Preliminary Study on SPES Membranes and PES/SPES Blend Membranes

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Abstract: SPES Membranes and PES/SPES blend membranes were cast from solutions. Both SPES and PES/SPES blend membranes had low methanol permeability and high proton conductivity indicating these membranes are excellent candidate membrane materials for direct methanol fuel cells (DMFCs) applications.

Key words: sulfonated poly (ether sulfone); poly (ether sulfone); blend membrane; methanol permeability; direct methanol fuel cells (DMFCs)
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It is well-known that perfluorosulfonate ionomer membranes, such as commercially available Nafion (DuPont) membranes, have been successfully used in hydrogen-oxygen type PEMFC. So Nafion membranes were used as PEM during the early years of the DMFC research. But Nafion membranes have high methanol permeability which resulted in decreasing energy conversion efficiency of DMFC. These have motivated great efforts in developping cost-effective hydrocarbon PEMs with lower methanol crossover, such as sulfonated poly (ether ether ketone) (SPEEK) membranes[1], sulfonated poly (ether sulfone) (SPES) membranes[2-3] and their blend membranes, for these membranes have lower methanol permeability than Nafion membranes. In the paper, both SPES membranes and PES/SPES blend membranes were prepared. Methanol permeability and proton conductivities of these membranes were investigated to evaluate their potential applications for DMFCs.

1 Experimental

1.1 Membrane preparation

SPES was synthesized with $ClSO_3H$ as sulfonating agent and CH_2Cl_2 as solvent at 25℃. Degree of sulfonation (DS) was measured by titrating with standard NaOH solution. SPES and PES/SPES blend Membranes were prepared by a normal casting process. Membranes were pretreated with 0.5 mol/L sulfuric acid solution.

1.2 Membrane characterization

The Infrared spectra were measured by a Bruker TENSOR27 FT-IR spectrometer. The methanol permeability (P) was measured using diffusion method. The transported methanol concentration in diffusion cell was analyzed by BF03430 Gas Chromatography. The normal conductivity measurements were performed in the two-electrode AC impedance mode using a CHI760B Electrochemical Analyzer/Workstation.

2 Results and discussion

2.1 Infrared (IR) spectra

FT-IR spectra of PES and SPES are showed in Fig.1. Comparing with the spectra of PES, the SPES absorption peak at ~1025 cm^{-1} is due to the aromatic $-SO_3H$ symmetric stretching vibrations[4], and the intensity of this characteristic peak increases as DS of SPES increases. The conclusion that $-SO_3H$ groups has been introduced into the polymer chains can be drawn.

2.2 SPES membranes

Fig.2 shows the methanol permeability and proton conductivity of SPES membranes at room temperature. It is clear that SPES membranes have good methanol barrier performance. Methanol permeability of SPES membrane increases as DS increases, which is lower than Nafion membrane. Obviously, proton conductivity of SPES membranes is higher than the PES membrane, and increases as DS increases. Proton conductivity of SPES membranes is high, but lower than Nafion membrane.

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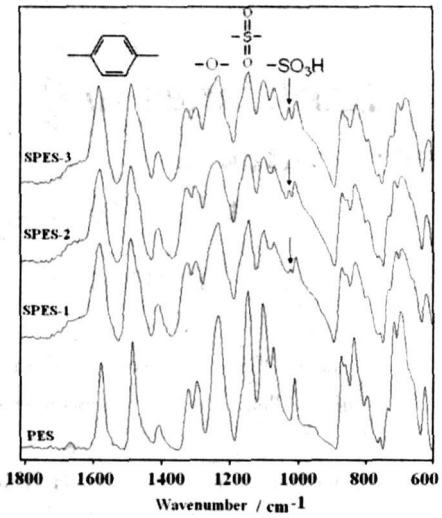

Fig. 1 FT-IR spectra of PES and SPES which DS of SPES-1, 2, 3 were 13.1%, 20.6% and 31.2%

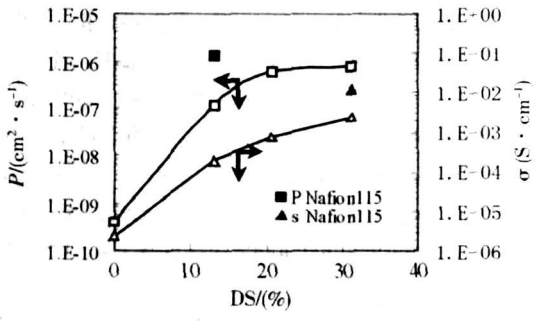

Fig. 2 Methanol permeability and proton conductivity of SPES membranes

2.3 PES/SPES blend membranes

Methanol permeability and proton conductivity of PES/SPES (DS of SPES is 31.2%) blend membranes at room temperature are given in Fig. 3. Methanol permeability of blend membranes reduces as the content of PES increases due to the phase separation behavior in blend membranes which improves methanol barrier performance of the blend membranes.

It is obvious that proton conductivity of blend membranes reduces as the content of PES increases. The addition of PES reduces concentration of —SO3H group in blend membranes, which results in reducing proton conductivity[5].

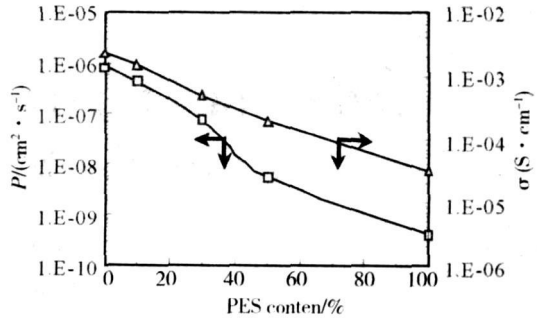

Fig. 3 Methanol permeability and proton conductivity of PES/SPES blend membranes

3 Conclusions

The presence of sulfonic acid groups in SPES was identified by FT-IR Spectra. Both proton conductivity and methanol permeability of SPES membrane increased as DS of SPES increased. The addition of PES led to reduction of proton conductivity of blend membranes. However PES/SPES blend membranes had excellent methanol barrier performance, which indicates these membranes are excellent candidate membrane materials for direct methanol fuel cells (DMFC) applications.

References:

[1] KREUER K D. On the development of proton conducting polymer membranes for hydrogen and methanol fuel cells[J]. J Membr Sci, 2001, 185: 29—39.

[2] IWASAKI, KATSUHIKO, et al. Polymer electrolyte and process for producing the same[P]. United States Patent 6, 087, 031 (2000).

[3] MA C S, ZHANG L, MUKERJEE S, et al. An investigation of proton conduction in select PEMs and reaction layer interfaces designed for elevated temperature operation[J]. J Membr Sci, 2003, 219: 123—136.

[4] DAI H, ZOU H, XU J, et al. Preparation and Properties of Sulfonated Polyethersulfone Proton Exchange Membrane[J]. Modern Plastics Processing And Applications, 2006, 18 (3): 22—25.

[5] SONG W S, LI L, WANG Y X, et al. Study on conductivity and mass transfer of blend membranes of sulfonated polyetheretherketone and polysulfone[J]. Membrane Science and Technology, 2004, 24 (3): 15—19.

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means that is better crystalline at sintering 800℃ for 24 h and better cycling performance.

Fig. 2 displays the relationship between cycling performance and discharge rate for the $LiAl_{0.1}Mn_{1.9}O_4$ and $LiMn_2O_4$. Although Al was doped $LiAl_{0.1}Mn_{1.9}O_4$, initial discharge capacity is decreased. Comparing with the $LiAl_{0.1}Mn_{1.9}O_4$ and $LiMn_2O_4$ of the discharge capacity the cycle number, the discharge capacity for $LiAl_{0.1}Mn_{1.9}O_4$ faded from 110 to 96 mA·h·g^{-1} with the capacity retention rate of 87.3% after 50 cycles. Whereas that the $LiMn_2O_4$ discharge capacity the cycle number was 67.8% after 50 cycles. This results are attributed to the doping of Al, which may reduce Mn valence and give rise to the suppression of Jahn—Teller distortion. So aluminum ions partly substituted manganese could effectively stabilize the spinel structure during the intercalation and deintercalation.

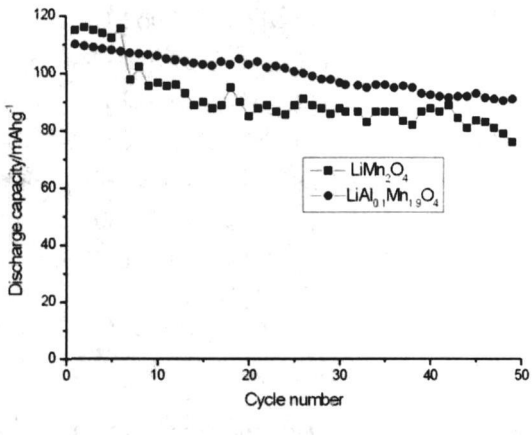

Fig. 2 The discharge capacity the cycle number for the $LiAl_{0.1}Mn_{1.9}O_4$ and $LiMn_2O_4$

References:

[1] ZHOU W J, BAO SH J, HE B L. Synthesis and electrochemical properties $LiAl_{0.05}Mn_{1.95}O_4$ by the ultrasonic assisted rheological phase method [J]. Electrochimica Acta, 2006, 51: 4701—4708.

[2] BAO SH J, LIANG Y Y, ZHOU W J. Synthesis and electrochemical properties of $LiAl_{0.1}Mn_2O_4$ by microwave-assisted sol-gel method [J]. J Power Sources, 2006, 154: 239—245.

溶胶—凝胶法合成 $LiAl_{0.1}Mn_{1.9}O_4$及其电化学性能

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摘 要: 通过溶胶—凝胶法合成 $LiAl_{0.1}Mn_{1.9}O_4$, XRD的结果表明掺杂少量的铝后并没有改变晶体的结构。利用恒流充放电测试手段比较研究了尖晶石型的 $LiAl_{0.1}Mn_{1.9}O_4$, 铝的掺杂后的 $LiAl_{0.1}Mn_{1.9}O_4$比没有掺杂的 $LiMn_2O_4$更好的可逆性能, 更好的循环性能。

关键词: 锂离子电池; $LiAl_{0.1}Mn_{1.9}O_4$; 溶胶—凝胶法; 尖晶石
中图分类号: TM911

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摘 要: 以氯磺酸为磺化剂, 以二氯甲烷为溶剂, 在室温下合成了磺化聚醚砜 (SPES), 并采用红外光谱证明了 SPES中 $-SO_3H$基团的存在。采用流延法制备了 SPES膜和 PES/SPES共混膜。SPES膜在室温下的电导率和甲醇透过系数随着磺化度的增大而增大。由于 PES/SPES共混膜存在相分离行为, 导致其甲醇透过系数随 PES的含量增加而降低。PES的加入降低了共混膜 $-SO_3H$基团的浓度, 导致共混膜的电导率也降低。所制备 SPES膜和 PES/SPES共混膜表现了较好的质子传导性能和阻醇性能, 有望作为直接甲醇燃料电池用质子交换膜。

关键词: 磺化聚醚砜; 聚醚砜; 共混膜; 甲醇透过系数; 直接甲醇燃料电池
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