

# Influence of the solvent in anode catalyst ink on the performance of a direct methanol fuel cell

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## Abstract

An optimal preparation method of electrodes has been sought to improve the performance of direct methanol fuel cell (DMFC). The electrodes were prepared with solvents of various polarities in catalyst ink and their single-cell performances were evaluated. A new equivalent circuit of methanol oxidation in DMFC anode has been introduced to find the origin of the difference in the anode performances. The performance of a single cell was high when less polar solvent was employed in catalyst ink. This has been attributed to the decrease in solubility of the ionomer (proton conductor) leading to the formation of a larger agglomerate with catalyst. Consequently, improved proton paths could decrease the pore electrolyte resistance in the catalyst layer. In addition, the secondary pores between those agglomerates became larger to make mass transfer process more facile.

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**Keywords:** Direct methanol fuel cell (DMFC); Catalyst ink; Impedance analysis; Pore electrolyte resistance; Equivalent circuit; Conditioning

## 1. Introduction

Past two decades have witnessed tremendous research progress in the field of direct methanol fuel cell (DMFC) based on polymer electrolyte membrane. There are various aspects that are addressed in the literature to improve the performance of DMFC. It is essential to optimize an electrode preparation method in order to improve the performance of DMFC. In the research field of polymer electrolyte fuel cells (PEFC), a number of attempts have been made to prepare electrodes to improve performance. In 1988, it was reported that by incorporating Nafion<sup>®</sup> into porous electrodes containing low platinum loadings (0.35 mg/cm<sup>2</sup>), the same level of performance could be achieved as with the electrodes having a high platinum loading [1]. Further improvements in the ionomer content in the catalyst layer were made by many other researchers [2–5]. There are also reports on DMFC [6–9]. Aricò et al. [6] found that the performance of both supported and unsupported catalysts vary with ionomer content. Wei et al. [7] used a decal transfer method to apply a thin film layer to a Nafion<sup>®</sup> membrane and found an enhancement in performance. Nordlund et al.

[8] added PTFE to the anode in order to make the morphology more favorable for carbon dioxide to evolve as a gas by creating the necessary pore.

It is known that Nafion<sup>®</sup> ionomer in organic solvents can be solubilized depending on dielectric constant ( $\epsilon$ ) of the solvent, namely, solution ( $\epsilon > 10$ ), colloid ( $3 < \epsilon < 10$ ) or precipitate ( $\epsilon < 3$ ) [10]. However, the role of the preparation method of the catalyst ink has hardly been reported. Nevertheless, there were some reports on performance improvement of PEMFC single cells with electrodes using *n*-butyl acetate ( $\epsilon = 5.01$ ) as a solvent for the catalyst ink [11,12].

For the cast ionomer and the polymer electrolyte in PEFC, sufficient hydration is necessary for stable proton conductivity. Thus, a conditioning process during an appropriate period is essential to achieve the stable performance of a single cell. This process results in changes in the catalyst layer as well as an increase of proton conductivity [12]. Changes in the interface with the catalyst due to swelling and slight dissolution of the ionomer cause a decrease of the charge transfer resistance resulting in an increase in the electrochemical active surface area (EAS). Furthermore, structural changes of the catalyst layer can affect the long-term performance of a single cell. However, reports on the changes of catalyst layer and their effects on the performance during the conditioning process are few.

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The present paper concerns the effect on the anode catalyst layer and the changes that occur during conditioning of the membrane electrode assembly (MEA) by changing solvent in the preparation of catalyst ink. Single-cell performance and the corresponding impedance analysis have been conducted.

## 2. Impedance elements in equivalent circuit

### 2.1. Basic elements

The impedance of a solid electrode having a smooth surface may be described by a simple model consisting of two impedance elements: charge transfer resistance ( $R_{ct}$ ) and double-layer capacitance ( $C_d$ ). To represent an electrolyte resistance ( $R_e$ ), one may additionally append a resistor. To describe porous DMFC anode and methanol electro-oxidation a few additional steps are required.

### 2.2. Porous layer

Porous electrodes in PEFC may be described using different models [13,14]. In general, there exists a cross-correlation between the geometry of the model and the simplicity of the impedance elements used. The second aspect of a porous electrode is given by mathematics. A model may be very descriptive for the real conditions in the porous regions, but the same model may be ineffective when it can not be defined by simple mathematical elements. Thus, the model used here is based on a relatively simple geometry, assuming a system of ‘homogeneous’ pores as suggested by Göhr [15]. The impedance of the porous layer may be expressed in terms of the macroscopic impedance elements such as  $Z_p$  (impedance of the pores filled by electrolyte),  $Z_m$  (impedance of the porous metal catalyst) and  $Z_q$  (impedance of the interface (porous layer/pore)).

The impedance  $Z_p$  and  $Z_m$  can reduce to resistive elements ( $R_p$  and  $R_m$ ). In this study the term  $R_m$  can be neglected assuming a value of zero. The expression for the total impedance ( $Z_{pl}$ ) in the porous layer may appear complex, but can be calculated by using the approach of Göhr [15] as given in Eq. (1):

$$Z_{pl} = \frac{\sqrt{R_p Z_q}}{\tanh(\sqrt{R_p/Z_q})} \quad (1)$$

### 2.3. Relaxation impedance ( $Z_K$ )

Relaxation impedance may be included in a model of Faradaic impedance ( $Z_F$ ) at non-equilibrium potential. The Faradaic impedance is composed of a potential-dependent charge transfer resistance ( $R_{ct}$ ) and time-dependent relaxation impedance as given in Eq. (2):

$$Z_F = \frac{R_{ct} Z_K}{R_{ct} + Z_K} \quad (2)$$

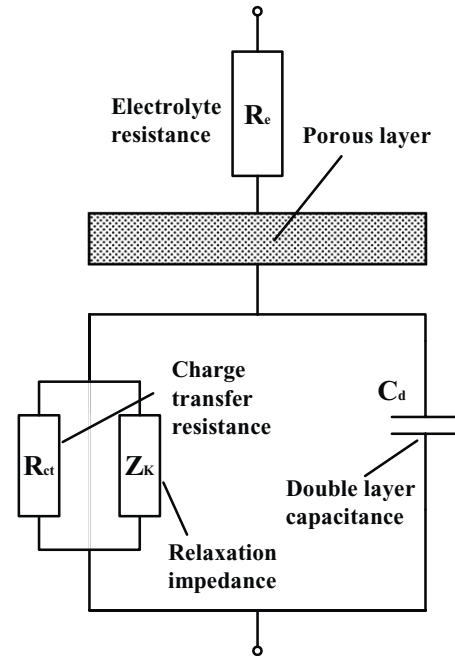


Fig. 1. Equivalent circuit for the evaluation of the DMFC anode impedance data.

According to Schiller et al. [16], impedance spectra of the Pt anode in a PEFC show strong time dependences and exhibit a pseudo-inductive contribution at the low frequency due to carbon monoxide poisoning. The pseudo-inductive behavior can be attributed to a surface relaxation process of the anode. It is already known that oxidation of adsorbed carbon monoxide in the mechanism of methanol oxidation is the rate-determining step at high temperature (ca. 80 °C) [17]. Thus, the same phenomena may be found in the DMFC anode and a relaxation impedance term should be included.

Therefore, total impedance ( $Z$ ) and equivalent circuit of DMFC anode in this study have been proposed as given in Eq. (3) and Fig. 1:

$$Z = R_e + Z_{pl} + \frac{1}{1/Z_F + j\omega C_d} \quad (3)$$

## 3. Experimental

### 3.1. Membrane electrode assembly

The cathode catalyst used was 47 wt.% Pt/C (Tanaka) and catalyst ink was prepared by dispersing appropriate amounts of catalyst in deionized water and isopropyl alcohol (IPA) with 5% Nafion<sup>®</sup> solution (1100 EW, Du Pont). The anode catalyst used for methanol electro-oxidation was 53 wt.% PtRu/C (Tanaka) and the catalyst ink was prepared by the same method. Besides IPA as solvent of the anode catalyst ink we used methanol (MeOH), dipropyl ketone (DPK) and *n*-butyl acetate (NBA). The catalyst ink was sprayed onto 10 cm<sup>2</sup> of carbon paper (TGPH-060, Toray) and additional

ionomer solution was sprayed onto the catalyst layer of each electrode in order to decrease the contact resistance with the polymer electrolyte membrane (Nafion<sup>®</sup> 117, Du Pont). The metal (Pt or PtRu) loading was 3 mg/cm<sup>2</sup> in each electrode and the total ionomer, including additional ionomer, loading was 30 wt.% for the cathode and 60 wt.% for the anode. A pair of electrodes (cathode and anode) were hot-pressed on both sides of the polymer electrolyte membrane at a temperature of 140 °C and with a pressure of 70 kgf/cm<sup>2</sup> for 150 s.

### 3.2. Operation of single-cell

All experiments including electrochemical measurements were conducted with cells which consisted of MEAs sandwiched between two graphite flow field plates. The active area of the cell was 10 cm<sup>2</sup>. In all the experiments operated in a fuel cell mode, 2 M methanol solution was pumped through the anode side at 5 mL/min and oxygen to the cathode side at a flow rate of 250 sccm. The temperature and pressure of single cells were held at 80 °C and atmospheric pressure, respectively. Oxygen gas was humidified by passing through a humidifier maintained at a temperature of 65 °C. Current–voltage curves were measured galvanostatically by using an electronic load (EL-500P, Daegil Electronics). Data were collected after hydration by circulating 2 M methanol solution through the anode for 2 h. Afterwards the cell voltage was measured every 6 or 12 h, and impedance measurements were carried out.

### 3.3. Characterization of electrodes

#### 3.3.1. Electrochemical impedance spectroscopy (EIS)

Impedance spectra were obtained from the operating cells with a potentiostat (IM6, Zahner). The anode was supplied with 2 M methanol solution (5 mL/min) at 80 °C and the cathode with a continuous stream of dry hydrogen (200 sccm) to make a dynamic hydrogen electrode (DHE) and to facilitate removal of permeated water. All anode impedance spectra reported here were measured between the anode and the DHE in the complete fuel cell. The frequency range was from 50 mHz to 1 kHz and the amplitude of sinusoidal current signal was adjusted so that the potential amplitude did not exceed 5 mV. Every spectrum was measured at a dc potential of 0.400 V (vs. DHE).

#### 3.3.2. Size distribution in catalyst ink

Agglomerate size distribution in catalyst ink was investigated with a light scattering instrument (PHOTAL ELS8000, Otsuka Electronics).

#### 3.3.3. Structure analysis of catalyst layer

The pore size distribution measurements were obtained both by Hg-porosimetry (Auto Pore II 9220, Micrometrics) and by the N<sub>2</sub> adsorption method (ASAP2010, Micrometrics). And the porous microstructure of anode was studied

with scanning electron microscopy (SEM) using S-4200 (Hitachi).

## 4. Results and discussion

### 4.1. Influence of solvents on the catalyst layer in the anode

Solvents with various dielectric constants such as methanol ( $\epsilon = 33.10$ ), isopropyl alcohol ( $\epsilon = 18.30$ ), dipropyl ketone ( $\epsilon = 12.60$ ) and *n*-butyl acetate ( $\epsilon = 5.01$ ) were chosen in the preparation of the anode catalyst ink. Fig. 2 shows the single-cell performance of each anode prepared with different solvents of catalyst ink. Since there was no mass transfer limitation under the experimental condition employed in this study, the polarization curve of the single cell could be divided into two regions [18]. At low currents, the cell voltage is dominated by the electrochemical kinetics of the anodic methanol oxidation (A). By increasing the current load, the cell voltage is further decreased due to the electric resistance of the fuel cell (B). In the region A, there is no difference in the single-cell performance of each anode that was prepared with catalyst inks of various solvents. The changes in polarity of solvent appeared to have no appreciable effect on the catalytic activity. However, a significant difference in the performance of each electrode was observed in the region B. The slope of the polarization curve in this region is the simple resistance to the flow of electrons through the material of the electrodes and the various interconnections, as well as the resistance to the flow of ions through the electrolyte [19]. Only resistances in the catalyst layer and contact resistance with polymer electrolyte appeared to vary with solvent since the polymer electrolyte was the same for all the electrodes. The ohmic resistance in the region B de-

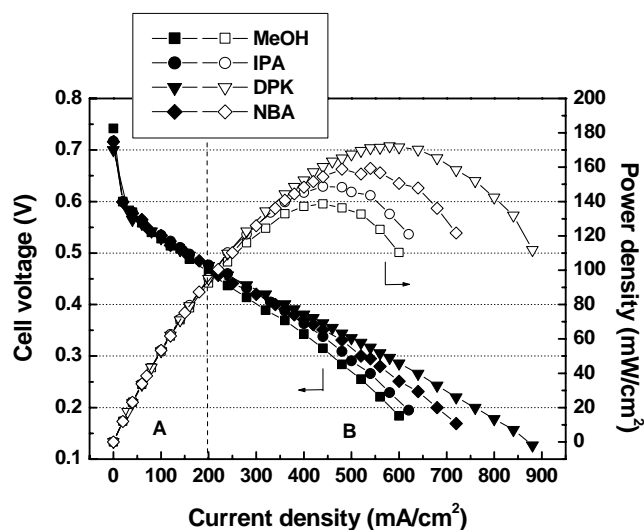


Fig. 2. Polarization curves for the MEAs with anodes using different solvents for the catalyst ink on 2 M MeOH/O<sub>2</sub> under 80 °C and atmospheric pressure.

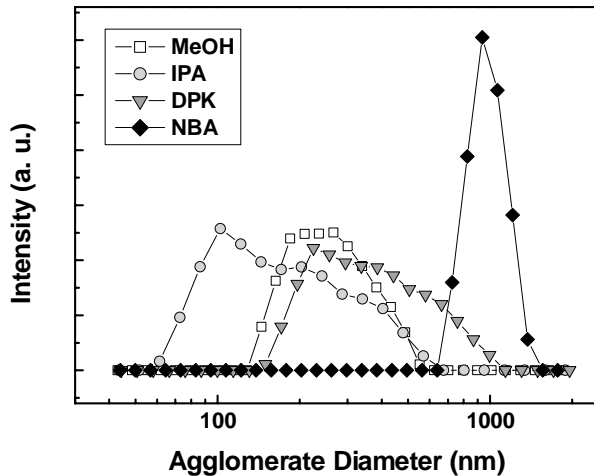


Fig. 3. Size distribution of agglomerates of catalyst and ionomer in different solvents.

creased in following order: MeOH ( $\epsilon = 33.10$ ) > IPA ( $\epsilon = 18.30$ ) > NBA ( $\epsilon = 5.01$ ) > DPK ( $\epsilon = 12.60$ ). Consequently the single-cell performance increased roughly as the solvent polarity decreased. In order to find out the reason for change in performance, one has to understand the fundamental mechanism of methanol electro-oxidation. Electro-oxidation occurs to produce protons, electrons and carbon dioxide when methanol solution comes to the active sites which is the interface of the catalyst and ionomer; proton and electron are transferred through the ionomer and catalyst respectively and carbon dioxide escapes to the outside. The reaction can be distributed into a mass transfer process and a charge transfer process.

We shall discuss the mass transfer process first. The ionomer in a less polar solvent became less soluble such that it precipitated in the agglomerated form. This state of ionomer could form relatively the large-sized agglomerates with the catalyst. This became clear through the investigation of agglomerate size distribution in catalyst ink by light scattering experiments. Fig. 3 shows the size distribution of the catalyst in the ionomer agglomerate of each catalyst ink. The intensity of the vertical axis indicates concentration of the agglomerate of a uniform diameter. It can be seen that the agglomerate in the catalyst ink using less polar solvent (DPK or NBA) was relatively large-sized. The size of the agglomerate was reflected in the structure of the catalyst layer through the drying process after spraying catalyst ink onto carbon paper. Because various sizes of the agglomerates formed by the catalyst and the ionomer, secondary pores existed between the agglomerates (Figs. 4 and 5). Fig. 4 shows the pore size distribution in anodes measured with an Hg porosimeter. The primary pores in this study were below 10 nm according to our supplementary experiment by  $N_2$  adsorption method, therefore, all the pores shown in Fig. 4 originated from the space between catalyst agglomerates. According to Nordlund et al. [8] and Uchida et al. [20], the secondary pores were mainly in the size range

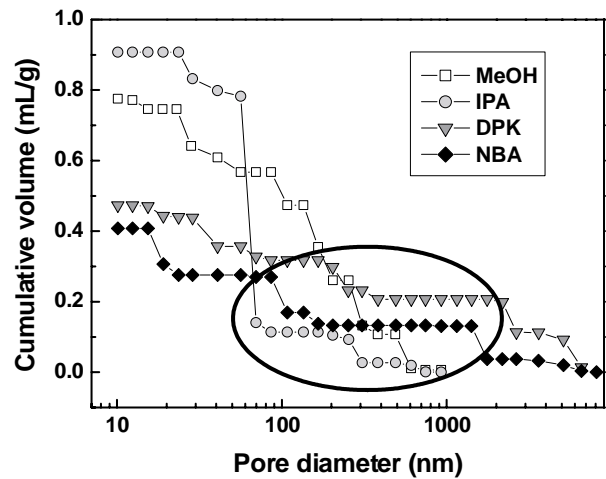


Fig. 4. Cumulative pore volume distribution of anodes prepared with catalyst ink using different solvents.

of 0.04–1.0  $\mu\text{m}$ . From Fig. 4, one can see that the secondary pore volume is larger in the case of DPK and NBA as evaluated from the area. SEM images of the catalyst layer show the formation of small and round agglomerates in the electrode, when polar solvents are used. However, they were connected with ionomer to form large dumbbell shapes in the electrode using DPK and NBA. From these observations, it can be proposed that single-cell performance should increase due to easy mass transfer in the case of the electrode prepared with a catalyst ink using less polar solvents like DPK or NBA. Mass transfer processes can be made easier by increase of the secondary pore volume in the catalyst layer by impregnating an ionomer and/or PTFE; PEMFC or DMFC with such electrodes exhibit improved performance [8,20]. But mass transfer processes seemed to have a minor effect on the performance in this study because there was no mass transfer limitation (Fig. 2).

Next, we shall discuss the charge transfer process. Resistances related to methanol electro-oxidation on the DMFC anode have been included in impedance data. Particularly, several elements related to anode impedance could be separated through a fitting process of measured data with an appropriate equivalent circuit. An equivalent circuit was constructed similar to Göhr [15] and Schiller et al. [16], and then the values of the constituent elements were fitted to the measured impedance data using Eq. (3) (Fig. 6).  $R_{ct}$ ,  $R_e$ ,  $R_p$  and  $R_m$  were mentioned previously.  $R_{ct}$  was the resistance for methanol electro-oxidation occurring at the interface of catalyst and ionomer. Therefore, this one was not only related to the effective area of the three-phase interface [21], but also reflects the mass transfer resistance [22].  $R_e$  was the resistance indicating proton conductivity. In general models,  $R_e$  has included the resistances of electrolyte membrane and cast ionomer in catalyst layer, but the latter could be separated from  $R_e$  to be represented by  $R_p$  as one element in the porous layer in this study. The resistance for electrons ( $R_m$ ) transferred through catalyst was excluded because of

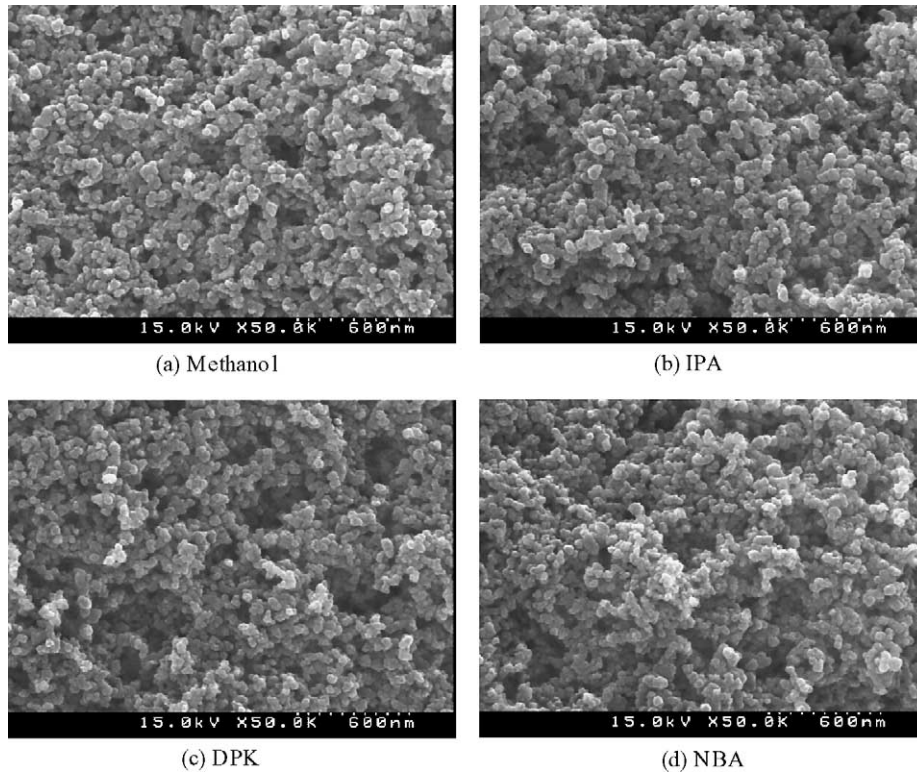


Fig. 5. SEM images of anodes prepared with catalyst ink using different solvents.

its negligible value. These three types of resistances for each electrode were compared in Fig. 7. The resistance of the cast ionomer in the porous catalyst layer,  $R_p$ , showed exactly the corresponding tendency with single-cell performance; however,  $R_e$  and  $R_{ct}$  did not have any significant difference between each electrode. Thus, these observations suggest that only the proton conductance of the cast ionomer in the catalyst layer could be affected mainly by changing solvents of different polarity. Since the ionomer having hydrophilic and hydrophobic realms simultaneously form different structures

depending on the polarity of solvent, the proton-transferring path in the agglomerates formed with catalyst seems to be changed dramatically.

4.2. Influence of solvent on the single-cell performance during MEA conditioning

For stable operation of the single cell, MEA conditioning is necessary and single-cell performance increases due

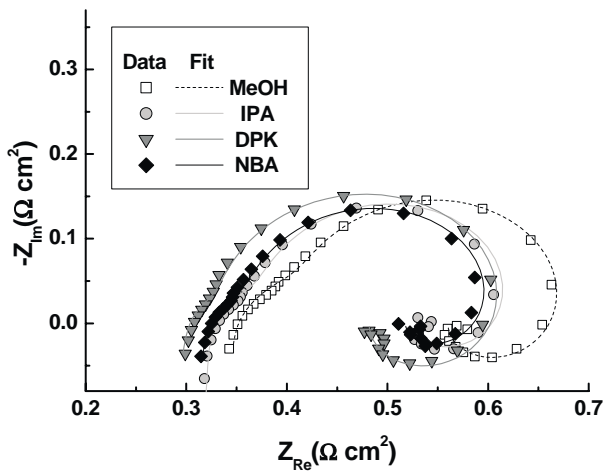


Fig. 6. Measured (symbols) and fitted (line, model of Fig. 1) impedance data of anodes prepared with catalyst ink using different solvents.

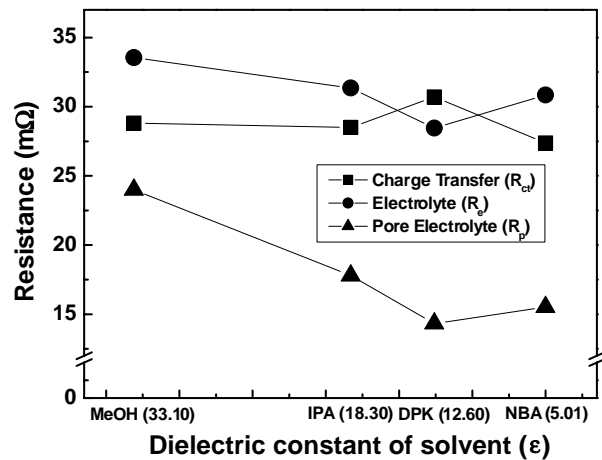


Fig. 7. Three kinds of resistances ((■) charge transfer resistance, (●) electrolyte resistance, (▲) pore electrolyte resistance, fitted with model of Fig. 1) for the process on the anodes prepared with catalyst ink using different solvents.

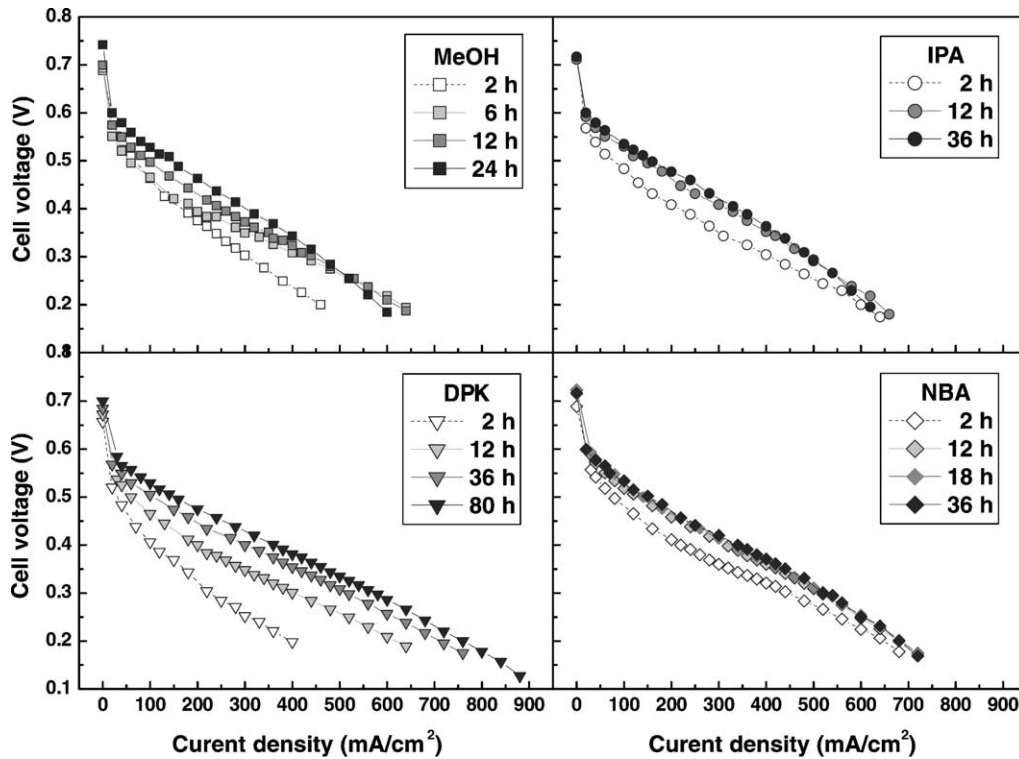


Fig. 8. Single-cell performance of anodes prepared with catalyst ink using different solvents during conditioning period.

to several factors. A detailed analysis of the factors increasing the performance during conditioning shall be the purpose of a future publication [12]. Single-cell performances vary depending on the solvent used for catalyst ink in this study as can be seen from Fig. 8. When polar solvents like MeOH or IPA were employed, the performance increased continuously for ca. 12 h but decreased slightly because the resistance increased especially in the region of high current density after that period. On the other hand, when less polar solvents like DPK or NBA were employed, there was no decline in performance in the region of high current density. In the representative impedance data (Fig. 9), resistances associated with polymer electrolyte of IPA electrode increased after 12 h.

Changes in the resistance of proton-conducting material seemed to be related to which kinds of solvents were used in the catalyst ink. The cast film made from a commercial Nafion<sup>®</sup> ionomer solution was poor, brittle and cracked. Furthermore, the resulting film was soluble at room temperature in polar solvents, especially in water and methanol [23,24]. At the end of the direct drying process of the ionomer solution, the remaining solvent was mainly water, which is a poor solvent for perfluorosulfonated ionomer (PFSI) [25]. Grot and Chadds [26] have suggested a solution to this problem. Solvents of high boiling point (above ca. 130 °C) may be added to the ionomer solution, followed by room-temperature evaporation of the mixture, which may lead to the formation of uncracked film with good mechanical properties after heating to 120 °C. DPK (bp 143.5 °C)

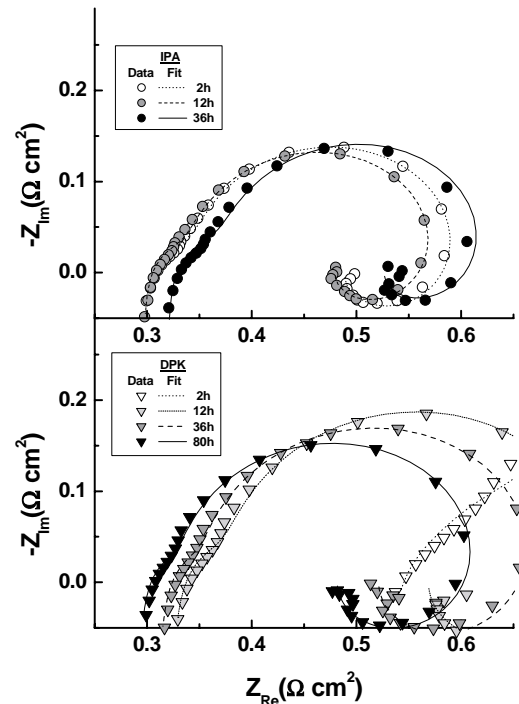


Fig. 9. Measured (symbols) and fitted (line, model of Fig. 1) impedance data of anodes prepared with catalyst ink using IPA and DPK during conditioning period.

and NBA (bp 126.0 °C), which have a higher boiling temperature than water, and could remain longer than alcoholic species like methanol (bp 64.5 °C) or IPA (bp 82.2 °C) even after the drying process. Therefore, when these solvents were employed, a stable cast ionomer, which was insoluble in polar methanol solution, could be obtained and their single-cell performance has been improved significantly and for an extended period.

## 5. Conclusions

The electrode prepared with less polar solvents (DPK or NBA) showed a higher single-cell performance. The main factors improving the performance were the decrease of the pore electrolyte resistance in the catalyst layer and secondary pore enlargement. Change of solvent did not affect the intrinsic activity of the catalyst but only the resistance of the proton-conducting material in the catalyst layer. Solvents of higher boiling point than water, like DPK and NBA, were found to be favorable in producing a stable cast ionomer even in the presence of methanol solution at the anode. The influence of these factors is confirmed by the investigation of single-cell performance during the conditioning period.

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