연료전지용 나피온-실리카 나노복합막에 있어서 친수성 SiO₂ 나노 입자의 효과

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Effect of hydrophilic SiO₂ nanoparticles on Nafion-silica nanocomposite membranes for fuel cell applications

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1. Introduction

Proton exchange membrane fuel cells (PEMFC)s have drawn much attention as a primary and auxiliary power source for transportation, stationary and portable applications [1],[2]. Perfluorosulfonic acid membranes such as the Nafion membranes are currently used as the electrolyte due to their favorable chemical and mechanical stabilities along with their high proton conductivity in the hydrated state [3]. However, Nafion shows a significant loss in conductivity at elevated temperatures due to dehydration of water from the membrane. The dehydration also results in membrane shrinkage and consequent poor contact which subsequently reduces the electrochemical performances.

In this study, a new approach to incorporate hydrophilic inorganic oxide particles such as SiO₂ is suggested to enhance the water retention property and the resulting proton conductivity under high temperature operating conditions. A simple and effective direct mixing method was performed to incorporate silica nanoparticles into PFSA matrix using identical surfactants to PFSA structure in order to obtain a homogenous distribution. The hybrid of Nafion-based silica membrane exhibits higher proton conductivity at a high temperature and at low RH than that of Nafion membrane. The observed characteristics of these composite membranes allow them to be used as candidate electrolytes for the high temperature operation of the PEMFCs.

2. Experimental

A mixture of Aerosil® 380 and surfactant was added to the 20 wt.% Nafion solution, and mechanically stirred for 1 day at 30°C to obtain a Nafion-SiO₂ nanocomposite. Moreover, Nafion-SiO₂ nanocomposite membranes were prepared by varying SiO₂ contents (1, 3 and 5 wt.%) via the same procedure.

This obtained solution was cast on a glass plate and heated at 60 °C for 6h. Then, the recast composite membranes were peeled off from the glass plate by adding some de-ionized water. The membranes were annealed in its sodium salt-form in order to enhance its mechanical properties before acidification. Finally, the membrane was acidified by heating at 80 °C in the solution of 3 wt.% H₂O₂, de-ionized water, 0.5 M H₂SO₄ and in de-ionized water for 2h successively. Here, all membranes were carefully prepared with a nominal thickness of 50 μm.

The total amount of water inside the membrane was calculated by weighing the membrane after immersing each membrane coupon into deionized water at 30oC for 24h. The ion exchange capacity (IEC) value was measured through the classical titration (ASTM D2187) method. Mechanical properties of the membranes were measured with an Instron mechanical testing machine (Shimadzu-Autograph AGS-J) following ASTM D882.

3. Results and Discussions

Membrane materials with high mechanical strength are required to avoid the membrane

breakage during MEA fabrication. There is a vast difference in mechanical strength between the membrane with and without silica. For this reason, silica acts as reinforcing agent to enhance tensile strength of the membrane after the formation of homogeneous inorganic phase by adding surfactants as shown in fig 1.

Similarly, the dimensional stability (fig 2) also shows the identical results, where silica contributes to the improvement of the stability of the resulting composite membrane even at high temperature. For the assurance of the proton conductivity, the IEC was also measured before the electrochemical measurements.
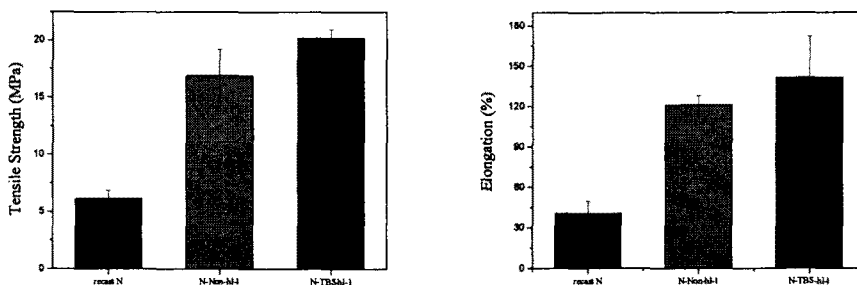

Fig. 1 The mechanical property of recast nafion and nafion composite membranes in wet states
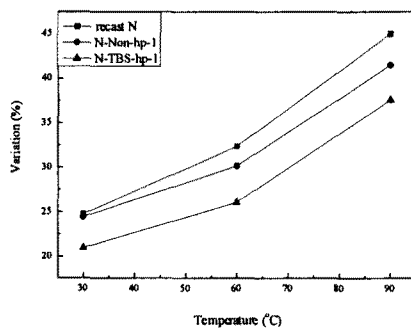

Fig. 2 Dimensional change of pristine and composite membranes as a function of temperature

Moreover, composite membrane appears quite homogeneous with no observable voids or defects. The proton conductivity of Nafion decreases at over 90 oC owing to fast evaporation of water molecules within the polymer matrix, however this problem can be solved by adding hydrophilic silica dispersed with particular surfactant. The dispersant could possibly be a factor for positive effects on the proton conductivity as well as on the electrochemical performance of the single cell.

Furthermore, the morphological changes and electrochemical performances of the membrane have to be evaluated.

Future Works

It is necessary to understand the effects of the dispersed silica over the membrane. For this, a precise study on the comparison of the composite membranes based on Nafion

and non-perfluorinated polymer electrolyte membranes containing various amount of silica is required. Further study should be focused on the membrane performances including molecular transport behaviour and membrane durability to hydrolysis, thermal or mechanical aging, and free radical attack.

References

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Acknowledgemetns