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Electrochemical Properties of Imidazole Sulphamate Ionic Liquid Grafted SPEEK and Doped by Ln_2O_3

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SPEEK membranes were grafted by imidazole sulphamate ionic liquid (SP) firstly, and then doped by Ln_2O_3. The experiment results show that SP can significantly improve the electrochemical properties of the membranes, like proton conductivity and methanol concentration, while grafting more SP on its backbone. The enhancement potentiation at proton conductivity was prominent in the low temperature section. After continuously doped by Ln_2O_3 nanoparticles, it seems that appropriate amount of Ln_2O_3, best methanol resistance reached. However, Ln_2O_3 had nothing to do with enhancement of proton conductivity even lower it. When doped by Ln_2O_3, coordination reaction occurs at the electron-donating groups which are riched on SPEEK backbone and generated mutual attraction between sulfonic acid groups, reducing the number of sulfonic acid groups and blocking the methanol diffusion path. This could ultimately lead to reducing methanol permeation concentration of the modified membranes. Specimen S0505 had overall excellent properties mentioned above.

Keywords: electrochemical properties, imidazole sulphamate ionic liquid, SPEEK, graft

1. INTRODUCTION

Sulfonated poly(etheretherketone) (SPEEK) membranes have been paid more attentions to its good properties comparing to Nafion membrane [1-3]. But, it is also has some insufficient should be enhanced at high temperature and low humidity. In the last decade, physical doping modification (SiO_2, Y_2O_3, W_2O_3, PES, PPSU, etc. [4-8]) and chemical grafting modification (PWA, ionic liquids, chemical crosslinking, etc. [9-13]) had been researched according to the improving its performance.

In the previous studies, it is found that Ionic liquid could slightly increased the proton conductivity by physical doping but does not meet the requirements of PEM methanol permeability and anti-swelling properties [14]. However, the doped particles or macromolecule are easier to outflow to reduce the performance and the service life due to physical blend. The overall performances are less than pure SPEEK. The proton exchange performances of SPEEK membrane increased, but the proton conductivity has not reached of 10^{-2} S•cm^{-1}. Thereby, choosing grafted SPEEK to improve overall application performance. 64.5% sulfonation degree of the SPEEK resin was selected in order to ensure the behaviors of methanol permeability and water swelling, and then grafted ionic liquid groups by a chemical substitution reaction to SPEEK to be formed novel polymer as SPEEK backbone with ionic liquid large molecule pendant. This technique differs from the doping modified. Through chemical grafting can solve the stability and working life of the membrane, and also can control the number of sulfonated functional groups on the side groups, greatly improve the proton conductivity. All over cannot be achieved by any other doping, blending technologies.

Rare earth oxide can be employed to maintenance of fuel cell anode (cathode). Wu [15] put Y_2O_3 into SPEEK system. Consequently, because of the neutral reactions happened between Y_2O_3 and sulfonic groups, proton conductivity was doomed to decreasing while methanol resistance enhanced excellently. Wang [16] blended both different molar ionic liquids and Y_2O_3 into SPEEK. As a result, both proton conductivity and methanol resistance of SPEEK/EB/Y_2O_3 were superior to pure one, but it seemed physical blend wasn't as steady as chemical one for long time used especially in high temperature and always destroyed polymer structural regularity.

In this paper, based on intermediate sulfonation SPEEK (63.05%), imidazole sulphamate ionic liquid (**SP**) was synthesized and grafted it to SPEEK backbones. Then doped the grafted SPEEK with certain amount Ln_2O_3 to prepare membranes to investigate the proton conductivity, methanol resistance and water uptake properties.

2. EXPERIMENTAL SECTION

2.1 The synthesize of grafted SPEEK membranes

Poly(etheretherketone), offered by Chemistry Department of Jilin University (Jilin, China), in form of particles. The same procedure was described in reference [7], and SPEEK had degree of sulfonation 63.05% (DS). $NaBH_4$ was utilized to carbonyl reduction of SPEEK (named as R-SPEEK) (figure 1, 2-3). Thirdly N-methylimidazole, offered by Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China), was at same molar ratio mixed with sulfamic acid from Ao Xin Chemical Co., Ltd at room temperature for 12 h to synthesize imidazole chloride ionic liquids **SP** (figure 1, 2-1). Equimolar quantities **SP** and $NaBH_4$ were sent to 50 mL dichloromethane to react 24 h at 40 °C to synthesize [Smin]SP_4 (figure 1, 2-2). Then certain amount sulfamic acid was grafted into SPEEK backbone by reacting with R-SPEEK solution (figure 1, 2-4). Finally, different molar mass Ln_2O_3, from Shanghai Huaming Gaona Rare Earth New Materials Co., Ltd with a particle size of 100 nm, was adopted into the grafted solution with mechanical stirring. Casting the SPEEK composites viscous solution onto a glass plat to dry to obtain grafted membranes. And the thickness of the membranes was about 100 μm. The chemical contents of membranes were shown in Table 1.

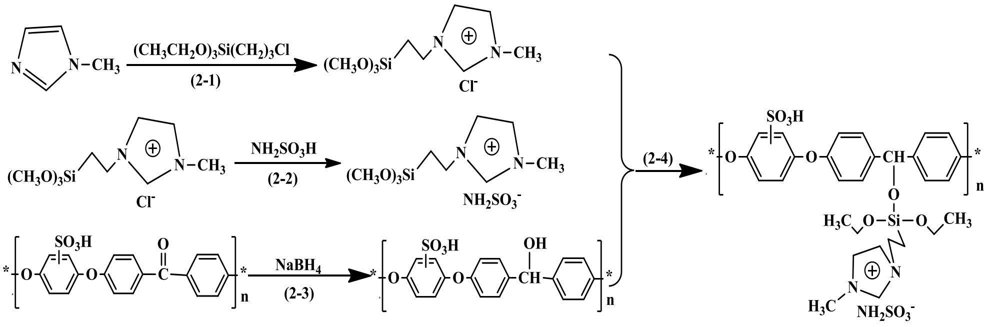

Figure 1. Synthesis of grafted SPEEK by imidazole sulphamate ionic liquid

Table 1. The chemical contents of grafted membranes

CODE	SPEEK (wt.%)	Ionic liquids (wt.%)	Ln_2O_3 (wt.%)
SPEEK	100	0	0
S0500	95	5	0
S1000	90	10	0
S0501	85	15	0
S0505	80	15	5
S0510	75	15	10

2.2 The characterization and testing

The chemical structure of the membranes were recorded by Fourier transform infrared (FTIR) spectra with AVATAR 370 infrared spectrometer (Thermo Nicolet Instrument Co., USA) in the scanning range of 500-4000 cm^{-1}. All specimens were liquid which characterized by painting on the surface of glass slide directly.

The EIS recorded over a frequency range of 1-10^6 Hz. All the membrane specimens were soked in 1mol/L hydrochloric acid solution for 24 h before tests, after then rinsed with de-ionized water several times. Then, the proton conductivity and resistance of membranes performance were calculated as described. Using a measurement cell way to measure the proton conductivity performance by AC Electrochemical Impedance Spectroscopy, the detailed mechanism was narrated in literature [17].

A self-made diaphragm diffusion cell was using to measure the methanol permeability of the membranes, which was closed to the one described in Ref [7]. Immersing the membranes into de-ionized water at 25 °C for 24 h, and then both of the thickness and areas were measured. Whereafter, the membranes were settled down at test temperature above 1h and then tested the methanol permeability. 70 mL 5 mol/L methanol was poured into the diffusion cell and equal volume de-ionized into the other. Magnetic stirrers were stirring in both compartments. The interrelationship of peak areas and methanol concentration were detailed in in Ref 7. The methanol permeability coefficient was calculated by the second law of Fick's diffusion.

Through measuring the dry and hydrous weight to calculate the water uptake (S_w) of the membrane detailed in Ref 7. The $mass_{dry}$ weight was measured by membrane specimens dried at 90 °C for 24 h were. Then, put it into deionized water for 24 h. The $mass_{wet}$ weight was quickly measured by membranes specimens wiped by blotting paper to remove the surface water. The S_w was calculated using equation $Sw=(m_{wet}-m_{dry})/m_{dry}\times100\%$.

3. RESULTS AND DISCUSSION

By far, SPEEK has been proved to be sulfonated successfully [18]. Then it was grafted by imidazole sulphamate ionic liquid. Comparing the curves of grafted membranes in figure 2, there are identical with the absorption peaks appearing at 1640 cm^{-1}, 1220 cm^{-1}, 1110 cm^{-1}, 1010 cm^{-1} and 739 cm^{-1}.

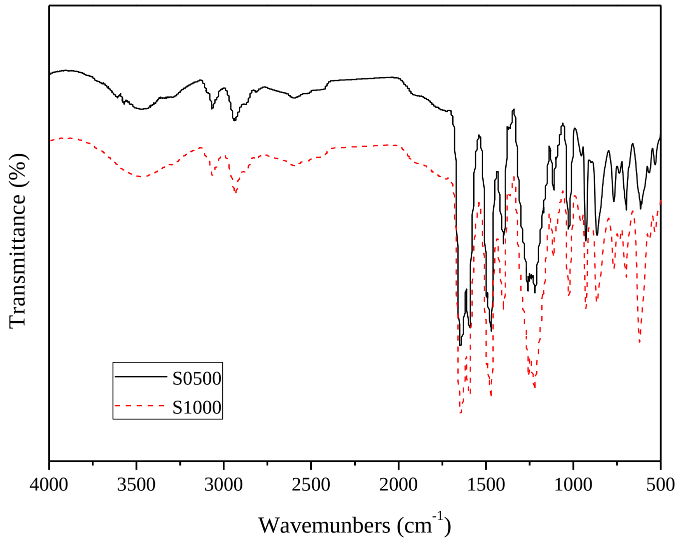

Figure 2. FT-IR spectra of imidazole sulphamate ionic liquid grafted SPEEK

Where there existed a wide absorption peak at 3400 cm^{-1} corresponded to O-H band stretching vibration then we got degree of reduction was 23.7 % accordingly. 1646 cm^{-1} is due to the Ar-C(=O)-Ar group characteristic peaks. 1188 cm^{-1} is the -Ar-O- group characteristic peaks, 1224 cm^{-1} is the O=S=O asymmetric stretching bond vibration peaks, 1080 cm^{-1} is the O=S=O bond symmetric stretching vibration peaks and 714 cm^{-1} is the S-O key symmetric stretching vibration peak, which are indicated that the main chain structures of SPEEK are not damaged. The multiple absorption peaks between 2800 cm^{-1} and 3000 cm^{-1} corresponded to C-H stretching vibration. Absorption peaks at 1427 cm^{-1} and 1570 cm^{-1} were assigned to imidazole symmetric stretching vibration, 667 cm^{-1} belonged to characteristic peaks of -Si-O-. Above all, it was confirmed that **SP** was successfully synthesized.

Comparing S0500 and S1000 infrared spectra, it is indicated that the peak area of S1000 is larger than S0500 at 667cm^{-1} due to the Si-O characteristic absorption peak. But the C-H stretching vibration peaks of -CH_2 and - CH_3 in S0505 are higher than S1000 which prove that the grafting rate in S1000 membrane is higher than S0500.

Table 2 was the proton conductivity of SPEEK membrane and ionic liquids grafted SPEEK membranes at 30 °C. Proton conductivity increased than pure SPEEK by ionic liquids grafted, and an order of magnitude higher than pure SPEEK membrane which reached above 10^{-3} S•cm^{-1}.

Table 2. Proton conductivity of SPEEK and grafted membranes at 30 °C

CODE	Thickness (cm)	Area (cm^2)	Impedance (Ω)	Proton conductivity (S·cm^{-1})
SPEEK	0.0079	0.1451	61.23	8.89×10^{-4}
S0500	0.0230	0.1451	32.93	4.81×10^{-3}
S1000	0.0165	0.1451	13.95	8.17×10^{-3}

The proton conductivity of the membranes as a function of temperature is shown in figure 3. As the temperature rising, the proton conductivity of the pure SPEEK membrane increased. The active participation of the proton transfer has been strengthened to improve the efficiency of their transitions in the membrane, resulting in proton conductivity increases. The proton conductivity of 64.5% DS pure SPEEK membrane was 1.82×10^{-4} S•cm^{-1} at 20 °C. But after grafted, all the proton conductivity increased to an order of magnitude higher than pure SPEEK membrane. B1000 reached 10^{-2} S•cm^{-1} at 40 °C. Combined table 1, it reached a maximum 2.28×10^{-2} S•cm^{-1} at 70 °C (S0500) and 2.74×10^{-2} S•cm^{-1} at 60 °C (S1000). S0500 and S1000 samples have the best performance of the proton conductivity properties, which may be due to the using of grafted imidazole sulphamate ionic liquids. In the same series component content of ionic liquid, imidazole sulphamate ionic liquids contains much more number of increasing relative acid groups. That can increase the number of protons activation and hydrophilic area in the membrane. The proton conductivity was easier and the temperature rises prompting more protons are activated. Thus, the proton conductivity is maximum. Due to the ions paired structure of ionic liquids with mobility which helps the proton conductivity in the membrane [19]. So, the proton conductivity of the membrane samples increases with temperature increasing.

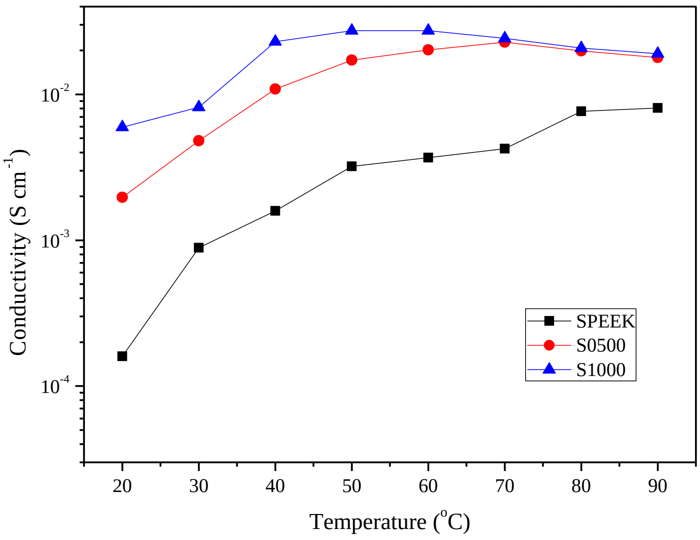

Figure 3. Proton conductivity of SPEEK and grafted membranes vs temperature

Since S05 series had shown high proton conductivity, but they were employed to continuously blend Ln_2O_3 for further modification at the same time. The proton conductivity of **SP** grafted and Ln_2O_3 doped SPEEK was shown in figure 4. It is indicated that Ln_2O_3 was significantly beneficial to promote proton conductivity. With the increasing contents of Ln_2O_3, it reacted with sulfonic groups where generating coordination bonds each other. This effect finally led to amount of sulfonic groups cut down then hindered proton transportation in membranes since sulfonic groups acted as H^+ transportation.

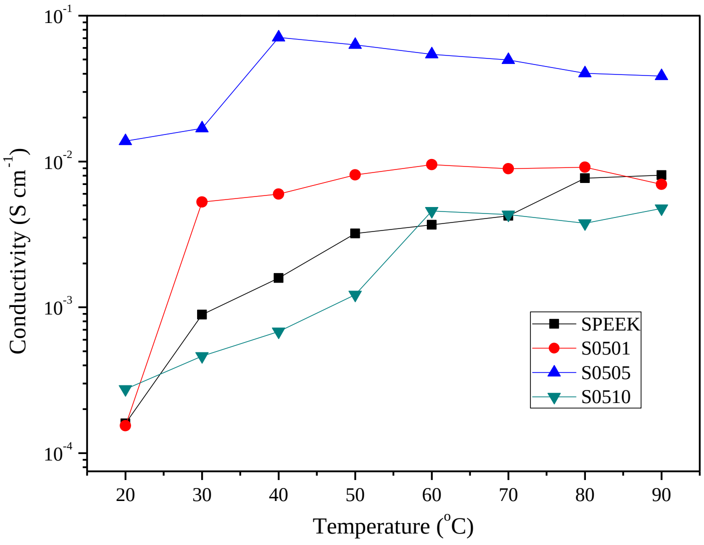

Figure 4. Proton conductivity of **SP** grafted and Ln_2O_3 doped SPEEK

Compared with B0501, the proton conductivity of S0505 membrane is much higher than S0501 membrane. Since protonated before the proton conductivity test of the samples, membrane samples are in acidic conditions. H^+ aggregated around Ln_2O_3 to help proton transfer between different sulfonic acid groups where a large number of H^+ environment, thereby improving the performance of the proton conductive membrane.

From figure 4, it is indicated that the proton conductivity of S0510 decreased significantly compared with S0505. This is because the hydrophilic groups were reduced with the Ln_2O_3 doping amount increasing. But the proton conductivity of the membrane is directly related to the content of the hydrophilic groups. That caused the reducing of proton conductivity. The proton conductivity of S0510 membrane remained relatively stable varies with temperature and far below of S0505. In the low temperature region, the proton conductivity of the S05 series membranes are higher than that of pure SPEEK. Such as the proton conductivity is up to 1.38×10^{-2} S•cm^{-1} at 20 °C, two order of magnitude higher than that of pure SPEEK at the same temperature. The proton conductivity of the membrane is reduced to 3.85×10^{-2} S•cm^{-1}, 477% of pure SPEEK membrane at 90 °C. That are probably due to the tetrafluoroborate ionic liquid has function of conductivity. SPEEK membrane has small number of activation protons at low temperature, the proton conductivity are mainly ionic liquid. Although membrane providing activation proton for migration are increased as the temperature rises, but due to excessive Ln_2O_3 content, the coordination reaction occurs between the sulfonic acid groups and Ln_2O_3 which caused the relative reduction in the number of sulfonic acid groups for proton conduction [20]. Thus, the proton conductivity of S0510 remained relatively stable with the temperature increasing.

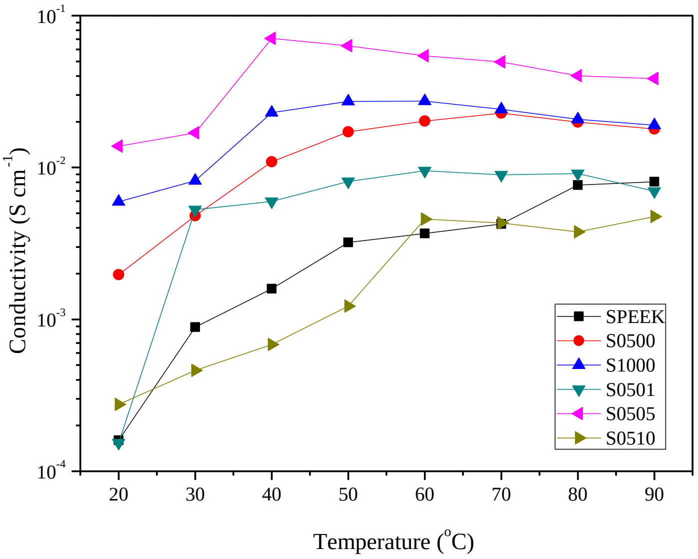

Figure 5. Conductivity of imidazole amino sulphamate ionic liquid modified SPEEK membranes as a function of temperature

Comparison the performances of ionic liquids grafted with different formulations of modified proton conductive membrane, the results are shown in figure 5. For the **SP** series membranes, the ionic liquid itself imidazole sulfamate containing sulfonic acid groups due to the number of sulfonic acid groups and proton transition vector relative increase. Simultaneously, the formation of hydrophilic regions is contributed to the proton conduction inside the membrane. But, Ln_2O_3 is a basic oxide. When the doping amount is higher than a certain value, Ln_2O_3 are easied to react coordinate with sulfonic acid groups in the SPEEK and reduce the relative amount of sulfonic acid groups in the membrane which plays a role in the proton conductivity, so that lead to decline of proton conductivity rate.

Through testing the methanol permeability of the grafted SPEEK and doped by Ln_2O_3, doping content membranes to obtain methanol concentration versus time curves at get deionized water side which are shown in figure 6. The curves show that the methanol concentration of various osmotic membranes indicated a tendency to increase linearly with time, the slope of the curves are essentially the same as that the methanol permeability coefficient substantially unchanged. The methanol permeation concentration at the water side of S1000 membrane was gradually increasing, methanol permeability increases and the increasing trend is most obvious. But the methanol permeation concentrations of other four membranes are all exceed 10^{-2} mol/L^{-1} within 90 min, more different between the curves slope or methanol permeability coefficient. The reasons may be that the introduction of imidazole sulphamate ionic liquid could form a larger number of water channel in the membrane, and cause a significant impact in the methanol permeation process. Therefore, the methanol concentration of crossover S0500 membrane is lower. But when increases sulphamate ionic liquid, the number of methanol permeable channels increased, so that methanol permeability concentration of S1000 membrane is increased. The methanol permeability concentrations of three membranes are substantially nonlinear increasing trend with the time increasing. While under the same infiltration time, all methanol permeate concentration at water side of the membranes were increased with the doping amount of yttrium oxide increasing. The methanol permeability concentration of modified membrane samples are higher than S0500 and the S0501 is maximum, which indicated that the rare particles may interact with ionic liquid and do not fully play its role of improvement hindered alcohol performance.

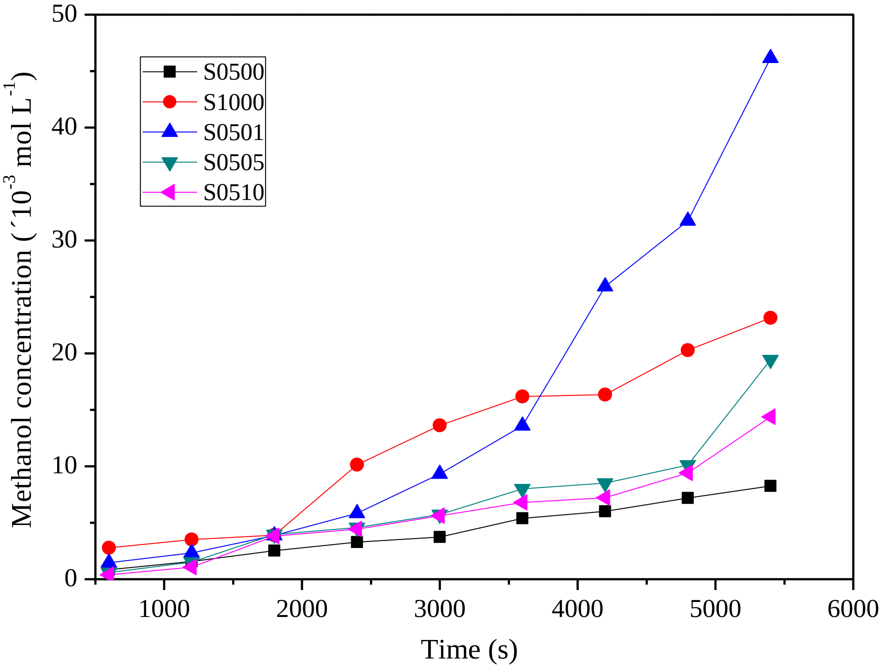

Figure 6. Methanol concentration of **SP** and Ln_2O_3 modified SPEEK membranes as a function of time

Obtained curves slope according to methanol permeation concentration versus time of pure water side as shown in Table 3, while calculated methanol permeability coefficient according to the formula. With the increase of Ln_2O_3 doping, methanol permeability coefficient appears a trend of rising. It is probably due to the occurrence of interaction between Ln_2O_3 and ionic liquid. Ln_2O_3, are not uniformly dispersed in the membranes and the modification is not obvious. But with the increase amount of Ln_2O_3, doping, ionic liquids relative increase in the proportion of the membrane, lead to the methanol crossover intensified. As for the S series membranes, the methanol permeability coefficient didn't appear to be much different when the doping amount of Ln_2O_3 rose from 1 to 10 percent. The reasons could be that on the one hand, the amount of ionic liquid increases with the doping increases in the proportion of the membrane. The introduction of hydrophilic phase and hydrophilic channels are in favor of penetration and diffusion of methanol molecules. On the other hand, Ln_2O_3 can generate coordination structure in SPEEK membrane or generate the mutual attraction between the sulfonic acid groups, reducing the number of sulfonic acid groups to some extent to block the methanol pathway. Thus, the methanol permeability coefficient of S series membranes have a trendency of ascends first and finally stable.

Table 3. Methanol permeability coefficient of SPEEK and grafted membranes

CODE	Thickness (cm)	Area (cm^2)	Straight Slope ($\times 10^{-6} mol\cdot L^{-1}\cdot s^{-1}$)	Methanol permeability coefficient ($\times 10^{-7} cm^2\cdot s^{-1}$)
SPEEK	0.0077	0.3451	5.80	7.76
S0500	0.0230	0.3451	1.90	7.60
S1000	0.0165	0.3451	4.50	12.93
S0501	0.0438	0.3451	1.60	12.19
S0505	0.0438	0.3451	2.80	11.10
S0510	0.0272	0.3451	2.70	11.82

The water absorption and swelling of ionic liquids grafted membranes were tested and the results are shown in figure 7 and 8. As the temperature rises, the water absorption and swelling of the series samples are increases as the curves shows. The increasing trend is more obvious with the temperature increased. Water absorption and swelling increased over the doping content. Water absorption of pure SPEEK membrane reached 60.1% at 90 °C and swelling was 34.1%. Water absorption of S0500 membrane reached 98.7% and the swelling was 69.8%. Water absorption of S1000 reached 116.5% and swelling was 88.5%. The water-swelling properties of doping membranes were less than pure SPEEK which indicated that the microstructure of the doping membrane were not dense due to the water absorption and swelling too high.

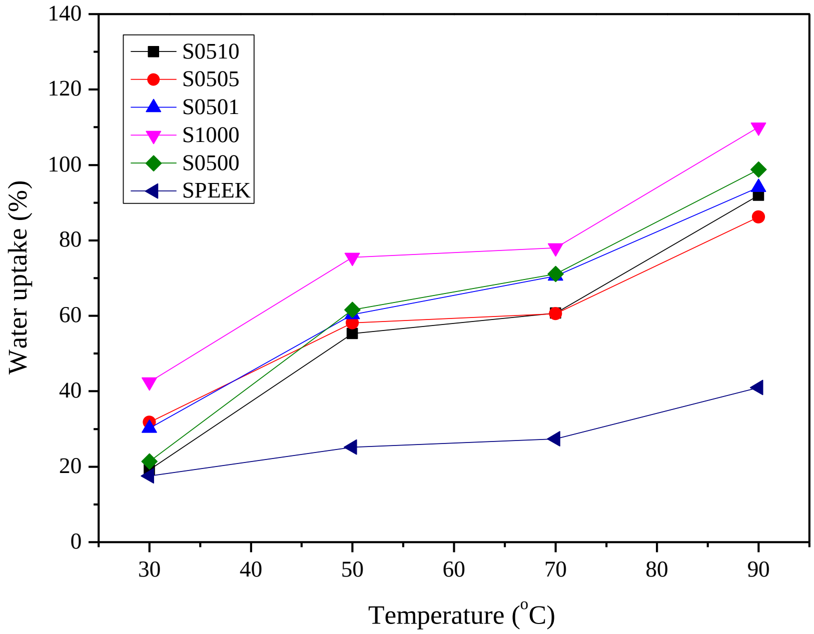

Figure 7. Water uptake of **SP** and Ln_2O_3 modified SPEEK membranes vs temperature

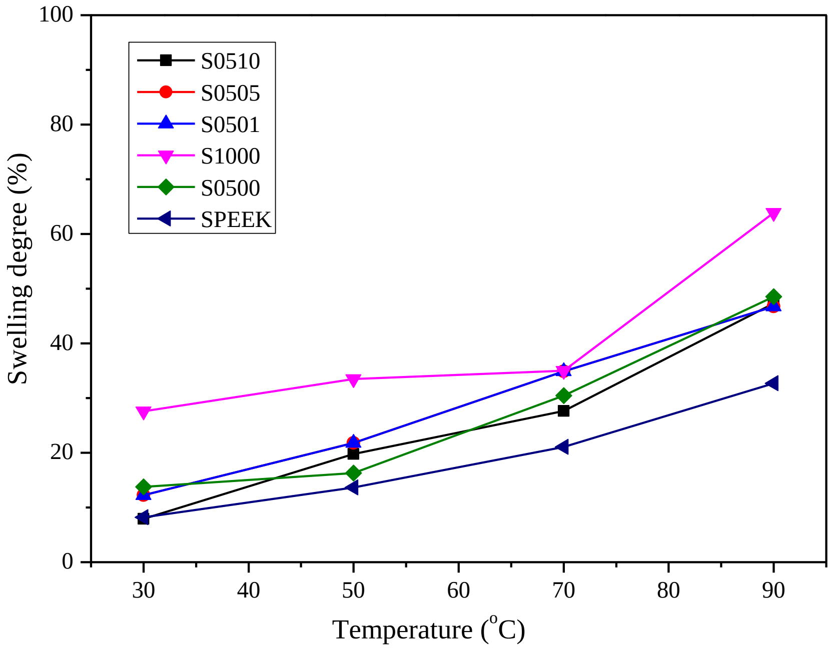

Figure 8. Swelling degree of **SP** and Ln_2O_3 modified SPEEK membranes vs temperature

After doping by Ln_2O_3, the increasing of water absorption of 05 series membranes (0501, 0505, 0510) still increased with temperature, but the trendency is less than 0500 series. The increase gradually decreased with the increasing of Ln_2O_3 content. All above improved that the added of Ln_2O_3 could enhance the structural stability of the membranes and relative reduced the water absorption. The swelling of 0510 series membranes are lowest which probably because the doping of Ln_2O_3. The electron-rich carbonyl groups in SPEEK mainly chain took place coordination reaction with it to enhance the stability of the grafed membranes.

4. CONCLUSIONS

SPEEK proton exchange membranes were grafted by imidazole sulphamate ionic liquid (**SP**) and doped by Ln_2O_3, and the grafting chemical structure of the membranes were validated by FT-IR analysis. **SP** can significantly improve the proton conductivity and methanol concentration of the composite membranes. Chemical graft could effectively avoid the loss of ionic liquid and extend the using life of membranes. The proton conductivity of S0505 membrane arrived 4×10^{-2} S•cm^{-1} after doped by Ln_2O_3. But the S0501 membrane has the highest methanol concentration upon 10^{-6} cm^2·s^{-1} which is higher than pure SPEEK. When doped by Ln_2O_3, coordination reaction took place at the electron-donating groups which are riched on SPEEK backbone and generated mutual attraction between sulfonic acid groups, reducing the number of sulfonic acid groups and blocking the methanol diffusion path. Above all are reducing methanol permeation concentration of the modified membranes. The water absorption and swelling degree of 0510 series were lowest. The 0500 and 0510 series were higher than 0510 and pure SPEEK membranes, which indicated that the introduction of ionic liquid structures could significantly reduce the resistance to water swelling performance. But the mixed of Ln_2O_3 nano-particals could improve the water swelling resistance performance of the membrane. S0501 and S0505 have the best water swelling resistance performance.

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