Short communication

Influence of dispersion solvent for catalyst ink containing sulfonated poly(ether ether ketone) on cathode behaviour in a direct methanol fuel cell

Kyung A Sung, Ho-Young Jung, Wan-Keun Kim, Ki-Yun Cho, Jung-Ki Park[*]

*Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology,
373-1 Guseong-Dong, Yuseong-Gu, Daejeon 305-701, Republic of Korea*

Abstract

Electrode properties are key determinants of the performance of the membrane-electrode assembly (MEA) in fuel cells. In this study, the influence of dispersion solvent for the catalyst ink on cathode properties and also on the cell performance is investigated. Cathodes containing sulfonated poly(ether ether ketone) (sPEEK) as an electrode binder are prepared with different dispersion solvents such as N,N-dimethylformamide (DMF), N,N-dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), and N-methyl-2-pyrrolidone (NMP). When DMF is used as a casting solvent, the sPEEK membrane exhibits a particular low proton conductivity. The high boiling points of DMSO and NMP as dispersion solvents for the cathode lead to a reduction in the pore volume of the cathode and, consequently, cause poor transport of oxygen at the cathode. A MEA based on a cathode using DMAc as a dispersion solvent gives the highest performance due to the high proton conductivity and good morphology of the cathode.
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1. Introduction

The direct methanol fuel cell (DMFC) has attracted much interest as a power source of portable electronic devices due to its ease of carriage, less safety concerns, and existing fuel supply infrastructure [1–3]. The main component of a DMFC is the membrane-electrode assembly (MEA), which is composed of a solid polymer electrolyte membrane sandwiched between a catalyzed anode and a cathode. The MEA is usually based on Nafion, and has several drawbacks such as high cost, high methanol permeability, and limited operational temperature. To solve these problems, several alternative membranes have been investigated and are mostly based on polyaromatic engineering plastics such as poly(etherketone)s (PEK), polysulfones (PSf), and polyimides (PI) [4–6]. Despite this research, there have been few studies of electrodes that might be compatible with the alternative membranes [7,8].

A high-performance electrode requires good adhesion between the membrane and the electrode, uniform Pt dispersion in the electrode, good ion conduction, and reactant/reaction product transport through electrode. These properties are influenced by the component materials and fabrication process of the electrode. Since the dispersion solvent for catalyst ink can affect the solubility of the electrode binder and the Pt dispersion, it will eventually determine the morphological properties of the electrode. This study examines the effect of the dispersion solvent on the properties of a cathode prepared using sulfonated poly(ether ether ketone) (sPEEK) as a binder and also investigates the electrochemical performance of the resulting DMFC.

2. Experimental

2.1. Synthesis of sPEEK and membrane preparation

As a material for both the membrane and the electrode binder, sPEEK was synthesized according to the procedure reported elsewhere [6,8]. The degree of sulfonation of the synthesized polymer was 61%, as determined by ^{1}H NMR analysis [9].

sPEEK membranes were prepared by a solution-casting method [10]. A sPEEK solution (10–15 wt%) in *N*-methyl-2-pyrrolidone (NMP) was directly cast on to a clean glass plate, and dried at 50 °C for 1 day and then again under vacuum at 100 °C for 12 h. The sPEEK film was peeled from the glass plate by submersing it in de-ionized water, and then was fully protonated using 1.0 M sulfuric acid solution at room temperature for 1 day.

2.2. Selection of dispersion solvent for catalyst ink

A dispersion solvent for catalyst ink is required to be both a good dispersant for the Pt catalyst and a good solvent for the electrode binder. To select candidates that meet these requirements, Pt dispersion and sPEEK solubility tests were performed on the most commonly used solvents. The solvents used in these tests are listed in Table 1.

For preparation of the catalyst solution, the mixtures of Pt and each solvent were prepared and stirred vigorously in an ultrasonic bath for 12 h. The mixtures were left for 1 day without additional handling and then the degree of Pt dispersion in each solvent was examined. The solubility of sPEEK in the solvent was determined simply by checking the optical transparency of the mixtures at room temperature.

2.3. Preparation of cathodes based on different dispersion solvents and their characterization

Catalyst inks for cathodes were prepared according to the following procedures: sPEEK solutions (5 wt%) were prepared using different dispersion solvents. Platinum black (ETEK Inc.) was added and the ratio of Pt black to pure sPEEK was 19:1. All mixtures were stirred vigorously to achieve a uniform dispersion of Pt. Each catalyst ink was applied to carbon paper (TGPH090, Toray) by a brushing technique. All the cathodes were prepared to contain the same amount of Pt loading, viz., $5 \, \text{mg cm}^{-2}$.

Table 1
Results of dispersion test of Pt and solubility test of sPEEK

	Pt dispersion test	sPEEK solubility test
Acetone	O	X
Acetonitrile	X	X
Deionized water	O	Δ^a
DMAc	O	O
DMF	O	O
DMSO	O	O
Ethanol	O	X
Isopropyl alcohol	X	X
Methanol	X	O
Methyl ethyl ketone	Δ^b	X
NMP	O	O
1-Propanol	X	X
Tetrahydrofuran	X	X
Toluene	X	X

[a] sPEEK was not dissolved at room temperature. It could be dissolved at 100 °C.
[b] Pt particles were well-dispersed for the 1st day, and then were precipitated.

To estimate the proton conductivity of catalyst layer indirectly, sPEEK membranes were solvent-casted separately using the dispersion solvents that had been used for preparation of the cathodes, and their proton conductivities were evaluated by ac impedance spectroscopy (1400 FRA and 1470E, Solartron) [11]. The morphological properties of the cathodes, including pore size distribution and porosity, were characterized by Hg-porosimetry (Autopore IV 9500, Micrometrics). To investigate oxygen transport through the cathode, linear sweep voltammetry was performed [12]. To make a dynamic hydrogen electrode (DHE) as the reference electrode, humidified hydrogen gas was supplied to the anode at a flow rate of 50 mL min^{-1}. The cathode, working electrode, were supplied with humidified oxygen gas at a flow rate of 50 mL min^{-1}. Linear sweep voltammograms at a 10 mV s^{-1} scan rate were recorded in the potential range from 1.5 to 0.0 V versus DHE.

2.4. MEA fabrication and its electrochemical characterization

Several MEAs were manufactured using the cathodes prepared with different dispersion solvents. To investigate the effect of the cathode on MEA performance, the same anode and sPEEK membrane were used. The catalyst ink for the anode was composed of 5 mg cm^{-2} of Pt/Ru (1:1, a/o) and Nafion solution (5 wt%, Dupont), and it was applied to carbon paper. The membrane was sandwiched between the anode and the cathode by hot-pressing at 130 °C for 3 min under 800 psi. The MEAs were then connected to a test station equipped with an electronic load (Won-A tech, Korea) and current–voltage curves at 60 °C were obtained galvanostatically. A 2.0 M methanol solution was supplied to the anode at 1.0 mL min^{-1} and oxygen to the cathode at a flow rate of 200 mL min^{-1}. Impedance measurements were performed on the operating cells using ac impedance spectroscopy. The ac signal had the amplitude of 10 mV and the frequency range was from 0.05 Hz to 10 kHz. All spectra were measured at a dc potential of 0.4 V.

3. Results and discussion

3.1. Selection of dispersion solvents for catalyst ink

Since a uniform dispersion can ensure a high utilization of Pt, the degree of Pt dispersion in various solvents was firstly examined. Visual observation for comparison of the degree of Pt dispersion in various solvents is shown in Fig. 1 and the results are listed in Table 1. The Pt particles in de-ionized water, ethanol, acetone, methyl ethyl ketone, NMP, *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc), and dimethyl sulfoxide (DMSO) are well-dispersed, while they are precipitated in acetonitrile, isopropyl alcohol, toluene, tetrahydrofuran, 1-propanol, and methanol. The solubility of sPEEK also needs to be taken into account in the preparation of a high-performance electrode since it can influence the contact area between Pt and electrode binder. As listed in Table 1, methanol and several aprotic polar solvents including NMP, DMF, DMAc, and DMSO are found to be good solvents of sPEEK.
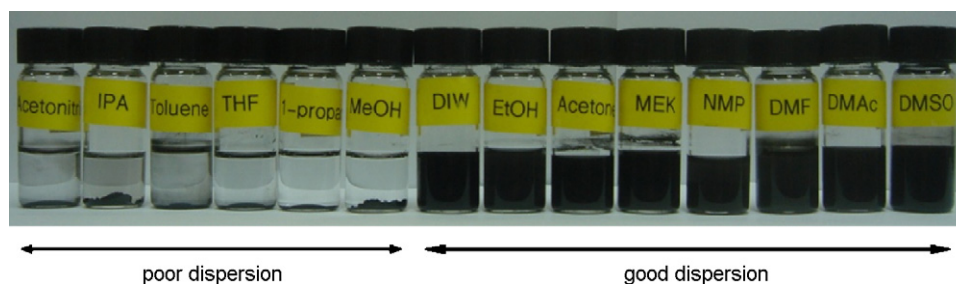
Fig. 1. Degree of Pt dispersion in various solvents.

Based on these results, DMF, DMAc, DMSO, and NMP, that were both good solvent of sPEEK and good dispersant of Pt, were selected as dispersion solvents in this study.

3.2. Proton conduction in catalyst layer

The proton conductivity of the catalyst layer is an important determinant of electrode performance and can provide useful information for optimization of the MEA structure [13]. Although there have been several reports of the proton conductivity of catalyst layer, the measurement methods were either impractical or too complex [14–16]. In this study, proton conductivity of sPEEK membranes using DMF, DMAc, DMSO, and NMP as a casting solvent were examined for easy and fast approximation of proton conductivity of the catalyst layer.

Table 2 lists the proton conductivity of the sPEEK membrane at 30 and 60 °C. The proton conductivity of the membrane using DMF as a casting solvent is found to be remarkably lower than those of the membranes based on other casting solvents. This is due to the fact that the nitrogen electron pairs of DMF are involved in hydrogen bonding with the sulfonic acid hydrogen atoms of sPEEK [9,17]. Since the sulfonic acid group of the sPEEK influences the number of charge carriers and the mobility of protons available for proton transport, the hydrogen bonding yields a reduction in proton conductivity.

3.3. Morphological properties of cathodes

The pore structures of cathodes prepared with different dispersion solvents were investigated by Hg-porosimetry. The total porosity of the cathodes using DMF, DMAc, DMSO, and NMP as dispersion solvents was 85, 86, 77 and 71%, respectively. In fact, the primary and secondary pores are especially important in determining electrode properties rather than the total pore volume [18]. It is known that the catalyst layer in the elec-

trode has two distinctive pore distributions, namely primary and secondary pores [19,20]. The former is identified as the space between the primary particles in the agglomerate, and the latter is the space between the agglomerates.

The pore size distributions of the cathodes based on different dispersion solvents, which were measured by mercury intrusion porosimetry, are shown in Fig. 2. There are two distinctive pore-size distributions with a boundary of around 100 nm. The small pores in this boundary are considered to be primary pores and the large ones up to 2–3 μm are secondary pores. Pores larger than the secondary pores are usually from the carbon paper or imperfections such as cracks and holes in catalyst layer [21], and are excluded in our investigation. In both primary and secondary regions, it is found that the cathodes using DMF and DMAc as dispersion solvents have larger pore volumes than those based on DMSO and NMP. This appears to be related to the boiling point of the dispersion solvents. Since the dispersion solvents selected in this study have relatively high boiling points, the pores in the cathodes may be partially filled with the residual solvents even after the heat treatment. The boiling points of DMSO and NMP are 189 and 202 °C, and are higher than those of DMF and DMAc, which are 153 and 165 °C. This would lead to a relatively slow evaporation of DMSO and NMP. Consequently, the cathodes based on DMSO and NMP as dispersion solvents exhibit smaller pore volumes than those based on DMF and
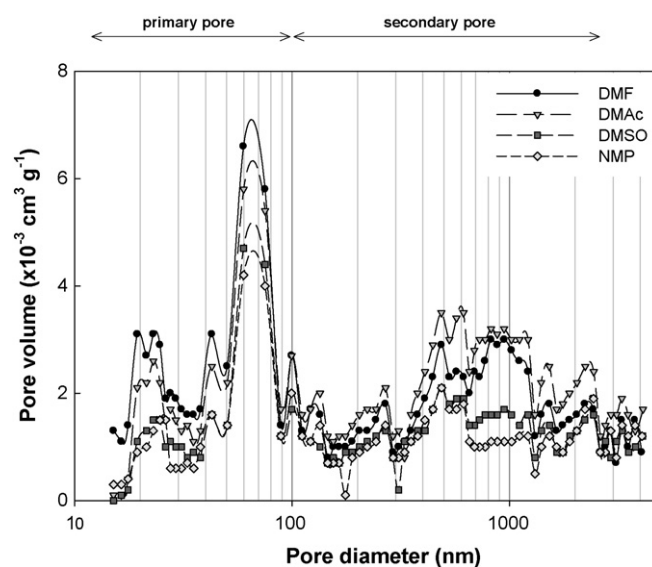
Table 2
Proton conductivities of sPEEK membranes based on different casting solvents

	Roton conductivity (S cm^{-1})	
	30 °C	60 °C
DMF	0.045	0.094
DMAc	0.086	0.130
DMSO	0.080	0.143
NMP	0.090	0.139

Fig. 2. Pore size distribution of cathodes based on different dispersion solvents.

DMAc. This dependency of pore volume on boiling point is in good agreement with the results of other publications [22,23].

Since, during cell operation, a complex flow of reactants and reaction products exists in the pore of the electrodes, the pore structure is very important for cell performance. In the cathode, a matter of a concern in this study, the pores must allow gaseous oxygen to reach the catalyst surface and support efficient removal of product water to prevent flooding. In this study, the controlled variable for preparation of the cathode is the dispersion solvent of catalyst ink, and thus it was expected that the difference in the pore volume in the cathode will result in a change of gaseous oxygen transport. This effect is investigated by means of linear sweep voltammetry for oxygen reduction, as discussed in the following section.

3.4. Oxygen transport at the cathode

The performance of an electrode is determined by the kinetics and reactant permeation properties [12]. In the cathode of a DMFC, oxygen is supplied and reduced in the presence of Pt by the following reaction:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O, \quad E_r = 1.23\,V$$
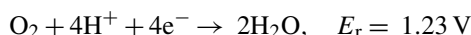
If potential of the electrode is made relatively more negative than the equilibrium potential, the reactant will be reduced [24]. In oxygen reduction, the equilibrium potential is shifted towards a lower potential than the theoretical reversible potential E_r because of its sluggish reaction kinetics. As shown in Fig. 3, the reduction currents of all cathodes are generated at the similar voltage, i.e., around 0.9 V (versus DHE). This means that the dispersion solvent for catalyst ink does not have much effect on the intrinsic kinetics of the cathode. By contrast, there is a remarkable difference in the limiting current of the various cathodes that is related to mass transport limitations. The plateau in the linear sweep voltammogram is indicative of an insufficient supply of oxygen to the reactive site of the cathode. Since mass transport in the cathode is determined mainly by the permeability of oxygen which, in turn, is largely governed by the pore

volume, the limiting current shows a similar change with the type of dispersion solvent as the pore volume. Cathodes using DMF and DMAc as dispersion solvents show higher limiting currents compared with those using DMSO and NMP, and these will be reflected in the single-cell performance.

3.5. Electrochemical characterization of single-cell

The effect of dispersion solvent for catalyst ink on DMFC performance is shown in Fig. 4. Although all the cells exhibit similar voltage–current behaviour up to 300 mA cm^{-2}, the voltage drop becomes significantly different in the region of higher current density, where mass-transfer is the dominant variable in determination of the cell performance. If gaseous oxygen transfer to the reaction site at the cathode is not successfully achieved, there will be a mass transfer limitation leading to a limitation in current density, which can cause deterioration of MEA performance. As shown in Fig. 4, the limiting current density of the MEA using NMP as a dispersion solvent for the catalyst ink is lowest, about 300 mA cm^{-2}, and the limiting current densities of other MEAs increase in the order of DMSO, DMF and DMAc. This pattern for the change in limiting current density is consistent with the pore volume behaviour in the cathode, as shown above. Since the dispersion solvents DMSO and NMP produce a relatively smaller pore volume in the cathode because of their high boiling points, gas feeding becomes more difficult for the cathodes based on these solvents, which results in a retardation of gas transport to the reaction sites. By contrast, MEAs based on DMF and DMAc as dispersion solvents for the catalyst ink give relatively higher limiting current densities that are greater than 400 mA cm^{-2} due to their higher pore volume. It is therefore concluded that the dispersion solvent used in electrode preparation influences the performance of DMFC significantly, particularly in the high current density region accompanying a considerable mass-transfer limitation.

The electrical resistances of the MEAs were measured by electrochemical impedance spectroscopy. The impedance spec-
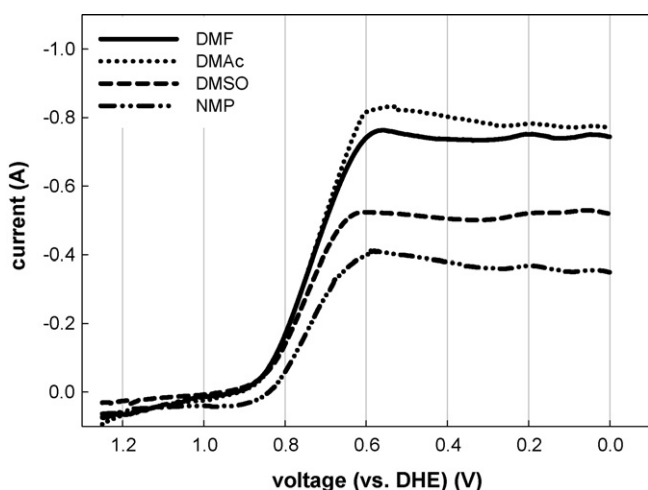

Fig. 3. Linear sweep voltammograms for oxygen reduction at cathodes using different dispersion solvents.
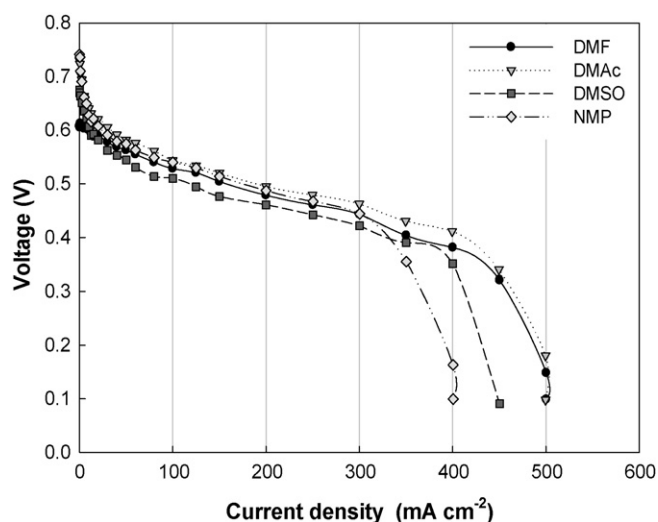

Fig. 4. Polarization curves for single-cells with cathodes based on different dispersion solvents at 60 °C.
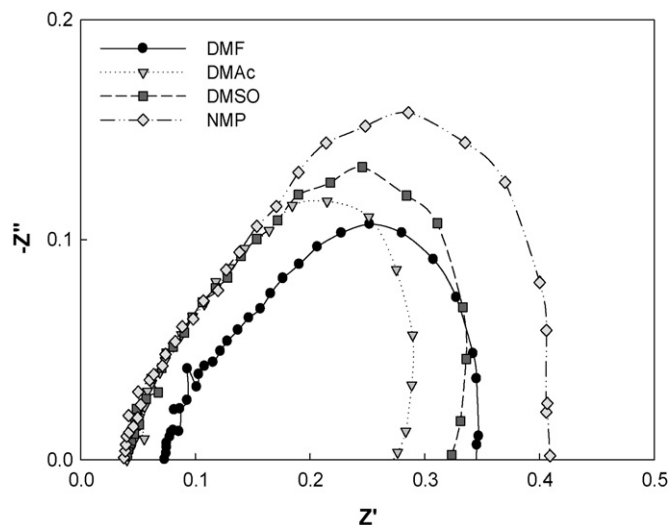
Fig. 5. Impedance spectra of single-cells with cathodes based on different dispersion solvents during cell operation at a dc potential of 0.4 V.

tra at 0.4 V of single-cells based on different dispersion solvents for the catalyst ink are presented in Fig. 5. It is remarkable that in the region of high frequency corresponding to bulk transport, there is a clear difference in the spectra between the MEA based on the dispersion solvent DMF and the MEAs based on other dispersion solvents. The MEA based on DMF shows a higher resistance in the high frequency region than the other MEAs, which have nearly the same resistance. This is attributed to the lower proton conductivity of the catalyst layer based on DMF.

4. Conclusions

A series of different cathodes with a sPEEK binder have been prepared from catalyst inks using different dispersion solvents. The type of dispersion solvent can significantly influence the proton conductivity of catalyst layer and also the pore morphology of the electrodes which, in turn, affects cell performance.

A cathode using DMF as a dispersion solvent exhibits the lowest proton conductivity of the catalyst layer due to hydrogen bonding between DMF and sPEEK. Cathodes prepared with DMF or DMAc as a dispersion solvent produce larger pore volumes than those based on DMSO and NMP. This is due to the

relatively lower boiling points of the former two solvents and influences oxygen transport behaviour at the cathode. As a consequence, MEAs based on cathodes using DMAc as a dispersion solvent produce the highest limiting current density and highest cell performance. These results demonstrate that the dispersion solvent used for the catalyst ink is obviously a key factor in the preparation of high-performance DMFCs.

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