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Use of Inner Ionomer Solution in Preparing Membrane-Electrode Assembly (MEA) for Fuel Cells and Its Characterization

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Abstract: Optimization of ionomer solution was conducted in order to improve the performance of MEAs in PEMFC. The interface between membrane and electrodes in MEAs is crucial region determining fuel cell performance as well as ORR reaction at cathode. Through the modification of Nafion ionomer content at the interface between membrane and electrodes, an optimal content was obtained with Nafion 115 membranes. Two times higher current density was obtained with the outer Nafion sprayed MEA compared with the non-sprayed one. In addition, the symmetrical impedance spectroscopy mode (SM) exhibited that the resistances of membrane area, proton hydration, and charge transfer decreased as the outer Nafion is sprayed. From the polarization curves and SM, the highest current density and the lowest resistance was obtained at the outer ionomer content of 0.15 mg cm^{-2}.

Keywords: *interfacial resistance, Nafion ionomer, membrane-electrode assembly (MEA), electrochemical impedance spectroscopy, proton exchange membrane fuel cells (PEMFC)*

1. Introduction

Since the industrial revolution, fossil fuels such as oil, coal, and natural gas have been widely used to meet the energy demand for automobiles, household, and stationary power plants. However, the byproducts from the combustion of the fossil fuel have caused severe environmental problems such as air pollution and global warming. In addition, the increasing price of fuel promotes the development of environmentally friendly energy sources. One of the most promising alternatives is fuel cells. Fuel cells are energy conversion devices which consume only hydrogen and oxygen in the production of electricity and water [1,2].

Of all fuel cells, proton exchange membrane fuel cells (PEMFC) have been developed for automobiles and residential applications. One of the most important components in PEMFC is membrane-electrode assembly (MEA). In order to improve the performance and durability of PEMFC, it is strongly needed to investigate the optimum condition of MEAs. The oxygen reduction reaction (ORR) is known as the most dominant resistance that limits the fuel cell performance. Thus, most MEA research has been contributed on the optimization of cathode catalyst layer with catalyst loading [3,4], various compositions of catalysts/Nafion ionomer solution [5], and polytetrafluoroethylene (PTFE) [6].

Electrochemical Impedance Spectroscopy (EIS) is a useful and powerful technique for the diagnosis of the resistive and capacitive characteristics in fuel cells [7,8]. Mostly, the impedance of fuel cells is measured

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with the feed of hydrogen and oxygen at anode and cathode, respectively. This in-situ impedance measurement provides comprehensive understandings on the charge transfer and mass transfer resistance during the fuel-cell operation. Gas diffusion layers [9], proton conductivity of Nafion membrane [10], CO tolerance of electrodes [11,12], catalyst-Nafion interface [13], and influence of each compartment [14] have been also examined by EIS measurement.

Especially, the symmetrical impedance spectroscopy (SM) enables to individually examine the effects of each gas in fuel cells [15]. For the symmetrical impedance measurement, same type of gas is injected to both anode and cathode compartments (H_2/H_2 or O_2/O_2). Injection of the hydrogen or oxygen gases to the both compartments shows the electrochemical processes occurring at the anode or cathode, respectively. Furthermore, the anode reaction can be divided into the three rate-limiting steps for proton hydration, charge transfer, and diffusion processes using the SM [16]. Interestingly, Himanen *et al.* reported that the obtained resistance contains not only membrane resistance, but also contact and ohmic resistances at electrodes [17]. However, quantitative studies on the interfacial resistance have not been carried out using the SM.

Few studies, however, have quantitatively examined the interfacial resistances between membrane and electrodes in MEAs even though the resistances have a significant role in improving fuel cell performance [18]. The interfacial resistance is defined as due to the presence of membrane-electrode interface, independent of bulk membrane or electronic component resistance. Similarly, Shin *et al.* (2002) implemented 8 wt% of Nafion ionomer in a mixture of catalyst slurry and additionally covered with 25 wt% of Nafion ionomer to improve the proton conduction at the interface [19]. Xie *et al.* (2005) suggested that a gradient Nafion distribution (i.e., higher concentration at membrane/catalyst interface) is beneficial to the proton conduction [20]. In order to investigate the MEAs, the measurement of polarization curve is the most common method because of its convenience. However, not only the various electrochemical processes and the operational conditions of the MEAs, but also the interfacial resistances are difficult to examine using that method [21].

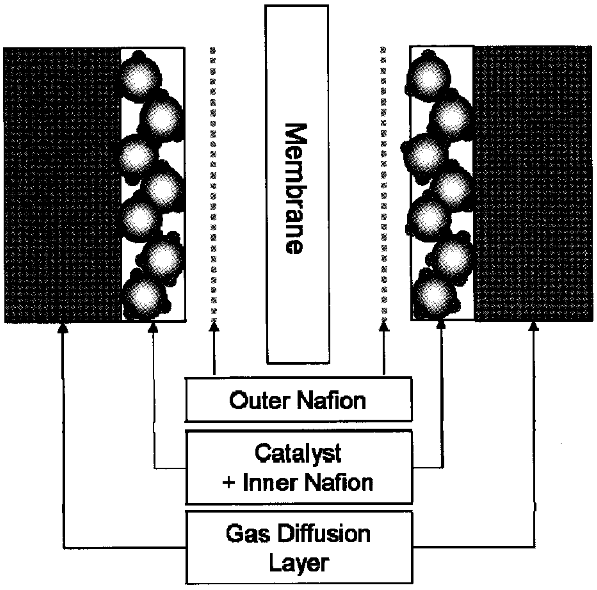

Fig. 1. A schematic diagram of the inner and outer Nafion in a MEA.

In this study, the optimum outer Nafion content was investigated in order to reduce the interfacial resistances between the membrane and electrodes by using polarization curves and the SM. For the investigation, the outer Nafion content of $0 \sim 0.45$ mg cm^{-2} were additionally sprayed on the identically prepared catalyst electrodes with 8 wt% of Nafion ionomer.

2. Experiments

2.1. MEA Fabrication

Commercial Nafion 115 membrane was provided by Dupont™ (USA). The catalyst powder, 40 wt% platinum deposited on Vulcan XC-72 (USA), was purchased from E-TEK®. Nafion® ionomer solution (5 wt% in alcohols/water, Aldrich, USA) and SIGRACET® GDL 10BC (SGL Carbon group, Germany) gas diffusion layer (GDL) was used as a binder in the catalyst layer and a backing electrode, respectively. For the preparation of the electrodes, a mixture of 8 wt% Nafion

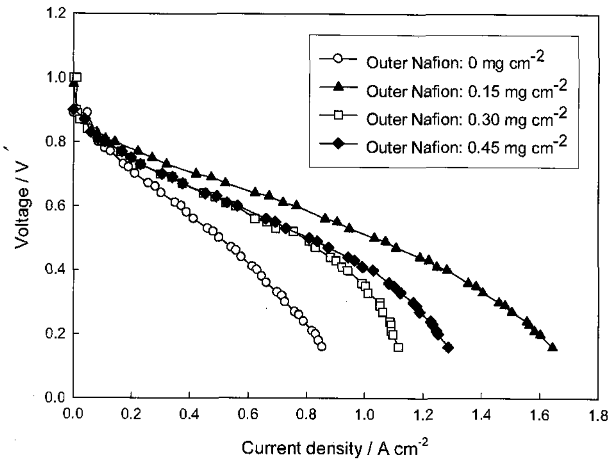

Fig. 5. Effects of the outer Nafion on polarization curves for H_2/O_2 operation at 60 °C with Nafion 115 membranes.

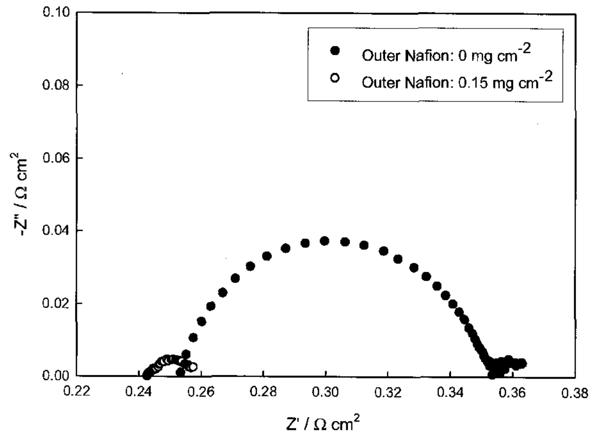

Fig. 6. The Nyquist plot of the Nafion 115 membrane using the SM (H_2/H_2) at 30°C.

addition, it is reported that 20~40% of ionomer is the optimum for PEMFC operation [20,24]. Therefore, the optimized ionomer preparation method is strongly required for the increase of platinum utilization and saving of manufacture cost. Interestingly, Xie *et al.* obtained better performance with the gradient catalyst layer at the membrane/catalyst interface due to the low ionic resistance [20]. Accordingly, it is known that higher ionomer content at the membrane/catalyst interface is required for low interfacial resistance from the highly connected ionic transport channels for proton, while lower ionomer content at the catalyst/GDL interface is needed for effective utilization of catalyst sites and mass transfer.

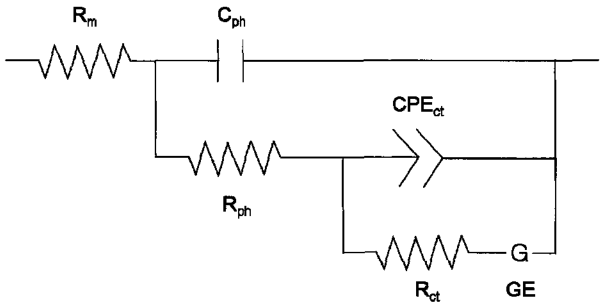

Fig. 7. A theoretical equivalent circuit for the SM (H_2/H_2) proposed by Meland *et al.* [16].

The effects of the presence of outer Nafion on polarization curves are shown in Fig. 5. Current density of each MEA increased as the content of outer Nafion between the membrane and electrodes was increased. The MEA without the outer Nafion showed low open circuit voltage and current density as 0.89 V and 0.37 A cm^{-2} at 0.6 V, respectively. This 0.6 V was adopted for the comparison of ohmic losses in MEAs [22], which are closely related with the interfacial resistances at the interface due to the sprayed outer Nafion. In this range, all the results exhibited the typical characteristics of ohmic losses; the current density linearly increased as the potential is decreased. Compared to other cases, the outer Nafion content of 0.15 mg cm^{-2} showed higher current density of 0.77 A cm^{-2}. This better performance is mainly obtained from the improvement in proton conduction by connecting ionic channels of both sides. However, the current density slightly decreased at the outer Nafion of 0.30 and 0.45 mg cm^{-2} due to the thickened pathway from anode to cathode. Thus, the optimum content of outer Nafion for Nafion 115 membranes was determined as 0.15 mg cm^{-2} based on the polarization curves.

The impedance spectra of MEAs without and with outer Nafion of 0.15 mg cm^{-2} are shown in Fig. 6. The obtained data was fitted by the theoretical equivalent circuit (Fig. 7) for the interpretation of each component proposed by Meland *et al.* [16]. Contrary to their results, one semi-circle superimposed at the intermediate frequency ranges in this study. The left intercept of the semi-circle at high frequency ranges represents the membrane area resistance, R_m, of the MEA, including the membrane resistance, contact resistance, and minor ohmic losses in electrodes [17]. The obtained R_m were 0.254 and 0.243 Ωcm^2, at 0 and 0.15 mg cm^{-2} of outer Nafion, respectively. The superimposed semi-circle represents the sum of proton hydration, R_{ph}, and charge transfer, Rct, resistances. The obtained $R_{ph} + R_{ct}$ of the cases were 101 and 17 $m\Omega$ cm^2, respectively. As the outer Nafion content increased, both R_m and $R_{ph} + R_{ct}$ decreased. This decrease of the resistances is closely related with the sprayed outer Nafion at the interface between membrane and electrode, is consistent with the improved current density in case of the outer Nafion sprayed electrodes.

4. Conclusions

One of the important losses in fuel cell is the ohmic resistances from the transport of charged species as well as the ORR resistance. In this study, optimum condition of ionomer solution was investigated to reduce the ohmic resistances at the surface of membrane and electrodes, thus higher current density was obtained at the outer Nafion content of 0.15 mg cm^{-2}. Similarly, the sprayed outer Nafion decreased all the resistances by improving the interface for proton conduction between the membrane and electrodes.

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