

The electrochemical kinetics study of methanol at electrocatalyst Pt-Ru/C and the methanol diffusion in the modified proton exchange membranes

Ning-Yih Hsu , Yu-Nong Chen, and Shi-Chern Yen

Department of Chemical Engineering

National Taiwan University

Taipei, Taiwan, 10674

scyen@ntu.edu.tw

1. Abstract

Pt-Ru/C catalyst has been applied extensively in direct methanol fuel cells for methanol electrochemical oxidation. In this study, a model for electrochemical kinetics of methanol has been developed for electrocatalyst Pt-Ru/C. The single cell performance of DMFC and AC impedance analysis were measured. The methanol crossover problem still remains a challenge for the applications of DMFC. The mechanism of methanol crossover and the effect of methanol concentration on the methanol crossover in the modified proton exchange membranes would also be investigated. With the aim of improving the membrane properties for DMFC applications, the modifications and treatments for Nafion-based membranes have been proposed and investigated. By treating membranes with the sol-gel method, the methanol permeability of the modified membrane could be reduced to one half of that in the Nafion membrane.

2. Introduction

Recently, liquid feed direct methanol fuel cells (DMFC) receive increasing attention. Conventional DMFC consist of a solid polymer electrolyte such as Nafion membrane with catalyzed electrodes bonded to both sides. However, DMFCs are also faced with a number of technical challenges: methanol crossover and slow anode kinetics. Recent advances in power densities have been attributed to improvements in the electrode structure rather than to progress in electrocatalysis: Pt-Ru alloys are still considered to be the best catalysts for methanol electrooxidation, and Pt is still frequently used as the oxygen reduction catalyst. A standard practice in

hydrogen-air fuel cell research consists in measuring cell impedances and considering them as cathode impedances [1]. Contributions of the anode of hydrogen fuel cell are usually negligible due to fast kinetics and mass transport of hydrogen oxidation reaction. Consequently, it is possible to eliminate contributions of the cathode in a DMFC by operating it without oxygen, so that protons are reduced and hydrogen is evolved. In order to diminish the methanol permeation through the membrane, two main directions can be followed: a development of new polymer electrolytes [2] or a modification of the structure of the conventional membranes. The present work is an attempt to improve the performance of Nafion in DMFCs by introducing inorganic fillers. The results of Antonucci et al. [3] might be considered as a good starting point for further optimization of the PFSI-based membranes. By introducing a small amount of silica powder in Nafion, a more crystalline polymer is produced [4]. In addition to this structural modification, the incorporation of hydrophilic inorganic particles may retain more water and may contribute to a better methanol exclusion. It also could advantageously influence the water transfer to the cathode. Here we report the properties of Nafion-based composite membranes which were modified by sol-gel method. In this way, we aim to improve the membranes conductivity and methanol permeation by taking advantage of the modified structure of and the water uptake properties of the inorganic fillers. The ratio of methanol permeability and conductivity as a combined characteristic of the membrane performance is determined for all specimens.

3. Experimental

3. 1. MEAs

The complete fabrication of gas diffusion electrodes (GDEs) is basically a three-step process; firstly, Toray carbon paper undergoes hydrophobic treatment, secondly, a thin PTFE/carbon layer is cast onto the treated surface, and lastly the catalyst layer is cast onto the surface of the supporting layer. The catalyst suspension was composed of Pt/C or Pt-Ru/C (Johnson Matthey) catalyst powder , 5wt.% Nafion solution (Dupont) and ethylene glycol (EG) (Aldrich). The finely ground catalyst powder was first mixed with EG, and then Nafion solution was slowly added with stirring. The mixture was agitated by means of ultrasonic waves (Sonicator XL-2020,

Heat Systems Inc.). The anode catalyst loading was 4mgPt-Ru/cm² and the cathode was 1.5mgPt/cm². Finally, these GDEs were hot-pressed onto Nafion 117 membranes at a temperature of 130°C and a pressure of 0.5kN/cm² to obtain the complete membrane electrode assemblies (MEAs). The operation conditions of single cell were 2M methanol on anode, air breathing on cathode, 40°C and atmospheric pressure. The frequency generator/analyzer was a Solartron SI 1260 Impedance controlled by a personal computer and coupled to a potentiostat instrument (Solartron 1287) that allows modulation of large dc currents. Impedance spectra were usually obtained at frequencies between 10000Hz and 0.001Hz. The amplitude of the sinusoidal potential signal was 10mV.

3. 2. Membranes

3. 2. 1. Nafion

The Nafion membranes (H⁺ form, EW 1100, DuPont) were first treated in a 3% hydrogen peroxide solution at 70°C for 1 hour and thoroughly washed with DI water 4~5 times in ultrasonic bath then kept in 0.5M sulfuric solution at 70°C for 1 hour and washed again with DI water 4~5 times in ultrasonic bath.

3. 2. 2. Sol-gel modified Nafion-based

We control the sol-gel solution composition and sol-gel reaction time to reach the lowest permeability and the highest conductivity. The composition was shown in the Table 1.

Table 1. Sol-gel solution composition

S.G-3	TEOS : H₂O : EtOH : HCl = 1/3 : 4.2 : 8.6 : 0.2
S.G-4	TEOS : H₂O : EtOH : HCl = 1 : 4.2 : 8.6 : 0.2
S.G-5	TEOS : H₂O : EtOH : HCl = 1/3 : 4.2 : 8.6 : 0.6
S.G-6	TEOS : H₂O : EtOH : HCl = 1 : 4.2 : 8.6 : 0.6

3. 3. Permeability

Methanol permeability of these membranes was determined using the typical

diaphragm diffusion cell. This glass cell consisted of two reservoirs each approximately 5 ml, separated by a vertical membrane. Prior to testing, membranes were hydrated in deionized water for at least 24 hr. Initially, one reservoir contained only water and the other reservoir contained a methanol/water mixture. Concentrations of methanol in the initially pure water reservoir were measured versus time using gas chromatography. For gas chromatography, 1 μ l samples were analyzed using a gas chromatograph fitted with a Porepak Q chromatographic column and a thermal conductivity detector.

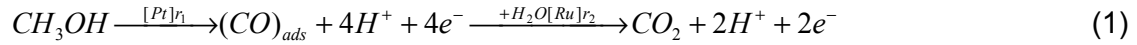
3. 4. Conductivity

The conductivity measurements were carried out by ac impedance spectroscopy. A sample of the membrane (1.5 cm in diameter) was placed between Pt disk and Pt wire electrodes. The disk which is connected to a Pt wire by spot welding is 1 cm in diameter and the wire is 0.1 cm in diameter. The Pt wires are connected to an Solartron SI1260 frequency response analyzer. The impedance is measured in the frequency range between 1 MHz and 1 Hz with a perturbation voltage amplitude of 10 mV. Z-view (Scribner) software is used to fit the impedance spectra. The membrane conductivity is calculated from the membrane resistance, R, according to $\sigma = 1/R \cdot l/A$, where l is the membrane thickness (in cm) and A is the surface of the electrode (in cm^2).

4. Results and discussion

Depending on the potential of DMFC, its Nyquist plots can have different features. Fig. 3. (a) and (b) show a series of Nyquist plots of Pt-Ru/C anode working with various dc potentials. A loop reflecting an inductive behavior appears at the low-frequency end when the potential is larger than 0.3V. The loop had been reported in the research of Muller et al. [5]. It is clear that increasing overpotential is helpful for the methanol oxidation. Therefore, the formation of the loops is due to the improvement of methanol electro-oxidation kinetics. The inductive behavior can be explained using the kinetic theory derived by Harrington and Conway [6] for reactions involving intermediate adsorbates. We assume the following mechanism for methanol

electrooxidation:



Methanol was adsorbed, mainly on Pt sites, with a rate r_1 to give $(CO)_{ads}$ as the dominating intermediate species. Oxidative removal of the adsorbate with a rate r_2 is rate-determining step under conditions relevant to fuel cell operation, i.e., low anode potentials ($E < 0.4V$ [RHE]) and high temperatures (ca. $100^\circ C$). It is furthermore assumed that mass transport limitations do not occur. The net rate of production of electrons r_e and the net rate of production of $(CO)_{ads}$ r_{CO} can be defined as follows.

$$r_e = 4r_1 + 2r_2 = \frac{i}{F} \quad (2)$$

$$r_{CO} = r_2 - r_1 = \frac{q_{CO}}{F} \frac{d\theta}{dt} \quad (3)$$

where θ is the fractional surface coverage of CO, and q_{CO} is the charge required for adsorption of CO to complete coverage. The full derivation is given in Ref. [6] This expression for the faradaic impedance leads to the equivalent circuit shown in Fig. 1.(b). When it is used to model the impedance behavior of the DMFC anode, the resulting shape of the Nyquist plots agrees well with the experimentally observed plots. The inductance L which means the current signal follows a voltage perturbation with a phase delay is due to slowness of $(CO)_{ads}$ coverage relaxation. R_{ct} serves to modify the phase-delay according to the reaction scheme, and the R_c arm of the circuit is associated with the part of the current response, which occurs without change in coverage. R_{ct} was the resistance for methanol electrode-oxidation occurring at the interface of catalyst and ionomer (dry Nafion solution). Therefore, this one was not only related to the effective area of the three-phase interface, but also reflects the mass transfer resistance [7]. R_m was the resistance indicating proton conductivity. In general models, R_m has included the resistances of electrolyte membrane and cast ionomer in catalyst layer, but the latter could be separated from R_m to be represented by R_i as one element in this study. It should be noted that flattening of the measured spectrum is frequently observed on technical electrodes. The reason for this distortion is believed to be the roughness of the catalytic layer. If

the different degrees of catalytic layer roughness and the non-uniform distribution of catalyst are concerned, the impedance for the Pt-Ru/C anode usually exhibits a non-semicircular response for Nyquist plots. As a result, only a constant-phase element (CPE) instead of the ideal capacitance could fit the experimental results more agreeably. This constant-phase element (CPE) can be used to study the practical electrode with the different degrees of surface roughness, physical non-uniformity or a non-uniform distribution of surface reaction sites [8]. The impedance of CPE is written as

$$Z = 1 / [T(l*w)^P] \quad (4)$$

Parameters: CPE-T, CPE-P

The CPE is defined by two values, CPE-T and CPE-P. If CPE-P equals 1 then the equation is identical to that of a capacitor. If CPE-P equals 0.5, a 45 degree line is produced on the Complex-Plane graph. When a CPE is placed in parallel to a resistor, a Cole-Element (depressed semi-circle) is produced. Often a CPE is used in a model in place of a capacitor to compensate for non-homogeneity in the system. For example, a rough or porous surface can cause a double-layer capacitance to appear as a constant phase element with a CPE-P value between 0.9 and 1. In fact, a capacitor is actually a constant phase element - one with a constant phase angle of 90 degrees. A CPE with CPE-P value of 0.5 can be used to produce an Infinite Length Warburg element. A Warburg element occurs when charge carrier diffuses through a material. Lower frequencies correspond to diffusion deeper into the material. If the material is thin, low frequencies will penetrate the entire thickness, creating a Finite Length Warburg element. If the material is thick enough so that the lowest frequencies applied do not fully penetrate the layer, it must be interpreted as infinite.

The most two important reactions in sol-gel process are hydrolysis and condensation. The hydrolysis rate and condensation rate could be controlled by adjusting the compositions of sol-gel solution. Firstly, S.G.-3 (TEOS : H₂O : EtOH : HCl = 1/3 : 4.2 : 8.6 : 0.2) was used to be a standard composition which could reduce methanol permeability. Then S.G.-4 (TEOS : H₂O : EtOH : HCl = 1 : 4.2 : 8.6 : 0.2) was applied to upgrade our compositions. It was found that methanol permeability could decrease obviously after 3 hours reaction time and then could decrease to 8.9X10⁻⁷cm²/s (nearly half to Nafion 1.7X10⁻⁶ cm²/s) after 75 hours reaction time.

S.G.-6 (TEOS : H₂O : EtOH : HCl = 1 : 4.2 : 8.6 : 0.6) could reach $8.9 \times 10^{-7} \text{ cm}^2/\text{s}$ after 6 hours reaction time but conductivities were decreased seriously. Membrane efficiency could be determined by the ratio of conductivity / permeability (C/P ratio). Although S.G.-6 could reach the lowest permeability quickly, S.G.-5 which conductivities were much higher than S.G.-6's had higher C/P ratio than S.G.-6.

5. Conclusion

The impedance behavior of a DMFC anode was studied. The faradaic impedance with constant phase element (CPE) was successfully modeled using a kinetic theory based on the most widely accepted reaction mechanism for methanol electrooxidation. An equivalent circuit was suggested whose elements are linked to kinetic parameters of the reaction and which explains the characteristic inductive behavior of the DMFC anode working without diffusion control. The different degrees of catalytic layer roughness and the non-uniform distribution of catalyst was successfully modeled and rationalized by CPE. Sol-gel modified Nafion membranes could reduce methanol permeability and still had enough proton conductivity. Permeability is independent of membrane thickness and concentration difference. Methanol permeability could be reduced to half of Nafion by modified Nafion membrane with Sol-Gel processing. The relative C/P ratio could be increased to 190% based on Nafion.

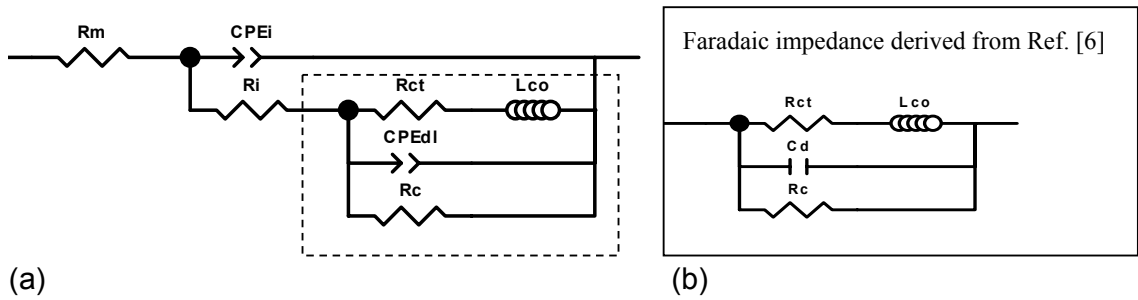


Fig. 1. Equivalent circuit for modeling the impedance of DMFC anodes. (a) our equivalent circuit, (b) Faradaic impedance derived from Ref. [6]

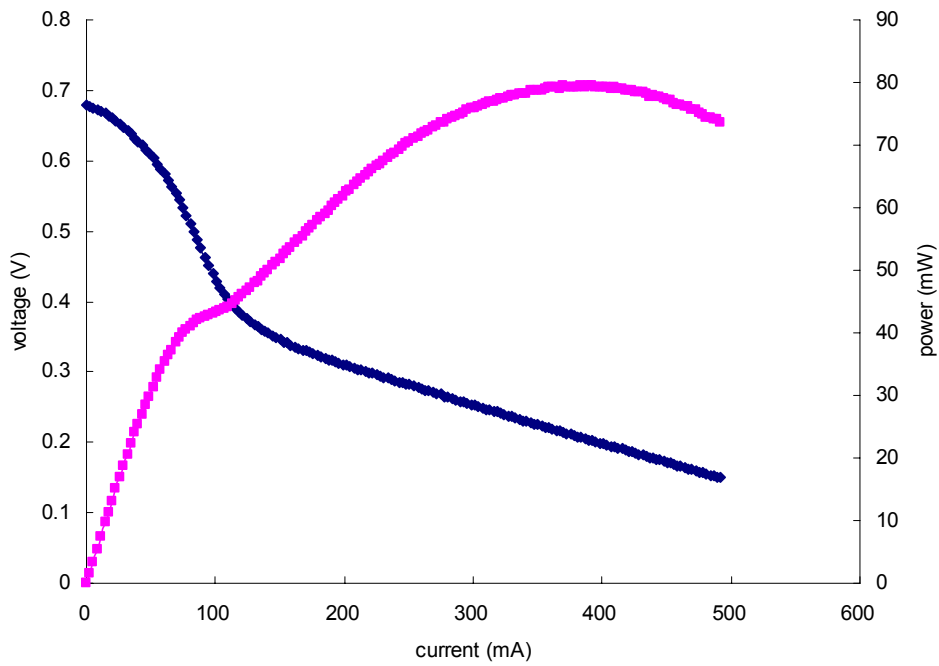
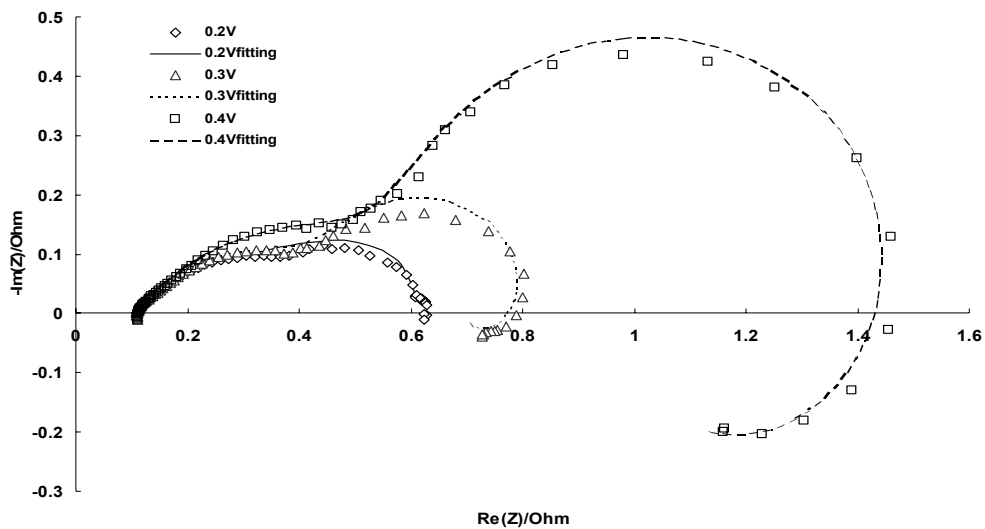
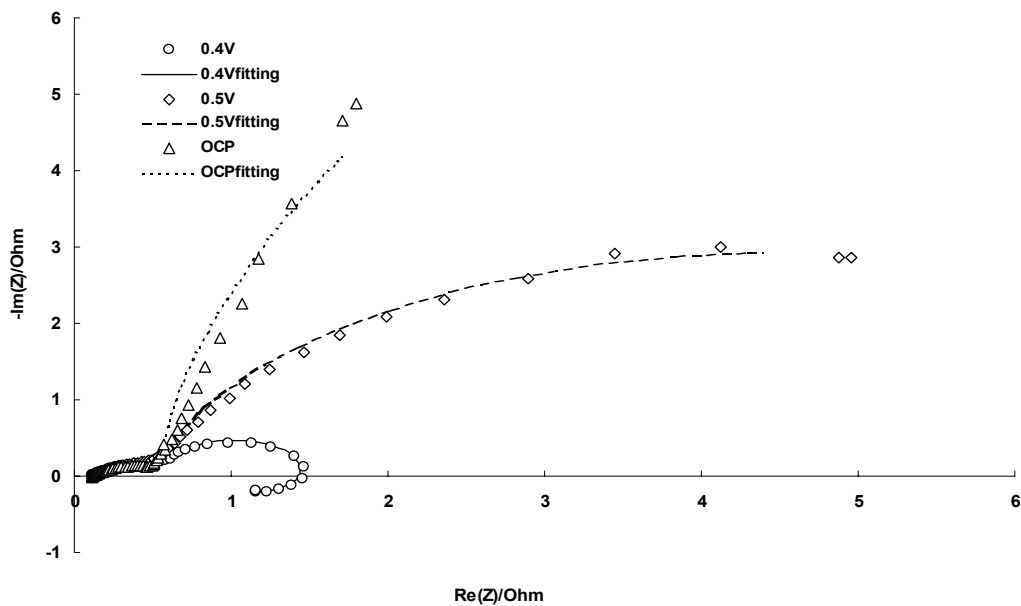


Fig. 2. Single cell performance curve of DMFC. Methanol concentration: 2M; air breathing; cell temperature:40 °C ; Pt loading: 1.5mg/cm², Pt-Ru loading: 4mg/cm², electrode area: 6.25cm².



(a)



(b)

Fig. 3. Pt-Ru/C anode Nyquist plots and fitting results at different potential (a) 0.2V~0.4V, (b) 0.4V~OCP. Methanol concentration: 2M; cell temperature: 40°C; Pt loading: 1.5mg/cm² Pt-Ru loading 4mg/cm²

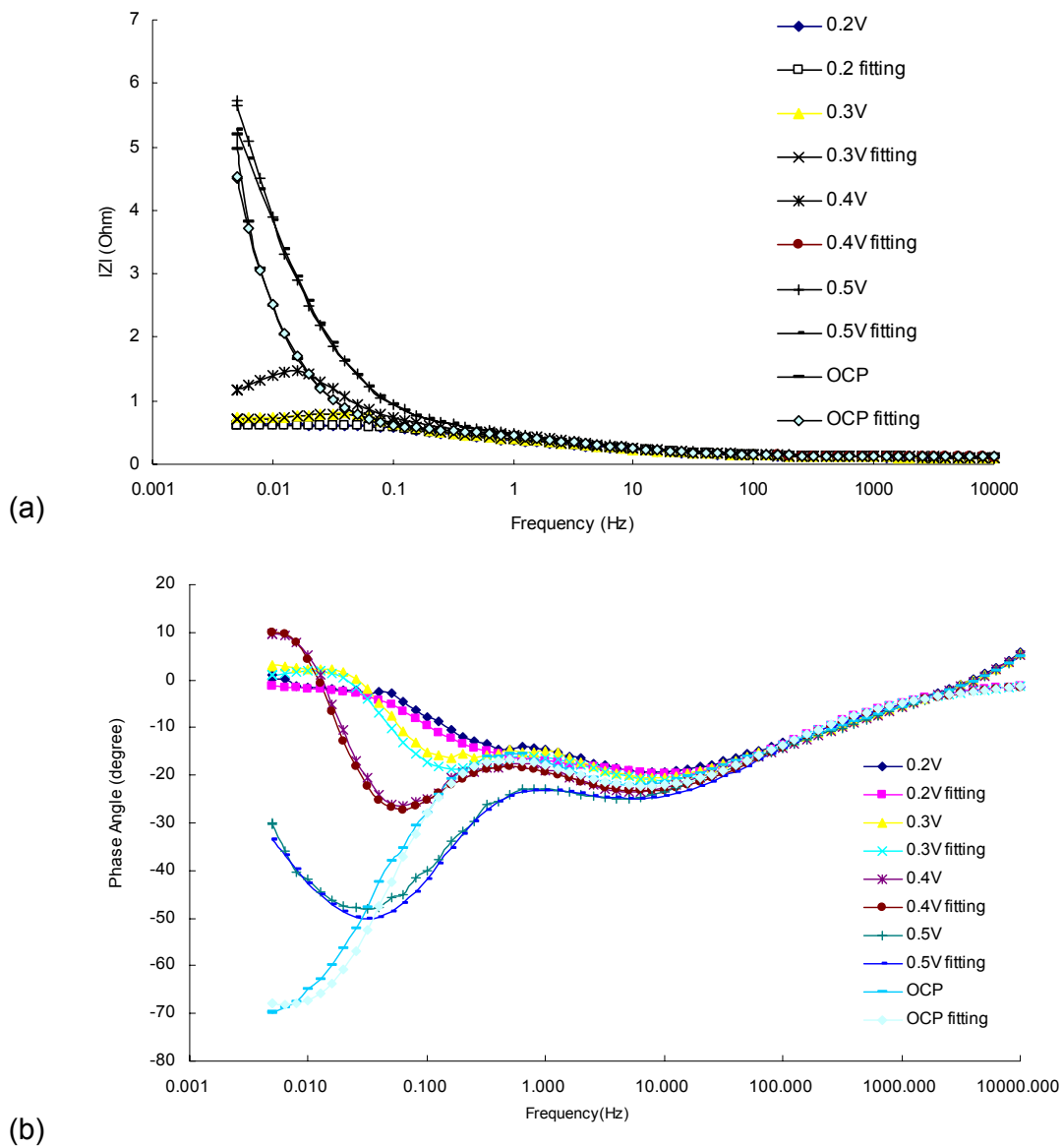
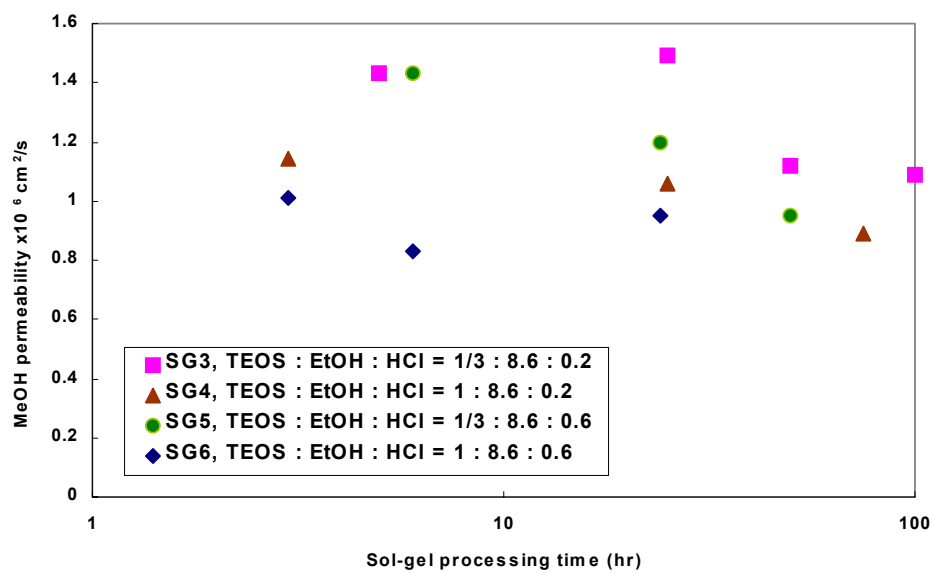
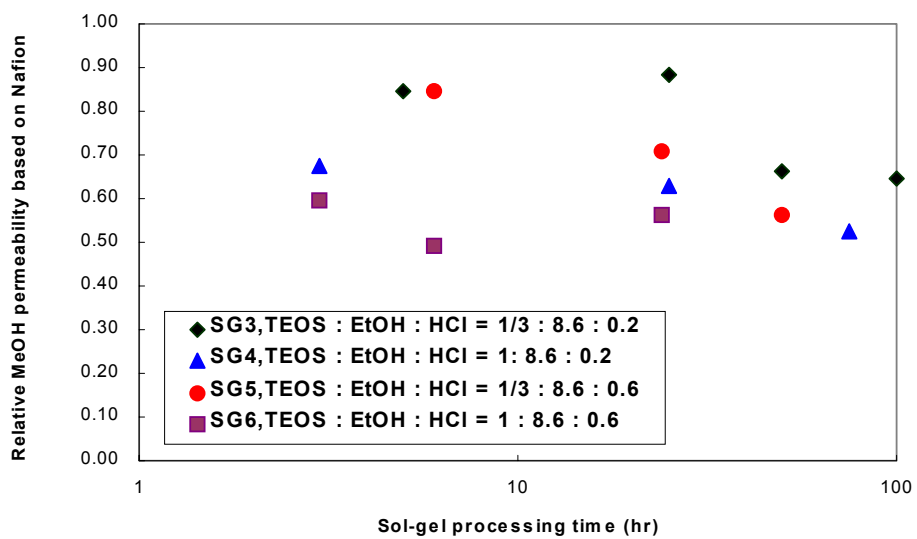


Fig. 4. Pt-Ru/C anode Bode plots and fitting results at different potential (a) magnitude v.s. frequency (b) phase angle v.s. frequency. Methanol concentration: 2M; air breathing; cell temperature: 40°C; Pt loading: 1.5mg/cm², Pt-Ru loading 4mg/cm².

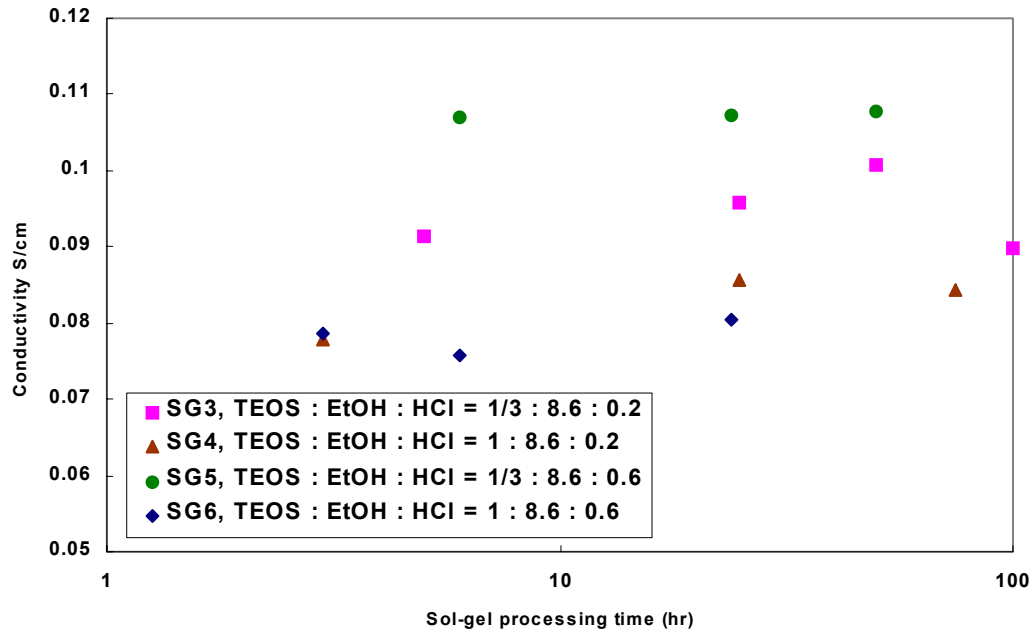


(a)

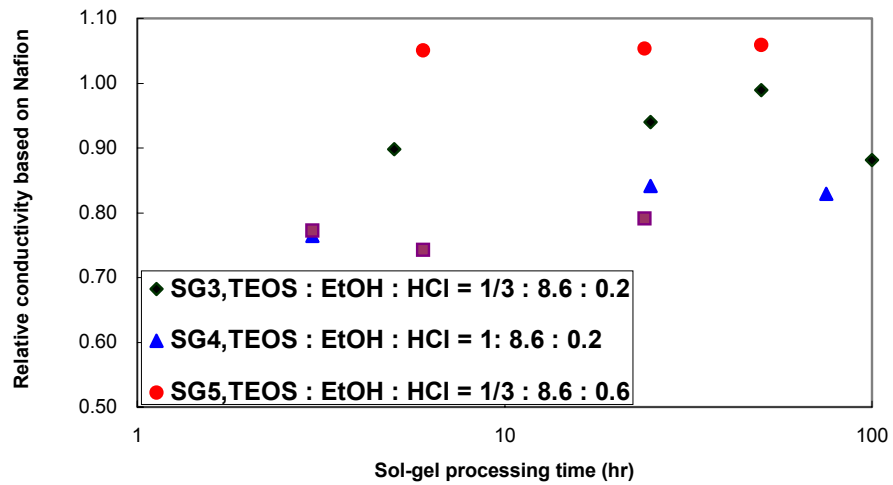


(b)

Fig. 5. Effect of Sol-gel compositions on methanol permeability.



(a)



(b)

Fig. 6. Effect of Sol-gel compositions on membrane conductivity.

Relative C/P base on Nafion

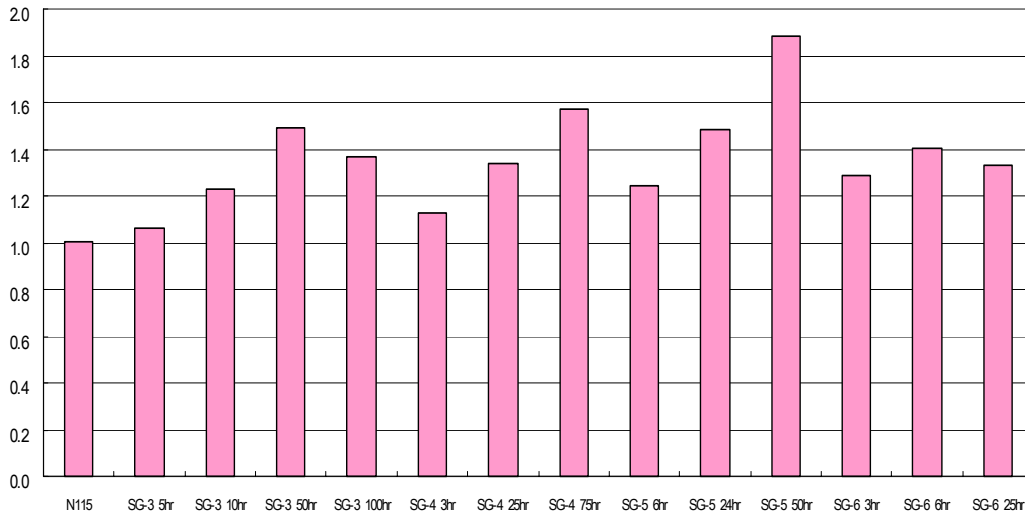


Fig. 7. The relative conductivity/ relative permeability (C/P) v.s. Sol-gel compositions with reaction time.

Table 2. Fitting parameters of our equivalent circuit for modeling the impedance of DMFC anodes.

	Rm	CPEi-T	CPEi-P	Ri	Rct	Lco	CPEdl-T	CPEdl-P	Rc
0.2V	0.10915	0.39083	0.60945	0.30527	0.73186	2.453	2.621	0.64	0.31224
0.3V	0.11077	0.45231	0.58382	0.42394	0.3268	4.381	4.06	0.92776	0.36784
0.4V	0.11166	0.459	0.56349	0.60265	0.35028	20.14	4.154	0.95385	1.026

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