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Study on a novel manufacturing process of membrane electrode assemblies for solid polymer electrolyte water electrolysis

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Abstract

A novel manufacturing process for catalyst coated membrane (CCM) was utilized to fabricate the membrane electrode assemblies (MEA) for solid polymer electrolyte (SPE) water electrolysis. The properties and performance of the modified CCM were analyzed and evaluated by SEM, electrochemistry impedance spectroscopy (EIS) and *I–V* curves. The characterizations reveal that the sprayed Nafion layers are very effective for increasing the reaction interface between SPE and the electrode catalyst layer. The test experiments show that the SPE water electrolyzer with new MEA structure can lower about 0.1 V of water electrolysis voltage at atmosphere pressure and 2 A cm^{-2}.

Keywords: Water electrolysis; Solid polymer electrolyte; Catalyst coated membrane; Membrane electrode assembly; Manufacturing process

1. Introduction

The first SPE electrolyzers were developed by General Electric Co. in 1966 for space applications [1]. Compared with water-alkaline electrolyzers, SPE water electrolyzers possess the following advantages: safety, low maintenance, higher energy efficiency, specific production capacity and a simple system [2,3]. At present, such electrolyzers are developed for the special purposes (spacecrafts, submarines, etc.), and also for the civil industry, such as power plants, analytical chemistry, nuclear reactors, hydrogen welding, metallurgy of especially pure metals and alloys, electronic industry [2,4]. Along with the research and development of fuel cell, SPE electrolyzers will play more and more important role in hydrogen production [5]. PEM electrolyzers can be also used in PV-hydrogen energy-storage system as a viable alternative for hydrogen generation from renewable energy sources [6].

The MEA is the core part of a SPE water electrolyzer and electrochemical reaction only takes place at ''triple-phase boundaries'', where reaction materials, electrolyte and electrically conducted catalysts contact together. Therefore, the interface between solid polymer electrolyte and catalyst layers should be as large as possible and contact resistance between them should be as small as possible [7].

At present, the fabrication processes of MEA for SPE water electrolysis include chemical plating [8–10], transfer method [11,12] and catalyst coated membrane technology [3], and besides, spraying or coating the catalysts onto a backing/current collector substrate was also used to prepare the MEA of SPE water electrolyzer [13]. MEAs made by using chemical plating method have large catalyst particle diameter and low surface area of catalysts and high catalyst loading, and thus possess lower performance. The membrane surface etching [9,10] and sand-blasting [9] were utilized to increase the membrane roughness and then enlarge the reaction interface between SPE and the electrode, but surface roughening weakened mechanical strength of membrane and then shortened the lifetime of

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MEA. Transfer method [11,12] and CCM [3] was used to prepare MEA for SPE water electrolysis, which can lower catalyst loading and enhance the adhesion between polymer electrolyte and catalyst layers and thus improve the performance of MEA for SPE water electrolysis.

In this paper, modified CCM technology was utilized to prepare MEA for SPE water electrolysis by spraying a layer of ionomer on the surface of membrane to enlarge the interface between solid polymer electrolyte and catalyst layers and thus improve the performance of MEA for SPE water electrolysis. Compared with conventional MEA preparation process, modified CCM technology has several advantages such as lower catalyst loading, larger interface and lower contact resistance between polymer electrolyte and catalyst layers, which indicates that the new CCM can improve the performance of SPE water electrolysis.

2. Experimental

2.1. Preparation of modified catalyst coated membrane for SPE water electrolysis

CCM with the novel structure was prepared by introducing a Nafion layer into interface between polymer electrolyte membrane and catalyst layer. Preparation of CCM with new structure was presented in detail as followings.

0.14 g of Nafion solution (5 wt%) and 0.14 g of NaOH aqueous solution (0.5 M) were mixed by supersonic for an hour and sprayed onto one side of Na^+ form Nafion 115 at 100 °C. Sprayed Nafion loading was about 0.7 mg cm^{-2}. A Nafion layer was also formed onto another side of Na^+ form Nafion 115 by the same method. And then modified membrane was treated for 30 min under 180 °C and vacuum, followed by rinsing in deionized water to remove excess NaOH.

IrO_2, which is used as the electrocatalyst for oxygen evolution, was prepared by using Adams method [14]. Pt black as the electrocatalyst for hydrogen evolution was obtained from Shanghai Chemical Reagent Company. An appropriate amount of electrocatalyst (IrO_2 or Pt black), 5 wt% Nafion solution (Dupont), 0.5 M NaOH aqueous solution and iso-propanol were dispersed by supersonic to obtain the catalyst ink. In order to transform H^+ form Nafion to Na^+ form Nafion, excess NaOH needs to be added to the catalyst ink. Catalyst ink was applied onto the modified Na^+ form Nafion 115 to form catalyst layer. A suitable composition of anode (or cathode) catalyst layer was 70 wt% IrO_2 (or Pt) and 30 wt% Nafion. The loading of IrO_2 is about 2.5 mg cm^{-2}, and the loading of nanometer Pt is about 2 mg cm^{-2}.

During the preparation of CCM with new structure, a piece of modified Na^+ form Nafion 115 was placed on a homemade vacuum device at 100 °C and the spraying process was carried out by using an air driven spray gun. The anode (or cathode) slurry was evenly sprayed into 5 cm^2 of square on both sides of modified membrane. The sprayed CCM was treated for 0.5 h under Ar and 195 °C and then was re-protonated to H^+ form CCM in 0.5 M sulfuric acid at 80 °C for an hour, followed by rinsing in deionized water to obtain the available CCM. This new structural CCM was denoted as CCM-1.

In order to make comparison, another CCM was obtained by the conventional CCM technology, and the CCM was denoted as CCM-2.

2.2. Characterization of CCMs

After the characterization of EIS and water electrolysis test, the surface and cross-sectional morphologies of CCM-1 and CCM-2 were analyzed by Hitachi S-4500 scanning electron microscope (SEM).

During water electrolysis at atmospheres temperature and atmosphere pressure and 1 A cm^{-2}, the impedence spectra were recorded with EG&G PAR potentiostat/galvanostat 263 A combined with a Perkin–Elmer 5210 frequency response analyzer in the frequency from 0.5 Hz to 50 kHz. Because the over-potential of hydrogen evolution on the Pt black is very small, so the cathode can be used as the counter electrode and reference electrode.

2.3. Evaluation of the SPE water electrolyzer

The CCM performance for water electrolysis was tested by using a single cell with an active area of 5 cm^2. Carbon paper served as cathode diffusion backing and carbon paper plated with gold was used as anode diffusion backing. In water electrolysis, the cell was run at 80 °C and ambient pressure.

3. Results and discussion

3.1. SEM images of Nafion 115 membrane and CCM before and after modification

Abrasion of membrane surface has already been mentioned in the literatures [9,15,16] as an interesting and efficient method to enlarge the active area of the electrodes and improve their adhesion to the membrane. However, the method lowered the mechanical strength of membrane and then lowered the lifetime of MEA.

The SEM photographs of the surface of Na^+ form Nafion 115 membrane before and after modification are shown in Figs. 1a and b, respectively. As shown in Figs. 1a and b, the surface of as-received Na^+ form Nafion 115 is very smooth, but there are many holes, pits and islands at micrometer scale on the surface of modified Na^+ form Nafion 115, so the surface of modified Na^+ form Nafion 115 membrane is much rougher than that of as-received Na^+ form Nafion 115.

Figs. 1c and d show the cross-sectional SEM images of CCM-2 and modified CCM-1, respectively. The thickness of anode and cathode catalyst layers are about 16 μm and 10 μm, respectively. As shown in Fig. 1d, the interface