클레이 나노복합재 자기조립 다층박막에 의한 Nafion 전해질 박막의 메탄올 투과 감소

Reduced Methanol Crossover of Nafion by Self-Assembled Clay-Nanocomposite Multilayers

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1. Introduction

The liquid feed direct methanol fuel cell (DMFC) is one of the promising candidates for the high energy density portable power source. For the practical DMFCs development of efficient fuel cell membranes is one of the major topics of current research [1-3]. Nafion, a perfluorosulfonate membrane developed by DuPont, has been commonly used for the membranes owing to good chemical and thermal resistance and ionic conductivity. But, Nafion membrane is subject to serious methanol crossover. The transported methanol through the membrane is oxidized by oxygen at the cathode leading to a significant decrease in cell potential and fuel efficiency.

In this work, we modified the Nafion membrane by depositing a very thin clay-nanocomposite multilayer on the membranes, in order to reduce the methanol crossover. The nanosheets of clay (saponite) were alternately deposited with the cationic polyelectrolyte (substituted ionic polyacetylenes) on the Nafion films by means of the layer-by-layer assembly [4].

2. Experimental

Nafion membrane (Nafion 117, 178 μm thick) was purchased from Aldrich. Poly (*N*-octadodecyl-2-ethynylpyridinium bromide) (PEPy-C18) with a long alkyl chain attached to the quaternized nitrogen in the pyridine ring was prepared by spontaneous polymerization of 2-ethynylpyridine according to the literature method [5]. Saponite was provided by Source Clay Minerals Repository, University of Missouri. The clay was exfoliated as described in the literature [6].

Substituted ionic polyacetylenes were dissolved in methanol (typically 0.1 wt%) and were used for build-up of polycation layers. The aqueous suspension of exfoliated saponite particles was used for the polyanion build-up. The literature procedure of layer-by-layer deposition was followed to build the multilayer films on the Nafion membrane [7].

Two-compartment glass cell (source and receiving compartment) separated by the membrane was used to test the methanol permeability. The methanol concentration transported through the membranes was determined by sampling a small amount of the solution from the receiving compartment.

Conductivity of the membrane, which was clamped in a conventional two probe cell, was measured by impedance analyzer (4194A, Hewlett-Packard Co.).

3. Results and Discussion

Multilayers of clay nanosheets and ionic polyacetylene PEPy-C18 were deposited onto Nafion membranes by layer-by-layer assembly method. UV/Vis absorption spectroscopy was used to monitor the consecutive build-up of the oppositely charged species. The absorption pattern due to polycation layers of PEPy-C18 was characterized by two absorption peaks at 471 and 502 nm (Figure 1). The inset in Figure 1 showed that the intensity of the absorption increased linearly as a function of deposition cycles. This indicated that the sequential assembly between the saponite nanosheets and polyacetylenes produced almost the same thickness of bilayer at the each deposition cycles.

TEM image of the cross-section of the multilayer films clearly showed that the clay sheet layers were lying parallel to the film surface and were regularly deposited, leading to an ordered nanocomposite multilayer. Thickness of the multilayer films was measured by ellipsometer. The 30-bilayer film of PEPy-18 and saponite deposited on a silicon wafer was estimated to be 156 nm thick. This means that the thickness of each bilayer is 5.2 nm in average.

Methanol permeability of the Nafion membranes deposited on its both side with 10-bilayer of clay/PEPy-C18 nanocomposites was determined using the permeation cell. The methanol concentration in the receiving compartment of the permeation cell increased linearly with time as shown in Figure 2. The methanol permeability of the membranes was calculated from the slope in the figure. The methanol permeability of the pristine Nafion membrane was estimated to be 1.91×10^{-6} cm^2/s, which was similar with the literatures value [8]. Only 10 bilayer nanocomposite films (ca. 0.1 μm thick) deposited on Nafion reduced the methanol permeability of the Nafion membrane (178 μm thick) to about a half and the determined value was 7.58×10^{-7} cm^2/s.

The in-plane proton conductivity of the membrane was measured by a two probe cell. The proton conductivity of Nafion membrane modified by the 10 bilayer nanocomposite was measured to be 0.124 S/cm, which was similar with the pristine Nafion (0.122 S/cm).

In conclusion, only 10 bilayer nanocomposite films with a thickness of 0.1 μm reduced the methanol permeability of the Nafion membrane to less than a half without deterioration of its in-plane proton conductivity.

4. References

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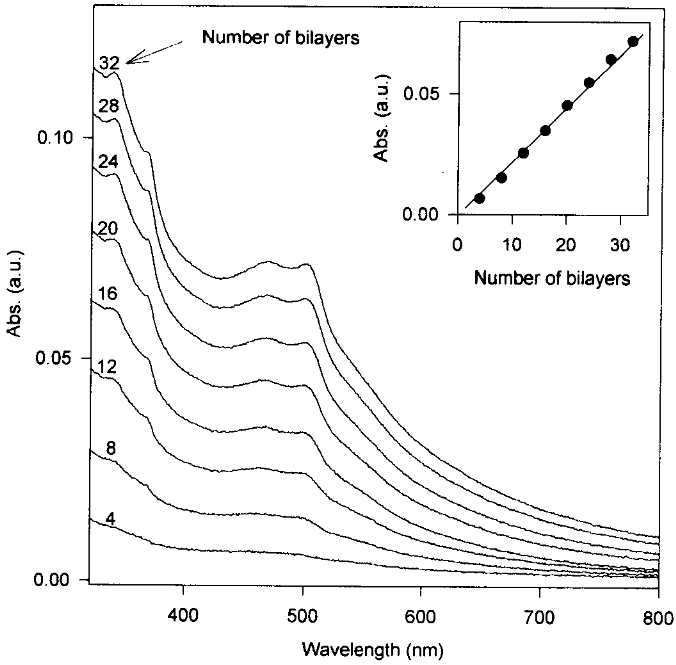

Figure 1. The absorption spectra of multilayered nanocomposite films of exfoliated clay nanosheets and ionic polyacetylenes as a function of the number of bilayers.

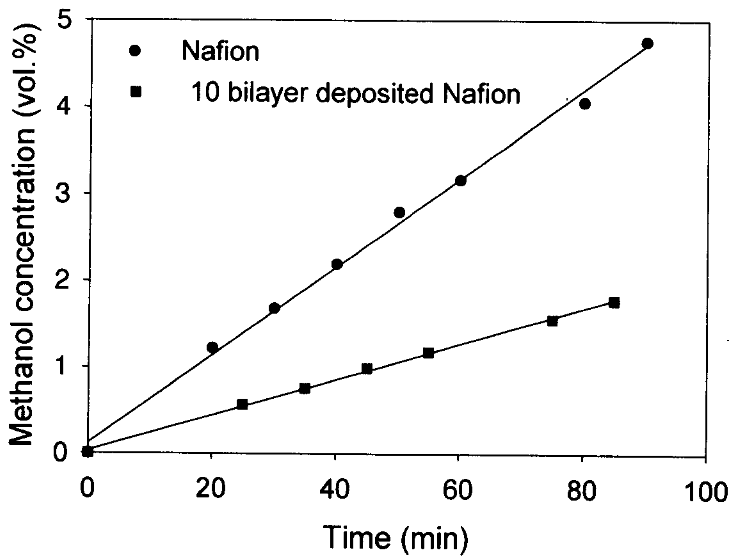

Figure 2. The methanol concentration in the receiving compartment of the permeation cell using a pristine Nafion and 10-bilayer clay-nanocomposite deposited Nafion as a membrane.