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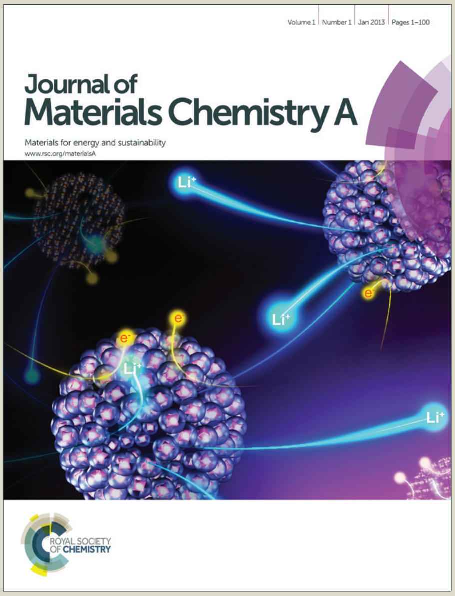

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Design and synthesis of cation-functionalized ionic liquid for application as electrolyte in proton exchange membrane fuel cell

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Functional design was conducted for ionic liquid (IL) by introducing –SO_3H to the cation, and an IL of N,N,N-trimethyl butylsulphonate ammonium hydrosulfate ([N1114SO_3H]HSO_4) was synthesized as the electrolyte in proton exchange membrane fuel cell (PEMFC). Subsequently, a series of single cell tests were carried out. The results show that the PEMFC with the designed IL as the electrolyte can offer a high cell performance. A maximum power density (MPD) of 90 mW cm^{-2} was obtained with the functionalized IL of [N1114SO_3H]HSO_4. While the MPD for the fuel cell with similar IL but not functionalized can only provide an MPD of around 60 mW cm^{-2}. Possible mechanisms behind the elevation of the fuel cell performance were investigated and discussed. The results show that the proton diffusion coefficient elevation of the functionalized IL is one important reason to explain the fuel cell performance elevation. Finally, theoretical calculation of the potential barrier for proton transportation in the two ILs was conducted. The results show that the potential barrier for the functionalized IL was lowered. All the results above imply that introducing functional group to the cation is a promising way for a high proton conductive ILs as the electrolyte in PEMFC.

1. Introduction

Ionic liquids (ILs) are salts with melting point below 100°C.[1, 2] ILs have received considerable attention in various research circles for their unique properties such as good electrochemical stability, low vapor pressure, high ionic conductivity, and functional designability.[3-6] Recently, ILs have been proposed as an alternative electrolyte for proton exchange membrane fuel cell (PEMFC),[7-14] which have been considered as an efficient and clean power source alternative to the conventional ones basing on fossil fuels causing environmental problems.[15, 16] ILs attracted consideration as alternatives electrolyte mainly because of their high ionic conductivity independent of liquid water [8, 17, 18] and the high cost of Nafion membrane.[19-23] Until now, imidazolium salts are the mostly investigated ILs as electrolyte for fuel cell. These ILs are excellent proton conductors as shown by studies.[8, 24] However, most of the fuel cells with imidazolium ILs can only provide extremely low performance, the maximum power density (MPD) are around 1 mW cm^{-2}.[25, 26] Several reasons such as unfavorable fuel cell structure,[26] low conductivity of the membrane-IL composite have been proposed to explain the low performance.[27] Recently, the impact of cation on the fuel cell performance was investigated.[28] It is found that the imidazolium cation may be an important reason for the poor performance of the fuel cell. Our previous investigation imply that the application of non-imidazolium IL of trimethylethyl amide hydrosulphate ([N1114]HSO_4) can lead to elevated performance. However, the performance was still low, and further works are needed to improve the performance of PEMFCs with ILs as electrolyte.

In the IL of [N1114]HSO_4, the negative effect from the cation was avoided by replacing the imidazolium cation with amide one, and improvement in fuel cell performance was obtained. However, preliminary calculations show that the potential barrier for proton transport remains almost the same as that of the imidazolium ones. Calculation shows that the potential barrier for the proton to hop to the cation is -340.39 a.u and -328.75 a.u for $[Emim]^+$ and $[N1114]^+$, respectively. Both are much high than that for the proton to hop to HSO_4^-, which is -691.36 a.u. Therefore, if the potential barrier for the proton to hop to the cation can be lowered, it shall be easier for the transport of proton in the ILs and may lead to increase in fuel cell performance. From this point of view, it is necessary for special functional design of the IL to be applied as electrolyte for fuel cell to lower the potential barrier for proton transport between the cations and anions. However, most of the ILs applied in fuel cell were not functional designed although functional modulation has been proposed for several years in various fields.[4, 29]

In the present work, design of cation was especially made by introducing functionalized group of-SO_3H to the cation of IL while keeping the anion also functionalized. As a result, the potential barrier for the proton to hop between the anion and cation are obviously lowered. In this IL, the proton can hop from one anion to the neighboring cation much easier and then to the next anion and so on. This shall make it easier than to hop from one anion to the cation with higher potential barrier in the case of [N111]HSO_4. Basing on the above analysis, a salt of N,N,N-trimethyl butylsulphonate ammonium hydrosulfate ([N1114SO_3H]HSO_4) was designed and synthesized as the –SO_3H is an excellent group for proton transport. A series of single cell tests were conducted and the results were compared with that of fuel cell with IL of [N1114]HSO_4, which is not functionalized with a –SO_3H group as in previous work.[28] The results implied that the cation-functionalized IL can offer improved fuel cell performance. Afterwards, electrochemical methods were applied to check possible mechanisms for the performance improvement. The results imply that the performance elevation is largely attributed to the elevation of proton transport efficient as a result of the functionalizing of the cation of the IL. To back the speculation of the mechanism, the electrochemical impedance spectroscopy (EIS) measurements were performed to measure and compare the proton diffusion coefficient of ILs composed of cations with and without –SO_3H at various temperatures. Finally, density functional theory (DFT) calculations were carried out to obtain the energy barrier for the proton to hop to and from the cation and anion of the IL. The results show that it is a promising way to functionalize both the cation and anion of the IL to improve the performance of PEMFC with IL as electrolyte.

2. Experimental section

2.1. Synthesis of [N1114SO_3H]HSO_4

All chemical reagents were used as received. Fig. 1 illustrates the IL preparing process. Firstly, trimethylamine water solution (33% wt) was added to 1,4-butylsulphonate (99.5%) in equal mol while being stirred magnetically. The system was stirred 4 hours in a flask immersed in a 70°C water bath. Subsequently, most of the water was rotate vaporized and a white solid was obtained. H_2SO_4 dissolved in distilled water was added in equal mol to the obtained solid and magnetically stirred 30 minutes to obtain a colorless solution. Most of the water in the solution was rotate vaporized and a colorless viscous liquid was obtained. The liquid was then dried *in vacuo* at 120 °C for 24 hours and a colorless transparent viscous liquid was obtained. The liquid can be confirmed to be [N1114SO_3H]HSO_4 with the help of ^{1}HNMR and element analysis.

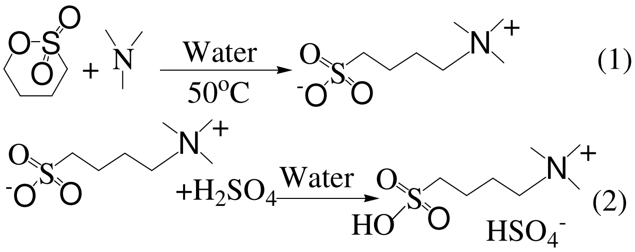


Fig. 1 Synthesizing process of [N1114SO_3H]HSO_4

2.3 Single cell test

The process is similar with that described in the previous work.[28] Briefly, a 45 mm×45 mm (with thickness of 200 μm) sized membrane of PVDF with a pore diameter of 20 μm was immersed in the [N1114SO_3H]HSO_4 solution in ethanol for 24 hours at room temperature. The wet membrane was then dried at 60°C for 24 hours to vaporize the ethanol, leaving pure IL in the membrane.

The membrane was then sandwiched between two pieces of carbon paper with Pt/C catalyst of 0.5 mg cm^{-2} to prepare a membrane electrode assembly (MEA) with an area of 2.5 cm× 2.5 cm. The MEA was subsequently clamped between two graphite blocks with serpentine flow channels for hydrogen and oxygen flow to set up a single cell. The hydrogen and oxygen was supplied from corresponding cylinder at a flow rate of 10 and 20 mL min^{-1}, respectively, without humiliation. The current and voltage were recorded with a multimeter (KIKUSUI) at 30, 50 and 70 °C.

2.3 Electrochemical tests

The tests have been described in detail in the former work and summarized here.[30] The experiments were conducted with the concentration of 10000 ppm IL. A saturated calomel electrode (SCE) and a platinum foil were used as the reference and the counter electrode, respectively.The cyclic voltammogram (CV) conducted from 0 to 1.4V at a scan rate of 20 mV s^{-1}. The influence of the IL on the catalytical ability of Pt/C towards oxygen reduction reaction (ORR) was studied with liner sweep method on PAR 2273 workstation (Princeton Applied Research, USA).

The supporting electrolyte for the electrochamical tests was H_2SO_4 solution (0.5 M). The working electrode was fabricated by casting Nafion impregnated Pt/C (Pt 60wt%, Johnson Matthey, UK) catalyst ink onto a glass carbon disk electrode with a diameter of 0.5 cm. The catalyst loading was 0.15 mg Pt cm^{-2}. The ORR tests were performed at rotation rate of 1000,1500,2000 and 2500 rpm. Subsequently, Levich plot was constructed with the limiting current density obtained above. The apparent number of electrons transferred (napp) was then calculated with the Levich plot slope with the help of Levich equations. The test temperature was controled to be 25°C with water bath.

The EIS measurements were performed on an electrochemical workstation (CHI 660A, CHI Company) to investigate the proton diffusion coefficient of both the ILs at various temperatures. The frequency was ranged from 0.01 to 100,000 Hz with an amplitude of 0.005 V with pure ionic liquid as electrolyte.

The viscosity of the two ILs at 70 °C was measred.

2.4 Theoretical calculation

All calculations were performed with B3LYP methods[31] in Gaussian 03 program.[32] The model containing [N1114] and [N114SO_3H] were constructed to simulate the structure of the cations of the IL. Full molecular models were applied for these cations of ionic liquids. All molecular structures were constructed with Gview program based the optimized results.

3. Results and discussion

3.1. Ionic liquid selection

This quaternary ammonium salt of [[N1114SO_3H] is selected because of its similar structure with that of [N1114]. Since the two ILs of [N1114SO_3H] and [N1114] are similar in structure only that the cation of the former is equipped with the -SO_3H, any difference in the fuel cell performance can be much safely attributed to the -SO_3H group. The -SO_3H was selected as a functionalizing group mainly because of its well known function for proton transport.[33, 34] Therefore, the IL in the present work was functionally designed.

The HSO_4^- anion was selected as the functional anion since it has a structural proton and is a potential proton conductor.[35]

3.2 Single cell test

The single cell test results at 50°C are presented in Fig. 2. For comparison, the single cell test result with IL of $[N1114]HSO_4$ in the previous work[28] was also presented here. The open circuit voltage (OCV) for the single cell with both ILs is nearly the same, both higher than 0.9V.

The current density can be higher than 240 mA cm^{-2} for the fuel cell with $[N1114SO_3H]HSO_4$. This is about 70 mA cm^{-2} higher than that with $[N1114]HSO_4$ as electrolyte. The MPD was also improved. The MPD for the single cell with $[N1114]HSO_4$ as electrolyte was found to be around 60 mW cm^{-2}. When the $-SO_3H$ was introduced to the cation, a MPD of 90 mW cm^{-2} was observed as shown in Fig. 2. Therefore, the fuel cell performance was improved significantly when the IL of $[N1114SO_3H]HSO_4$ was used as electrolyte.

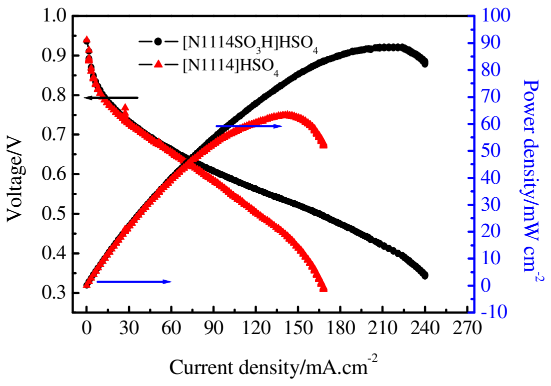


Fig.2 Polarization curves of fuel cells with the two Ils at 50 °C

The single cell test was also conducted at 30 and 70°C, and the results are presented together with that obtained with $[N1114]HSO_4$ in Fig. 3. It can be seen that the MPD at 30 °C is around 70 mW cm^{-2}. This is also higher than that with $[N1114]HSO_4$ at the same temperature, which is around 45 mW cm^{-2}. The MPD at 30 °C is lower than that observed at 50 °C. This may be explained by the lower conductivity and more sluggish electrode reaction. However, the MPD decreased dramatically to merely 30 mW cm^{-2} to 70 °C. This may be explained by the increased difficulty for the IL to be carried uniformly in the membrane as a result of decrease in viscosity. se refer to the previous work.[28] It should be noted that the MPD of $[N1114SO_3H]HSO_4$ is slightly lower (around 1 mW cm^{-2}) than that if $[N1114]HSO_4$, although the former was expected to be higher. This may also be explained by the leaching of the ILs from the membrane. As the viscosity of $[N1114SO_3H]HSO_4$ is lower than that of the $[N1114]HSO_4$, the leaching of $[N1114SO_3H]HSO_4$ is more serious. To back this explain, the viscosity of the two ILs were measured at 70 °C. The viscosity is 175 and 154 cP for $[N1114]HSO_4$ and $[N1114SO_3H]HSO_4$ respectively. This means that it is more difficult for $[N1114SO_3H]HSO_4$ to distribute uniformly than it is for the $[N1114]HSO_4$. This cause lower MPD for $[N1114SO_3H]HSO_4$.

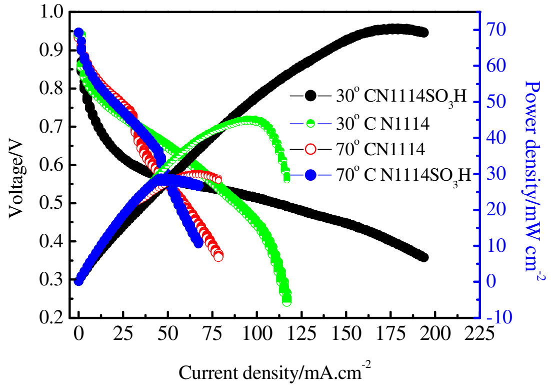


Fig.3 Polarization curves of fuel cell at 30 and 70 °C

3.3 Electrochemical tests

The performance elevation may be attributed to several reasons. Since IL may significantly affect the Pt/C catalyst activity, this possible effect from the two ILs was firstly investigated with electrochemical tests.

3.3.1 CV test

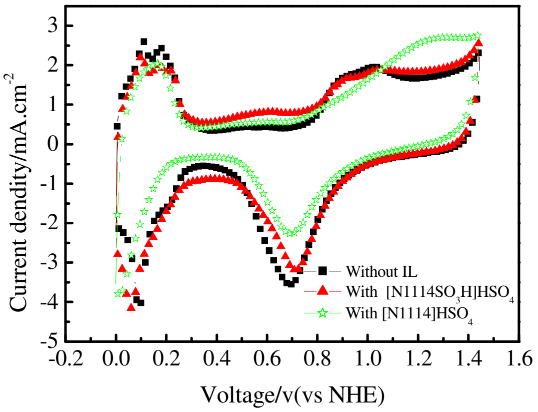


Fig. 4 Cyclic voltammograms for Pt/C in 0.5 M H_2SO_4 with $[N1114SO_3H]HSO_4$ and $[N1114]HSO_4$ at 25°C. scan rate=20 mV.s^{-1}

Fig.4 shows the results of CV conducted in H_2SO_4 solution containing $[N1114]HSO_4$ and $[N1114SO_3H]HSO_4$, respectively. It shows that no significant decrease of electrochemical active surface area (EAS) was observed with 10000 ppm $[N1114]HSO_4$ or $[N1114SO_3H]HSO_4$ added. The EAS calculated according to the method described in reference [36] are around 70 $m^2.g^{-1}$ when the two ILs were added. This value is much near that of the Pt/C catalyst without addition of IL. The results imply that both ILs has no significant negative influence on the EAS of the Pt/C catalyst. Therefore, the single cell performance elevation can not be attributed to the change in the EAS of the Pt/C catalyst.

3.3.2 ORR test

The ORR results at different rotation were presented in Fig. 5 for [N1114SO$_3$H]HSO$_4$ and Fig.6 for [N1114]HSO$_4$. It can be seen that the onset potential for ORR is 0.84V with presence of [N1114SO$_3$H]HSO$_4$. The onset potential for ORR with presence of [N1114HSO$_4$ is around 0.82V. Both the value is near that for ORR on Pt/C catalyst in electrolyte of 0.5 M HSO$_4$.[37] Although the onset potential is slightly different, this difference can not be a main reason to cause the significant difference in fuel cell performance. This is backed by the single cell tests shown in Fig. 3, which shows that the OCV for the fuel cell with both ILs are nearly the same of 0.95 V. Therefore, the CV and ORR tests imply that the fuel cell performance elevation can not be attributed to the compatibility of the IL with Pt/C catalyst.

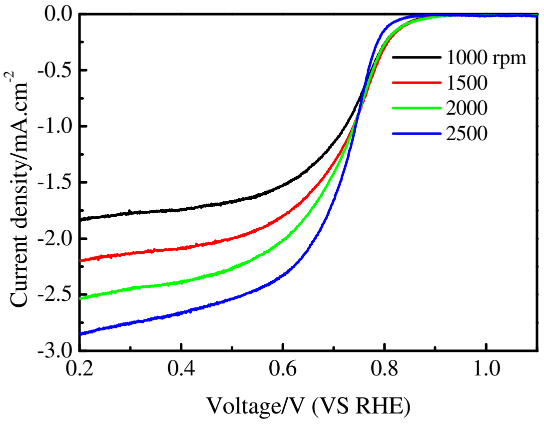


Fig. 5 ORR tests at various rotation rate with [N1114SO$_3$H]HSO$_4$

To investigate the apparent number of electrons transferred (napp) for the ORR reaction with ILs added, the limit current density was plotted vs rotating rate. A plot of i^{-1} versus $\omega^{-1/2}$ for various IL concentration yields straight lines presented in Fig. 7 is known as Koutecky- Levich or (levich plot). The plots slope can allow one to assess napp involved in the oxygen reduction reaction with the help of Eq (3) and Eq (4). Where i_k is the kinetic current density, the value can be obtained by extrapolating the Levich plots to $\omega^{-1/2}$ of 0, 1/B is the Levich plot slope, 0.2 is a constant when the rotation rate ω is expressed in rpm, Co is oxygen solubility in the electrolyte at 25°C (1.1 × 10^{-3} mol L^{-3}), D$_0$(1.4 ×10^{-5} cm.s^{-1})[38] is the oxygen diffusivity and ν (0.09 cm^{2}s^{-1}) is the kinetic viscosity of the electrolyte measured with the viscometer. In this case, the slope for Levich line is 15.93 and 16.11 for [N1114SO$_3$H]HSO$_4$ and [N1114]HSO$_4$, respectively. The napp for [N1114SO$_3$H]HSO$_4$ and [N1114]HSO$_4$ was calculated to be 3.77 and 3.53. This means that the favorable 4-eletron path for ORR is not significantly influenced by either [N1114SO$_3$H]HSO$_4$ or [N1114]HSO$_4$. Therefore, the fuel cell performance elevation cannot be attributed to the change in napp, and other mechanism for the performance elevation should be found.

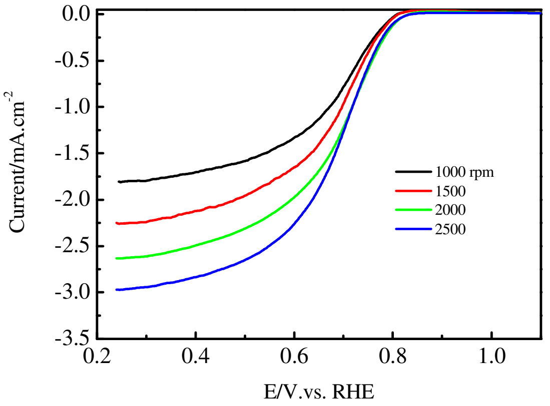


Fig. 6 ORR tests at various rotation rate with [N1114]HSO$_4$

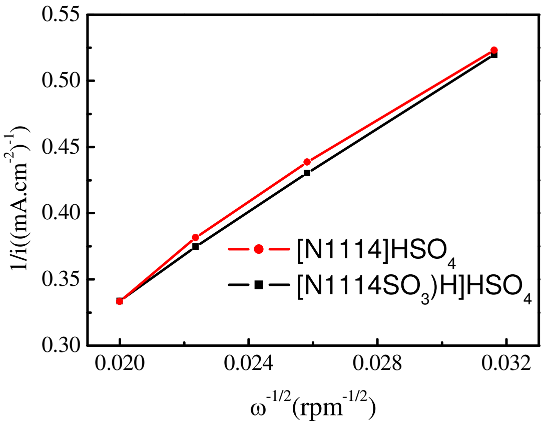


Fig. 7 Levich plot for ORR with[N1114SO$_3$H]HSO$_4$ and [N1114]HSO$_4$

$$\frac{1}{i}=\frac{1}{i_k}+\frac{1}{B\omega^{1/2}} \qquad (3)$$

$$B=0.2nFC_0D_0^{2/3}\gamma^{-1/6} \qquad (4)$$

Since the test conditions were kept to be the same except that the cation, the performance elevation may be largely attributed to the introduction of –SO$_3$H to the cation. Firstly, comparing with the ILs with only anion functionalized for proton transportation, like [N1114]HSO$_4$, the hoping distance for the proton in [N1114SO$_3$H]HSO$_4$ is shortened. As afore mentioned, the proton has to jump over the cation during the transportation in IL of [N1114]HSO$_4$ as the cation is not proton acceptor. However, in [N1114SO$_3$H]HSO$_4$, the cation is equipped with –SO$_3$H. As a result, the proton can hop from the anion to its neighboring cation and to the next anion and so on as shown. Thus, the hoping distance was shortened, making it easier for the proton to transport in the IL. As a result, the fuel cell performance was elevated.

Besides the longer hopping distance, the energy for the proton to hop over the [N1114] may be much higher since the cation cannot accept the proton. Therefore, there may be higher energy barriers near the cation in the transporting path in IL of [N1114]HSO_4. While the energy barriers may be lowered in IL of [N1114SO_3H]HSO_4 since both the cation and anion is proton acceptor. Because of the two reasons mentioned above, it may became easier for the proton to transport in the IL of cation equipped with –SO_3H, and this may be the reason for the performance elevation. To back the speculation above, the proton diffusion coefficient was measured with EIS.

3.3.3 EIS measurement

The EIS results are presented in Fig. 8. For both of the ILs, a small semicircle in high frequency region and a line in low frequency region were observed. Basing on the results, the proton diffusion coefficient (D cm^2 s^{-1}) was calculated according to Equal (5)[39], where A is the surface area of the electrode, which is 6.25×10^{-4} m^2. n is the number of the electrons per molecule attending the electronic transfer reaction, and this is 1 and 2 for [N1114]HSO_4, and [N1114SO_3H]HSO_4. F is the Faraday constant (96485C mol^{-1}). C is the concentration of active proton, which is 1.05 ×10^4 mol m^{-3} and 6.934×10^3 mol m^{-3} for [N1114SO_3H]HSO_4 and [N1114]HSO_4, respectively at 25 °C. R is the gas constant(8.314 JK^{-1} mol^{-1},). T is the testing temperature, and σ is the slope of the line Z'-$\omega^{-1/2}$ shown in Fig 9, which can be obtained from the line of Z'-$\omega^{-1/2}$, where ω is the angular frequency. The slop was found to be 1368 and 27632 for [N1114SO_3H]HSO_4 and [N1114]HSO_4, respectively at 25 °C. The D was calculated to be 2.8 ×10^{-12} cm^2 s^{-1} and 2.5 ×10^{-13} cm^2 s^{-1}for [N1114SO_3H]HSO_4 and [N1114]HSO_4, respectively. The results imply that the proton diffusion coefficient of [N1114SO_3H]HSO_4 is about 10 time that of the [N1114]HSO_4. The coefficients at other temperatures were also measured and the results are shown in Fig. 10. It can be seen that the proton diffusion coefficients of [N1114SO_3H]HSO_4 are higher than that of [N1114]HSO_4 at all the testing temperatures. The higher proton diffusion coefficient of [N1114SO_3H]HSO_4 means it is much easier for the proton to transport in the IL with cation equipped –SO_3H. This is in constant with the speculation. Therefore, the results imply that the introduction of functional group is an efficient way to improve the proton conductivity, which is an important factor for electrolytes of PEMFC.

$$D=0.5*\left(\frac{RT}{AN^2R^2C\sigma}\right)^2 \qquad (5)$$

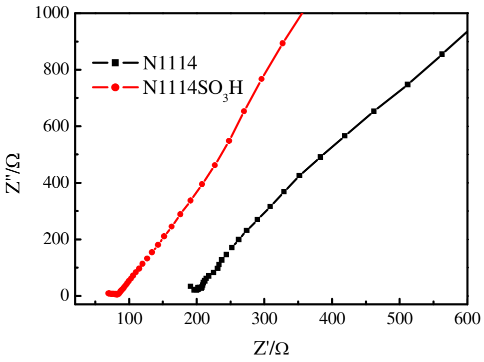


Fig. 8 Electrochemical impedance spectroscopy of the ILs

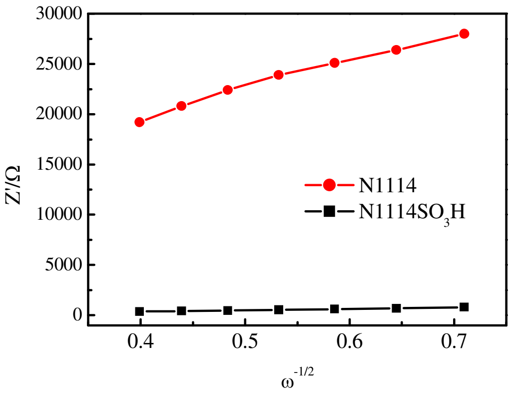


Fig. 9 Z'-ω line for calculation of the proton diffusion coefficient

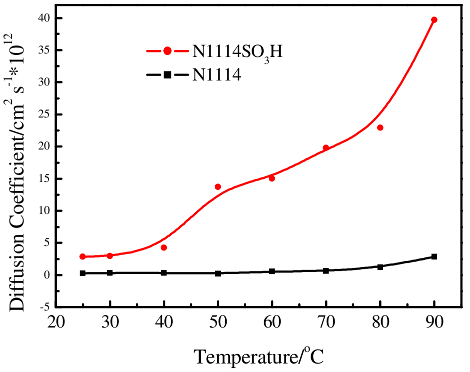


Fig. 10 Proton diffusion coefficient as a function of temperature

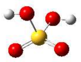
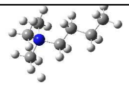
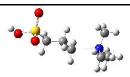
It should be noted that there are also some other ILs with both cation and anion functionalized although not clearly declared by the authors. However, the functional group for proton exchange is largely not especially selected, and most of the "functional group" are nitrogens forming the cation ring since the nitrogen can function as the proton acceptor via hydrogen bond.[40] For example, IL of 2,5-diphenyl-1,3,4-oxadiazole (DOD) with a super strong acid bis(trifluoromethane sulfonyl)imide (HTFSI) (DODTFSI) is one kind of these ILs. Still another IL of benzimidazolium bis(trifluoromethanesulfonyl)imide (HBIMTFSI) was investigated as proton conductor for PEM.

However, most of the ILs contain imidazolium cations, and the negative effect on the catalysts can not be avoided. As a result, the fuel cells with these ILs as electrolyte perform rather poorly. The MPD for the ILs with both ILs is lower than 1 mW cm^{-2}. Thus it is important to select IL as electrolyte for PEMFC. They should be high in proton transport and low in negative effect on the fuel cell catalysts at the same time, and high ionic conductivity merely is not enough.

3.4 Theoretical calculation

To further investigate the mechanism for the cell performance elevation after introduction of $–SO_3H$. The potential barrier for the proton to transport via the two ILs was calculated. The barrier for HSO_4^- was also calculated. The results are presented in Table-1. It shows that the potential barrier for the proton to transport via the HSO_4^- is -691.36 a.u. While that via the N1114 is -328.75 a.u, and this is almost 400 a.u higher than that for HSO_4^-. The potential barrier for the proton to transport via the cation decreased to -905.41 a.u. when the cation is equipped with $–SO_3H$

Table-1 Calculation result

	H-HSO_4	H-[N1114]	H-[$N1114SO_3H$]
Structure			
Energy/a.u	-691.36	-328.75	-905.41

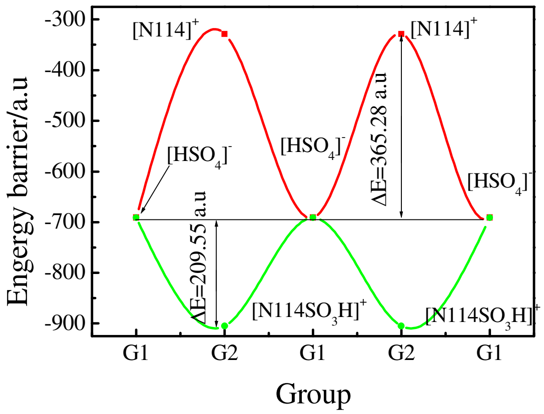


Fig. 11 Energy barrier on the paths for the proton to transport through the two ionic liquids

Fig. 11 is obtained basing on the theoretical calculation results above. It depicts the potential barrier on the paths for proton to transport in IL of [N1114]HSO_4 and [$N1114SO_3H$]HSO_4. It can be seen that the proton has to cover energy barrier of about 365.28 a.u in the IL of [N1114]HSO_4. However, this barrier in the cation-functionalized IL of [$N1114SO_3H$]HSO_4 is decreased to be 209.55 a.u. This means that the potential for the proton to transport has been lowered in the IL with cation functionalized. This lower potential may explains why the fuel cell performance was elevated since it becomes easier for the proton to transport in the IL after the cation was functionalized with $–SO_3H$. The calculation results agree well with the EIS results.

4. Conclusion

Functional desigen was especailly conducted for the cation of an IL for application as electrolyte for PEMFC. Single cell tests were conducted and the results show that fuel cell with the designed IL can offer much higher performance in terms of maximum power density than that with IL not especially designed. The mechanims for the performance elevation were discussed with the help of electrochemical tests. It is specualated that the performance elevation is mainly attributed to lower potential barrier for the proton transportation as a result of the introdcution of the $–SO_3H$ to the cation. Theoretical calculation was conducted to back the conclusion. The results imply that it is a promising way to elevate the performance of the PEMFC with IL as electrolyet by functional designing of the ILs. The results may open a new door to select, design and synthesis for ILs proposed as electrolyte for fuel cell.

Acknowledgements

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.Notes and references

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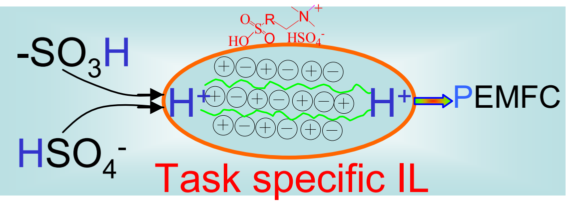

$-SO_3H$ was introduced to design cation of ionic liquid specifically as electrolyte for PEMFC