SHORT COMMUNICATION

Surface-charged polyacrylonitrile/poly(vinyl alcohol) (PAN/PVA) colloids used to prepare proton conducting materials

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Abstract: Proton exchange membranes exhibiting a well-organized structure were successfully prepared by a novel self-assembling technique using surface-charged latex nanoparticles as building blocks. The nanoparticles were synthesized in water by free-radical copolymerization. Free-standing membranes were obtained by casting the polymer emulsions followed by a cross-linking reaction. The acquired membrane exhibited a high proton conductivity of 0.04 S cm^{-1} with an ion exchange capacity (*IEC*) as low as 0.48 mmol g^{-1}. The enhanced proton conductivity is thought to be derived from the formation of a co-continuous ionic network for ion channels by the closely packed surface-charged latex nanoparticles, facilitating proton transportation in the membranes.

Keywords: polyacrylonitrile; poly(vinyl alcohol); proton conductivity; ion exchange capacity; fuel cell.

INTRODUCTION

Proton-conducting polymer electrolyte membranes (PEM) are one of the most critical components for polymer electrolyte membrane fuel cells (PEMFCs) and direct methanol fuel cells (DMFCs). Most of the PEMs are ionomers consisting of a hydrophobic backbone with pendant cation exchange sites, such as –SO$_3^-$. The ionic aggregation and the nanoscale phase separation of ionic and nonionic components resulted in the formation of bi-continuous structures for membranes exhibiting proton conductivity.[1,2] However, the long-range patterned organization of hydrophilic clusters into a hydrophobic phase does not exist in PEMs,[3] which suggests that a low content of clusters does not induce the formation of percolation paths. Increasing the content of cation exchange site faci -

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litates the transformation from insulator to ion conductor (percolation threshold) for the polymers, which is ascribed to the formation of interconnected ionic domains. However, a continuous increment in the content of ionic sites may result in a deterioration of mechanical properties of the membranes because of the high hydrophilic property of the polymer. Therefore, it is essential to reasonably control the amount of ionic group in order to avoid a sharp decrease of the proton conductivity or a deterioration of the mechanical properties of the membranes.

Although there are many archetypal structures to choose from in order to design a polymer with a particular molecular structure which would promote phase separation, the synthetic pathways available are not quite so rich.[4] Furthermore, membranes casting from ionomer solutions usually did not lead to a precisely controlled structure (Fig. 1) to improve proton transport by optimizing the connectivity of the ionic domains.
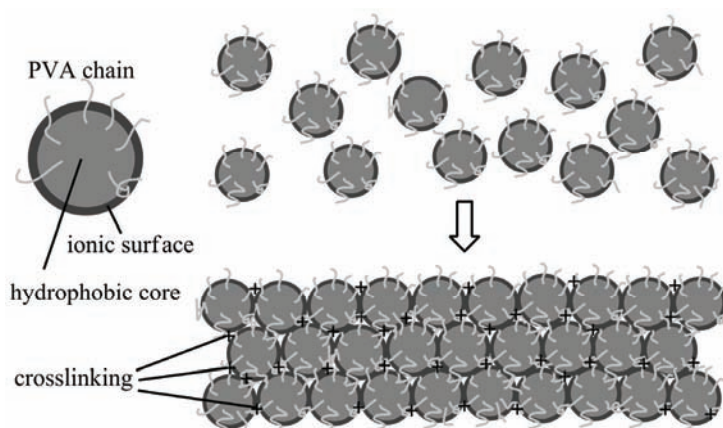

Fig. 1. Schematic diagram showing the surface-charged latex nanoparticles and membrane formation *via* the self-assembly of the nanoparticles.

Self-assembling of latex nanoparticles were applied for the preparation of templating semiconductors or conducting polymers. The polystyrene particles used to template doped π-conjugated polymers were found to decrease the percolation threshold for electrical conductivity.[5] Surface-charged latex nanoparticles were used to build blocks for PEMs exhibiting a linear relationship between conductivity and ion exchange capacity (*IEC*) values even at low *IEC* values, probably due to the disappearance or shifting to very low of percolation thresholds for membranes with bi-continuous structures.[6,7] In this work, the efforts were mainly focused on the preparation and characterization of novel proton exchange membranes, increasing the co-continuous ionic network for ion channels and facilitating proton transportation. A novel method to prepare proton--conducting membranes *via* surface-charged polymer colloids self-assembling te-

chniques, followed by a cross-linking reaction, is demonstrated. A schematic diagram showing the surface-charged late x nanoparticl es and the mem brane formation is shown in Fi g. 1. The surface- charged latex nanoparticles were packed and linked together as bui lding blocks medium for proton conductive membranes. In this way, a proton conductive m embrane with controlled micro/nanoscale structure and optimized connectivity of the ionic domains was formed.

EXPERIMENTAL

Sample preparation

A hy drophobic monomer, a crylonitrile (AN), a cross-linker , *N,N*'-methylenebisacrylamide (BIS), and a charged monomer, sodium vinylsulfonate (SVS, 25 % c ontent in distill ed water), were chosen for the nanoparticle sy ntheses by free-radical emulsion copolymerization in an a queous poly(vinyl alcohol) (PVA, deg ree of poly merization a nd saponif cation wer e 1700 an d 98–9 9 %, respecti vely) solution. During the nanoparticle synthesis reactio n, th e PVA serve d as a poly meric dispersant, preve nting the colloi dal particles fr om ag gregation. The PVA chains assembled the spheres to form latex films and the hydroxyl groups (–OH) in PVA were cross-linked in the following membrane preparation process, constraining the swelling of the membrane and providing mechanical strength. The sy nthesis in aqueous emulsions should re sult i n charged gro ups b eing att ached to t he surface of the p articles.[8] Vario us amounts of SVS were introduced into the system to obtain particles with different contents of charges for diff erent membranes. AN (14.0 g) , BIS (1.0 g) and SVS (1.0–4.0 g) were add ed into 80.0 g of a n aqueous PV A solution contai ning 4.0 g of P VA under vigorous stirring and then heated under a nitrogen at mosphere to the incubation temperature of 65 °C. The reaction was initiated by adding dropwise an ammonium persulfate (APS) solution.

The free-standi ng membranes were prep ared by direct ca sting of the e mulsion onto a clean glass slide, followed by drying under n ormal pressure at ambient temperature. Then the membrane with a thic kness of about 120 µm was immersed into an acetone solution containing 5 wt. % glutaradehy de (G A) and 0.5 % HCl (volu me fr action). The reaction wa s maintained at 40 °C for 4 h, whereby cross-linked membranes were subsequently obtained. In addition, the as-received membranes were treated with a 1.0 M H_2SO_4 solution overnight and then washed three tim es with distill ed water before measurements of the proton conductivity and ionic content. Naf on[®] 117 (1100 EW, 177.8 µm thickness, commercially extruded film) was purchased from Aldrich and used as received without any further purification.

Measurements

The FTIR anal ysis was p erformed on a Nico let MX–1E FTIR spectro meter. The m orphology of the particle membrane was studied by scanning el ectron microscopy (SEM), using a Jeol JSM-5900LV electron microscope.

The proton conductivities of the particle membranes were evaluated by measuring the ac impedance spe ctra using a So lartron ac i mpedance system (1260 i mpedance analy zer, 128 7 electrochemical interface, Zplot software) in the frequen cy range of 1 MHz to 1 Hz. Th e membranes of 0.59 c m^2 in are a were sandwiched betw een two platinum bl ocking electrodes. All membranes were pre-hy drated in wat er for at least 2 4 h and then qui ckly enclosed in a sealable cell to maintain hy dration during i mpedance measurements. The *IEC* values of the membranes were measured by the classical titration method.

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RESULTS AND DISCUSSION

The FTIR spectra of the membranes before and after the cross-linking reaction are shown in Fig. 2. With respect to the membrane after cross-linking with GA, the membrane showed different absorption bands in the spectra as compared with the pristine membrane. The bands at 1000 and 1038 cm^{-1} correspond to the vibration of C–O and C–O–C bonds due to acetal or semi-acetal formation after the cross-linking reaction, respectively. The band at 1717 cm^{-1} was assigned to the absorption of the carbonyl groups of non-conjugated aldehydes.[9] In addition, two important peaks at 2934 and 2862 cm^{-1} were ascribed to the absorptions of the stretch vibration of C–H bonds related to aldehydes.[10] These FTIR spectral changes shown in Fig. 2 confirm the acetalization that occurred inter molecular between PVA and GA.
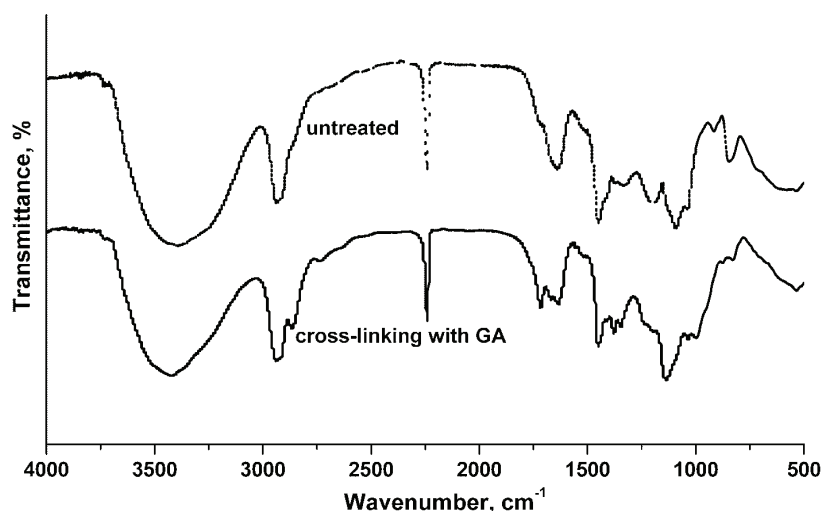

Fig. 2. FTIR Spectra of particle membranes obtained before and after the cross-linking reaction.

Before the cross-linking reaction, cohesion of the spheres was achieved mainly through intersphere chain entanglement of PVA. The water solubility of the PVA chains enabled the film to swell excessively in water, preventing measurement of the conductivity and *IEC*. After the cross-linking reaction, the films showed constrained swelling and adequate mechanical strength.

An SEM cross-section image of a cross-linked membrane obtained from the surface-charged polymer colloids is shown in Fig. 3. It may be observed that the particles are individually well dispersed and packed closely within the membrane, suggesting that the structure of the particles remained after the preparation and cross-linking reaction of the membrane. The well dispersed structure of the particles is believed to facilitate the formation of network for ion channels.
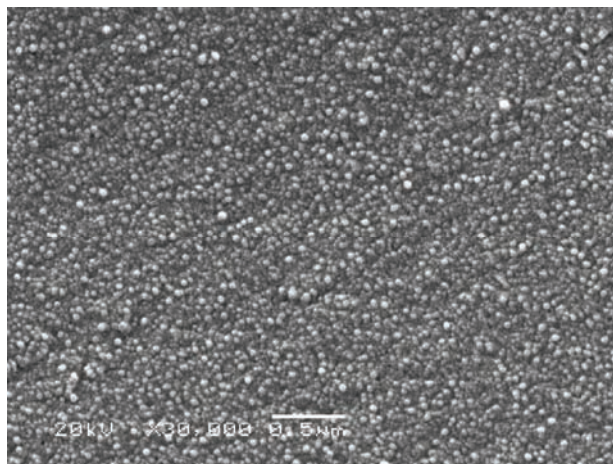
Fig. 3. SEM Cross-sectional image of a particle membrane with an *IEC* value of 0.28 mmol g^{-1}.

Proton con ductivity can vary with diff erent experimental approaches and instruments. For comparison, the proto n conductivity of Nafion ® 117 was measured under the same conditions and resulted in a value of 0.020 S cm^{-1} at 20 °C. As shown in Table I, the proton con ductivity of the particle membranes was high even for an *IEC* as low as 0.18 mm ol g^{-1}. The values of the proton conductivit y increased al most linearly with *IEC*, re aching 0. 040 S cm $^{-1}$ for an *IEC* of 0.48 mmol g^{-1}. It is generally accepted that a higher value of the *IEC* is desirable to achieve higher proton con ductivity in p olymer ele ctrolyte membranes. As compared with Nafion ® 117 (*IEC* of 0.9 1 mmol g^{-1}) under the same condition, t he particle membrane had a com parative proton conductivity, in addi tion to an *IEC* of 0.28 mmol g^{-1}, which is much lower than that of a Nafion 117 membrane of 0.91 mmol g^{-1}.

TABLE I. *IEC* and proton conductivity (δ) of the membranes

Membrane sample	SVS content[a], wt. %	*IEC* / mmol g^{-1}	δ[b] / S cm^{-1}
Membrane-1 5		0.18	0.010
Membrane-2 8		0.28	0.020
Membrane-3 12		0.36	0.028
Membrane-4 17		0.48	0.040
Nafion® 117	–	0.91	0.020

[a]SVS contents in feed; [b]measured at 20 °C

It is believed that the difference be tween the conductivit y of the particle membranes and the Nafion ® 117 membrane lies in the connectiv ity of t he conduction pathways. In a mem brane made from random or graft copol ymers, the charges are uniformly distributed res ulting in a la ck of phase separation. T he high conductivity only oc curs where there is sufficient connecti on between t he

charged regions for a conti nuous pathway to exist, often associated with a high *IEC*. For the surface-charged latex m embranes, the particles packe d closely and the cation exchange sites ($-SO_3^-$) are spread am ong adjacent particles, facili - tating phase separation during m embrane drying. When the thin   film sw ells i n water, the lo calized charg e clusters may diffuse to f orm a co-con tinuous i onic network and so provide continu ous pat hways, even at a low   char ge content. In this case, the percolation threshold shifts to much lower values. In effect, the lo w percolation threshold can be attributed to an efficient organization of the charges within the membrane. It is known that   the proton conductivit y of an ordered arrangement of proton conductive nanodomains is higher than that of a rando mly arranged one.[11–13] Thus, t he particle membranes have the advant age of impro- ving proton conductivity by the formation of a continuous conduction pathway.

CONCLUSIONS

Proton exchange membranes exhibiting well-organized structures were suc- cessfully prepared by self-assembling and cross-linking reaction of surfac e-char- ged poly mer colloids. The well-organized structure as reve aled by SEM facile- tated the formation of continuo us conduction pathways, thus i mproving the pro- ton conducti vity of the particle   membranes. The novel   method for preparing membranes with an ordered microstructure is recognized to be u seful in the d e- sign of both PEMs and ion-conducting membranes for use in battery applications, electrosynthesis and water purification.

И З В О Д

ПРИМЕНА ПОВРШИНСКИ НАЕЛЕКТРИСАНИХ КОЛОИДНИХ ЧЕСТИЦА
ПОЛИ(АКРИЛОНИТРИЛ)/ПОЛИ(ВИНИЛАЛКОХОЛА) (PAN/PVA)
У ПРОТОН ПРОВОДНИМ МАТЕРИЈАЛИМА

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У овоме раду је приказана израда протон проводних мембрана добро дефинисане структуре применом нове технике „само-организације" површински наелектрисаних нано- честица. Наночестице су синтетисане емулзионом кополимеризацијом у присуству слободних радикала као иницијатора. Полимерне мембране су добијене поступком извлачења латекса и накнадним умрежавањем колоидних честица. Добијене полимерне мембране су показивале велику протонску проводљивост од око 0,0 4 S cm^{-1} при релативно ниском јоноизмењи- вачком капацитету (*IEC*) од 0,48 mmol g^{-1}. Претпоставља се да је повећана протонска про- водљивост мембрана последица континуалне мреже јонских канала, настале густим пако- вањем површински наелектрисаних наночестица, чиме је олакшан транспорт протона кроз мембрану.

REFERENCES

1. L. Rubatat, A. L. Rollet, G. Gebel, O. Diat, *Macromolecules* **35** (2002) 4050
2. Y. A. Elabd, E. Napadensky, C. W. Walker, K. I. Winey, *Macromolecules* **39** (2006) 399
3. K. A. Mauritz, R. B. Moore, *Chem. Rev.* **104** (2004) 4535
4. Y. Yang, S. Holdcroft, *Fuel Cells* **5** (2005) 171
5. R. Mezzenga, J. Ruokolainen, G. H. Fredrickson, E. J. Kra mer, D. Moses, A. J. Heeger, O. Ikkala, *Science* **299** (2003) 1872
6. J. Gao, D. Lee, Y. S. Yang, S. Holdcroft, B. J. Frisken, *Macromolecules* **38** (2005) 5854
7. J. Gao, D. Lee, Y. S. Yang, S. Holdcroft, B. J. Frisken, *Macromolecules* **39** (2006) 8060
8. J. H. Kim, M. Chainey, M. S. El-Aasser, J. W. Vanderhoff, *J. Polym. Sci., Part A: Polym. Chem.* **30** (1992) 171
9. W. M. de Azevedo, J. M. de Souza, J. V. de Melo, *Synth. Met.* **100** (1999) 241
10. H. S. Mansur, R. L. Oréfice, A. A. P. Mansur, *Polymer* **45** (2004) 7193
11. E. M. W. Tsang, Z. B. Zhang, Z. Q. Shi, T. Soboleva, S. H oldcroft, *J. Am. Chem. Soc.* **129** (2007) 15106
12. R. Maki-Ontto, K. de Moel, E. Polushki n, G. A. van Eken stein, G. ten Brink e, O. Ikkala, *Adv. Mater.* **14** (2002) 357
13. T. Tezuke, K. Tadanage, A. Hay ashi, M. Tatsu misago, *J. Am. Chem. Soc.* **128** (2006) 16470.

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