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Evaluation of impregnated nanocomposite membranes for aqueous methanol electrochemical reforming

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ABSTRACT

In this work, we present the methanol electrolysis performance of the bimetallic Pt–Pd impregnated Nafion based nanocomposite polymer electrolyte membrane prepared by non-equilibrium impregnation–reduction (NEIR) method. The different atomic concentrations of Pt–Pd impregnated nanocomposite membranes were subjected to X-ray diffraction for their structural characteristics. The effect of various parameters such as methanol concentration, cell voltage and temperature on the cell performance was investigated. Further, the bimetallic concentration and catalyst loading were also optimized for methanol electrolysis. The results indicated that the bimetallic Pt–Pd of a ratio 70:30 impregnated Nafion based nano-composite membrane showed the best performance on the methanol electrolysis.

1. Introduction

The increase in the need of energy consumption to the futuristic world has led the scientists to search for a new and clean energy source. Hydrogen has high energy density and is considered as a most promising energy carrier for providing a clean and sustainable energy system to prevent from the climate changes related to the use of other fuels, especially the use of fossil fuels [1,2]. Electrolysis is a best option for producing hydrogen very quickly and conveniently. Particularly, electrolysis of aqueous methanol is a promising method for onsite hydrogen production, and it has been reported that very high purity hydrogen can be generated by electrolysis of methanol–water mixture at a very low operating voltage, compared to water electrolysis [2,3]. In a methanol electrolysis cell, methanol is fed to the anodic compartment where it can be completely oxidized in the presence of water, producing carbon dioxide and protons, i.e.,:

$$\text{At Anode}: CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^- \quad E_a^0 = -0.016\,\text{V vs SHE}. \tag{1}$$

Carbon dioxide evolves in the form of gaseous phase, whereas the electrons circulate in the external circuit and protons crossover the polymer electrolyte membrane, reaching the cathodic compartment where they are reduced by the electrons coming from the external circuit, thus producing hydrogen as follows:

$$\text{At Cathode}: 6H^+ + 6e^- \rightarrow 3H_2 \quad E_c^0 = 0\,\text{V vs SHE}. \tag{2}$$

This corresponds to the overall decomposition of methanol into hydrogen and carbon dioxide:

$$\text{Overall}: CH_3OH + H_2O \rightarrow 3H_2 + CO_2 \quad E^0 = -0.016\,\text{V vs SHE}. \tag{3}$$

Hydrogen production by aqueous methanol electrolysis is simple in principle [4], in the patent by Narayanan et al. [5] who first described hydrogen production by electrolysis of aqueous organic solutions. There are several studies on aqueous methanol electrolysis have been reported and most of the works are focused on catalyst development and parameter optimizations [2–6]. However, it is well known that Nafion perfluorosulfonic acid polymers are commonly used as electrolyte membranes due to their excellent thermal and chemical stability, and their disadvantage is that they are quite permeable to methanol [7–9]. Methanol crossover may reduce the cell performance [10], purity of hydrogen and conversion loss in lost fuel. In addition cathode catalyst layer is poisoned by CO due to methanol oxidation intermediate. In order to mitigate the effect of methanol crossover in direct methanol fuel cells, a number of techniques have been reported [10–13] and the modification of Nafion without decreasing its proton conductivity is

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one of the important techniques, such as hybridizing the Nafion membrane with sulfonated organic silica, zeolites, conducting polymers and polymer composites, metallic nanoparticles, heteropolyacids and composite organic/inorganic thin films onto the Nafion membrane [14]. Among the others, the surface modification of Nafion membrane with incorporation of palladium (Pd) layers and Pd nanoclusters is an interest of recent research [15].

It has been widely reported that the Pt catalyzed membrane is suitable for electrolyzer applications because of the use of a Pt-catalyzed membrane as an anode for methanol oxidation offers advantages over conventional cells [16–19]. Furthermore, the addition of Pd suppresses the methanol permeation and enhances proton conductivity which makes the bimetallic Pt–Pd/Nafion nanocomposite as the promising membrane for methanol electrolysis. To the best of our knowledge, so far no one has studied the Pt–Pd impregnated Nafion nanocomposite membrane for methanol electrolysis. On the other hand, the catalyzed membrane preparation is an attractive as it involves only simple steps and also for application processes. Furthermore, the development of a nanocatalyzed membrane by the non-equilibrium impregnation–reduction (NEIR) method is one of the best methods for electrolyzer applications [17,20,21]. Hence, in this study, bimetallic Pt–Pd nanophase was impregnated to modify the Nafion membrane. The Pt–Pd impregnated Nafion based nanocomposite polymer electrolyte membranes fabricated by NEIR method were investigated for methanol electrolyzer applications.

2. Experimental procedure

The methodology used for membrane pre-treatment and Pt–Pd impregnated nanocomposite membrane preparation method has been reported already in our previous work [22]. The reproducibility of the Pt–Pd impregnated nanocomposite membranes varies with the fabrication procedure. However, the reproducibility of the Pt–Pd impregnated nanocomposite membranes extents to keep fabrication procedure identical [21]. Hence we keep the fabrication procedure identical to facilitate the reproducibility. Accordingly, Pt–Pd was deposited on one side of Nafion membrane and was used as an anode (Fig. 1). On the other hand, 40% Pt/C (Duralyst, USA) was used as a cathode catalyst with 1 mg cm^{-2} loading. The electrocatalyst slurry was prepared by dispersing a 40% Pt/C in water and followed by sonication at room temperature for 30 min. A 5 wt.% of Nafion ionomer, and isopropyl alcohol were added to the mixture and again sonicated at room temperature, and then the obtained slurry was coated onto the membrane using decal transfer method. In decal transfer method the above prepared catalyst ink was applied on a polyimide film and dried at 100 °C. The catalyst coated polyimide film was placed on pretreated membrane and was hot pressed to 1000 psi at 130 °C for 3 min. Later, the polyimide film was peeled off, leaving a uniform layer of the catalyst on the membrane. Finally again MEAs were hot pressed with microporous layer coated gas diffusion layer (GDL) with uniform holes on anode side and without holes on cathode side. The pressure was maintained to 1000 psi for 3 min at 130 °C (Fig. 2). For comparative evaluation, a normal MEA with both side 40% Pt/C catalysts was prepared by decal transfer method.

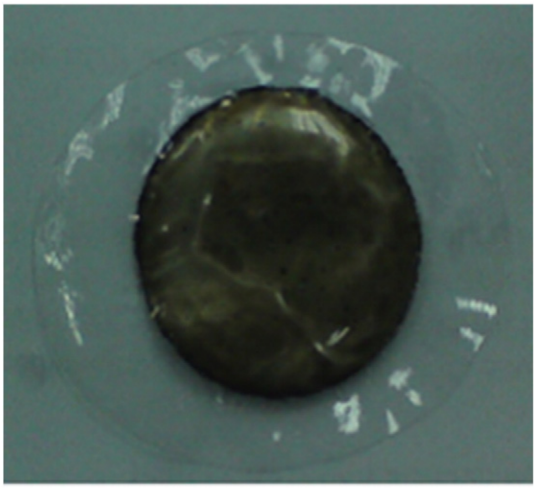

Fig. 1. Pt–Pd impregnated nanocomposite membrane.

X-ray diffraction (XRD) patterns of Pt–Pd/Nafion nanocomposite membranes were acquired at room temperature with an X'pert PRO PANalytical diffractometer using Cu-k$_\alpha$ radiation as source and operated at 40 kV. The samples were scanned in the 2θ ranging from 10 to 80° for 2 s in the step scan mode.

Single cell experiments were performed by placing the Pt–Pd impregnated Nafion nanocomposite MEA between two gaskets of thickness 0.25 mm and inserted between two graphite plates with straight parallel grooves and 10 cm^2 active areas. The above items were clamped together using nuts and bolts, by applying uniform torque, to assemble the single cell. The cell had provision for heating, temperature control and suitable ports for feeding the reactants and removal of products.

The electrolysis was conducted to generate hydrogen at the cathode, by applying current across the two terminals of the electrolyzer using a programmable DC power supply unit having constant current and voltage mode provisions. Hydrogen production rate was calculated from the cell current and was cross examined by gas volume measurement. The purity of hydrogen gas was checked by using a calibrated hydrogen purity analyzer (NOVA Gas Analyzer).

3. Results and discussions

3.1. Physical characterizations

3.1.1. XRD

XRD patterns of different ratios of Pt–Pd layered Nafion 117 membranes and pure Nafion 117 membrane are shown in Fig. 3. The samples showed the crystalline characteristic peaks around at 2θ = 40, 47 and 68° which represented (1 1 1), (2 0 0), and (2 2 0) lattice planes, respectively, of face-centered cubic (*fcc*) structure of Pt and Pd [23]. A broad hump observed at 17° revealed the amorphous nature of Nafion membrane [24]. It was confirmed that the face centered cubic structure

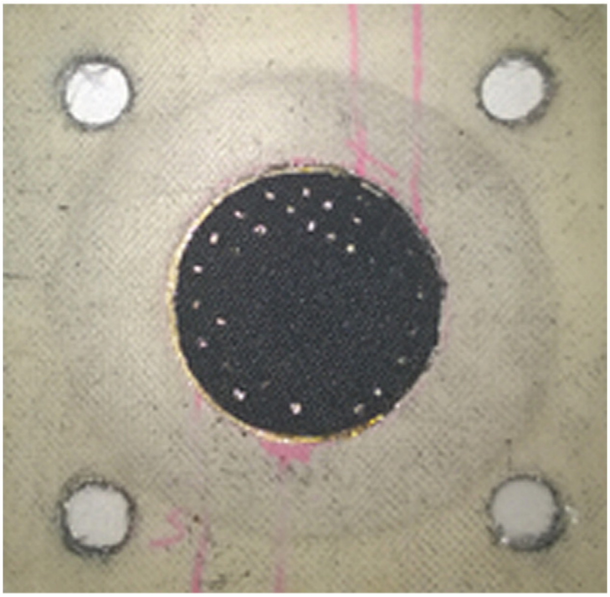

Fig. 2. MEA with gasket.