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Preparation and characterization of partial-cocrystallized catalyst-coated membrane for solid polymer electrolyte water electrolysis

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ABSTRACT

A novel catalyst-coated membrane (CCM) for solid polymer electrolyte water electrolysis was fabricated by together crystallizing partial-crystallized Nafion membrane and catalyst layers. The properties and performance of the partial-cocrystallized CCM (PCCCM) were evaluated and analyzed by destructive soaking test, scanning electron microscope, mercury intrusion and single cell test. The results revealed that the optimum annealing temperature and time for fabricating partial-crystallized Nafion membrane and PCCCM was 100 °C for 4 h and 120 °C for 4 h, respectively. The PCCCM not only possessed much stronger cohesion between membrane and catalyst layers, but also had higher porosity than conventional CCM. The electrolysis voltage of the SPE water electrolyser with the new CCM was as low as 1.748 V at 2000 mA cm⁻² under 80 °C and atmospheric pressure. Moreover, there was no obvious increase of electrolysis voltage during stability test conducted under 2000 mA cm⁻² for about 180 h.

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1. Introduction

With the extensive consumption and coming shortage of fossil fuels, developing new clean energy techniques is imperative. Hydrogen, the cleanest energy carrier, can be produced from renewable energy sources in various ways. Compared with other hydrogen production methods, solid polymer electrolyte (SPE) water electrolysis possesses the advantages of safety, simplicity, high energy efficiency, high specific production capacity and low maintenance [1–3].

Membrane electrode assembly (MEA) is the core part of SPE water electrolyser. High-performance MEA for SPE water

electrolysis should possess the following characteristics: (1) ample triple-phase boundaries; (2) excellent electron conductivity of catalyst layers; (3) strong adhesion and thus low proton transfer resistance between catalyst layers and membrane [4]; (4) proper porosity and thus high mass transfer ability of catalyst layers [5]; (5) high chemical and physical durability in operation [6,7]. The performance of electrolysers strongly depends on the properties of MEA. However, works on the research and development of MEAs are very limited compared with those on the catalysts [4,5,7,8].

At present, the MEA preparation methods can be classified into two modes according to the different supports of catalyst

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layers, i.e. gas diffusion electrode (GDE) mode and catalyst coated membrane (CCM) mode, adopting gas diffusion layer and solid polymer electrolyte as support, respectively. It has been well demonstrated that CCM has lower catalyst loading, thinner catalyst layers and much more hydrophilic catalyst layers compared with GDE [9,10]. Therefore, most of the MEAs for SPE water electrolysis were fabricated by the CCM method. However, the catalyst layers of the CCM are prone to peel off from the membrane for the following reasons: (1) the different swelling degrees between membrane and catalyst layers in water, (2) the large amount of gas generation in catalyst layers during water electrolysis, and (3) the nonuniformity of compression force between the land and under the channel. The delamination of CCM would increase the contact resistance between membrane and catalyst layers, and shorten the life of SPE water electrolyser [4,7,8]. Besides, the poorer gas transmission ability of catalyst layers of CCM compared with that of GDE is prone to decrease the utilization of catalysts [5].

To increase the adhesion between membrane and catalyst layers, several methods have been studied. Millet et al. [11] increased the adhesion of electrode to membrane by chemically reducing noble metal cationic species within Nafion membrane. However, MEA fabricated by this method had large catalyst particle size, high catalyst loading, and was prone to induce H_2 and O_2 diffusion for the deep penetration of catalysts into the membrane. Besides, Millet et al. [12] also employed surface etching method to increase the roughness factor of membrane, which increased the adherence strength between membrane and catalyst layers. In spite of that, surface etching treatment lowered the mechanical strength of membrane. Recently, other methods have been explored to increase the interfacial contact strength between membrane and catalyst layers, including modified CCM technology [4] and spraying CCM under irradiation method [7]. Nevertheless, the increase of the adherence is limited due to the non-integrated character of the membrane and catalyst layers.

The gas transfer ability of catalyst layers is also an important factor influencing the performance of SPE water electrolyser. To increase the gas transfer ability of catalyst layers, Xu et al. [5] added PTFE to catalyst layer and annealed it at 340°C . But annealing at temperature higher than 270°C can lead to the decomposition of the side chains of Nafion and consequently decrease proton conductivity of catalyst layers [13]. Chen et al. [14] adopted the Nafion-pyrolyzed method to minimize mass transport limitation in unitized regenerative fuel cell. This method effectively enhanced the performance of fuel cell mode; nevertheless the improvement of the electrolysis mode was not obvious due to the decrease of proton conductivity.

In our previous work, by together crystallizing amorphous membrane and catalyst layers, we fabricated cocrystalline CCM which not only effectively decreased the electrolysis voltage but also enhanced stability of SPE water electrolyser [15]. However, for the weak mechanical strength of amorphous Nafion membrane, it was easy to break up for the membrane during the process of fabricating CCM. Therefore, in this research, we further developed partial-cocrystallized CCM. Study results indicated that the partial-cocrystallized CCM also showed remarkably lower electrolysis voltage and better stability under high current density compared with conventional CCM.

2. Experimental

2.1. Preparation of Nafion membrane and partial-cocrystallized CCM

The partial-cocrystallized CCM was prepared by together crystallizing the partial-crystallized Nafion membrane and catalyst layers. The details of fabrication Nafion membrane and partial-cocrystallized CCM are described as follows.

Firstly, the Nafion solution (5 wt. %, DuPont) was heated at 60°C for 10 h to remove the solvent. Then the obtained Nafion ionomer was redissolved in N, N-dimethylacetamide (DMAc) with 10 wt. % of the Nafion content. The Nafion/DMAc solution was cast onto a glass substrate and dried at 60°C for 35 h. Finally, the resulting membrane was treated at elevated temperature. The thickness of the obtained partial-crystallized membrane was about $120\ \mu\text{m}$, which was close to Nafion 115 membrane (DuPont). All Nafion membranes were pre-treated by 5 vol. % H_2O_2 aqueous solution at 80°C for 40 min, then $0.5\ \text{mol L}^{-1}$ H_2SO_4 at 80°C for 30 min, and finally rinsed with the deionized water.

Iridium black (95 wt. %, Johnson Matthey) and 70 wt. % Pt/C (Johnson Matthey) were used as the anode and cathode catalysts, respectively. A homogeneous ink consisted of catalyst (Iridium black or Pt/C), Nafion solution (5 wt. %, DuPont) and isopropanol was sprayed onto each side of the cast partial-crystallized membrane. The composition of catalyst layers was 75 wt. % catalyst (Iridium black or Pt/C) and 25 wt. % Nafion. After being dried at 80°C and vacuum for 1 h, the sprayed CCM was annealing crystallized at different temperatures and time. The obtained partial-cocrystallized CCM was named CCM-1. For comparison, another two CCMs, CCM-2 and CCM-3, were also made by the same procedure, except that their catalyst layers were sprayed on Nafion 115 membrane, and that CCM-2 did not undergo the annealing crystallization treatment. The catalyst loading of all the CCMs was $2.0\ \text{mg cm}^{-2}$ for iridium black and $1.0\ \text{mg cm}^{-2}$ for Pt/C.

2.2. Physical characterization

XRD (X-Ray Diffraction) patterns were recorded on Rigaku D/MAX 2500/PC (using $\text{Cu K}\alpha$ radiation, $\lambda = 0.154\ \text{nm}$ at 40 kV and 200 mA). Scanning electron microscope (SEM) (JSM 6360-LV) was employed to observe the cross-sections of the CCMs. The porosities of the CCMs were measured by the mercury intrusion method with a PoremasterGT60 (Quantachrome). The pressure was from 1.478×10^8 (2.143×10^4 psi) to 1.933×10^8 Pa (2.804×10^4 psi) and the mercury contact angle was 140° . Destructive soaking test was conducted by soaking the MEA in anhydrous ethanol.

The proton conductivities of the Nafion 115 membranes were carried out under fully hydrated conditions at 80°C by using a cell with a pair of pressure-attached copper electrodes coating gold. The ohmic resistance (R) was measured by electrochemistry impedance spectroscopy (EIS) using Solartron 1287 Electrochemical Interface in conjunction with Solartron 1260 Frequency Response Analyzer in frequency from 1 MHz to 10 Hz. The conductivities (σ , S cm^{-1}) were obtained using $\sigma = d/RWh$, where d , W and h are the distance

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