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Influence of the composition of isopropyl alcohol/water mixture solvents in catalyst ink solutions on proton exchange membrane fuel cell performance

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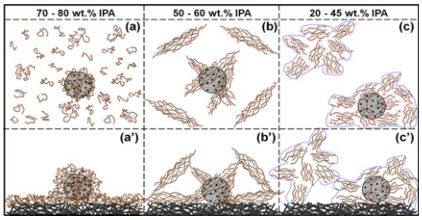
HIGHLIGHTS

- ► Pt surface area increases with decreasing IPA content of catalyst solution.
- ► Fuel cell performance increases with decreasing IPA content of catalyst solution.
- ► Pt surface area depends on solubility parameter of catalyst ink solvent.

GRAPHICAL ABSTRACT



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ABSTRACT

We study the morphology of Nafion in the dilute IPA (isopropyl alcohol)/water mixture solutions containing 20–100 wt.% of IPA and in the Pt–C/Nafion gas diffusion electrodes (GDEs; where Pt–C is the carbon powder deposited on its surface with Pt particles), which are prepared by spraying on the carbon paper surfaces with a layer of Pt–C, Nafion and IPA/water ink solution. The fuel cell performance of the GDEs strongly depends on the Nafion morphology in the ink solutions. A lower IPA content in the Pt–C/Nafion ink solutions results in the formation of larger and higher negatively charged Nafion aggregated particles, which leads to higher steric hindrance of the deposition of Nafion ionomer on the surface of Pt–C particles and thus a thinner Nafion film in contact on the Pt–C particle surfaces. The thinner Nafion film in contact with the Pt particles in the CL increases the chances of the Pt particles in contact with the H_2/O_2 gas, leading to a higher fuel cell performance.

1. Introduction

Nafion (a trade name of Du Pont) is an ionomer with a chemical structure that consists of a hydrophobic perfluorocarbon backbone ($-[(CF_2-CF_2)_x-(CF_2-CF)_y]-$) and hydrophilic sulfonated vinylether side chains ($-OCF_2-CF(CF_3)-O-CF_2-SO_3H$) [1–4]. It is an indispensable part of the proton exchange membrane (PEM) and a component of the catalyst ink solutions used in fabricating the membrane electrode assemblies (MEAs) of proton exchange membrane fuel cells (PEMFCs) [5,6]. A high-performance MEA requires a combination of effective contact at the three-phase boundary, high Pt (platinum) catalyst utilization, good proton conduction, and facile H_2 and O_2 reactants and water product transport to and from Pt active sites in the catalyst layer (CL). A Nafion ionomer in the CL helps to increase the three-dimensional zone of catalytic activity. Nafion serves as the physical binder and proton conductor in the CLs and facilitates the molecular interaction among the Pt particles; the Nafion ionomer may also play a key role in determining the final microstructure and properties of the CLs [7]. The catalyst ink solutions for MEA fabrications consist of Pt–C (Pt on a carbon powder support), the Nafion ionomer, and solvents. The molecular interactions of the Nafion ionomer and the

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solvents control the Nafion molecular conformations in the solutions and thus the final microstructure of Nafion in the CLs. Thus, it is important to understand the Nafion solution properties to obtain a high performance MEA.

Several studies have been devoted to the properties of Nafion solutions as well as the morphology of Nafion ionomers in dilute solutions containing various solvents [8–18]. Alcohol/water mixture solvents, especially isopropyl alcohol (IPA) and water mixtures, are the most common solvents used in preparing catalyst ink solutions. The structures of Nafion ionomers in water and methyl alcohols have been investigated using small angle neutron scattering (SANS), small angle X-ray scattering (SAXS), and electron spin resonance (ESR) for Nafion concentrations ranging from 1 to 22 wt.% [8–13]. The results showed that Nafion hydrophobic perfluorocarbon backbones aggregated and formed compact cylinders in solvents, with the hydrophilic sulfonated vinylether side chains surrounding the surfaces of the aggregated cylinders and in contact with the solvents. Dynamic light scattering (DLS) investigations have been carried out in dilute Nafion/ethanol–water (ethanol/water = 50/50 vol ratio) [14], Nafion/water [15], and Nafion/methanol–water (methanol/water = 4/1 wt. ratio) solutions [16]. Two modes of Nafion particle size distribution were found. The authors attributed these two aggregates to the hydrophobic inter-polymer fluorocarbon backbone interactions and the hydrophilic inter-polymer vinylether sulfonic acidic ion pair interactions. The morphology of commercial Nafion membranes has also been investigated using SAXS and SANS [18–31], wide angle X-ray diffraction [20,24,25,28], atomic force microscopy [30,31], and electron microscopy [30,31]. The SAXS and SANS data reveal that the Nafion membranes are composed assemblies of bundles of fibrils, which correspond to elongated polymeric aggregates surrounded with ionic charges. Most of the commercial Nafion membranes were obtained from Du Pont Co. and were prepared by extrusion. Few studies in the literature have reported on the molecular morphology of Nafion solution casting membranes and CLs fabricated using Nafion/Pt–C ink solutions. The influence of solvents of the Pt–C/Nafion catalyst ink solutions on the Nafion thin film morphology of CLs and on the fuel cell performance is still not clear to us.

There are three CL processing methods, i.e., decal method [32], gas diffusion layer (GDL)-based method [33], and membrane-based or catalyst-coated membrane (CCM) method [34] have been reported in literature. Uchida et al. [33] and Shin et al. [35] prepared electrodes using GDL-based method and reported that the dielectric constant ε of solvent used for the Pt–C/Nafion catalyst ink solutions determines the state of the Nafion ionomer in the solutions. Depending on the ε value, the Nafion solvent mixture can be in the form of solution ($\varepsilon > 10$), colloids ($10 > \varepsilon > 3$), and precipitates ($\varepsilon < 3$). Fuel cell performance and electrochemical analyses revealed that the electrode prepared by a colloidal method had a better results compared to those of the solution method. These authors mentioned that the colloidal method appeared to secure continuity of the ionomer network and higher porosity in the CL, resulting in higher proton conductivity, less mass transfer resistance, and higher fuel cell performance. The effect of the organic solvents with various εs, including isopropyl alcohol, ethanol, methanol, amyl alcohol, acetone, ethylene glycol, 1,2 propylene glycol, 1,3 propylene glycol, diethyl oxalate, dimethyl ether, ethylene glycol diethyl ether, water/ethylene glycol mixture, butyl acetate/glycerol mixture, ethanol/glycerol mixture, isopropyl alcohol/glycerol mixture, water/glycerol mixture etc., on the structure of CLs and the fuel cell performance of MEAs were further studied by using decal [36,37], GDL-based [38,39], and CCM [40] processing methods. All these papers discussed the morphology of CLs and the fuel cell performance of MEAs based on the ε value of the solvent of catalyst ink solutions.

Nafion has been reported to possess dual solubility parameters δs, i.e. $\delta_1 = 9.7$ cal$^{0.5}$ cm$^{-1.5}$ for the perfluorocarbon backbone and $\delta_2 = 17.3$ cal$^{0.5}$ cm$^{-1.5}$ for the sulfonated vinylether side chains [41]. In previous work [16–18], we showed the morphology of Nafion ionomer in the dilute solutions and in the solution casting membranes depends not only on the ε but also on the δ of the solvents. However, the study of the influence of δ of the solvent of catalyst ink solution on the morphology of Nafion ionomer in CLs and the fuel cell performance have not been reported in literature. Alcohol/water mixture solvents, especially isopropyl alcohol (IPA) and water mixtures, are the most common solvents used in preparing catalyst ink solutions. The physical properties of Nafion in IPA/water mixture solutions as a function of their compositions have rarely been investigated and discussed; thus, the optimum IPA/water wt. ratio of the catalyst ink solutions for the MEA CL fabrication remains unclear. In this work, we examine how the composition of the IPA/water mixture solvents influences the morphology of Nafion molecules in the solutions, the properties of the Pt–C/Nafion (where Pt–C is the carbon powder with 38 wt.% Pt particles deposited on its surface) catalyst ink solutions, and the Pt–C/Nafion microstructures of the CLs prepared by using GDL-based method. The morphology of Nafion ionomers in the IPA/water mixture solutions with various IPA concentrations ($\varepsilon > 10$) is observed and discussed based on the inter-molecular hydrogen bonding, εs, and δs of the mixture solvents. The results were correlated with the Pt electrochemical active surface areas (ECSAs) of the CLs and their performance in fuel cells, in an attempt to correlate the composition of the IPA/water mixture solvent of the Pt–C/Nafion ink solutions with the Pt ECSAs in the CLs and with the fuel cell performance. The main purpose of this study is to find the optimum IPA/water composition of the Pt–C/Nafion ink solutions for CL fabrication and MEA preparation.

2. Experimental

2.1. Viscosity of IPA/water mixture solvents

The flow times of the IPA (reagent grade, J.T. Baker)/water mixture solutions with the IPA concentration varied from 0.0 wt.% to 100.0 wt.% were measured at 25 °C using an Ubbelohde viscometer. The viscosity of each mixture solution was calculated from its flow time, using the viscosity of pure water (i.e., 0.890 cP at 25 °C) as reference [42]. The data were averaged over 3 measurements.

2.2. Nafion solutions preparation

A commercial Nafion solution (Du Pont Co., sulfonic acid equivalent weight of Nafion = ~1100 g equiv^{-1}) containing 20 wt.% of Nafion and 80 wt.% of aliphatic alcohol and water mixture solvent was heated at 60 °C (below $T_g = \sim 105$ °C of Nafion) under ambient pressure for 1 h and then at 60 °C under vacuum for 48 h to obtain a solid Nafion resin. The solid Nafion resin was then dissolved in a series of IPA/water mixture solvents, in which the IPA concentration was varied from 20 wt.% to 100 wt.%, to prepare Nafion solutions. A total of 9 Nafion solutions (in which the solvent compositions were [IPA]/[IPA + water] = 100, 80, 70, 60, 55, 50, 45, 40, and 20 wt.%) were prepared. All of the solutions had a Nafion concentration of 0.6 mg mL^{-1}.

2.3. Dynamic light scattering (DLS) of dilute Nafion solutions

DLS hydrodynamic radius (R_h) distribution measurements of 0.6 mg mL^{-1} Nafion in IPA/water mixture solutions with various IPA concentrations were carried out with a 256-channel autocorrelator (model BI9000, Brookhaven Co.) at 25 °C. An Ar ion laser