

Functionalized zeolite A–nafion composite membranes for direct methanol fuel cells

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Received 11 April 2007; received in revised form 13 June 2007; accepted 20 June 2007

Abstract

A series of composite membranes based on zeolite A and Nafion 117 have been fabricated for direct methanol fuel cells. The external surface of zeolite A has been modified to enhance the interface bonding between inorganic zeolite crystals and Nafion ionomer. The modified zeolite samples have been characterised using a combination of thermal analysis and spectroscopic techniques. Methanol permeability of Nafion 117 could be reduced by as much as 86% by incorporating functionalised zeolite NaA crystals into the membrane. The effect of different functionalisation level is discussed.

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Keywords: Zeolite NaA; Nafion; Composite membrane; Functionalisation; FTIR spectroscopy; Thermal analysis; Proton conductivity; Methanol permeability; Direct methanol fuel cell

1. Introduction

Fuel cell technology has been rapidly advancing over the recent years. In particular, direct methanol fuel cells (DMFC) have demonstrated a good deal of potential for practical applications. In terms of performance, it is essential for the DMFC membrane to have a high proton conductivity and a low permeability to methanol. Nafion, a membrane material manufactured by DuPont, is still the most widely used for DMFC. Although Nafion has a high proton conductivity, it suffers from severe methanol crossover, which restricts the performance of the fuel cell. Indeed, methanol can easily diffuse through Nafion under the concentration gradient which occurs in an operating fuel cell. In addition, protonated methanol or protons solvated by methanol can be transported through the membrane by means of electro-osmotic drag [1]. Methanol crossover leads to a significant decrease in both the fuel efficiency of the cell and in the open circuit voltage due to the presence of the “mixed potential” caused by the methanol oxidation at the cathode. In order to overcome these problems, a wide range of composite membranes based on

Nafion or other ion-conducting polymers have been prepared and evaluated. Materials which have been combined with the ion conducting polymer include calcium phosphate [2], montmorillonite (MMT) [3,4], chabazite and clinoptilolite [5] and TiO₂ nano-powder [6]. These materials show a range of useful properties, however, few authors have studied the influence of surface functionalisation of the particles, or the effect of particle size.

In this study Nafion–zeolite NaA composite membranes have been prepared in order to suppress methanol crossover. Zeolite NaA has been selected for this study since its low Si/Al ratio provides a hydrophilic (organophobic) character that allows for preferential adsorption of water, and therefore, preferential proton transfer, whereas methanol is excluded from the zeolite channels. Zeolite NaA membranes have been used for the separation of alcohols including methanol from water [7] suggesting that this zeolite would be very suitable for the preparation of composite membranes.

However, zeolite NaA is known to be unstable in strong mineral acids, and it is not known whether the acidic conditions in the hydrated Nafion will lead to significant breakdown of the zeolite crystals. In addition, poor interfacial compatibility between zeolite crystals and glassy polymer matrix has been

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reported by a number of authors [8–12] who attributed this effect to the presence of pinholes between the zeolite particles and Nafion. The size of these opening is in the nanometer range [13], which facilitates the methanol transport. In this work, we attempt to overcome this problem by functionalising the surface of the zeolite to make it more compatible with the polymer matrix. This has been achieved by grafting organic chains onto the inorganic surface using silane-based coupling agents such as 3-aminopropyltrimethoxysilane (APTS) [14]. The functionalised zeolite NaA has been characterised in detail and the effect of functionalizing the zeolite surface on the properties of a Nafion–zeolite composite membrane has been evaluated. In addition, this study aims to demonstrate that the degree of the zeolite modification can be quantified using a combination of thermal analysis and infrared spectroscopy. Indeed, it is important to establish the most favourable degree of modification in order to achieve good crosslinking between the polymer and the zeolite in combination with the optimum properties of the zeolite surface to minimise the membrane methanol permeability and maximise its proton conductivity.

2. Experimental

2.1. Chemical modification method

In order to functionalise the surface of the zeolite with APTS a procedure, based on the method reported by Plueddemann and others [14,15], was developed. Two parent samples of zeolite NaA were utilised in this work, NaA zeolite with a micron-range particle size of 2–3 μm (NaA-M) and zeolite NaA with a submicron particle size of ~ 300 nm (NaA-S). In a typical preparation, a mixture of 1.0 g zeolite NaA powder, 1 ml of APTS and 30 ml of dichloromethane (DCM) was stirred for 24 h at room temperature. After the reaction, the excess reagent was eliminated by repeated centrifugation (6000 rpm), decanting and re-dispersion by ultrasonication in ethanol. The recovered solid was dried at 100 $^{\circ}\text{C}$ for 24 h (the prepared materials were denoted as NaA-F1M or NaA-F1S). In order to investigate the effect of the degree of functionalisation, the procedure was repeated for some samples (these materials were denoted as NaA-F2M or NaA-F2S). The obtained white APTS-functionalised zeolite powders were used for the composite membrane fabrication.

2.2. Characterisation

X-ray diffraction (XRD) patterns of modified and unmodified zeolite crystals were obtained to monitor possible changes in crystallinity during the functionalisation process. For the infrared characterisation, self-supporting zeolite discs (~ 10 mg, 13-mm diameter) were placed into a Pyrex vacuum cell fitted with BaF₂ windows. The cell was installed inside the sample compartment of an FTIR spectrometer Nicolet Protégé 460. The cell was attached to a greaseless vacuum system and the cell temperature was externally controlled between 30 and 500 $^{\circ}\text{C}$. Following the sample disc activation at 30 $^{\circ}\text{C}$ and 10^{-5} Torr for 1 h, the infrared spectrum of the zeolite was collected. The cell

temperature was then steadily increased to the desired temperature (the temperature ramp was 10 $^{\circ}\text{C}/\text{min}$) and the stepwise desorption of various species was monitored by IR spectroscopy to the maximum temperature of 500 $^{\circ}\text{C}$, averaging 200 scans at an instrument resolution of 2 cm^{-1} and a spectral range of 4000–1300 cm^{-1} . Infrared spectra were analysed (including integration, subtraction and determination of peak positions) using specialised Nicolet software, Omnic 4.1.

Thermal analysis of the samples (both thermal gravimetric analysis, TGA, and differential scanning calorimetry, DSC) was undertaken in flowing nitrogen or air with a temperature ramp of 10 $^{\circ}\text{C}/\text{min}$ to the maximum of 800 $^{\circ}\text{C}$ using a STA-1500 Rheometric Scientific instrument.

2.3. Membrane preparation

Composite membranes were produced using a solution casting method. Nafion was purchased from Aldrich as a 5 wt.% solution in a mixture of low molecular weight alcohols and water. Methanol (99.99%), ethanol (99.7%) and *N,N*-dimethylformamide (DMF) (+99%) were used without further purification. Deionized water was used for the preparation of all aqueous solutions.

Composite mixtures were prepared by combining five volumes of the Nafion solution, five volumes of methanol/ethanol mixture (15 vol.% methanol solution in ethanol), three volumes of DMF [5], and the desired amount of zeolite NaA powder. Two different zeolite powders with particle sizes of 2–3 μm (Valfor[®] CP100, PQ corporation) and ~ 300 nm (Nanoscape, Germany) were evaluated. The mixture was dispersed by mechanical stirring and ultrasonication for 1–3 h, depending on the concentration of zeolite NaA.

The milky mixture was poured into a glass Petri dish and heated in a vacuum oven at 80 $^{\circ}\text{C}$ for 20 h and 150 $^{\circ}\text{C}$ for 4 h in order to evaporate the solvents. After cooling, the membrane was gently separated from the dish. The thickness of the membrane was controlled by the amount of the composite mixture used.

2.4. Proton conductivity measurements

The proton conductivity of the membranes was determined by AC impedance using a two-electrode measuring cell. This method is suitable for measuring the conductivity across the membrane, as appropriate for fuel cell applications [16]. The proton conductivity of the membranes was measured in a boric acid solution at pH 4.7 at a constant temperature of 35 $^{\circ}\text{C}$. Platinum electrodes (2 mm diameter) were placed on each side of the membrane and a pressure of 1.9 N cm^{-2} was applied to ensure a good contact between the electrodes and the membrane.

Prior to the testing, each membrane was boiled in 5% H₂O₂ solution for 1 h and in boric acid solution (pH=4.7) for 1 h, and then rinsed in deionized water, followed by equilibration for 48 h at 35 $^{\circ}\text{C}$. The AC impedance spectrum of membranes was obtained using an Autolab PGSTAT30 Frequency Response Analyzer (FRA) at three different locations on each membrane. Measurements were made with a perturbation voltage of 5 mV in the frequency range from 100 Hz to 1 MHz at 35 $^{\circ}\text{C}$. The resistance value was determined from the high frequency intercept of the

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