Electrochemical characterization of Polymer Electrolyte Membrane Water Electrolysis Cells

C. Rozain, P. Millet*

Institut de Chimie Moléculaire et des Matériaux d'Orsay, UMR CNRS n° 8182, Université Paris Sud 11, 15 rue Georges Clémenceau, 91405 Orsay cedex, France

ARTICLE INFO

ABSTRACT

The purpose of this paper is to report on the electrochemical characterization of Polymer Electrolyte Membrane (PEM) water electrolysis cells. Results were obtained using membrane-electrode assemblies containing unsupported IrO_2 catalyst at anode for the oxygen evolution reaction (OER) and carbon-supported platinum nano-particles at the cathode for the hydrogen evolution reaction (HER). Roughness factors of anodes and cathodes have been determined using an internal reference electrode. Individual cell voltage contributions have also been measured as a function of operating current density. Cell impedance spectra have been measured at different cell voltages along the polarization curve. It is shown that charge transfer processes are major cell impedance contributors at voltages up to 1.8-1.9 V. At higher cell voltages, cell impedances are mainly resistive. It is shown that the impedance associated with the HER is negligible and that the two time-constants observed on experimental impedance spectra can both be attributed to the OER. Possible mechanism options are discussed. Finally, some results related to the EIS characterization of PEM water electrolysis stacks are also reported.

1. Introduction

Increasing shares of renewable energy sources (intermittent electricity) in the energy mix are calling for appropriate energy storage solutions. In spite of excellent charging/discharging efficiencies, electrochemical devices such as batteries offer inappropriately low storage capacities and the need for chemical energy carriers is commonly acknowledged. Among a handful of potential candidates, molecular hydrogen (H_2) is usually considered as one of the most promising. There are few natural reserves of gaseous hydrogen which has to be extracted from natural feedstocks. In the industry sector, hydrogen is produced from natural hydrocarbons (natural gas, oil and coal), using steam reforming or gasification processes. The annual production is in the 50- billion tons range [1]. As a result, large amounts of carbon dioxide, a gas which is considered as responsible for increasing greenhouse effects and associated climate changes, are emitted in the atmosphere (0.3–0.4 m^3CO_2/m^3H_2) [2]. Water is a CO_2-free source of molecular hydrogen and a lot of R&D is carried out on the subject in view of the so-called "hydrogen economy" [3]. The total amount of energy required to split one mole of liquid water into gaseous hydrogen and oxygen is (in standard conditions), $\Delta H° = +285$ kJ.mol^{-1}. The enthalpy change remains approximately constant over the 25 °C - 1000 °C temperature range which is accessible to conventional chemical technology. The Gibbs free energy change of the water splitting reaction becomes negative at approximately 2,500 K. Therefore, the direct thermal dissociation of water is difficult to achieve because few materials can sustain such high operating temperatures and because the separation of gaseous hydrogen and oxygen in such conditions remains a very challenging task. Thermo-chemical cycles can be used to reduce the operating temperature [4]. Besides thermal processes, electricity can also be used to split water at much lower temperatures. Among three main water electrolysis technologies (alkaline, PEM and Solid Oxide) [5], the Polymer Electrolyte Membrane (PEM) process, which is specifically considered in this paper, is perceived as a key process for transforming zero-carbon electricity sources into the supply of zero-carbon hydrogen and oxygen for miscellaneous end-uses [6]. In state-of-art technology, a PEM water electrolyzer can now operate at 1 A.cm^{-2} with a high-heating-value (HHV) efficiency close to 75-80% and the multiple A.cm^{-2} range is becoming accessible. In addition, PEM water electrolysis offers the possibility of delivering pressurized hydrogen to facilitate hydrogen storage in pressurized containers [7]. Main scientific contributions in the field have been recently reviewed [8]. Increasing R&D investments are being made by public funding agencies and private companies to develop electrolysis units in the 100-250 Nm^3 H_2/hour delivery range and in the 10^4-10^5 hours operation range that would allow PEM water electrolysis to compete with the more mature alkaline process. Efficiency and durability issues

* Corresponding author. Tel.: +33 1 6915 4812.
E-mail address: pierre.millet@u-psud.fr (P. Millet).

are therefore critical and a better understanding of the performances of conventional membrane-electrode assemblies (MEAs) is required.

In this context, the purpose of this paper is to report on the electrochemical characterization of PEM water electrolysis cells using MEAs that contain Nafion as solid polymer electrolyte, iridium oxide as anodic catalyst for the oxygen evolution reaction (OER) and carbon-supported platinum as cathodic catalyst for the hydrogen evolution reaction (HER).

2. Experimental

2.1. Chemicals and materials

MEAs were prepared using PTFE-reinforced Nafion (du Pont) as solid polymer electrolyte (SPE). Unsupported iridium dioxide (Surepure Chem.) was used at the anode for the OER (loading $\approx$ 1.5 mg.cm^{-2}). Carbon-supported platinum nano-particles (Sigma Aldrich Co.) was used at the cathode for the HER (loading $\approx$ 0.5 mg Pt.cm^{-2}). Catalytic inks containing catalysts powders were sprayed automatically over the surface of the SPE using a catalytic ink printer (ExactaCoat, Sono Tek Co.).

2.2. Electrochemical characterization

A computer-controlled ModuLab Potentiostat/Galvanostat (Solartron Analytical Co.) equipped with an external 12V-60A booster was used to perform EIS measurements on laboratory cells in the 100 kHz-1 mHz frequency range. Short (10 cm long) electric cables were used to minimize parasite impedance effects. A VPM3 Multipotentiostat (Biologic Co.) was used to perform batch EIS measurements on the PEM stack. EIS spectra reported here were not corrected for any possible parasite inductive effects. Experimental impedance spectra were fitted using the EC-Lab software (Biologic Co.).

3. Detailed Description Of The Pem Water Electrolysis Cell

3.1. Cell components

Fig. 1-a shows the cross-section of the PEM water electrolysis cell. The active component at the center of the cell (label 1 in Fig. 1 a) is the MEA. MEAs are made of a thin (usually $\approx$ 50-200 μm thick) proton-conducting polymeric film (also called solid polymer electrolyte or SPE) with two porous catalytic layers platted on each side. In conventional PEM systems, the SPE is usually made of perfluoro-sulfonated polymer, as in fuel cell technology. Nafion® from DuPont [9] is a standard SPE material. The central grey area in Fig. 1a is the PTFE fibre which is used for mechanical reinforcement. The acidity and ionic conductivity of Nafion® products is equivalent to that of 1 M sulfuric acid aqueous solutions. This is why platinum-group metals (PGMs) are used as electrocatalysts (non-PGM metals are prone to corrosion/dissolution in such strong acidic media). The SPE is surface coated with two catalytic layers, a thin (0.1-1 μm thick) layer of carbon-supported platinum nano-particles at the cathode for the HER (label 2 in Fig. 1a) and a thicker (1-5 μm thick) layer of un-supported IrO$_2$ particles at the anode for the OER (label 2′ in Fig. 1a). Catalysts particles must be strongly bonded to the SPE surface to sustain the large mechanical constraints that occur during operating due to the massive production of gases. In addition, catalytic layers must be sufficiently porous to let gases go away from interfaces, and sufficiently conductive in order to let current flow homogeneously and to reduce parasite ohmic resistances. The MEA is clamped between two porous current collectors. In the anodic compartment, the current collector (label 3′ in Fig. 1-a) is usually a millimeter thick porous titanium disc obtained by thermal sintering of titanium powder. The microstructure of the disc (in terms of porosity and tortuosity) is a key factor that needs to be optimized because this is the place where two opposite flows (liquid water towards the anode and oxygen gas away from the anode) coexist [10]. Inappropriate porosities may yield mass transport limitations. Optimal porosity values may differ as a function of the nominal operating current density since, according to Faraday's law, the gas production is directly related to the current flowing across the cell. In the cathodic compartment, a similar titanium disc can be used. Alternatively (since titanium discs are rather expensive), a gas-diffusion-layer (GDL) similar to those found in PEM fuel cells can also be used (label 3 in Fig. 1-a). The microstructure of the cathodic current collector is less critical than the anodic one because at the cathode, the hydrogen gaseous production and the flow of liquid water (due to the electro-osmotic drag across the cell, i.e. hydration water molecules transported by protons) are both co-linear, away from the MEA. Two titanium end-plates delimit the PEM cell (labels 5 and 5′ in Fig. 1-a). Biphasic liquid–gas mixtures can circulate in channels or machined grooves in the thickness of the end-plates, just like in PEM fuel cells. Alternatively, less-expensive titanium grids can also be used as cell spacers (labels 4 and 4′ in Fig. 1-a). Individual PEM cells (usually in the 4–7 mm thick range) can be stacked together in order to increase gas production. A total of fifty to sixty cells is nowadays common good practice in industrial systems whereas in alkaline water electrolysis technology, several hundred cells can be clamped together.

3.2. Electrical equivalent circuit of a PEM water electrolysis cell

Fig. 1-b shows the equivalent electrical circuit of the PEM water electrolysis cell. Each charge transfer interface is modelled using the parallel connection of a polarization resistance and a constant phase element (Q) [11]. Constant phase elements are used to take into account deviations of double layers from ideal capacitive behaviours due to surface roughness, polycrystallinity and anion adsorption (sulfonate ions in PEM cells). Diffusion impedances are added in series to account for possible mass transport limitations of hydrogen and oxygen gases away from the interfaces across porous current collectors. Interface impedances are also series connected to ohmic resistances to account for electronic (metals) and ionic (SPE) conductivity of cell components. It will be shown in the following that the ohmic resistance of the PEM cell is a critical parameter that can quite significantly impact the overall performances of the PEM cell and that needs to be minimized. Details of the different circuit components are:

R^c_Ω and R^a_Ω (Ω.cm^2): electronic resistance of electron-conducting metallic cell components at cathode and anode respectively.

R^{el} (Ω.cm^2): ionic resistance of the SPE.

R^c_{ct} (Ω.cm^2): cathodic polarization resistance associated with the HER.

R^a_{ct} (Ω.cm^2): anodic polarization resistance associated with the OER.

Q^c_{dl} (F.cm^{-2}.s^{n-1}): cathodic constant phase element of the cathode/electrolyte interface; n is related to the angle of rotation of a purely capacitive line on complex plane plots [11].

Q^a_{dl} (F.cm^{-2}.s^{n-1}): anodic constant phase element of the anode/electrolyte interface.

Z^c_D (Ω.cm^2): cathodic diffusion impedance due to H$_2$ transport away from the cathode.

Z^a_D (Ω.cm^2): anodic diffusion impedance due to O$_2$ transport away from the anode and/or to H$_2$O transport to the anode.