

Nafion/PTFE composite membranes for direct methanol fuel cell applications

Hsiu-Li Lin^{a,b,*}, T. Leon Yu^{a,b}, Li-Ning Huang^b, Li-Chung Chen^a,
Kun-Sheng Shen^b, Guo-Bin Jung^b

^a Department of Chemical Engineering and Materials Science, Yuan Ze University, Nei-Li, Taoyuan 32026, Taiwan

^b Fuel Cell Center, Yuan Ze University, Nei-Li, Taoyuan 32026, Taiwan

Received 5 December 2004; received in revised form 14 February 2005; accepted 15 February 2005

Available online 31 March 2005

Abstract

Using dynamic light scattering and scanning electron microscope (SEM), it is shown that a high-carbon-number alcohol/water, i.e., 2-propanol/water, mixed solvent is more effective than low-carbon-number alcohol/water, i.e., ethanol/water and methanol/water, mixed solvents in dispersing Nafion molecules. Thus, it is a better solvent for the preparation of Nafion/PTFE (poly(tetrafluoroethylene)) composite membranes. The performance of direct methanol fuel cells (DMFCs) with a Nafion/PTFE composite membrane, which was prepared in-house, a commercial Nafion-117 membrane, or a commercial Nafion-112 membrane were investigated by feeding various concentrations, i.e., 2–5 M, of methanol to the anode. The Nafion/PTFE composite membrane gave a better DMFC performance than that obtained with Nafion-117 or Nafion-112 membranes. Using a DMFC model and varying the methanol concentration at the anode, cell voltage data were analyzed with respect to methanol concentration and cell current. The results indicate that inserting porous PTFE into Nafion polymer causes a reduction not only in methanol diffusion cross-over but also in the electro-osmosis of methanol cross-over in the membrane.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Nafion; Poly(tetrafluoroethylene); Composite membrane; Direct methanol fuel cell

1. Introduction

The perfluorosulfonated ionomer (PFSI) membrane is successful as a proton exchange membrane (PEM) for fuel cells. It is generally accepted that PEM fuel cells present an attractive alternative to traditional power sources, due to their high efficiency and pollution-free operation. Nevertheless, the high cost of the cell components is an impediment to their commercialization. One of the primary contributors to the high cost of PEM fuel cells is the PFSI membrane. Recent research reports have shown [1–8] that cost reduction can be realized by replacing the PFSI membrane with a PFSI-based composite membrane. Composite membranes may be pre-

pared by impregnation of a low-cost microporous support material with a PFSI solution. The most common PFSI solution and porous membrane for preparing composite membranes are Nafion solution, a registered trademark of DuPont, and porous polytetrafluoroethylene (PTFE) membrane, respectively. It is important to note that the composite membranes contain much less of the expensive PFSI resin than traditional PFSI membranes such as Nafion-117, thus the cost of composite membranes is much lower. They also offer other advantages such as good mechanical strength in both the swollen and the unswollen states, good thermo-stability, and thinner thickness (the thickness of composite membranes prepared in the author's laboratory is around 20 μm , whereas the thickness of Nafion-117 and Nafion-112 membranes is around 175 and 50 μm , respectively).

Nafion has a chemical structure with a hydrophobic tetrafluoride backbone and hydrophilic ionic side-chains. It

* Corresponding author. Tel.: +886 3 4638 800x2568;

fax: +886 3 4559 373.

E-mail address: sherry@saturn.yzu.edu.tw (H.-L. Lin).

has been reported [9] that Nafion polymers aggregate in dilute low alcohol and water solvents and form fringed, cylindrical rods with ionic side chains located on the periphery of the rods. These aggregates cause a problem for impregnating porous PTFE membranes with Nafion solutions, i.e., the pores of PTFE membranes are not fully impregnated by Nafion resin because of the larger sizes of the Nafion aggregates compared with the pore sizes of the PTFE membranes.

Yeo [10] determined the solubility parameter using the swelling method and found dual solubility parameters for Nafion: one ($\delta = 20.6 \text{ J}^{1/2} \text{ cm}^{-3/2}$) was attributed to the Nafion organic backbone and the other ($\delta = 34.2 \text{ J}^{1/2} \text{ cm}^{-3/2}$) was attributed to the ionic side-chains. The aggregation of Nafion molecules in the solvents depends strongly on the dielectric constant and the solubility of the solvents. In this paper, dynamic light scattering (DLS) has been used to measure the particle-size distributions of dilute Nafion in various low alcohol/water mixture solvents, i.e., methanol/water, ethanol/water and 2-propanol/water, that have different solubility parameters. The data show that the particle sizes of Nafion molecular aggregates decrease while the solubility parameter of solvent is close to the solubility parameter of the Nafion backbone ($\delta = 20.6 \text{ J}^{1/2} \text{ cm}^{-3/2}$). Nafion has the smallest aggregate size in 2-propanol/water solvent and the largest aggregate size in methanol/water solvent. Thus, Nafion/PTFE composite membranes have been prepared by impregnating porous PTFE membranes with a 2-propanol/water mixture solvent, which has better compatibility with the Nafion backbone than the other alcohols. The small size of the Nafion aggregates cause Nafion molecules to be easily plugged into the micropores of the PTFE membranes and results in a better fuel/oxidant barrier property. Comparison is undertaken of the physical properties and the performance of direct methanol fuel cells (DMFCs) with composite membranes or Nafion-series membranes, provided by DuPont Co. It has been reported [6,8,11–13] that a Nafion/PTFE (NP-) composite membrane gives better performance in a H_2/O_2 polymer electrolyte membrane fuel cell (PEMFC) than DuPont Nafion-series membranes. On the other hand, few papers have examined the performance of DMFCs prepared with NP-composite membranes. This study demonstrates that the NP-composite membrane gives better DMFC performance than DuPont Nafion-series membranes.

2. Experimental

2.1. Materials

The Nafion solution (DuPont Co.) was 5 wt.% of 1100 EW Nafion diluted in a mixed solvent of water, propanol, methanol, and unspecified ethers [14]. The mixed solvent was evaporated at 60°C under vacuum for 1 h to obtain a pure Nafion solid resin. The latter was used to prepare Nafion solutions with specified solvents. A porous polytetrafluoroethylene membrane (PTFE membrane, Yue-Ming-Tai Chemical

Ind. Co., Taichung, Taiwan) with a thickness of $18 \pm 3 \mu\text{m}$, pore sizes of $0.5 \pm 0.1 \mu\text{m}$, and a porosity of $52 \pm 5\%$ was used as a supporting material for the composite membranes. Methanol, ethanol, and 2-propanol (chemical reagents, Riedel de Hae Co., Germany) were used to prepare the Nafion solutions.

2.2. Particle-size distributions of Nafion solutions

The Nafion particle-size distributions of three 1 mg cm^{-3} Nafion solutions prepared with various solvents, i.e., methanol/water (4/1 wt. ratio), ethanol/water (4/1 wt. ratio), and 2-propanol/water (4/1 wt. ratio), were investigated by means of dynamic light scattering (DLS, model BI9000, Brookhaven Co., New York, USA) with a 25 mW He–Ne laser (wavelength $\lambda = 632.8 \text{ nm}$, Spectra Physics Co., USA). The DLS field correlation functions $g^{(1)}(t)$ of Nafion solutions were obtained at 30°C with a scattering angle of $\theta = 30^\circ$. The Nafion particle-size distributions were calculated from $g^{(1)}(t)$ using CONTIN software.

2.3. Preparation of Nafion/PTFE composite membranes

The porous PTFE membranes were mounted on $12 \text{ cm} \times 12 \text{ cm}$ steel frames and boiled in acetone at 55°C for 1 h. Each pretreated PTFE membrane was impregnated with a 5 wt.% Nafion/2-propanol/water (with 2-propanol/water = 4/1 in wt. ratio) solution for 24 h. The impregnated membranes were then annealed at 120°C for 1 h. After annealing, the membranes were swollen with distilled water for 24 h. Finally, the membranes were swollen with 1N sulfuric acid for 4 h. The final composition (wt. ratio) of the composite membrane was PTFE/Nafion/water = 42.5/49.5/8.0, and the thickness was $20 \pm 3 \mu\text{m}$.

2.4. Characterization of Nafion/PTFE composite membranes

The morphology of the surfaces of the composite membranes was studied by means of a scanning electron microscope (SEM, model JSM-5600, Jeol Co., Japan). The sample surface was coated with gold powder under vacuum. The ionic conductivity (σ) was calculated from the measured current resistance (R), i.e.,

$$\sigma = l/(A \times R) \quad (1)$$

where A is the cross-sectional area of the membrane and l is the thickness. The value of R was determined with an a.c. impedance system (model SA1125B, Solartron Co., UK). A device for holding the membrane was located between the probes. The testing device with the membrane was kept in a thermostat at a relative humidity of 95% and a temperature of 70°C . The membrane area, A , for R measurement was 3.14 cm^2 . The proton resistance r per unit area of a membrane

was obtained from Eq. (2):

$$r = l/\sigma = AR \quad (2)$$

Methanol cross-over in membranes was investigated with an apparatus designed in-hand. A device for holding the membrane was located centrally so as to separate a container into two vessels, with each vessel having a volume of 102 ml. At the beginning of the methanol cross-over test, vessel-1 was filled with 3 M methanol/water solution and vessel-2 was filled with pure water. The whole apparatus was maintained at a temperature of 25 °C. The methanol passing across the membrane was characterized by measuring the methanol concentration of vessel-2 (C_2) versus testing time using a gas chromatograph (GC, HP Co. model 8590A) with a capillary column (Agilent Co., 30 m × 0.53 mm × 20 μm) and a TCD detector. The carrier gas for GC was helium and the injection sample size was 0.2 μL. The injector, oven, and detector temperatures of the GC were 120, 100, and 130 °C, respectively. The normalized methanol cross-over rate was calculated as:

$$X_r = C_2 \times l/(A' \times 10 \text{ h}) \quad [(\text{wt.}\% \text{ MeOH}) \text{ cm}^{-1} \text{ h}^{-1}] \quad (3)$$

where X_r is the normalized rate of methanol cross-over, C_2 (in units of wt.%) the methanol concentration of vessel-2 at a testing time of 10 h, $A' = 5.31 \text{ cm}^2$ is the cross-sectional area of membrane for methanol cross-over measurements, and l the thickness of the membrane. If it is assumed that the quantity of methanol cross-over from vessel-1 to vessel-2 is much smaller than the total quantity of water in vessel-2 and that the density of water is 1 g cm^{-3} at 25 °C, then the total weight of water in vessel-2 is 102 g and the molar rate, q , of methanol cross-over per unit area of membrane in 1 s is:

$$\begin{aligned} q &= X_r/l [\text{wt.}\% \text{ cm}^{-2} \text{ h}^{-1}] \\ &= X_r/l [102 \text{ g (wt.}\% \text{ MeOH}) \text{ cm}^{-2} \text{ h}^{-1}] \\ &\quad \times [32 \text{ g (mol MeOH)}^{-1} 3600 \text{ s h}^{-1}]^{-1} \\ &= X_r/l \times 8.854 \times 10^{-4} [(\text{mol MeOH}) \text{ cm}^{-2} \text{ s}^{-1}] \quad (4) \end{aligned}$$

where 32 g mol^{-1} is the molecular weight of methanol.

2.5. Performance test of direct methanol fuel cell

The Nafion membranes obtained from DuPont Co., i.e., Nafion-117 and Nafion-112, and the NP-composite membrane prepared as above were used for the preparation of membrane electrode assemblies (MEAs). The gas-diffusion layer of the MEA was carbon paper (E-TEK Co.) pretreated with FEP resin (DuPont Co.). The Pt–Ru catalyst (E-TEK Pt–Ru/C catalyst with 40 wt.% Pt–Ru) loading of the anode was 4.0 mg cm^{-2} and the Pt catalyst (E-TEK Pt/C catalyst with 40 wt.% Pt) of the cathode was 2.0 mg cm^{-2} .

The performance of single cells prepared from Nafion-112, Nafion-117, or NP-composite membranes was tested at 70 °C using a Globe Tech Computer Cell GT testing system (Electrochem, Inc.). The input flow rate of methanol at

the anode was 5 ml min^{-1} with methanol concentrations of 2, 3, 4, and 5 M, and the cathode input O_2 flow rate was 150 ml min^{-1} .

3. Results and discussion

3.1. Dynamic light scattering study of Nafion alcohol/water solutions

The solubility, δ , and dielectric constant, ϵ , of water, methanol, ethanol, and 2-propanol [15,16] are listed in Table 1. The dual-solubility of Nafion [10] is also shown. The data indicate that 2-propanol has a better solubility with the Nafion fluorocarbon backbone whilst methanol has a better solubility with Nafion ionic side chain. The dielectric constant of the solvents decreases in the following sequence: water < methanol < ethanol < 2-propanol, which indicates that the polyelectrolyte effect of Nafion in various solvents decreases in the following sequence of water > methanol > ethanol > 2-propanol.

The particle-size distributions of 1.0 mg cm^{-3} Nafion in methanol/water, ethanol/water, and 2-propanol/water solutions (with a wt. ratio of alcohol/water = 4/1) are given in Fig. 1. These were obtained from DLS measurements at 30 °C with a scattering angle of $\theta = 30^\circ$. From ESR [9] and small-angle scattering data [17–19], it was concluded that Nafion molecules aggregate in a dilute methanol/water solution, i.e., [Nafion] ≤ 0.1 wt.%, through hydrophobic interaction of fluorocarbon backbone to form primary cylindrically aggregated particles with ionic side-chains located around the periphery of the cylinders. The primary aggregates can form secondary ionic aggregates through ionic side-chains, the number of which increases with increasing Nafion concentration [9,19]. The data in Fig. 1 show that there is a large particle-size distribution, i.e., $2 \times 10^4 \text{ nm}$, of Nafion molecules in the methanol/water mixture solvent. There are two modes of particle-size distribution in Nafion/ethanol/water and Nafion/2-propanol/water solutions (middle and top of Fig. 1, respectively), in which the aggregated Nafion particles are smaller than those in the methanol/water mixture solvent. The larger particle distributions (average particle size $\langle \xi \rangle \geq 10^3 \text{ nm}$) in these three alcohol/water mixture solvents are attributed to the secondary ionic aggregates of Nafion molecules [9,19]. The smaller particle distributions are attributed to the sizes of the single

Table 1
Solubility parameters (δ) and dielectric (ϵ) constants of Nafion, water, and alcohols

Solvent	$\delta \text{ (J}^{1/2} \text{ cm}^{-3/2}\text{)}$	ϵ
Nafion	20.6 (backbone), 34.2 (side chain)	
Water	47.9	78.4
Methanol	29.7	32.7
Ethanol	26.0	24.5
2-Propanol	23.5	19.9

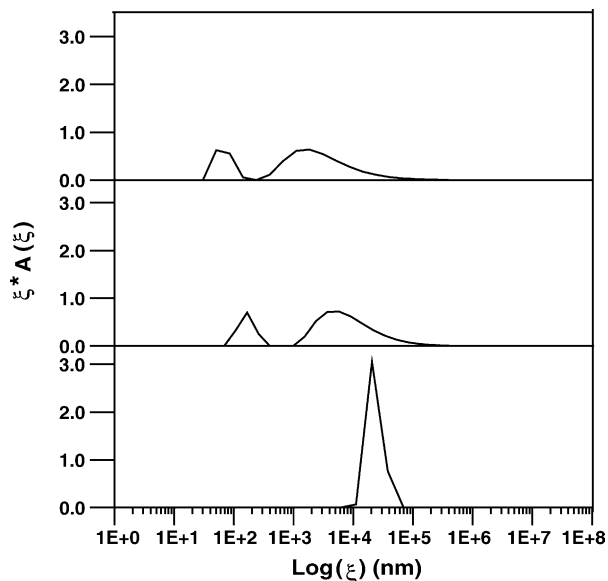


Fig. 1. DLS particle sizes (ξ) distributions ($A(\xi)$) of 1 mg cm^{-3} Nafion solutions with solvents: $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ (bottom), $\text{C}_2\text{H}_5\text{OH}/\text{H}_2\text{O}$ (middle), and $\text{C}_3\text{H}_7\text{OH}/\text{H}_2\text{O}$ (top); alcohol/ H_2O wt. ratio = 4/1; scattering angle $\theta = 30^\circ$; 30°C .

polymer chains and the smaller primary aggregated particles. As the solvent is varied from methanol to ethanol and then to 2-propanol, the dielectric constant (ϵ) of alcohol decreases and the difference between solubility of alcohol and that of the Nafion backbone (i.e., $20.6 \text{ J}^{1/2} \text{ cm}^{-3/2}$) decreases, thus both the degree of Nafion primary backbone aggregation and the secondary ionic aggregation decreases and the Nafion aggregated particle size in the solvents decreases in the sequence methanol/water > ethanol/water > 2-propanol/water.

3.2. SEM study of morphology of Nafion/PTFE composite membranes

A scanning electron micrograph of the surface of the porous PTFE membrane is shown in Fig. 2. It is seen that

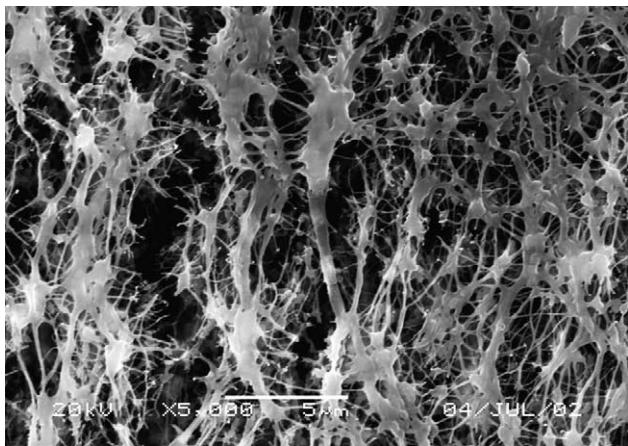


Fig. 2. Scanning electron micrograph of surface of porous PTFE membrane (5000 \times).

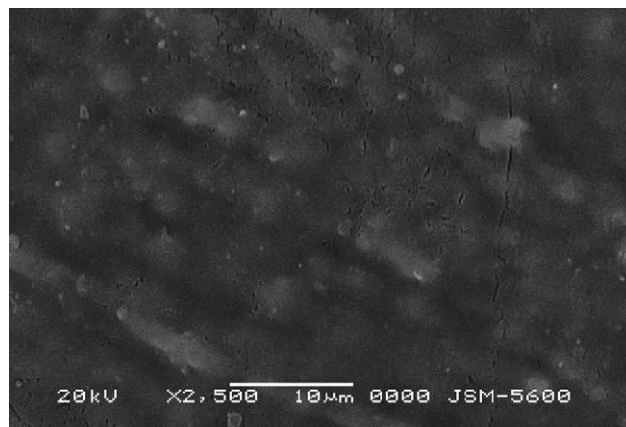


Fig. 3. Scanning electron micrograph of surface of composite membrane prepared by impregnating porous PTFE membrane in Nafion/2-propanol/water (2-propanol/water = 4/1 wt. ratio) solution (2500 \times).

there are fibres and knots in the membrane with enclosed micropores. A micrograph of the surface of the composite membrane, which was prepared by impregnating porous PTFE membrane with Nafion/2-propanol/water solution (with a 2-propanol/water wt. ratio = 4/1) is shown in Fig. 3. The surface of PTFE membrane is completely covered and filled with Nafion resin and no micropores are observed, which indicates that the porous PTFE membrane is well impregnated with Nafion resin. By contrast, a micrograph (Fig. 4) of the surface of composite membrane, which was prepared by impregnating porous PTFE membrane with 5 wt.% Nafion solution as received from DuPont Co., reveals the presence of micropores. This observation shows that the porous PTFE membrane is not well impregnated with Nafion resin solution as received from DuPont Co., since it contains water, methanol, ethanol, and 2-propanol mixture solvents and has larger aggregated Nafion particles. It is obvious that the smaller aggregated Nafion particle sizes in a 2-propanol/water mixture solvent causes easier plugging of Nafion molecules in the micropores of PTFE membranes and this results in the formation of less micropores in NP-composite membranes.

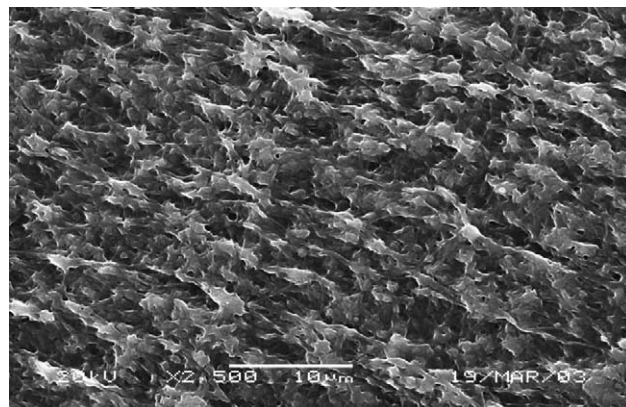


Fig. 4. Scanning electron micrograph of surface of composite membrane prepared by impregnating porous PTFE membrane in 5 wt.% Nafion solution as received from DuPont Co. (2500 \times).

Table 2
Resistance and conductivity of membranes at 70 °C and a relative humidity of 95% (Eq. (1))

Membrane	l (cm)	R (Ω)	σ ($S\text{ cm}^{-1}$)	$r=l/\sigma$ ($\text{cm}^2\text{ S}^{-1}$)
Nafion-117	0.0175	0.552	1.01×10^{-2}	1.730
Nafion-112	0.0050	0.162	9.82×10^{-3}	0.509
NP-composite	0.0020	0.192	3.31×10^{-3}	0.604

3.3. Conductivity measurements

The conductivity of the composite membranes was measured using an a.c. impedance system at 70 °C with a relative humidity of 95%. The conductivity σ and the proton resistance per unit area, $r=l/\sigma$, of Nafion-117, Nafion-112, and NP-composite membranes are listed in Table 2. The data are the average values of three measurements and the standard deviations are around $\pm 5\%$. The conductivity σ of the NP-composite membrane is lower than that of Nafion-117 and Nafion-112 membranes, due to the poor conductivity of the PTFE membrane. On the other hand, because of its smaller thickness, the composite membrane has an r value that is lower than that of the Nafion-117 membrane.

3.4. Methanol cross-over measurements

Methanol cross-over tests of Nafion-112, Nafion-117, and NP-composite membranes were performed at 25 °C with a 3 M methanol aqueous solution in vessel-1. The X_r and q values are summarized in Table 3. Since PTFE is an excellent barrier to the cross-over the membrane, it is found that X_r increases in the following sequence: NP-composite < Nafion-117 \leq Nafion-112. Though the NP-composite membrane has the lowest X_r value, the rate of methanol cross-over per unit area q , which is not normalized by the membrane thickness, increases in the order: Nafion-117 < NP-composite < Nafion-112, because the NP-composite membrane has the lowest thickness.

3.5. Performance of direct methanol fuel cell

The NP-composite, Nafion-117, and Nafion-112 membranes were used to prepare membrane electrode assemblies (MEAs) that were evaluated in DMFCs. The potential and the power density of a single cell versus current density for DMFCs operated at 70 °C are shown in Fig. 5. The concentration of methanol feed at the anode site was 2 M. The data show that the voltages of the single cells fall as the current density increases. The voltage loss at low current densities is

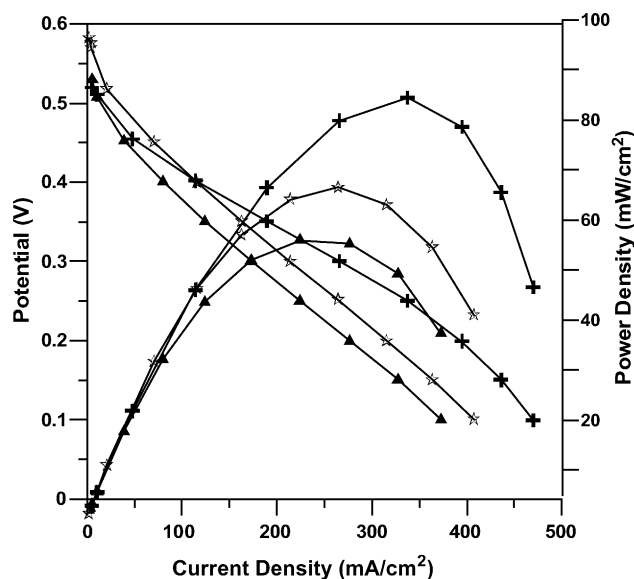


Fig. 5. DMFC single cell performance test at 70 °C; concentration of feed methanol is 2 M. MEAs prepared from: (★) Nafion 117; (▲) Nafion 112; (+) NP-composite membrane.

due to the interfacial resistance and is called the activation-polarization region I ($i < 30\text{ mA cm}^{-2}$) [20]. An efficient catalyst will help to alleviate the activation polarization. Region II ($30\text{ mA cm}^{-2} < i < 320\text{ mA cm}^{-2}$) occurs at current densities higher than region I and is characterized by a linear fall with increasing current density, the so-called ohmic loss. This behaviour is due to the resistance to the flow of ions through the polymer electrolyte membrane and is related to $r=l/\sigma$ [20–22]. The other reason for the decrease in voltage with increasing current density is related to the methanol cross-over rate q [20–22]. The cross-over of one methanol molecule from the anode to the cathode, where it reacts and wastes six electrons rather than providing an external current. Region III at $i > 320\text{ mA cm}^{-2}$ shows a final additional drop in voltage due to the depletion of species at the diffuser and catalyst layer interface and is termed the concentration-polarization region [22].

The data in Fig. 5 show that in region II the NP-composite membrane has the highest voltage, and thus the highest power density. The voltage (or power density) of MEAs prepared from these three membranes decreases in the order: NP-composite > Nafion-117 > Nafion-112. As mentioned in a previous section, the decline in voltage with increasing current is due to ohmic loss and methanol cross-over. The q_r values, the product of the rate of methanol cross-over and

Table 3
 X_r , q , and q_r data

Membrane	l (cm)	X_r (wt.% $\text{cm}^{-1}\text{ h}^{-1}$)	q mol MeOH ($\text{cm}^{-2}\text{ s}^{-1}$)	q_r mol MeOH ($\text{s}^{-2}\text{ S}^{-1}$)
Nafion-117	0.0175	0.0032	1.619×10^{-4}	2.801×10^{-4}
Nafion-112	0.0050	0.0035	6.198×10^{-4}	3.155×10^{-4}
NP-composite	0.0020	0.0010	4.427×10^{-4}	2.675×10^{-4}

the proton resistance per unit area, of the three membranes are also given in the table and are found to increase in the sequence: NP-composite < Nafion-117 < Nafion-112. The q_r values are quite consistent with the single-cell DMFC performance data shown in Fig. 5.

3.6. Effect of methanol concentration feed at anode on DMFC performance

It is known that the introduction of PTFE in the Nafion membrane will cause a reduction in proton conductance and methanol cross-over. The following sections examine the effect of methanol concentration feed at anode, and thus the methanol cross-over in the membrane, on the DMFC voltage. The cell voltage of a DMFC can be written as:

$$\begin{aligned} V &= E - \eta_{\text{an}} - \eta_{\text{cat}} - \eta_{\text{ohm}} - \eta_{\text{xov}} \\ &= E - A_1 \ln[i/i_0] - \eta_{\text{ohm}} - \eta_{\text{xov}} \end{aligned} \quad (5)$$

where V is the cell voltage, E the reversible open-circuit voltage, η_{an} the overvoltage of the anode, η_{cat} the overvoltage of the cathode, i the current density, i_0 the current density at which the overvoltage begins to move from zero, A_1 essentially the sum of slope of the polarization curves for the anode and the cathode, η_{ohm} the ohmic overpotential, η_{xov} the overpotential produced by methanol cross-over.

The ohmic overpotential η_{ohm} of a membrane can be calculated from the resistance, i.e.,

$$\eta_{\text{ohm}} = i \cdot l / \sigma \quad (6)$$

where l and σ are thickness and conductivity of the membrane, respectively.

The methanol cross-over causes depolarization losses at the cathode and loss of fuel. It is expected that when the methanol concentration feed in the anode is above a critical value, there will be a decrease in the cell voltage as a result of higher rates of methanol transport through the membrane. Permeation of water and/or methanol through an electrolyte membrane will take place under: (i) the driving force of the concentration differential (ΔC) across the membrane; (ii) the pressure differential ΔP across the membrane that acts on the permeate at the membrane–permeate interface; (iii) the electro-osmotic flux of methanol, which is accompanied by the electro-osmotic flux of water caused by protons dragging solvated water molecules through the membrane. By assuming (i) Fick diffusion and a linear concentration gradient through the thickness of the membrane, i.e., the methanol diffusivity D is independent of the concentration differential $\Delta C = C_{\text{an}} - C_{\text{cat}}$, where C_{an} and C_{cat} are the concentrations of methanol on the anode and the cathode sides, respectively, and (ii) that the permeate from the anode to the cathode is entrained in the carrier gas flow at a rate proportional to the methanol concentration at the cathode C_{cat} , the overvoltage η_{xov} due to methanol cross-over can be calculated [21] as

follows:

$$\begin{aligned} \eta_{\text{xov}} &= \chi J_{\text{MeOH}} \\ &= \chi (DC_{\text{an}}/l + \lambda i/nF) / (1 + D/kl + K_p \Delta P/kl) \end{aligned} \quad (7)$$

where χ is a constant, J_{MeOH} the flux of methanol cross-over, D the diffusion coefficient of methanol across the membrane, λ the number of moles of methanol per proton transferred by electro-osmosis, n the number of electrons involved in the reaction, F the Faraday constant, k a mass transfer coefficient for the cathode backing layer and flow channel, K_p a constant related to the hydraulic permeability across a pure Nafion membrane, ΔP the pressure differential across the membrane.

Eq. (7) predicts that the flux of methanol cross-over has a current-independent term that is affected by the methanol feed concentration at the anode, and a current-dependent term (producing an iR -like drop) due to electro-osmosis of methanol.

Substituting Eqs. (6) and (7) into Eq. (5), yields:

$$\begin{aligned} V &= E - A_1 \ln[i/i_0] - il/\sigma - \chi (DC_{\text{an}}/l + \lambda i/nF) / \\ &\quad (1 + D/kl + K_p \Delta P/kl) \end{aligned} \quad (8)$$

Rearranging Eq. (8) and separating the C_{an} -dependent and i -dependent term gives:

$$V(i, C_{\text{an}}) = E - A_1 \ln[i/i_0] - A_2 C_{\text{an}} - A_3 i \quad (9)$$

with

$$A_2 = \chi D / (l + D/k + K_p \Delta P/k) \quad (10)$$

$$\begin{aligned} A_3 &= l/\sigma + \chi \lambda / [nF(1 + D/kl + K_p \Delta P/kl)] \\ &= l/\sigma + A_{\text{eos}}(\text{MeOH}) \end{aligned} \quad (11)$$

In Eq. (11), $A_{\text{eos}}(\text{MeOH}) = \chi \lambda / [nF(1 + D/kl + K_p \Delta P/kl)]$, which is a term that relates the overvoltage to the electro-osmosis of methanol cross-over in the membrane. The equations describing A_2 and A_3 are valid only in region II [20–22] and a large overflow of water from cathode to anode may occur at a high current density namely $i > 350 \text{ mA cm}^{-2}$ due to the high production of water from the electrochemical reaction at the cathode. The parameter A_2 can be obtained from the slope of the plot of $V(i, C_{\text{an}})$ versus C_{an} at a fixed current density i with $330 \text{ mA cm}^{-2} > i > i_0$. The parameter A_3 can be obtained from the slope of the plot of $V(i, C_{\text{an}})$ versus i at a fixed methanol feed concentration at the anode C_{an} .

The unit area proton resistance, l/σ , of Nafion-112 membrane is close to that of the NP-composite membrane. In order to reduce the difference in overvoltage difference between two DMFCs, which results from the difference in l/σ between the membranes, MEAs prepared from Nafion-112 and NP-composite membranes were used to study the effect of introducing porous PTFE into Nafion polymer on methanol cross-over in the membrane. The single cell voltage and power density versus current curves for a DMFC at

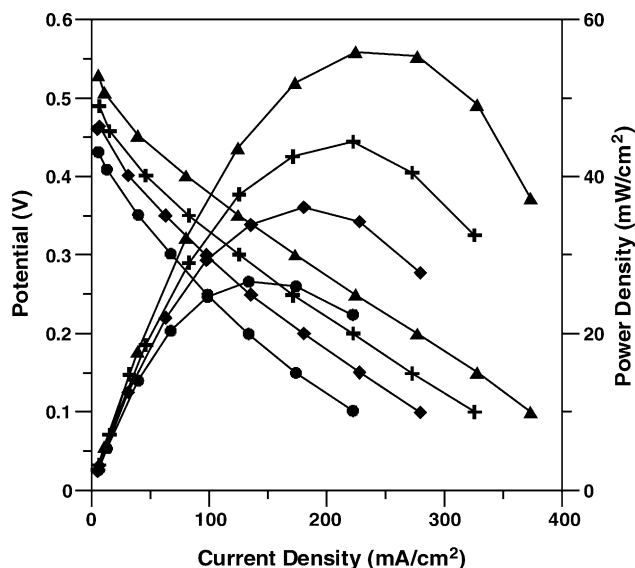


Fig. 6. DMFC single cell test (potential and power density vs. current density) at 70 °C. MEAs prepared from Nafion-112. Concentrations of feed methanol: (▲) 2 M; (+) 3 M; (◆) 4 M; (●) 5 M.

70 °C with an MEA prepared with a Nafion-112 membrane and methanol feed concentrations at anode of 2, 3, 4, and 5 M are given in Fig. 6. The corresponding plots with an MEA prepared from the NP-composite membrane are given in Fig. 7. Plots of $V(i, C_{an})$ versus C_{an} for an MEA made from Nafion-112 membrane and operated at current densities of 100, 150, 200, and 250 mA cm⁻² are presented in Fig. 8. The corresponding data for an MEA made from the NP-composite are shown in Fig. 9. The A_2 parameters of Nafion-112 and NP-composite membranes can be obtained from the slopes of the plots of Figs. 8 and 9, respectively, and are listed in Table 4. The relationship between $V(i, C_{an})$ and i

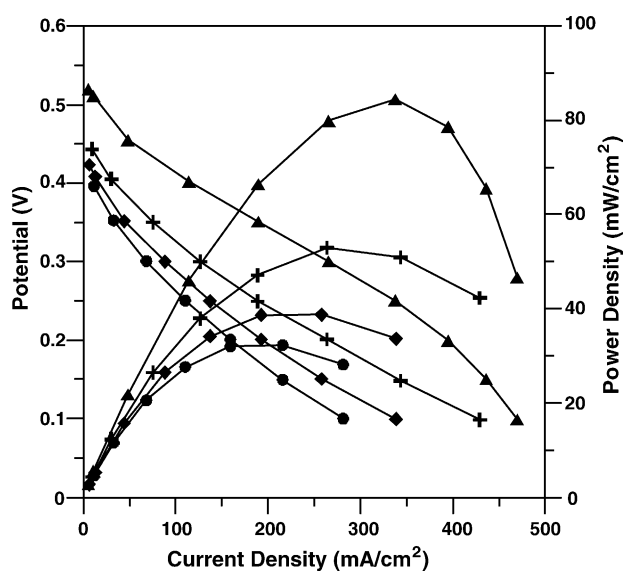


Fig. 7. DMFC single cell test (potential and power density vs. current density) at 70 °C. MEAs prepared from Nafion/PTFE composite membrane. The concentrations of feed methanol: (▲) 2 M; (+) 3 M; (◆) 4 M; (●) 5 M.

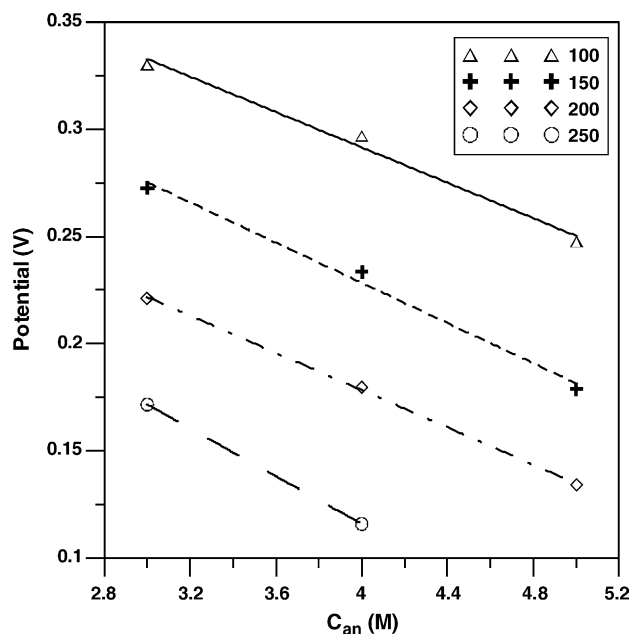


Fig. 8. Plots of $V(i, C_{an})$ vs. C_{an} for MEA made from Nafion-112 membrane and operated at current densities $i = 100$ mA cm⁻² (Δ), 150 mA cm⁻² (+), 200 mA cm⁻² (◇), and 250 mA cm⁻² (○).

for MEAs made from the Nafion-112 membrane and the NP-composite membrane with 350 mA cm⁻² $> i > 100$ mA cm⁻² and methanol feed concentrations at the anode of 2, 3, 4, and 5 M are given in Figs. 10 and 11, respectively. The A_3 parameters of Nafion-112 and NP-composite membranes can be obtained from the slopes of the plots in Figs. 10 and 11, respectively, and are shown in Table 5.

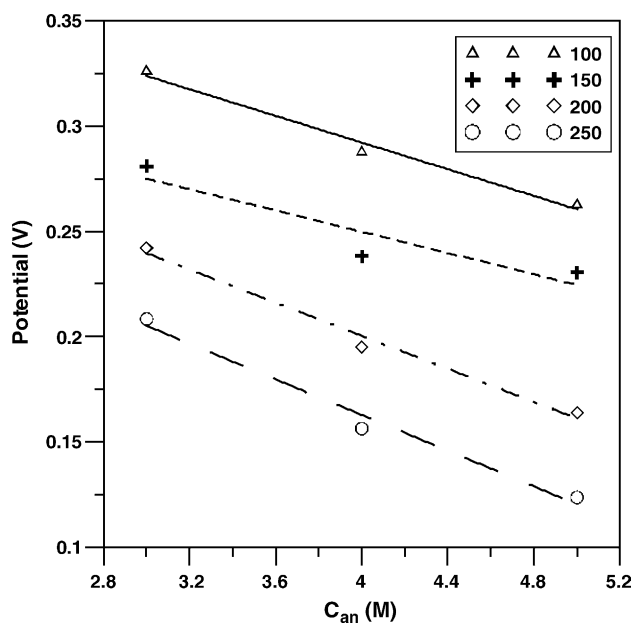


Fig. 9. $V(i, C_{an})$ vs. C_{an} for MEA made from NP-composite membrane and operated at current densities $i = 100$ mA cm⁻² (Δ), 150 mA cm⁻² (+), 200 mA cm⁻² (◇), and 250 mA cm⁻² (○).

Table 4
Parameter A_2 from Eqs. (9) and (10)

Current density (mA cm ⁻²)	A_2 of Nafion-112 V (M_{MeOH}^{-1})	A_2 of NP-composite V (M_{MeOH}^{-1})
100	4.13×10^{-2}	3.16×10^{-2}
150	4.69×10^{-2}	2.52×10^{-2}
200	4.35×10^{-2}	3.92×10^{-2}
250	5.58×10^{-2}	4.24×10^{-2}

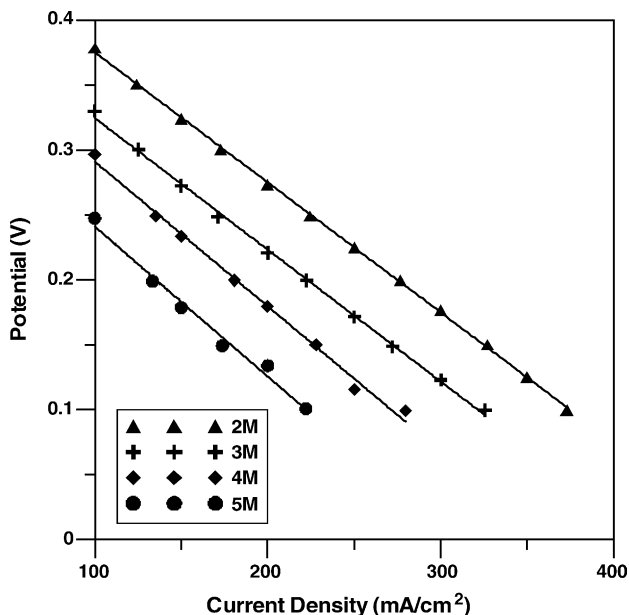


Fig. 10. $V(i, C_{\text{an}})$ vs. i for MEA made from Nafion-112 membrane with $350 \text{ mA cm}^{-2} > i > 100 \text{ mA cm}^{-2}$ and methanol feed concentrations are: 2 M (\blacktriangle), 3 M (+), 4 M (\blacklozenge), and 5 M (\bullet).

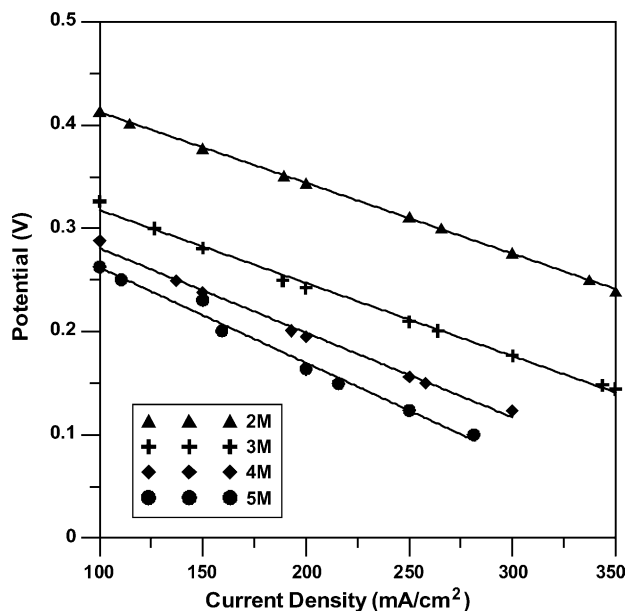


Fig. 11. $V(i, C_{\text{an}})$ vs. i for MEA made from NP-composite membrane with $350 \text{ mA cm}^{-2} > i > 100 \text{ mA cm}^{-2}$ and methanol feed concentrations: 2 M (\blacktriangle), 3 M (+), 4 M (\blacklozenge), and 5 M (\bullet).

Table 5
Parameter A_3 from Eqs. (9) and (11)

[MeOH] (M)	A_3 of Nafion-112 (V cm ² mA ⁻¹)	A_3 of NP-composite (V cm ² mA ⁻¹)
2	1.010×10^{-3}	6.860×10^{-4}
3	1.015×10^{-3}	7.073×10^{-4}
4	1.112×10^{-3}	8.188×10^{-4}
5	1.150×10^{-3}	9.230×10^{-4}

Table 6
Parameter $A_{\text{eos}}(\text{MeOH})$ from Eq. (11)

[MeOH] (M)	$A_{\text{eos}}(\text{MeOH})$ of Nafion-112 (V cm ² mA ⁻¹)	$A_{\text{eos}}(\text{MeOH})$ of NP-composite (V cm ² mA ⁻¹)
2	5.01×10^{-4}	0.820×10^{-4}
3	5.06×10^{-4}	1.03×10^{-4}
4	6.03×10^{-4}	2.15×10^{-4}
5	6.41×10^{-4}	3.19×10^{-4}

A_2 is a parameter that relates overvoltage to methanol diffusion cross-over in the membrane. The values in Table 4 show that the NP-composite membrane has a smaller A_2 value than Nafion-112, which suggests a lower overvoltage caused by methanol diffusion cross-over in the NP-composite membrane than by methanol diffusion cross-over in the Nafion-112 membrane. The A_3 parameters of NP-composite and Nafion-112 membranes are also summarized in Table 5. A_3 is a parameter that relates the overvoltage to a combination of proton resistance, l/σ , and the electro-osmosis of methanol, $A_{\text{eos}}(\text{MeOH})$, in the membrane. $A_{\text{eos}}(\text{MeOH})$ can be obtained by subtracting l/σ (listed in Table 2) from A_3 . The $A_{\text{eos}}(\text{MeOH})$ data for Nafion-112 and NP-composite membranes are given in Table 6 and it is seen that the NP-composite membrane has the smaller value. This indicates that the overvoltage caused by electro-osmosis of methanol is lower in the NP-composite membrane than in the Nafion-112 membrane. The lower A_2 and $A_{\text{eos}}(\text{MeOH})$ values for the NP-composite membrane suggest that introducing porous PTFE into Nafion polymer causes a reduction not only in methanol diffusion cross-over but also in electro-osmosis of methanol cross-over in the membrane.

4. Conclusions

A study has been conducted of the application of Nafion/PTFE composite membranes in DMFCs. It is found that introducing porous PTFE into Nafion polymer causes reductions in both methanol diffusion and methanol electro-osmosis cross-over in the membranes. One way to reduce the methanol cross-over for the unmodified pure Nafion membrane is to increase the membrane thickness. The experimental results reveal that although increasing the membrane thickness causes Nafion-117 (thickness $\sim 175 \mu\text{m}$) to have a lower methanol cross-over rate than the NP-composite membrane (thickness $\sim 20 \mu\text{m}$), it also causes Nafion-117 to have

a higher proton resistance than the NP-composite membrane. The combination of these two factors results in the NP-composite membrane giving a better DMFC performance than Nafion-117. Compared with a low-thickness Nafion-112 membrane (thickness $\sim 50 \mu\text{m}$), the experimental data indicate that the NP-composite membrane has higher proton resistance and lower methanol cross-over values. Further investigations of DMFC performance with various methanol feed concentrations at the anode have revealed that the NP-composite membrane had lower A_2 and $A_{\text{eos}}(\text{MeOH})$ values, which are parameters that relate overvoltage to diffusion and electro-osmosis of methanol cross-over in the membrane, respectively. A combination of the results for proton resistance and $A_{\text{eos}}(\text{MeOH})$ causes the NP-composite membrane to have a lower A_3 value, which is a parameter related to the current-dependent overvoltage, than Nafion-112 membrane, and thus a better DMFC performance.

Acknowledgement

The authors are grateful for financial support from the Energy Council, Ministry of Economy of ROC, through grant 93-D0122.

References

- [1] R.M. Penner, C.R. Martin, *J. Electrochem. Soc.* 132 (1985) 514–515.
- [2] C. Liu, C.R. Martin, *J. Electrochem. Soc.* 137 (1990) 510–517.
- [3] C. Liu, C.R. Martin, *J. Electrochem. Soc.* 137 (1990) 3114–3120.
- [4] M.W. Verbrugge, R.F. Hill, E.W. Schneider, *AIChE J.* 38 (1992) 93–97.
- [5] B. Bahar, A.R. Hobson, J. Kolde, US Patent 5,547,551 (1996).
- [6] K.M. Nouel, P.S. Fedkiw, *Electrochim. Acta* 43 (1998) 2381–2387.
- [7] A.E. Steck, C. Stone, US Patent 5,834,523 (1998).
- [8] F. Liu, B. Yi, D. Xing, J. Yu, H. Zhang, *J. Membr. Sci.* 212 (2003) 213–223.
- [9] E. Szajdzinska-Pietek, S. Schlick, *Langmuir* 10 (1994) 2188–2196.
- [10] R.S. Yeo, *Polymer* 21 (1980) 432–435.
- [11] J. Shim, H.Y. Ha, S.A. Hong, I.H. Oh, *J. Power Sources* 109 (2002) 412–417.
- [12] H.-L. Lin, T.L. Yu, K.-S. Shen, L.-N. Huang, *J. Membr. Sci.* 237 (2004) 1–7.
- [13] T.L. Yu, H.-L. Lin, K.-S. Shen, Y.C. Chang, G.-B. Jung, J.C. Huang, *J. Polym. Res.* 11 (2004) 217–224.
- [14] W.G.F. Grot, Nafion perfluorinated membranes product bulletin, DuPont Polymer Products Department (1986).
- [15] E.A. Grulke, in: J. Brandrup, E.H. Immergut (Eds.), *Polymer Handbook*, 3rd ed., Wiley, New York, 1989 (Chapter VII).
- [16] D.W. Van Krevelen, P.J. Hoftyzer, *Properties of Polymers*, 2nd ed., Elsevier, Amsterdam, 1976 (Chapter 7).
- [17] P. Alderbert, B. Dreyfus, M. Pineri, *Macromolecules* 19 (1986) 2651–2653.
- [18] B. Loppinet, G. Gebel, C.E. Williams, *J. Phys. Chem. B* 101 (1997) 1884–1892.
- [19] S.J. Lee, T.L. Yu, H.-L. Lin, W.H. Liu, C.L. Lai, *Polymer* 25 (2004) 2853–2862.
- [20] J. Larminie, A. Dicks, *Fuel Cell Systems Explained*, Wiley, Chichester, England, 2000 (Chapter 3).
- [21] K. Scott, W. Taama, J. Cruickshank, *J. Power Sources* 65 (1997) 159–171.
- [22] G. Murgia, L. Pisani, A.K. Shukla, K. Scott, *J. Electrochem. Soc.* 150 (9) (2003) 1231–1245.