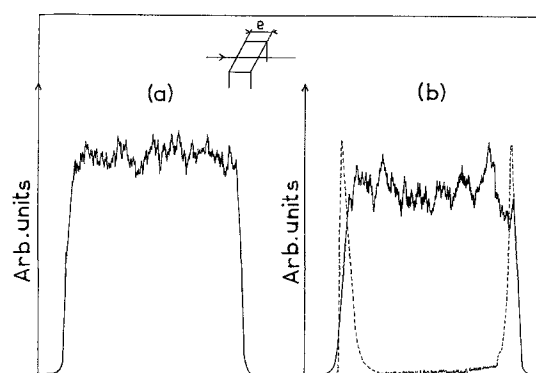

Fig. 1. Electron microprobe concentration profiles across the membrane thickness (e) in arbitrary scale. (a) Nafion–platinum exchanged sample. (b) Nafion–platinum exchanged sample treated with a $15 g l^{-1}$ $NaBH_4$ solution for 2 h (– – –) and Na^+ profile (——).

platinum-exchanged Nafion membrane is soaked at room temperature in a reducing aqueous solution of $NaBH_4$, precipitation of metallic platinum occurs into the membrane. The platinum metal concentration is not homogeneously distributed across the membrane thickness but predominates near its surfaces (Fig. 1b). After the precipitation, sodium ions are homogeneously distributed along the membrane thickness (Fig. 1b). This phenomenon can be explained as follows: once the platinum-exchanged membrane is soaked in the reducing solution, the cations located near the surface are reduced to the metallic state, thus creating a chemical potential gradient between the bulk of the membrane and its surfaces. Platinum cations diffuse toward the surface of the membrane where they are reduced, while an opposite sodium flux maintains electroneutrality. When the precipitation is over, each sulfonate is associated with a sodium counter-ion.

By changing the concentration of the reducing agent it is possible to obtain more or less localized layers of metallic platinum (Fig. 2). We can see that the higher the concentration of the reducer, the larger the layers of the platinum.

To increase the amount of platinum thus deposited, successive loading–precipitation cycles can be performed (Fig. 3). After four cycles, the area near the surfaces of the membrane become saturated with metallic particles, and the layers begin to broaden.
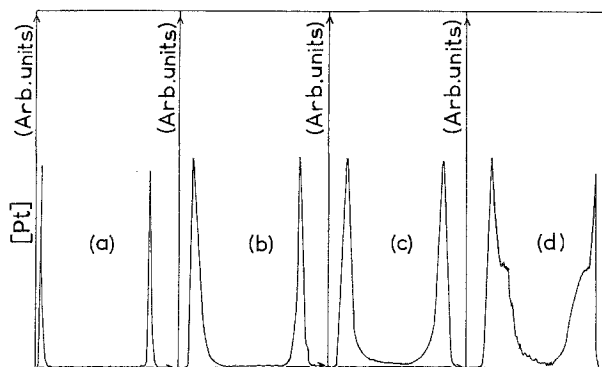

Fig. 2. Platinum concentration profiles obtained with platinum exchanged samples treated at room temperature for 2 h in a $NaBH_4$ solution: (a) 1; (b) 15; (c) 40; and (d) $80 g l^{-1}$.
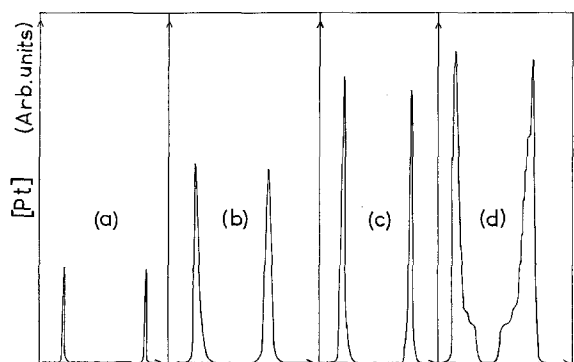
Fig. 3. Platinum concentration profiles obtained after (a) 1, (b) 2, (c) 3 and (d) 4 cycles of precipitation by a $1\,gl^{-1}$ $NaBH_4$ solution for 2 h.

Figure 4 shows the increase of the average size of the Pt particles (determined by X-ray diffraction and TEM analysis) with the number of cycles. The maximum size observed of 90 Å is in good agreement with results previously mentioned in the literature [23].

3.2. Application to SPE water electrolysis

To realize efficient composites for SPE water electrolysis application, the bonding of the electrodes onto the SPE is critical. Two conditions must be met:

(1) The metallic electrode must be located not too far inside the membrane to avoid low faradaic yield due to gas diffusion through the membrane.

(2) The metallic electrode must be located simultaneously inside the membrane (where it acts as an electrocatalyst) and outside, on the surface of the membrane (where it acts as a current collector). Furthermore, those two regions must be in contact to ensure electron transport and good adherence of the electrode under high mechanical tension during gas evolution.

Several experimental parameters such as cationic precursor salt and reducing agent concentration, time
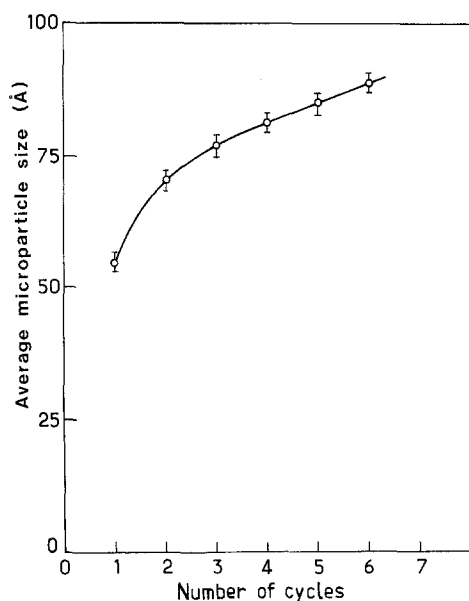

Fig. 4. Variation of the average microparticulate size within the SPE with the number of cycles of precipitation.

Table 1. Optimal values of parameters for the realization of Pt/Nafion/Pt SPE composites

Loading	$[Pt(NH_3)_4]Cl_2 . H_2O$ $10^{-2}M$ 15 min
Precipitation	$NaBH_4$ $3\,gl^{-1}$ 2 h
Number of cycles	2

of loading and reduction, number of loading–precipitation cycles and temperature determine the platinum loading, the thickness and porosity of the external part of the electrode and the localization of the precipitates within the SPE.

Optimal conditions for the realization of such SPE–Pt composites, in which the electrodes and the SPE are strongly interpenetrated, have been empirically determined and are compiled in Table 1. A Pt/Nafion/Pt $(2.3\,cm^2)$ composite was prepared under the conditions given in Table 1.

A loading of $1.13\,mg\,cm^{-2}$ of metallic platinum was obtained. Figure 5 shows the Pt concentration–distance profile obtained by microprobe analysis. The shape of the curve in the internal part of the membrane indicates that metallic platinum is present inside the SPE.

Figure 6 shows transmission micrographs of both the external and internal parts of the electrode. The interpenetration of the metallic electrode and the SPE is clearly apparent and three different regions can be distinguished: (1) the external part of the electrode, whose thickness is approximately 0.2 μm; (2) a second region of approximately 2 μm thickness, within the membrane, where the small metallic platinum particles are in contact with each other; (3) a third region about 10 μm thick where the metallic platinum particles are isolated and useless for the electrochemical reactions; a small amount of catalyst is thus lost.

Figure 7 shows the temperature dependence of the cell voltage–current density relation obtained after 200 h of continuous electrolysis at 1 A cm^{-2} and 80° C. The two-compartment cell shown in Fig. 8 was used for the masurements. The platinized membrane was pressed between two Pt current collectors made of Pt gauze (196 mesh cm^{-2}) welded onto a perforated Pt foil (0.2 mm thick). Lower loadings of metallic platinum of ca 0.1–0.2 mg cm^{-2} can be obtained with this technique when, prior to the two-step procedure of loading and precipitation of the precursor salt, the membrane is soaked in water at ca 150° C under a
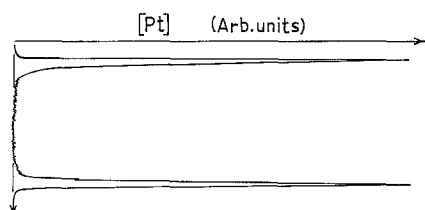

Fig. 5. Platinum concentration profile obtained for a sample prepared according to the procedure described in Table 1.

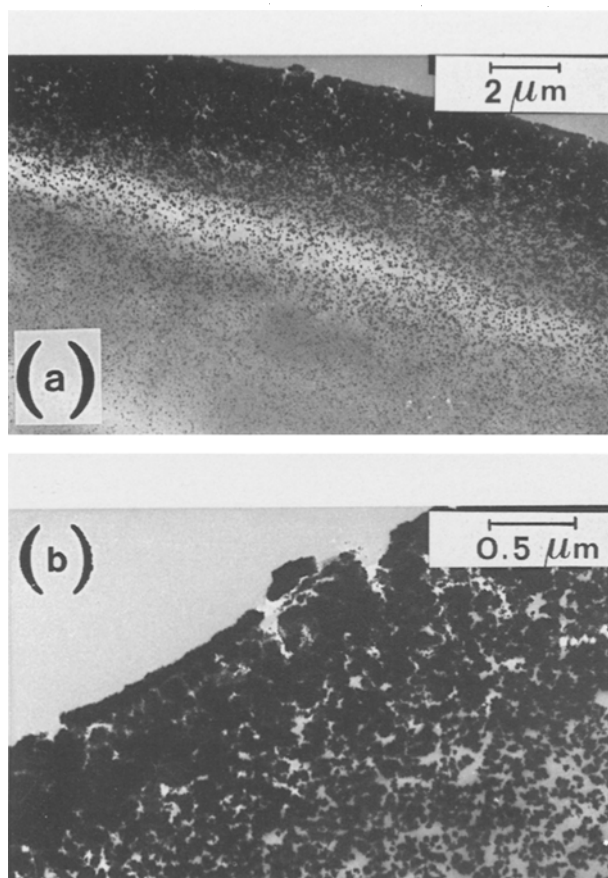Fig. 6. Electron transmission micrographs of a Pt/Nafion/Pt composite showing the interpenetration of the electrode and the SPE.

Fig. 8. Cell used for the experiments. (1) SPE composite, (2) platinum current collectors, (3) Viton gaskets, (4) circulating pumps and (5) gas–electrolyte separators.

pressure of several atmospheres for 1 h. But with such low loadings poisoning sensitivity and mechanical instability at high current densities $(1\,A\,cm^{-2})$ can shorten the life of the samples.

3.3. Iridium electrochemical deposition

It is well known that oxygen evolution on iridium requires a lower overpotential at a given current density than on platinum [24–26]. The electrochemical performances of the Pt/Nafion/Pt composite prepared according to the procedure described in the two previous sections can be improved by incorporating iridium into the anode. Because the chemical precipitation of iridium by a reducing solution is much more
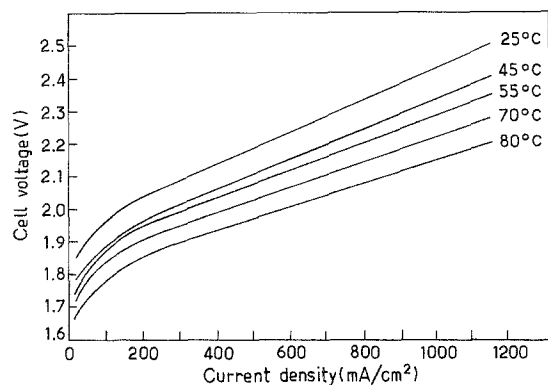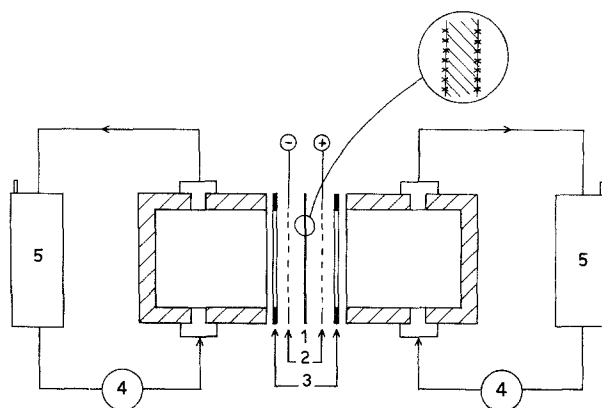
difficult to perform than for platinum (iridium compounds are more stable), and in order to obtain low iridium loadings, an electrochemical procedure was adopted. $20\,cm^3$ of a 0.008 M solution of iridium were prepared according to the procedure described in the experimental section. Then, a Pt/Nafion/Pt composite (Pt loading: $1.13\,mg\,cm^{-2}$) prepared as previously described, was mounted in the two-compartment cell (Fig. 8). $5\,cm^3$ of the iridium solution were introduced for 10 min to the left compartment of the cell while water was introduced to the right one. The iridium solution was then removed and replaced by water, and a current density of $0.5\,A\,cm^{-2}$ was passed through the cell for 45 min, the cathode being the electrode facing the side of the membrane where iridium had been incorporated. Thus, iridium was reduced (under hydrogen evolution) inside the Nafion on the platinum particles. An iridium loading of ca $0.2\,mg\,cm^{-2}$ was obtained.

The new Pt–Ir/Nafion/Pt composite was used for water electrolysis with Pt–Ir as anode and Pt as cathode using the two-compartment cell (Fig. 8). Figure 9 shows the Pt and Ir concentration–distance profile. Figure 10 shows the temperature dependence of the cell voltage–current density relation. A comparison with Fig. 7 outlines the improvement due to the incorporation of iridium. The iridium loading can be adjusted between 0.1 and $0.3\,mg\,cm^{-2}$ depending on the time of reduction.

The reproducibility of this method of plating has been tested on samples up to $150\,cm^2$, and the electrochemical performances have been maintained over 5000 h of continuous electrolysis without irreversible
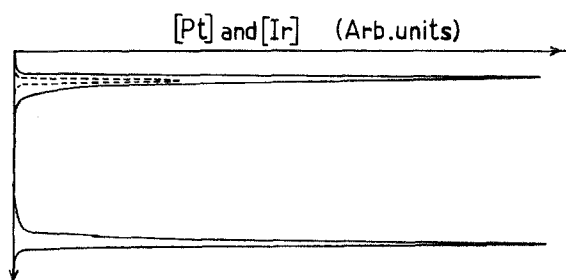

Fig. 7. Cell voltage–current density relation with temperature (atmospheric pressure). Platinum as anode and cathode.

Fig. 9. Platinum (——) and iridium (– – –) concentration profiles obtained after Ir electrodeposition.
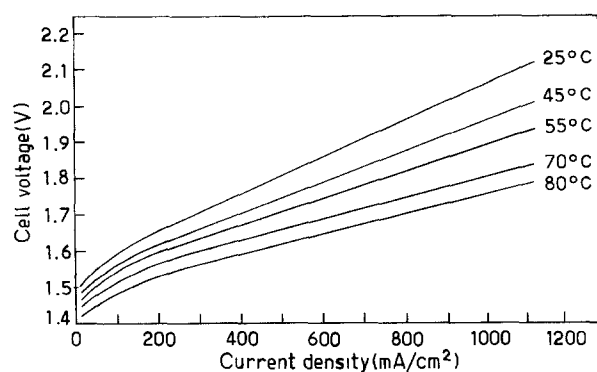
Fig. 10. Cell voltage–current density relation with temperature (atmospheric pressure). Pt as cathode and Pt–Ir as anode.

degradation. The purity of oxygen was measured using an Icare gas analyser, and was found to be above 99.97%, hydrogen being the main impurity. The purity of hydrogen was not measured.

4. Conclusion

The new procedure described in this paper for the preparation of SPE–electrocatalyst composites can be used for hydrogen and oxygen generation by SPE water electrolysis. This procedure is simple (preparation at room temperature and atmospheric pressure), rapid (2 h) and reproducible even for the preparation of high surface samples. The composites thus obtained present good electrochemical properties, low catalyst loadings, long-time stability and high energetic efficiencies.

According to the results obtained, the requirements for an ideal electrode structure for electrolysis application are as follows: the metallic and the polymeric phases must strongly interpenetrate each other in order to improve the electrode adherence. This electrode has two roles to play. The first role is that of current collector and involves the external zone. The structure must be sufficiently porous to allow fluid transport (reactants and products), but mechanical stability and electronic conductivity must be preserved. The second role is that of electrocatalyst and is realized by the internal zone. This part must have a high specific area in order to decrease the local current densities. This is realized by the dispersion of tiny metallic particles into the Nafion matrix over a thickness of several μm. However, this thickness must not be too large in order to avoid O_2 and H_2 diffusion across the Nafion membrane, which could be dangerous and would decrease the faradaic yield.

Further investigations are under way to study each electrode separately as well as the mixed electroreduction of iridium and ruthenium compounds and the phenomenon of localized precipitation.

References

[1] P. W. T. Lu and S. Srinivasan, *J. Appl. Electrochem.* **9** (1979) 269.
[2] S. Stucki and R. Muller, 'Proceedings of the 3rd World Hydrogen Energy Conference (WHEC)', Tokyo, Japan (1980) Vol. 4, p. 1799.
[3] H. Takenaka, E. Torikai, Y. Kawami and N. Wakabayashi, *Int. J. Hydrogen Energy* **7** (1982) 397.
[4] R. S. Yeo, in 'Perfluorinated Ionomer Membranes' (edited by A. Eisenberg and H. L. Yeager), ACS Symposium Series 180 (1982) p. 453.
[5] M. Donner, T. Botts, J. Mc. Breen, A. Mezzina, F. Salzano and C. Yang, 'Proceedings of the 4th WHEC', Pasadena, California, USA (1982) Vol. 1, p. 117.
[6] G. G. Scherer, 'Proceedings of the 6th WHEC', Vienna, Austria (1986) Vol. 1, p. 382.
[7] J. P. Masson, R. Molina, E. Roth, G. Gaussens and F. Lemaire, 'Proceedings of the 3rd WHEC', Tokyo, Japan (1980) Vol. 1, p. 99.
[8] A. Katayama-Akamata, H. Nakajima, K. Fujikawa and H. Kita, *Electrochim. Acta* **28** (1983) 777.
[9] H. Kita, F. Fujikawa and H. Nakajima, *Electrochim. Acta* **29** (1984) 1721.
[10] H. Nakajima, Y. Takakuwa, H. Kikuchi, F. Fujikawa and H. Kita, *Electrochim. Acta* **32** (1987) 791.
[11] W. A. Titterington and J. F. Austin, 'Ext. Abst.', ECS Fall Meeting, New York (1974) p. 576.
[12] L. J. Nuttall, 'Proceedings of the 1st WHEC', Miami Beach, Florida (1976) p. 6B-21.
[13] L. J. Nuttall and J. H. Russell, 'Proceedings of the 2nd WHEC', Zurich, Switzerland (1978) Vol. 1, p. 391.
[14] J. H. Russel, 'Proceedings of the 3rd WHEC', Tokyo, Japan (1980) Vol. 1, p. 3.
[15] R. J. Lawrence and L. D. Wood, US Patent 4,272,353, 9 June (1981).
[16] A. B. La Conti, E. N. Balko, T. G. Coker and A. G. Fragala, 'Proceedings of the Symposium on Ion Exchange, Transport and Interfacial Properties', The Electrochemical Society (1981) p. 318.
[17] H. Takenaka and E. Torikai, Kokai Tokyo Koho (Japan Patent) 55,38934 (1980).
[18] G. Scherer, H. Devantay, R. Oberlin and S. Stucki, 'Dechema Monographien', Band 98, Verlag Chemie (1985) p. 407.
[19] R. Oberlin and M. Fisher, 'Proceedings of the 6th WHEC', Vienna, Austria (1986) Vol. 1, p. 333.
[20] R. Durand, P. Millet and M. Pineri, French Patent EN 87 17 637, 17 Dec. (1987).
[21] A. Michas, J. M. Kelly, R. Durand, M. Pineri and J. M. D. Coey, *J. Membrane Sci.* **29** (1986) 239.
[22] P. Beutler and H. Gamsjager, *J. Chem. Soc. Chem. Common.* (1976) 554.
[23] K. Itaya, H. Takahashi and I. Uchida, *J. Electroanal. Chem.* **208** (1986) 373.
[24] A. Damjanovic, A. Dey and J. O'M Bockris, *J. Electrochem. Soc.* **113** (1966) 739.
[25] M. H. Miles and M. A. Thomason, *J. Electrochem. Soc.* **123** (1976) 145.
[26] M. H. Miles, E. A. Klaus, B. P. Gunn, J. R. Locker and W. E. Serafin, *Electrochim. Acta* **23** (1978) 521.