Journal of Power Sources 240 (2013) 525–529

Contents lists available at SciVerse ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Short communication

A cocrystallized catalyst-coated membrane with high performance for solid polymer electrolyte water electrolysis

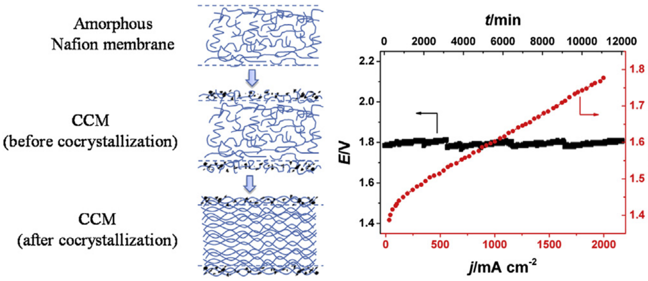
Xunying Wang [a,b], Zhi-Gang Shao [a,*], Guangfu Li [a,b], Linsong Zhang [a,b], Yun Zhao [a,b], Wangting Lu [a,b], Baolian Yi [a]

[a] Fuel Cell System and Engineering Laboratory, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, PR China
[b] Graduate School of the Chinese Academy of Sciences, Beijing 100039, PR China

HIGHLIGHTS

- Amorphous Nafion membrane and catalyst layers were crystallized together.
- Reinforced bonding between membrane and catalyst layers.
- Voltage of water electrolysis was 1.777 V at 80 °C and 2 A cm^{-2}
- Cocrystallized catalyst coated membrane exhibited high stability.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 7 December 2012
Received in revised form
11 April 2013
Accepted 12 April 2013
Available online 20 April 2013

Keywords:
Solid polymer electrolyte water electrolysis
Catalyst-coated membrane
Cocrystallization treatment
High performance

ABSTRACT

A cocrystallized catalyst-coated membrane (CCM) is prepared by together heating amorphous Nafion membrane and catalyst layers at 120 °C to develop the membrane electrode assembly for solid polymer electrolyte (SPE) water electrolysis. The cocrystallization treatment effectively reinforces the bonding between membrane and catalyst layers, and increases the hydrophobicity of the catalyst layers. The SPE water electrolyser with the cocrystallized CCM decreased cell voltage by 0.09 V at 2000 mA cm^{-2} at 80 °C and improved the stability in comparison with the conventional CCM.

1. Introduction

Solid polymer electrolyte (SPE) water electrolysis is a promising method for hydrogen production especially from renewable energy sources [1–4]. Compared with the conventional alkaline water electrolyser, SPE water electrolyser possesses the advantages of safety, simplicity, high energy efficiency, high specific production capacity and low maintenance [3].

Membrane electrode assembly (MEA) is the key component of SPE water electrolyser. However, the recent works on SPE water electrolysis have been mainly focused on catalyst [5–7]. To the best of our knowledge, reports on the research and development of MEAs have been very limited [8–10]. At present, the preparation of MEA for SPE water electrolysis is similar to that for proton exchange membrane fuel cell, and most of the MEAs have been prepared by the catalyst-coated membrane (CCM) method [11–13]. Compared

---

* Corresponding author. Tel.: +86 411 84379153; fax: +86 411 84379185.
E-mail address: zhgshao@dicp.ac.cn (Z.-G. Shao).

0378-7753/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jpowsour.2013.04.069

with the gas diffusion electrode, the CCM has been demonstrated to have lower catalyst loading, thinner and much more hydrophilic catalyst layers [11]. 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) large amount of gas generation in catalyst layers during water electrolysis, and (3) nonuniformity of compression force between the land and under the channel [14,15]. In addition, the complete hydrophilicity of catalyst layers of CCM makes against the gas transmission, thus decreases the utilization ratio of the catalysts [9]. To increase the adhesion of the electrode to the membrane, Millet et al. [16] chemically reduced noble metal cationic species within Nafion membrane. However, CCM fabricated by this method had large catalyst particle size and high catalyst loading, and was prone to induce H_2 and O_2 diffusion for the deep penetration of catalysts into the membrane. To enhance the hydrophobicity of the catalyst layer, Xu et al. [9] added PTFE into the conventional hydrophilic catalyst layer and annealed the catalyst layer at 340 °C. However, annealing catalyst layer at temperature higher than 270 °C can lead to the decomposition of the side chains of Nafion and consequently decrease proton conductivity of catalyst layer [17].

In this work, we prepared the cocrystallized CCM by together crystallizing amorphous Nafion membrane and catalyst layers at 120 °C. The resulting CCM reinforced the bonding between membrane and catalyst layers and increased the hydrophobicity of the catalyst layers. Serial cell tests indicated that the cocrystallized CCM had much better performance than the conventional CCM.

2. Experimental

2.1. Preparation of Nafion membrane and cocrystallized CCM

The cocrystallized CCM was prepared by together crystallizing amorphous Nafion membrane and catalyst layers. The details of casting Nafion membrane and fabricating the cocrystallized CCM are described as follows.

Firstly, the Nafion solution (5 wt.%, Du Pont) 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 Nafion content. The Nafion/DMAc solution was cast onto a flat glass substrate and dried at 60 °C for 35 h. The thickness of the obtained amorphous membrane was about 120 μm. For comparison, the crystallized membrane was prepared by annealing the amorphous Nafion membrane at 120 °C and vacuum for 4 h. All Nafion membranes were successively pre-treated by 5 vol.% H_2O_2 and 0.5 mol L^{-1} H_2SO_4, and then rinsed with the deionized water.

Iridium black (Johnson Matthey) and Pt/C (70 wt.%, Johnson Matthey) were used as the anode and cathode catalysts, respectively. Homogeneous ink consisting of catalyst (iridium black or Pt/C), Nafion solution (5 wt.%, Du Pont) and isopropanol was sprayed onto the amorphous membrane to form the catalyst layers. After being dried at 80 °C under vacuum for 1 h, the CCM was cocrystallized at 120 °C under vacuum for 4 h. This cocrystallized CCM was denoted as CCM-1. For comparison, another two conventional CCMs, CCM-2 and CCM-3, were made by the same procedure, except that their catalyst layers were sprayed on home-made crystallized membrane and commercial Nafion 115 membrane (Du Pont), respectively, and that they did not undergo the cocrystallization treatment. The catalyst loading of all the CCMs was about 2.0 mg cm^{-2} for iridium black and 1.0 mg cm^{-2} for Pt/C.

2.2. Physical characterization of CCM

JSM 6360-LV and NOVA NanoSEM 450 Scanning electron microscope (SEM) were employed to observe the cross-sections and surfaces of the CCMs, respectively. Destructive test was conducted by soaking the MEA in anhydrous ethanol. X-ray diffraction (XRD) patterns were recorded on Rigaku D/MAX 2500/PC X-ray diffractometer using Cu Kα radiation ($\lambda = 0.154056$ nm). The contact angle on the anode surface of CCM was measured by the KRŰSS DSA100 Drop Shape Analysis System.

2.3. Evaluation of water electrolysis performance

Porous titanium (Pt plated, 0.7 mm in thickness) and wet-proof carbon paper (Toray, TGP-H-60) served as the anode and cathode diffusion layer, respectively. The CCM and the carbon paper were hot pressed together at 120 °C and 0.5 MPa for 1 min. A home-made electrolysis test stand was used to evaluate the performance of the CCM. The SPE water electrolyser performance was evaluated at atmosphere pressure and 80 °C. Electrochemistry impedance spectroscopy (EIS) was carried out at 1.45 V by Solartron 1287 Electrochemical Interface in conjunction with Solartron 1260 Frequency Response Analyzer in frequency from 0.1 Hz to 10 kHz [18]. The impedance diagrams were analyzed and modelled using the ZView program of Solartron, version 3.0. The stability tests were conducted under 2000 mA cm^{-2} at atmosphere pressure and 80 °C.

3. Results and discussion

Nafion membrane cast at low temperature (between room temperature and 80 °C) was essentially amorphous, and annealing it at temperature higher than its glass transition temperature (T_g, 100 °C) can fuse its fluorocarbon chains together and therefore increase crystallinity of membrane [19, 20]. However, fabricating the CCM at a higher temperature may decrease the proton conductivity of Nafion. Therefore, the thermal treatment of CCM should be carefully controlled at a temperature lower than 140 °C [21]. Thus, we cast the amorphous Nafion membrane at 60 °C, and further annealed it together with the catalyst layers at 120 °C under vacuum for 4 h to get the cocrystallized CCM-1, as described in Fig. 1. In the amorphous

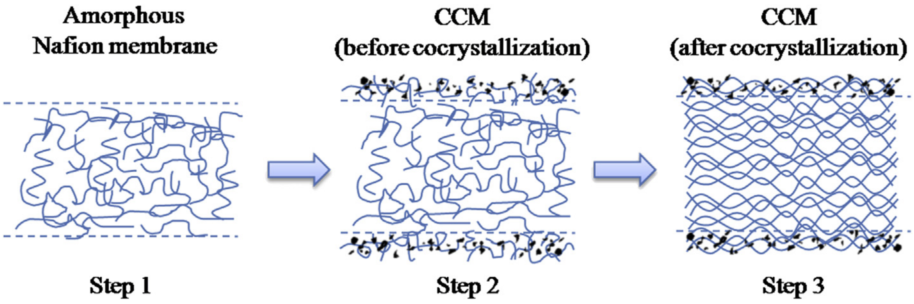


Fig. 1. Schematic illustration for the cocrystallized CCM fabrication.