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 2500 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. Noble metal based electrocatalysts have to be used to avoid corrosion of the electrodes in contact with the highly acid electrolyte.

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. In two previous papers, 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 2500 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.
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(NH₃)₄]Cl₂·H₂O, K₂IrCl₆ and RuCl₃·H₂O (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 cm²) 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 microamperes 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. 1. Schematic diagram of a dynamic hydrogen electrode (DHE): 1-reference electrode; 2-membrane strip; 3-SPE® composite.

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