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Note

A NOVEL KIND OF PROTON EXCHANGE MEMBRANE: CHARACTERS AND PROTON TRANSPORT MECHANISM

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Abstract A novel proton exchange membrane (PEM) was designed and prepared from a polymer containing calix[4]arene as the functional unit to transport proton. The proton-conductivity of this membrane is about the same order of magnitude as that of Nafion® 112 membrane. It is of interest to note that very different from most of the currently known PEMs, this membrane can transport proton without the help of water or other solvents. It is deduced that the protons are transported via an ion tunneling model. This opens up a new avenue for a new type of solvent-free PEMs to be applied in the development of new H_2/O_2 fuel cells.

Keywords: Proton exchange membrane; Calix[4]arene; Proton transport mechanism.

INTRODUCTION

Recently, proton exchange membrane fuel cells (PEMFCs) are attracting considerable interest as the most promising power sources in electrochemistry[1–3] and energy-source technology[4, 5]. The proton exchange membranes (PEMs) are the key component of PEMFCs, their common typical example is Nafion® membranes of DuPont Company, a type of poly(perfluorosulfonic acid) (PSFA) membranes, used in H_2/O_2 fuel cells normally. The functional groups for proton exchange in the PSFA are the sulfonic groups (—SO_3H) bonding on the backbone of the fluorocarbon polymer.

The protonic conductivities of Nafion® membranes will decrease dramatically when they dehydrate, or even become insulators when the relative humidity is lower than 15%[6]. Moreover, some other technical problems would be brought to the fuel cell system by water, for example, the operating temperature of fuel cell is limited at about 353 K for keeping water content in Nafion® membranes[7]. In this paper, a novel proton exchange membrane was designed and prepared from a new polymer containing calix[4]arene as the functional unit to transport proton (Scheme 1). The isotopic tracing (deuteroxide) method approved that this calixarene based membrane can transport proton without the help of water and no water was transported during the proton transportation. A model of proton tunnel is used to discuss and interpret the special proton transport mechanism of this novel calixarene based membrane.

EXPERIMENTAL

Materials and Reagents

All chemicals and solvents used were available from market. The deuteroxide (purity > 99.8%) was purchased from Beijing No. 4 Chemical Industry Company. Nafion® 112 membrane was purchased from DuPont and was pretreated according to the literature[8] before use.

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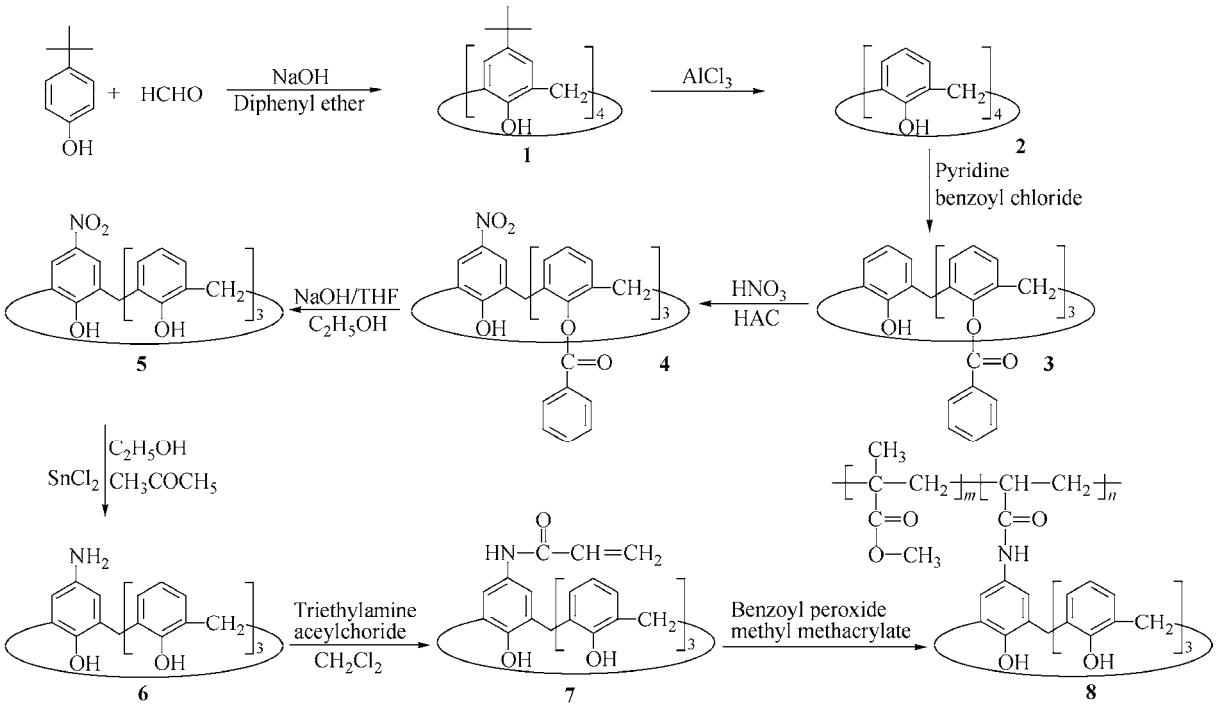

Scheme 1 Synthesis routine of the copolymer

Preparation of Calix[4]arene Containing Polymeric Membranes

The copolymer material (copolymer **8**) containing calix[4]arene derivative (compound **7**) was synthesized by the method reported in the literature[9]. The calix[4]arene derivative (**7**) content in the copolymer (**8**) was about 5 wt%). Tested by gel permeation chromatography, the molecular weight (M_n) of the target copolymer was about 2.9×10^4 and the polydispersity index (PDI) was about 11.

The solution of the copolymer (**8**) in chloroform (about 10 wt%) was poured onto an aluminum mold. A film was formed after chloroform evaporated completely at ambient temperature, and the target membrane was obtained. It was named as TJ-1 membrane. In order to compare with TJ-1 membrane, a membrane made of poly(methyl methacrylate) (PMMA), and another membrane made from calix[4]arene derivative (about 5 wt%) mixed in poly(methyl methacrylate) (PMMA + C) were prepared.

Measurements of Structure and Properties of TJ-1 Membrane

For TJ-1 membrane, the SEM was observed by using a Stereoscan 360 SEM. The horizontal surface was observed with a Benyuan 4000 AFM. The TG and DTG were measured by using a NETZSCH STA 449 A thermal analyzer from 323 K to 873 K.

The XRD of the calix[4]arene derivative (**7**), TJ-1 membrane, PMMA+C membrane and PMMA membrane were measured respectively by using a Bruker D8 XRD (40 mA-40 kV, Cu, λ = 0.154 nm).

Measurements of the Ability to Transport Proton of TJ-1 Membrane

AC impedance method used to measure protonic conductivity of PEMs was described in many reported works[10]. However, TJ-1 membrane was a hydrophobic membrane, it could not hold water inner and there were no mobilizable protons. So the common AC impedance method is not suitable to measure the protonic conductivity of TJ-1 membrane. In this paper the used measurement device (Fig. 1), consisted of two symmetric "L"-type compartments, looked like a "U"-tube. The membrane was fixed in middle of the device to separate the two parts, the effective transporting area of the membrane was about 20 cm^2. In experiments, each cell beside the membranes were filled with 250 mL of hydrochloric acid (pH = 3.01) as source phase or NaOH solution (pH = 10.96) as receiving phase individually. Both the source phase and the receiving phase were stirred and

protected by the nitrogen atmosphere to avoid the influence of carbon dioxide. The experiment temperature was controlled at (293 ± 0.5) K. The pH changes of each phase after transport were recorded by pH-meter (Cyberscan 510). A time span of 12 h was set for each single measurement. All the reported results here were the average results of at least three parallel experiments. Then the Nafion® 112 membrane was used instead of TJ-1 membrane to test. The results were then analyzed and compared.

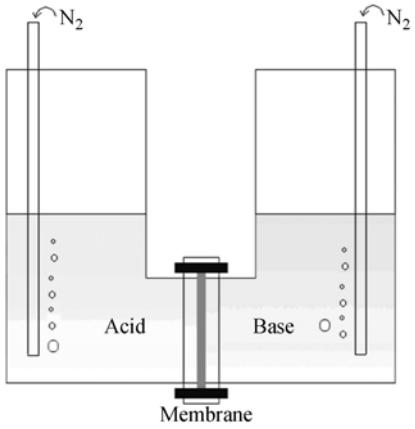

Fig. 1 Proton conductivity measurement device

Confirmation of the Proton Transporting Characteristic of TJ-1 Membrane

It was reported that the IR spectrum of deuteroxide (D_2O) had a characteristic peak about 2540 cm^{-1} while water (H_2O) has no absorption peak at the same wave number[11]. Thus in this experiment the deuteroxide was selected as the tracer of water, and FT-IR spectrum was used to detect D_2O to show the transport movement of water across membrane during proton transport. According to our experimental results, the deuteroxide could be detected by FT-IR spectrum even when the volume percentage of D_2O in solution was about 1%. Therefore, 100 mL deuteroxide and 100mL water were added in the source phase while in the receiving phase was still 200 mL water (no D_2O). The IR-spectra of the receiving phase solution then were detected respectively before and after proton transport and the peak at about 2540 cm^{-1} of wave number was used to confirm whether water transport happened while proton transported.

RESULTS AND DISCUSSION

SEM, AFM, TG/DTG and XRD

The SEM image of TJ-1 membrane showed that was even and compact, and its thickness was approximately 30 μm. The AFM image showed no penetrable hole in TJ-1 membrane. The TG showed no weight-loss when the temperature was under 373 K. It indicated the TJ-1 membrane was thermo stable under 373 K.

Both the patterns of PMMA+C membrane and PMMA membrane in Fig. 2 have a broad XRD peak at 10°–20° angle. Only the XRD of TJ-1 membrane has a sharp and strong peak at about 32° in addition to the broad peak at 10°–20° angle, which reveals that TJ-1 membrane contains a suitable range of ordered structure. Calculated by Bragg Equation, the interplanar spacing in the TJ-1 membrane was about 0.145 nm. Whereas this distance is longer than the O—H covalent bond (about 0.092 nm), it is near the hydrogen bond (about 0.163 nm) in dimeric water. It was believed that the ordered molecular structure in TJ-1 membrane was constructed by hydrogen bonds. In addition, since the diameter of H_2O molecules was about 2.6 nm, which is larger than the inter-planar spacing in TJ-1 membrane, this makes it difficult for the water molecule to pass through the TJ-1 membrane.

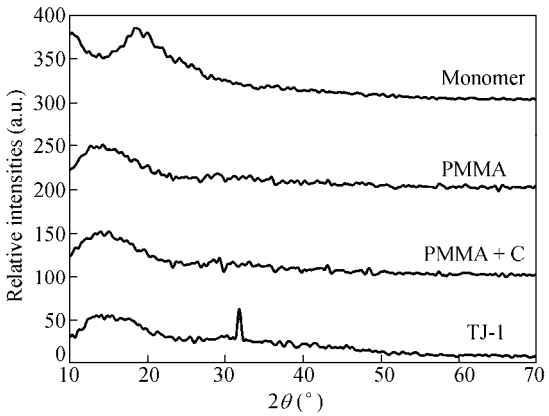

Fig. 2 XRD spectra of TJ-1 membrane

Proton Transport Experiments

The results of TJ-1 membrane's and Nafion® 112 membrane's proton transport experiments are listed in Table 1, pH_{a0} is the pH value of source phase before transport, pH_{b0} is the pH value of receiving phase before transport, pH_{at} and pH_{bt} are the pH values of source phase and receiving phase after transport. Tran% is the rate of the transported proton concentration across through the membranes and the initial proton concentration of source phase. The results in Table.1 indicated that TJ-1 membrane had obvious ability to transport proton, that is about the same order of magnitude as the Nafion® 112 membrane, though the proton transport ability of TJ-1 membrane was lower than the Nafion® 112 membranes', as this designed experimental condition was not the best for TJ-1 membrane.

Table 1. Results of proton transport

	pH_{a0}	pH_{at}	pH_{b0}	pH_{bt}	Tran%
TJ-1	3.01	3.28	10.96	10.55	57.34%
Nafion®112	3.01	3.95	10.96	4.32	98.22%

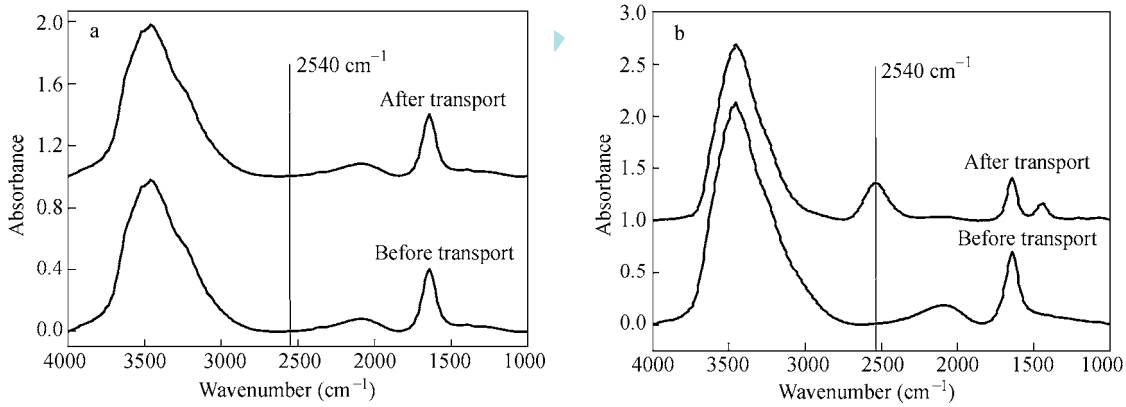

Fig. 3 The receiving phase solution's IR absorption of TJ-1 (a) and Nafion® 112 membrane (b)

The results of IR-tracing test showed the difference in proton transport between TJ-1 membrane and Nafion® 112 membrane (Fig. 3). For TJ-1 membrane, no absorption peak at 2540 cm^{-1} was detected out in the IR spectra of their receiving phase solution after proton transport. It indicated that water in the source phase was not transported through TJ-1 membrane while proton was transported through the membrane. While for Nafion® 112 membrane, an obvious absorption peak at 2540 cm^{-1} was detected out in the receiving phase solution after

proton transport; it indicated that water in the source phase was transported through Nafion® 112 membrane when proton was transported through the membrane. It showed that no water participated in the proton transport process in TJ-1 membrane, which is totally different from Nafion® 112 membrane.

Discussion on the Characters and Proton Transport Mechanism of TJ-1 Membrane

Calix[4]arene, the cyclic oligomer with a hydrophobic cavity composed of benzene rings, is an excellent receptor. It has typical supramolecular abilities to recognize and transport proton or metal ions[12, 13]. The TJ-1 membrane was obtained by introducing calix[4]arene into the main chain of polymer, which is a kind of hydrophobic membrane, water is difficult to enter into its micro pores to form hydrophilic microenvironment around the calix[4]arene unit. Furthermore, the acidity of phenol group of calix[4]arene is much weaker than $-SO_3H$, $-H_2PO_4$ and $-COOH$. The experiments also proved that TJ-1 membrane had no need of water for proton transport. Based on the principle of ion channel in supramolecular chemistry[14], a model of H^+ (proton) channel is proposed in this paper to explain the proton transporting mechanism of TJ-1 membrane (Fig. 4).

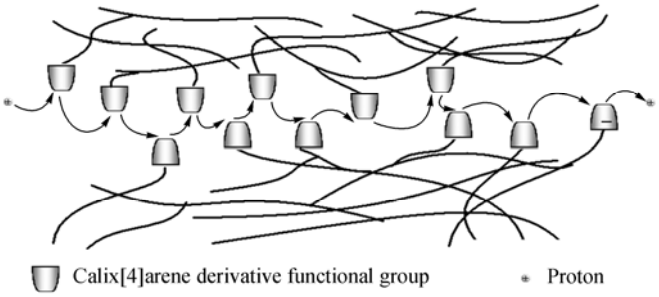

Fig. 4 Illustration of the proton transport mechanism of TJ-1 membrane

As illustrated by Fig. 4, the polymer chains twisted together to form a lot of micro vacancy or interval, which joined up each other to form some inner path or pipe inside TJ-1 membrane. While the calixarene units bonded in the polymer chain are as the “grip” or “stair step” in the path, which might help proton to pass through the inner path conveniently and complete proton transport across through TJ-1 membrane. It was calixarene that made the inner micro vacancy or interval inside TJ-1 membrane into a kind of special tunnel to transport proton, which was called “proton channel”.

Although every calixarene unit contained four phenol groups in its molecule, their acidity was much weaker than the common organic acidic groups such as sulfonic group or carboxyl group etc. But calixarene unit was easy to form intermolecular hydrogen bonds between their phenol groups, which could stabilize the negative ion or radical group. The hydrogen atom on the phenol groups of calixarene unit would depart from the neutral molecule when excited and leave a negative oxygen ion (Ar—O—) on the polymer chain. In common, this type of ion-pair was unstable and would annihilate at once. But in calix[4]arene, the negative oxygen ion would be stable because of conjugation of the intermolecular hydrogen bonds. Thus the stabilized negative oxygen ion would play the role like a vacant site to draw proton. These “proton-vacant sites” distributed on the polymer chain of TJ-1 membrane and could be looked on as a “hole” to accept proton. When proton near the “hole” was drawn to it and combined with it, a new “hole” was formed and left on the polymer. Continuously in this way, the proton would hop from one “hole” to another “hole” to complete proton transport, and a special proton channel was so formed in TJ-1 membrane. Moreover, because of the supramolecular recognition of this proton channel, only proton could be transported while water molecule could not be transported. That is why TJ-1 membrane is distinguished from Nafion® membranes and other reported PEMs essentially.

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