Short communication

Nano-TiO$_2$-coated polymer electrolyte membranes for direct methanol fuel cells

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Abstract

Composite polymer electrolyte membranes with nano-TiO$_2$ films are fabricated by deposition of titania nanoparticles from a sol solution. Measurements of ion conductivity, methanol permeability and single-cell performance of the modified Nafion membranes are conducted. The TiO$_2$ films adhere well and are crack-free. The protonic conductivity of the composite membranes decreases with increasing titania content, but methanol permeability is reduced. Preliminary tests on a single-cell of a direct methanol fuel cell (DMFC) indicate that a titania-coated membrane with 0.009 mg cm^{-2} content gives the highest cell voltage and maximum power density.
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Keywords: TiO$_2$ film; Composite membrane; Direct methanol fuel cell; Protonic conductivity; Methanol permeability

1. Introduction

The direct methanol fuel cell (DMFC) has potential uses in portable devices and in automobiles, because of its low weight and simple system features. This type of fuel cell does not, however, match the present high performance of hydrogen polymer-electrolyte fuel cells (PEMFCs). One of the main impediments to the practical realization of the DMFC as a power source is cross-over of methanol through the polymer electrolyte membrane (PEM). The methanol permeation reduces the fraction of useful methanol since the methanol passed to the cathode is converted into carbon dioxide. The formation of a mixed potential at the cathode due to the methanol permeation leads to additional losses so that the cell voltage is lowered and the electric power decreases.

Intensive research efforts to decrease the cross-over of methanol are focused mainly on the development of new PEMs [1–5], the development of methanol-tolerant cathode catalysts [6,7], the insertion of catalytically active particles into the PEM [8], the introduction of special coatings with methanol-blocking properties [9,10], surface-modified Nafion membranes using plasma etching and palladium-sputtering and Pd-layered Nafion membranes [11–14]. Adjemian et al. [15] and Jung et al. [16] have modified commercial Nafion 115 membranes by a sol–gel reaction with tetraethoxysilane (TEOS) and have applied them to a H$_2$/O$_2$ fuel cell and a DMFC. It was found that silica incorporated into the membrane decreased the proton conductivity of membrane at low temperature (<100 °C). The nano-silica/Nafion composite membranes prepared by plasma-enhanced chemical vapour deposition (PECVD) exhibited a methanol permeability that was reduced by 40%, but had an ion conductivity that was similar to the unmodified Nafion membranes [17]. A nanocomposite, re-cast, Nafion hybrid membrane that contains titanium oxide as an inorganic filler has been reported [18]. The introduction of the TiO$_2$ particles endows the composite membrane with good mechanical and thermal resistance and improves the water uptake and ion-exchange capacity in comparison with commercial Nafion membranes.

Several physical and chemical techniques such as sputtering, chemical vapour deposition (CVD), light-induced CVD, the sol–gel method and spray pyrolysis have been used to prepare thin films of titania. Among these, the relatively simple sol–gel method is the most widely used since it allows easy control over factors like film thickness and porosity [19]. In the present work, a Nafion membrane is coated with nano-TiO$_2$ by a simple sol–gel procedure. Compared with the commercial Nafion membrane,

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the modified membrane exhibits low methanol permeability and good cell performance for DMFC applications.

2. Experimental

2.1. Preparation of titania nanoparticles sols

Titanium tetraisopropoxide (TTIP) (97%, Aldrich), ethanol (99.5%, Aldrich), water, HCl (37%) and PEG 1000 (average molecular weight 1000, Aldrich) were used as the starting materials. The TTIP (2.5 ml) was added dropwise to a solution of 10 ml ethanol and 0.6 ml HCl at room temperature, and stirred for an hour. Water (10 ml) and 3% (mole percent with respect to Ti isopropoxide) of PEG 1000 were then introduced to the mixture. All additions were accompanied by vigorous stirring at 80 °C to allow the formation of a stable, homogenous and transparent sol solution.

2.2. Preparation of TiO$_2$-layed membranes

The titania sol formed by the procedure described above was deposited on the surface of Nafion^{TM} 112 membranes by spin coating. The membranes coated by titania sol were taken out and dried at 60 °C under UV irradiation for 12 h in air. The light source consisted of 10 photochemical lamps (each of 30 W) which had a maximum output at a wavelength of 300 nm. The experiments were conducted in a Rayonet photochemical reactor that was equipped with the aforementioned lamps.

2.3. Measurement of protonic conductivity and methanol permeability

Protonic conductivity measurements were performed on the membranes in a typical two-electrode cell at various temperatures. An impedance spectroscopic method was used in the frequency range of 10 Hz–100 kHz. A sample of the membrane (1.3 cm in diameter) was placed between two platinum disc electrodes and measured in the potentiostatic mode with ac, amplitude of 10 mV.

Methanol permeability was measured by means of an electrochemical technique [20–22]. A single-stack fuel cell was assembled from a membrane–electrode assembly (MEA), two stainless–steel plates with flow manifolds on the supply sides for fuel and water, and two Teflon gaskets. The cell assembly is described in detail elsewhere [23]. During measurement, nitrogen was introduced into the cathode side at a rate of 500 cm^3 per min and a positive voltage was applied using a power supply. A 1 M C$_2$H$_5$OH solution was pumped into the anode side of the cell at 2 ml per min by means of a micropump. The reaction occurring at the cathode is the oxidation of methanol that crosses through the membrane. When the applied voltage is sufficiently enough to oxidize rapidly all the methanol diffusing to the cathode side, a limiting current is achieved. The diffusion coefficient of methanol can be estimated from the limiting current.

2.4. Measurement of single-cell performance of a DMFC

The MEA for the DMFC test cell was made by hot-pressing the pretreated membrane together with an anode sheet and a cathode sheet. The anode sheet was carbon paper (SGL, Germany) with a carbon-supported Pt and Pt–Ru catalyst layer. The cathode sheet was a carbon paper with a carbon-supported 40 wt.% Pt catalyst layer supplied by E-TEK. The catalyst loadings at the anode and cathode were 3 and 2 mg cm^{-2}, respectively and the effective electrode area was 6 cm^2. The fuel was 2 M C$_2$H$_5$OH delivered at 2 ml per min by a micropump. The oxygen flow was regulated by a flowmeter at 500 cm^3 per min. The operating temperature was 80 °C.

3. Results and discussion

Simple hydrolysis with water was conducted at an ageing temperature of 80 °C. This temperature was chosen as it has been reported [24] to be sufficient for the formation of highly crystalline anatase nanoparticles. A transmission electron micrograph of the TiO$_2$ particles is shown in Fig. 1. It is found that the average particle size is 20 nm, and that the above PEG-aided sol–gel process produces a very stable colloidal solution.

As water is added together with PEG in the hydrolysis mixture, some water molecules will associate with the PEG through hydrogen bonding. This feature will loosen the PEG chains in due course. The free, non-associated water molecules are readily available to TTIP for hydrolysis in the early stages. As hydrolysis exhausts the supply of free water, water will be drawn from the associated water. The sol particles formed by the sol–gel reaction are covered by PEG chains to form particle–PEG complexes [25]. Further physical cross-linking and agglomeration of these particulate complexes leads to an inorganic–polymer composite.
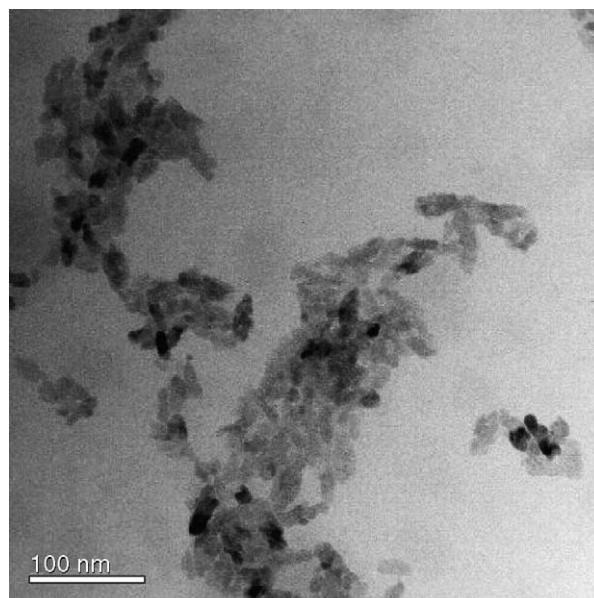

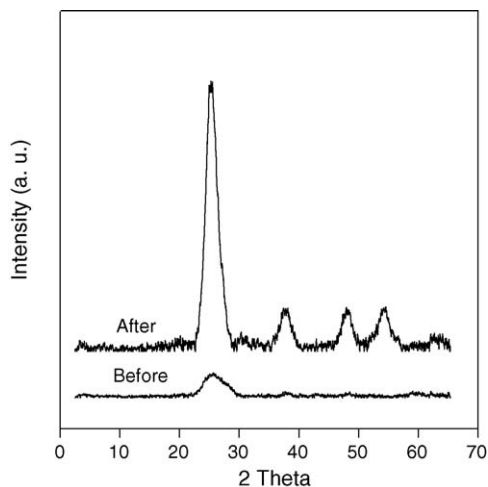Fig. 1. Transmission electron micrograph of titania nanoparticles.

Fig. 2. X-ray diffraction patterns of TiO$_2$ thin films fabricated on Si(100) discs from a colloidal dispersion before and after hydrodynamic ageing treatment.

X-ray diffraction patterns of thin films of TiO$_2$ coated on Si(100) from the colloidal dispersion are presented in Fig. 2. Peaks for the anatase phase and those for the rutile phase are not observed if the TiO$_2$ colloidal dispersion has not been subjected to the hydrodynamic ageing process, This indicates that the the film consists of amorphous TiO$_2$ particles. By contrast, a clear peak at $2\theta = 25.8$ (101) appears if the TiO$_2$ colloidal dispersion is subjected to the ageing treatment. This is the characteristic peak of the anatase phase. All the relatively sharp peaks could be indexed as anatase TiO$_2$, as they basically in agreement with the reported values (JCPDS No. 21–1272).

Thin films of TiO$_2$ were formed on the Nafion membrane by dip coating. The titania content was controlled by the TiO$_2$ concentration in sol and the coated times. The data presented in Fig. 3 show that the titania content increases with the TiO$_2$ concentration in the sol. Initially, the titania content increases slowly. When the TiO$_2$ concentration in the sol is more than 1.5 wt.%, the titania content increases rapidly. This may be caused by an increase in viscosity with titania content. Scanning electron micrographs of TiO$_2$-coated Nafion membranes are presented
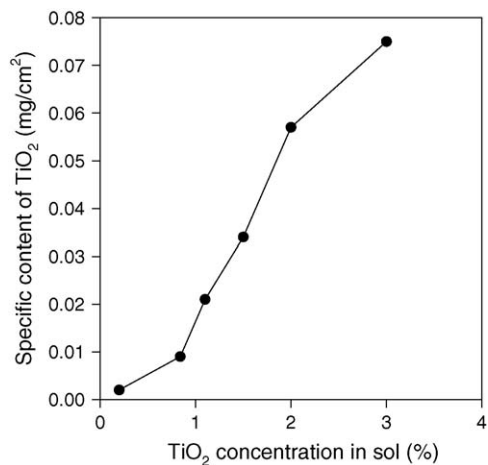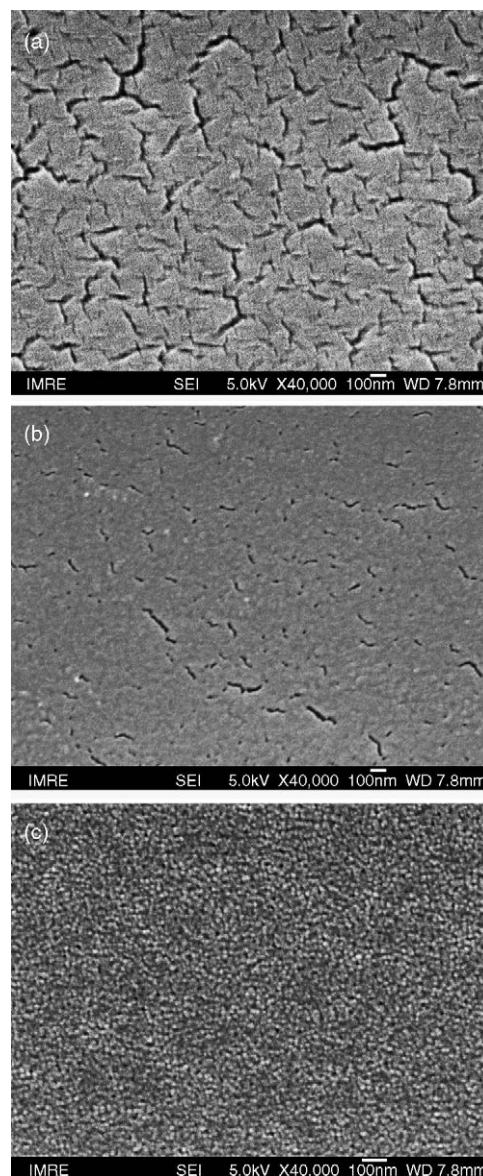

Fig. 4. Scanning electron micrographs of TiO$_2$-coated Nafion membranes for different contents of TiO$_2$: (a) bare Nafion; (b) 0.002 mg cm^{-2}; and (c) 0.021 mg cm^{-2}.

in Fig. 4. The films are constructed from aggregates of nano-sized, single-crystal (from XRD measurements) TiO$_2$ particles. The TiO$_2$ film is dense and appears to be well attached to the membrane, but some cracks in the membrane coated by dilute titania sol are not covered by the TiO$_2$ film (Fig. 4b). The TiO$_2$ film on membranes that are coated by a thick titania sol are very dense and no cracks are present (Fig. 4c).

The protonic conductivity of nano-TiO$_2$-coated Nafion membranes at 25 and 85 °C is shown in Fig. 5. The corresponding values for uncoated Nafion 112 membrane are 0.027 and 0.041 S cm^{-1}, which are similar to those reported by other authors [26,27]. As shown in Fig. 5, the protonic conductivity decreases with increasing titania content. This trend is consistent with that exhibited by Palladium- or silica-modified membranes, as reported by others [20,28]. Arrhenius plots of conductivity
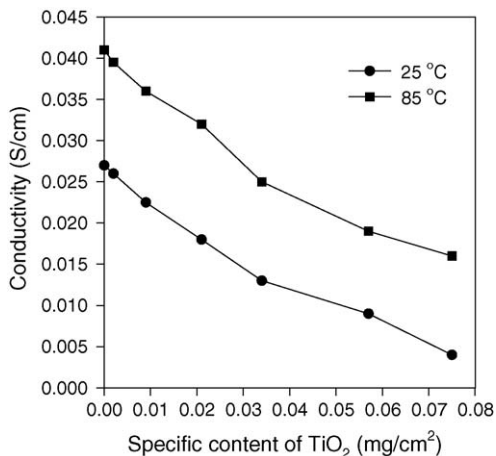

Fig. 3. TiO$_2$ content on surface of membrane as a function of TiO$_2$ concentration in sol.

Fig. 5. Effect of TiO_2 content on surface of membrane on protonic conductivity of TiO_2-coated Nafion membranes at different temperatures.

Fig. 6. Temperature dependence of uncoated and coated Nafion 112 membranes (titania content: $0.009\,mg\,cm^{-2}$) on conductivity.

as a function of temperature for uncoated and coated Nafion 112 (titania content: $0.009\,mg\,cm^{-2}$) are presented in Fig. 6. From the slope of the linear regression, the activation energy (E_a) for proton migration is 6.4 and $7.1\,kJ\,mol^{-1}$ for Nafion 112 and coated Nafion 112 (titania content: $0.009\,mg\,cm^{-2}$), respectively. This means that proton migration in the titania-coated Nafion 112 membrane is more influenced by temperature variation. The value obtained for Nafion 112 is similar to that reported by Silva et al. [26].

The methanol permeability at 25 and $85\,°C$ is shown in Fig. 7 as a function of the TiO_2 content formed on the Nafion 112 membrane. The permeabilities of the coated membranes decrease with increasing TiO_2 content, namely, from 3.2×10^{-6} to $1.7 \times 10^{-6}\,cm^2\,s^{-1}$ at $25\,°C$, and from 12.5×10^{-6} to $4.6 \times 10^{-6}\,cm^2\,s^{-1}$ at $85\,°C$. Thus, rise in temperature leads to a strong increase in permeation by a factor of about 3. The methanol permeability of the unmodified Nafion membrane is 3.6×10^{-6} and $13 \times 10^{-6}\,cm^2\,s^{-1}$ at 25 and $85\,°C$, respectively. This demonstrates that the permeation rate of uncoated membrane is dominated by the temperature dependence of the Nafion matrix. The methanol permeability of a nano-TiO_2–coated mem-
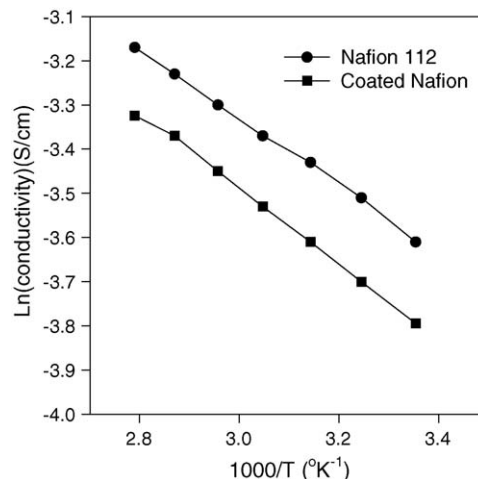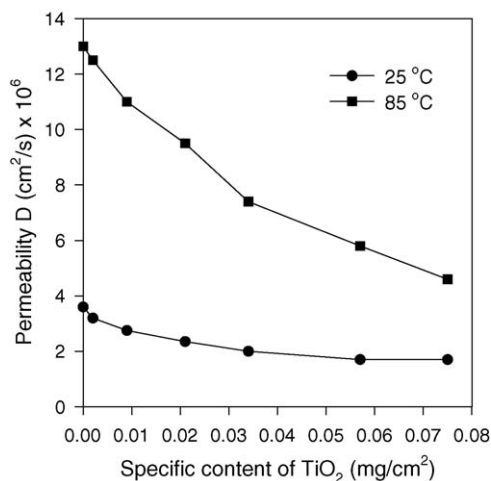

Fig. 7. Effect of TiO_2 content on surface of membrane on methanol permeability through TiO_2-coated Nafion membranes at different temperatures.
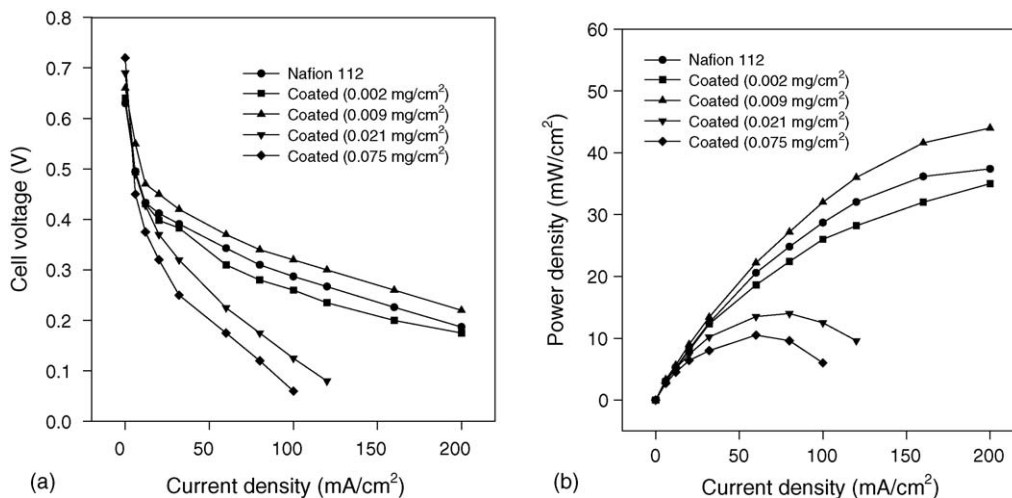

Fig. 8. (a) Current–voltage curves and (b) output power of single DMFC cell with uncoated and coated TiO_2-Nafion membranes at operating temperature of $80\,°C$.

brane with a high titania content ($0.075\,\text{mg cm}^{-2}$) at 25 and
85 °C is reduced by upto about 53 and 65%, respectively, com-
pared with the corresponding values for uncoated Nafion. A
possible reason for this behaviour is that the nanoscale titania
particles cover the cracks in the membrane. A TiO_2 film with
high content in the membrane displays a mesoporous network
texture, which hinders the permeation of methanol. In view of
the methanol permeability data, the poor resistance to methanol
cross-over of the membranes with low titania content may be
due to incomplete coverage of the cracks in the membrane.

The polarization curves obtained for the fuel cells equipped
with uncoated or coated membranes and operated under the
same conditions of oxygen feed at cathode and 2 M methanol
solution at anode are shown in Fig. 8. The cell with a titania-
coated membrane with a content of $0.009\,\text{mg cm}^{-2}$ exhibits
a higher voltage than cells with a Nafion membrane or with
the other coated membranes. The lower ($0.002\,\text{mg cm}^{-2}$) and
higher-titania content ($0.021, 0.075\,\text{mg cm}^{-2}$) membranes give
a lower cell voltage compared with Nafion 112. The Nafion
membrane delivers a maxium power density of $37\,\text{mV cm}^{-2}$ at
a current density of $200\,\text{mA cm}^{-2}$. A maximum power density
of $44\,\text{mW cm}^{-2}$ is obtained from a fuel cell that employs the
titania-coated membrane with a $0.009\,\text{mg cm}^{-2}$ content. The
decrease in voltage of cells using membranes with 0.021 and
$0.075\,\text{mg cm}^{-2}$ titania may be due to an increase in contact resis-
tance. In the presence of a titania film, the problem of methanol
cross-over is ameliorated but the protonic conductivity is
decreased.

4. Conclusions

Nano-TiO_2–Nafion composite membranes have been pre-
pared by a simple sol–gel procedure. Highly crystalline TiO_2
anatase nanoparticles are formed in an ethanol–water solution.
X-ray diffraction analysis shows that the TiO_2 particles have an
appreciable crystallinity that is further refined by ageing treat-
ment at 80 °C. The TiO_2 film on membranes that are coated by
a thick titania sol is very dense and no cracks are formed. The
protonic conductivity of the composite membranes decreases
with increasing titania content, but their methanol permeabil-
ity is also reduced. Preliminary tests on a single cell of a direct
methanol fuel cell indicate that a titania-coated membrane with
$0.009\,\text{mg cm}^{-2}$ content gives the highest cell voltage and the
greatest maximum power density.

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