The effect of the MEA preparation procedure on both ethanol crossover and DEFC performance

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Abstract

In the present work, the changes of Nafion®-115 membrane porosity in the presence of ethanol aqueous solutions of different concentrations were determined by weighing vacuum-dried and ethanol solution-equilibrated membranes. It was found that membrane porosity increases as ethanol concentration increases. *Membrane electrode assemblies* (MEAs) have been prepared by following both the conventional and the decal transfer method. The ethanol crossover through these two MEAs was electrochemically quantified by a voltammetric method. A 10 h stability test of *direct ethanol fuel cell* (DEFC) at a current density of 50 mA cm^{-2} was carried out. It was found that the electrode preparation procedure has an obvious effect on ethanol crossover and direct ethanol fuel cell's performance and stability. The single DEFC test results showed that about 15 and 34% of the original peak power density was lost after 10 h of life test for the MEAs prepared by the decal transfer method and the conventional method, respectively. *Electrochemical impedance spectrum* (EIS) results of the MEAs showed that, in the case of the membrane electrode assembly prepared by the following decal transfer method, the internal cell resistance was almost the same, 0.236 Ω cm^2 before the life test and 0.239 Ω cm^2 after 10 h of life test, while the respective values for the membrane electrode assembly by the conventional method are 0.289 and 0.435 Ω cm^2. It is supposed that the improved cell performance with MEA by the decal transfer method could be resorted to both a better contact between the catalyst layer and the electrolyte membrane and higher catalyst utilization. Furthermore, based on the experimental results, the increased internal cell resistance and the degraded single DEFC performance could be attributed to the delamination of the catalyst layer from the electrolyte membrane.
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1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) have been actively and widely developed for both stationary and mobile applications due to their compactness, zero-pollution, high output energy density at room temperature and their excellent easiness of start-up and shut-down in the system operation [1–5]. However, there are difficulties in hydrogen supply infrastructure or fuel reforming technology with the clean-up of impurities such as carbon monoxide and sulfur compounds. Undoubtedly, one of the most direct solutions to the fueling problem would be to develop fuel cells that operate on a liquid fuel. *Direct methanol fuel cells* (DMFCs) had been actively investigated since 1960s [6] and much progress has been made in recent years [7]. However, the perfluorosulphonate, Nafion® membranes manufactured by E.I. Du Pont Nemours and Co. in 1972 are quite permeable for methanol [8,9] to the oxygen cathode, which is one of the main factors significantly affecting DMFCs performance, and in this way lowering the fuel cell efficiency with a loss

of more than 50% at lower current densities [10]. In addition, methanol is relatively toxic and inflammable, and it is neither a primary nor a renewable fuel. On the other hand, as a naturally available and renewable material, ethanol is considered to be an attractive substitute for methanol with positive impact on both economy and environment [11–13]. Moreover, ethanol combustion will cause no rise in global concentrations of greenhouse gases. It should also be noted that ethanol itself and the intermediate products of its oxidation are less toxic than the other alcohols [14]. To our knowledge, the research and development of DEFC have been concentrated on both the ethanol electro-oxidation mechanism [15–19] and the identification of ethanol oxidation products over electrocatalysts [20–23]. There are few publications concerning the performance [24] of DEFC and ethanol crossover from the anode to the cathode through Nafion® membrane [25,26].

In the present investigation, Nafion® membrane porosity in the presence of the ethanol aqueous solutions with different concentrations at ambient temperature was determined. Membrane electrode assemblies were prepared by both the conventional method and the decal transfer method. The ethanol crossover has been electrochemically determined by the voltammetric method. A 10 h DEFC life test at a current density of $50\,mA\,cm^{-2}$ was carried out. The techniques of single fuel cell test, electrochemical impedance spectroscopy (EIS) were applied to investigate the cell performance degradation of the MEAs fabricated by different methods: (a) the conventional method and (b) the decal transfer method.

2. Experimental

2.1. Membrane porosity measurement

Nafion®-115 membranes were adequately pretreated by boiling them successively in 3 wt.% hydrogen peroxide, deionized water, $0.5\,mol\,L^{-1}$ sulfuric acid and deionized water again, 1 h for each step [27,28]. In order to quantify membrane porosity, the Nafion®-115 membrane samples were immersed in ethanol aqueous solutions with different ethanol concentrations and equilibrated for 36 h at ambient temperature. After that, the membrane was removed from the solution and the excess liquid was wiped from its surface by the use of a filter paper. The weight of swollen membranes was determined by using an accurate balance. After drying at 60 °C in vacuum for 24 h the weight of the membranes was determined again. Each sample porosity was determined for at least three times and the results were within the experimental error.

2.2. Membrane electrode assembly (MEA) preparation

MEAs were fabricated by the conventional method (CON) and the modified decal transfer method (DTM) for electrode preparation which both are schematically represented in Fig. 1. For the sake of simplicity, the MEAs prepared by
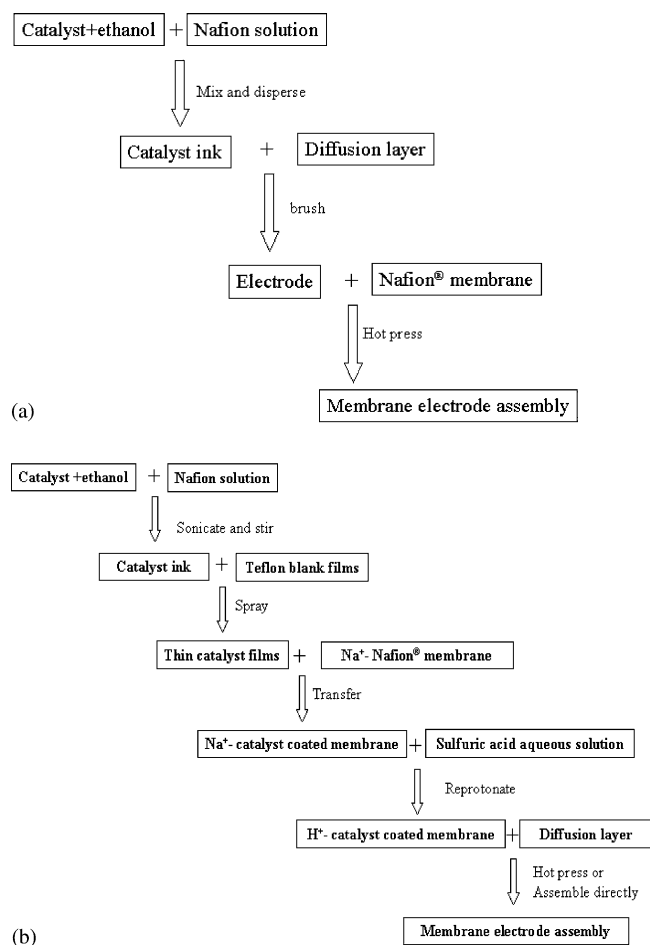

Fig. 1. Schematic presentation of the detailed electrode preparation procedures for: (a) the conventional method and (b) the decal transfer method.

the CON or the DTM are here denoted as MEA-CON and MEA-DTM, respectively. The main difference between these two electrode preparation procedures is that the catalyst layer was applied onto the gas diffusion layers for MEA-CON or onto the electrolyte membrane for MEA-DTM with a transfer process at higher temperature value. The conventional electrode preparation procedure has been previously described in detail [29]. Here, a detailed procedure for the DTM is presented. Pre-treated H⁺ form Nafion®-115 membranes were converted into the Na⁺ form by successively boiling them in $0.5\,mol\,L^{-1}$ NaOH aqueous solution and deionized water, for 1 h each step. PtRu black of nominal 1:1 atomic ratio and Pt black purchased from Johnson Matthey Corp. were used as the anode and cathode catalysts, respectively. Catalyst inks were prepared by adding 5% of Nafion solution (1100 equiv. weight) to the pre-wetted by water and ethanol well-dispersed catalyst inks. The solubilized Nafion was converted into the Na⁺ form by adding an appropriate amount of NaOH aqueous solution. Appropriate amounts of well-dispersed anode and cathode inks were uniformly sprayed by a gunnite to Teflon decal blanks with a given size to give metal loadings of about $3.0\,mg\,cm^{-2}$ for both the anode and the cathode, respectively. The *catalyst-coated membrane* (CCM)