RSC Advances

Volume 1 | Number 1 | Jan 2013 | Pages 1–100

RSC Advances

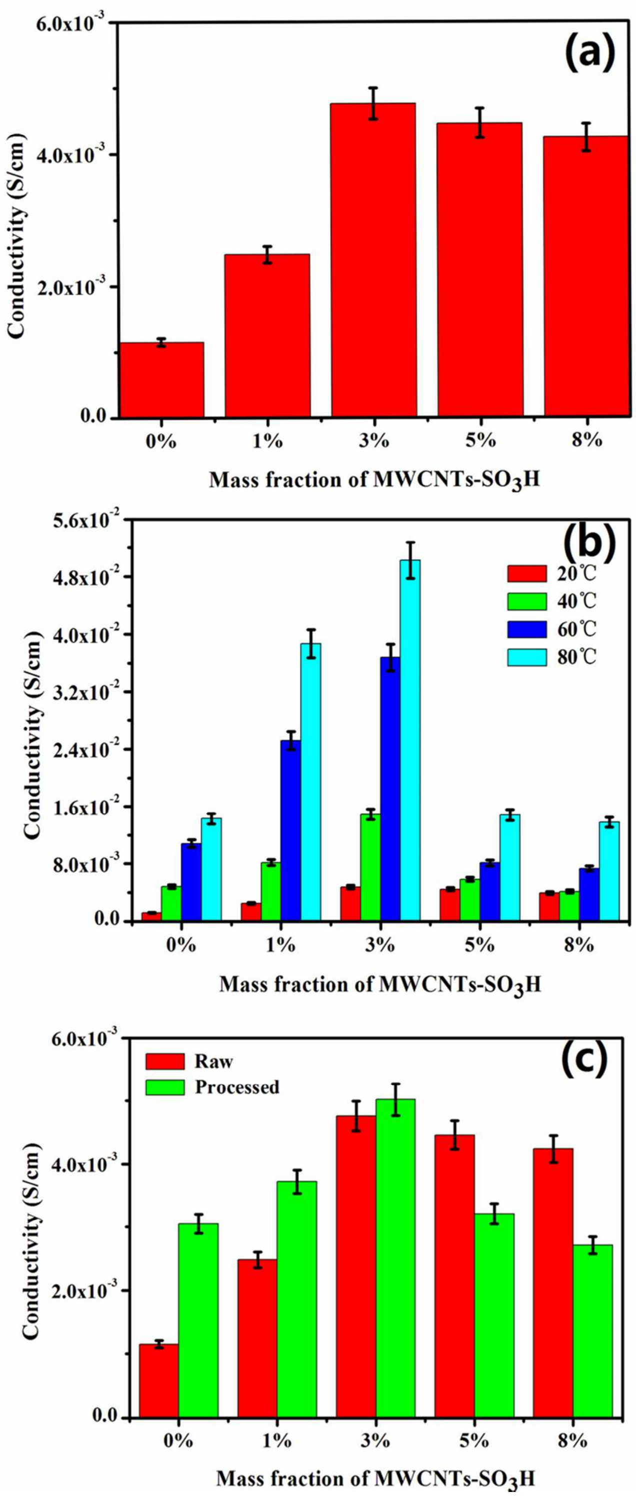
www.rsc.org/advances

ROYAL SOCIETY OF CHEMISTRY

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

The reinforcement of sulfonated carbon nanotube using acyl chloride method on proton conductivity of sulfonated polyarylene ether nitriles was investigated.



Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Sulfonated carbon nanotube synergistically enhanced proton conductivity of sulfonated polyarylene ether nitriles

M. N. Feng,[a] Z. J. Pu,[a] P. L. Zheng,[a] K. Jia[*a] and X. B. Liu[*a]

Received (in XXX, XXX) XthXXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

The addition of a small amount of sulfonated multi-walled carbon nanotubes (3 wt%) to the sulfonated polyarylene ether nitriles (SPEN) proton exchange membrane using acyl chloride method was proved to be an effective way to increase mechanical behaviour and proton conductivity performances.

Proton exchange membranes (PEMs), as the key components of polymer fuel cells, provide effective ionic pathway for proton transfer while prevent the mixing of reactant gases.[1] An ideal PEM is required to be capable of efficiently transferring protons, good resistance to the high-temperature, humid and oxidative environment.[2] Currently, the sulfonated tetrafluoroethylene based fluoropolymers, named as Nafion, are widely used as PEMs.[3] However, Nafion shows some disadvantages of high cost, strong temperature dependence, low strength at certain humidity and weak thermal stability, etc.[4] Thus, two means have been proposed to solve the above difficulties. One is the modification of Nafion proton exchange membranes;[5] the other is seeking novel proton exchange membranes to alternate Nafion, especially in terms of cost and mechanical performance. At the present stage, much effort has gone into the development of PEMs via polymer modification method,[6] while it is of great urgency to develop novel PEMs. For instance, more and more researches focus on the polybenzimidazoles, polyimides, poly(arylene ether sulfone), poly(arylene ether ketone), and poly(arylene ether sulfone ketone), etc.[7, 8, 9] But these PEMs require the addition of a great deal of sulfonic acid conductors to increase conductivity, which cause excessively water-swollen or sobulity,[3] resulting in the low heat resistance and bad mechanical performances.

Aromatic polyarylene ether nitriles (PEN), a fascinating material, have been widely investigated in the past decades because of their high thermal and thermo-oxidative stabilities, favourable dielectric, chemical inertia and excellent mechanical performance.[10] It was reported that nitrile groups have been introduced into the polymer matrix to achieve the aim of decreasing swelling of membranes by enhancing intermolecular interactions,[11] which is one of the foundations of better thermal stability and strength of membranes. Sulfonated polyarylene ether nitriles (SPEN), as a family of copolymers with different ratios of hydroquinonesulfonic acid potassium salt (SQH) and 4,4'-Biphenol(BP), is expected to inherit the better performances of PEN. According to the previous research,[12] SPEN possesses stable thermal property, excellent mechanical performance, better solubility and machinability, while relative low proton conductivity, which restrict the wide application. To address this issue, multi-walled carbon nanotubes (MWCNTs), as a kind of nanomaterials, have large aspect ratio and present a unique combination of mechanical and thermal properties, attracting extensive attention worldwide as an ideal filler to enhance the strength of composites.[13] Liu et al. reported that the addition of CNTs into Nafion membranes could improve the mechanical properties of the composite membrane effectively. [14] However, the method used for the dispersion of CNTs, i.e., a ball-milling method followed by solvent casting, is not appropriate for scaling up and has no significant improvement in performance.[15, 16] Joo et al. reported that sulfonic acid functionalized CNTs/sPAS composite membrane prepared for direct methanol fuel cell applications improved in ionic conductivity and decreased in permeability, while the tensile strength is still relatively low.[15] In addition, many researches adopt the sulfonic acid,[16] decomposing $(NH_4)_2SO_4$,[17] and sulfanilic acid [18] to decorate CNTs and obtain the S-CNTs (S-SWCNTs or S-MWCNTs). Nevertheless, the harsh compounds were involved in these experiments and the reaction temperature was either too low (2 ℃) or too high (235 ℃) to control. On the contrary, acyl chloride method is readily controllable to fabricate MWCNTs-SO_3H and this method has not yet been reported according our best knowledge.

Therefore, in the present work, the polymer of principal focus is the acid form of sulfonated PEN with a SQH/BP ratio of 7/3 via nucleophilic aromatic substitution reaction. The SPEN was successfully synthesized by control the degree of sulfonation to obtain the membranes of high heat resistance and mechanical performance. Meanwhile, the proton conductivity was also investigated in detail.

The SPEN was synthesized from BP, SQH and 2, 6-difluorobenzonitrile (DFBN) via nucleophilic aromatic substitution reaction in *N*-methylpyrrolidone (NMP) with K_2CO_3 as catalyst, according to the similar procedure in literature.[19] Furthermore, SPEN was purified several times by alcohol and deionized water to remove the unreacted bisphenol and inorganic salt.

The MWCNTs-SO_3H powder is prepared by the acyl chloride method. In the typical experiment, 3 g of acidulated MWCNTs (MWCNTs-COOH), 96 mL $SOCl_2$ and 5 mL N,N-dimethylformamide (DMF) were added in 250 mL round-bottom flask under nitrogen atmosphere to prevent $SOCl_2$ decomposing or reacting with water. Then the mixture was refluxed with magnetic force stirring at 70 ℃ for 72 h. After removing the excess $SOCl_2$ solvent by reduced pressure distillation, the blackish block was obtained. Then, the remaining solid was reacted with excessive acid potassium salt in NMP at room temperature, washed by deionized water several times and dried at a vacuum at 50 ℃ overnight. The MWCNTs-SO_3H powder was finally obtained.

The MWCNTs-SO_3H/PEN nanocomposites were prepared generally via solution-casting a mixture of SPEN resin and MWCNTs-SO_3H powder, combining with ultrasonic dispersion technology. The weight-measure of MWCNTs-SO_3H (0 wt%; 1 wt%; 3 wt%; 5 wt%; 8 wt%) was added in dimethylacetamide (DMAc) under sonication for 45 min to disperse completely. Meanwhile, a certain amount of SPEN was dissolved in DMAc with mechanical stirring. The mixture of SPEN resin and the previously-ultrasonicated MWCNTs-SO_3H powder were heated for 1 h after the SPEN was totally dissolved and then, the mixture was put on a clean preheated glass plate and cast solvents using a sequential mode of temperature program at 80 ℃, 100 ℃, 120 ℃, 140℃, 160 ℃ for 2 h, respectively. Then it was cooled to room temperature naturally, the MWCNTs-SO_3H/SPEN nanocomposites were obtained.

The FTIR spectra of MWCNTs-COOH and MWCNTs-SO_3H powders are shown in **Fig. 1** to evidence the forming of sulfonated MWCNTs. The absorption band at 3432 cm^{-1} belongs to the -OH stretching vibration on the surface of MWCNTs. Characteristic absorption band of the carbonyl can be observed at 1640 cm^{-1}. The characteristic absorption bands at 1167 and 1136 cm^{-1} are assigned to the asymmetric and symmetric stretching vibrations of S=O in the sulfonic acid groups. Besides, the band at 1368 cm^{-1} is attributed to the SO_2 telescopic absorption peak of sulfonate acid groups. All these can confirm successful incorporation of sulfonate acid groups into MWCNTs surface.

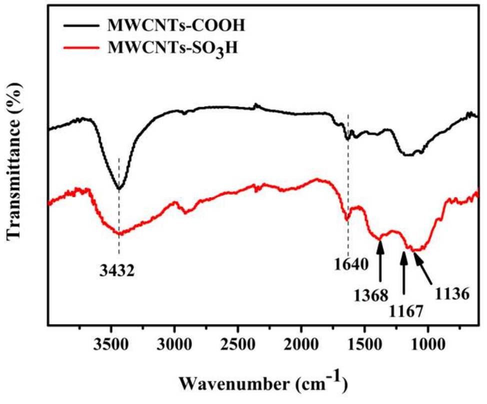


Figure 1. The FTIR spectra of MWCNTs-COOH and MWCNTs-SO_3H powders

The cross-sectional SEM images of 3 wt% MWCNTs -SO_3H/SPEN and 8 wt% MWCNTs -SO_3H/SPEN nanocomposites at the scale bar of 10μm and 3μm, respectively are shown in **Fig. 2**. As shown in **Fig. 2(a)** and **(b)**, the 3 wt% MWCNTs-SO_3H powder has better dispersion and the phase interface between MWCNTs-SO_3H and SPEN matrix is vague and has no obvious pullout phenomenon, verifying that MWCNTs-SO_3H powder are embedded in the SPEN matrix finely. This may be caused by the fact that the sulfonic acid groups between surface of MWCNTs and SPEN matrix chain could form hydrogen bond, enhancing the compatibility of matrix and MWCNTs. Besides, sulfonated MWCNTs could reduce the surface polarity and intermolecular force of MWCNTs, ameliorating the dispersion state in polymer matrix. Nevertheless, the interface compatibility and dispersion state of 8 wt% MWCNTs-SO_3H are obviously weak and bad, which can be seen from the **Fig. 2(c)** and **(d)**. The aggregation of 8 wt% MWCNTs-SO_3H is also very serious, which can affect the performance of the composite strongly. Therefore, the 3 wt% MWCNTs-SO_3H/SPEN composite films present better dispersion and compatibility, which is the prerequisite for better performance and of vital importance to the further study and application.

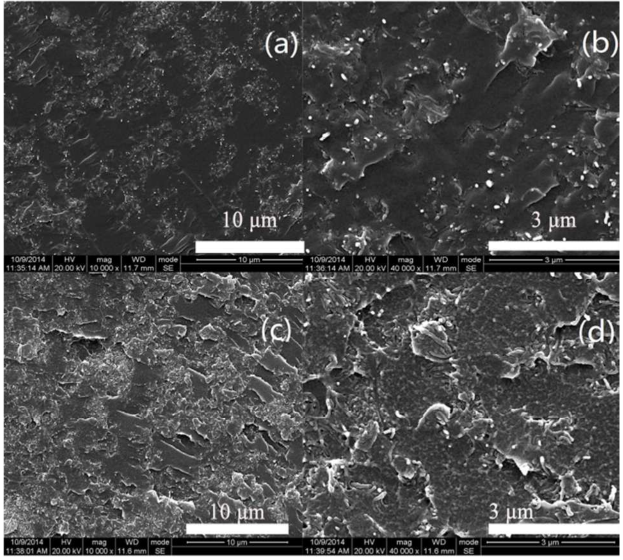


Figure 2. The SEM images of cross section morphology of the (a, b) 3 wt% MWCNTs -SO_3H/SPEN and (c, d) 8 wt% MWCNTs-SO_3H/SPEN nanocomposites at the scale bar of 10μm and 3μm, respectively

TGA was used to further confirm the successful forming of MWCNTs-SO_3H powder. **Fig. 3(a)** presents the decomposition states of MWCNTs-SO_3H and MWCNTs-COOH. The initial decomposition temperature of MWCNTs-COOH powder is about 150 ºC (the decomposition temperature of oxhydryl group in the surface of MWCNTs-COOH), while the MWCNTs-COOH powder is about 230 ºC, which is the decomposition temperature of sulfonic acid groups. Compared these two curves, the MWCNTs-SO_3H powder has been successful forming via the acyl chloride method. The thermogravimetric analysis of composite membranes and neat SPEN membrane are illustrated in **Fig. 3(b).** All the composite membranes have better thermodynamic stability and the initial decomposition temperatures (＞200 ºC) are also higher than the neat SPEN membrane. Besides, the 3 wt% MWCNTs-SO_3H/SPEN composite membrane presents the optimal thermal property compared with other content of composite membranes. This may be caused by the good compatibility between filler and matrix, which is accordant with the results of SEM images. Besides, the SPEN molecular possesses massive rigid aromatic ring structure and oxygen ether bond, establishing better foundation for the good thermodynamic stability of SPEN composite membrane.

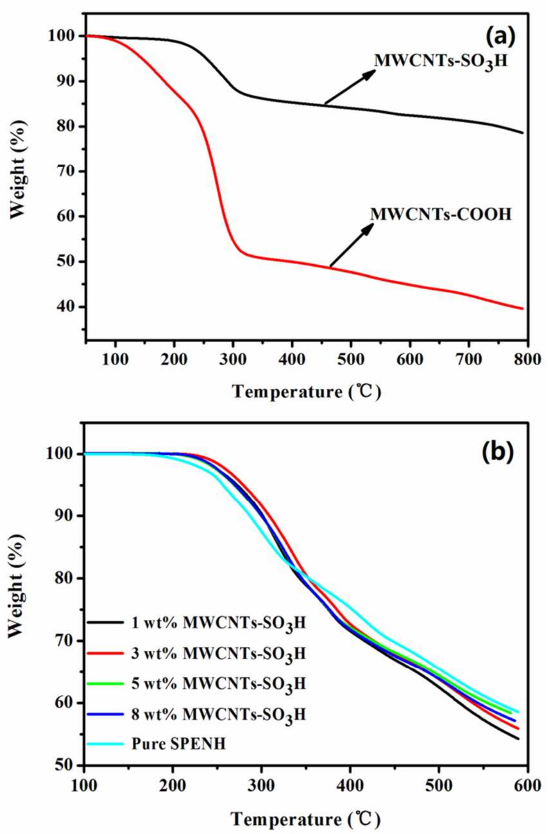


Figure 3. The TGA curves of (a) MWCNTs-COOH and MWCNTs-SO$_3$H, (b) pure SPEN and MWCNTs-SO$_3$H/SPEN composite membranes

Fig. 4 presents the representative curves of tensile test of the composite membranes (a: Tensile strength, b:Tensile modulus). It can be seen that both the tensile strength and modulus reach their highest values at the 3 wt% MWCNTs-SO$_3$Hloading (97.48 MPa, 2458 MPa), and then decrease with further addition of fillers. The effect of this phenomenon is related to the dispersion of filler in PEN matrix chains and the interfacial adhesion of the organic component and inorganic component. When the loading is low, the polymer solubility is affected by the penetration difficult degree of small molecules and the polymer movement. Besides, the dispersion state and interfacial adhesion are also gradually enhanced up to the threshold value. After that, the reunion phenomenon becomes serious and the SPEN matrix is broken by the fillers seriously. Even so, the mechanical properties of 8 wt% MWCNTs-SO$_3$H/SPEN are still higher than that of neat SPEN membrane, demonstrating that grafting massive sulfonic acid groups could fully exert the excellent mechanical property of MWCNTs. It should be noted that the obtained MWCNTs-SO$_3$H/SPEN membranes exhibit much larger tensile strength than the commercial Nafion 117 membrane (10 MPa).[20] In this aspect, the composite can widen their potential application in many special engineering areas.

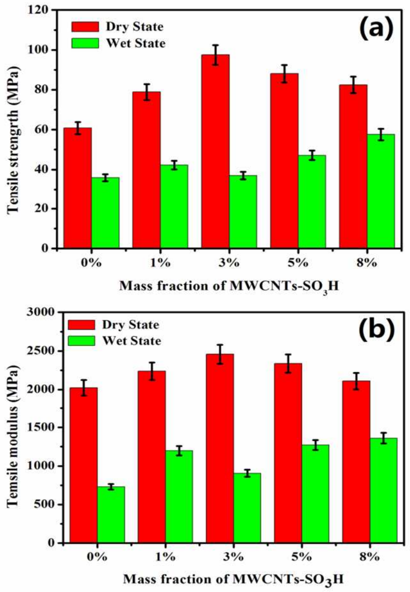


Figure 4. Tensile strength of neat SPEN membrane and MWCNTs -SO$_3$H/SPEN composite membranes prepared in different conditions

Fig. 5(a) shows the conductivity of neat SPEN and MWCNTs-SO$_3$H/SPEN composite membranes immersed in deionized water for 24 h at the room temperature. The proton conductivity reaches the highest value for the loading content of 3 wt% MWCNTs-SO$_3$H sample, indicating that MWCNTs-SO$_3$H could form ion cluster structure and enhance the proton transfer efficiency. With the addition of MWCNTs-SO$_3$H, the local agglomeration becomes more and more serious and interfere the proton transfer to a certain degree, which is corresponding with the morphology characteristics. This shows that the continuous network structure may form when the MWCNTs-SO$_3$H in SPEN matrix reach a certain number, resulting in the rapid increase of proton transfer channel and giving full play the electrical properties of carbon nanotubes. The results display that the filler is a better intensifier to SPEN membrane and also prove that acyl chloride method modified MWCNTs is a successful technique to enhance proton conductivity of SPEN membrane.

Fig. 5(b) presents the variation of proton conductivity with the MWCNTs-SO$_3$H loading content at different temperature. In general, proton conductivities increases with temperature, which is attributed to the increased motion transmissibility of water molecular and form more hydronium ion, resulting in the increased transmission rate. According to previous report,[21] though the proton conductivity of commercial Nafion membranes in 100% RH at different temperatures is slightly higher than that of MWCNTs-SO$_3$H/SPEN composite membranes, the real values are approximate, which is attributed to the large rigidity of SPEN backbone and relatively weak proton carrying capacity.

In order to investigate the effect of shift state of sulfonic acid groups onto the proton transfer, the SPEN membranes were firstly incubated in water at room temperature for 24 h, followed by drying in the oven for 12 h and another round water incubation for 24 h. The proton conductivity of raw and processed SPEN membranes with different content of filler was shown in **Fig. 5(c)**. In low filler content, the proton conductivity of second time water processed SPEN membranes is higher than the original SPEN, suggesting that more sulfonic acid groups expose to the surface of SPEN membranes, which is the contribution of loose and incremental excess proton transfer channel. In contrast, the conductivity decreases as the water uptake time in the higher filler loading, owing to inseparable and untidy proton transfer channel, which block the transfer of sulfonic acid groups. Besides, the minimum change of proton conductivity is 3 wt% MWCNTs-SO_3H, displaying that the SPEN composite membranes contained 3 wt% MWCNTs-SO_3H has optimal stability and possess enormous potential applications in the field of new energy.

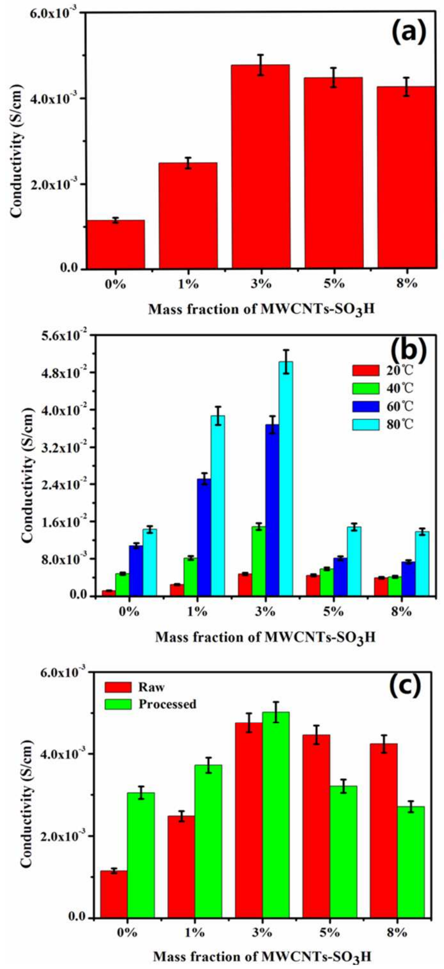


Figure 5. The influence of sulfonated MWCNTs on proton conductivity at different conditions: (a) room temperature, (b) the tendency as the variety of temperature, and (c) the second time water treatment

Conclusions

To address the issue of relative poor mechanical behaviour and low proton conductivity of SPEN composite membranes, the sulfonated MWCNTs fabricated by acyl chloride method was explored as a new filler. The FTIR and TGA measurement confirmed that the MWCNTs-SO_3H has been formed successfully and the MWCNTs-SO_3H/SPEN composite membranes have outstanding thermal stability (> 200 ºC), especially for the 3wt% MWCNTs-SO_3H loading. The mechanical property achieved a maximum of 97.48 MPa and 2458 MPa, which exhibited much larger tensile strength than the commercial Nafion 117 membrane. Besides, the proton conductivity also improved significantly as the addition of MWCNTs-SO_3H powder to a certain value. These improvements are attributed to the addition of MWCNTs-SO_3H powder ameliorate the dispersion state and compatibility with SPEN matrix and provided more excess proton transfer channel. Therefore, the sulfonated MWCNTs fabricated by acyl chloride method is a promising filler to improve the performance of SPEN composite membranes.

Acknowledgements

The authors wish to thank for financial support of this work from the National Natural Science Foundation (Nos. 51173021, 51373028, 51403029) and "863" National Major Program of High Technology (2012AA03A212).

Notes and references

[a] High Temperature Resistant Polymer and Functional Composites Key Laboratory of Sichuan Province, School of Microelectronics and Solid-States Electronics, University of Electronic Science and Technology of China, Chengdu 610054, China. E-mail: jiakun@uestc.edu.cn; liuxb@uestc.edu.cn, Tel:+86-28-83207326

[1] B. J. Yao, X. L. Yan, Y. Ding, Z. J. Lu, D. X. Dong, H. Ishida, M. Litt and L. Zhu, *Macromolecules*, 2014, **47**, 1039–1045.

[2] S. Steven, V. Ramani, J. M. Fenton, H. R. Kunz, M. T. Shawaand R. A. Weiss, *J Membr Sci*, 2005, **256**, 122–133.

[3] Y. Fang, T. T. Wang, R. Y. Miao, L. Tang and X. D. Wang, *Electrochim Acta*, 2010, **55**, 2404–2408.

[4] X. F. Li, D. J. Chen, D. Xu, C. J. Zhao, Z. Wang, H. Lu and H. Na, *J Membr Sci*, 2006, **275**, 134–140.

[5] H. W. Zhang and P. K. Shen, *Chem Rev*, 2012, **112**, 2780−2832.

[6] R.W. Kopitzke, C. Linkous, H. Randoph, R. Anderson and G.L. Nelson, *J Electrochem Soc*, 2000, **147**, 1667-1681.

[7] S. W. Chen, Y. Yin, H. Kita and K. I. Okamoto, *J Polym Sci Part A: Polym Chem*, 2007, **45**, 2797−2811.

[8] D. J. Jones and J.Rozière, *J Membr Sci*, 2001, **185**, 41–58.

[9] S. K. Park and S. Y. Kim, *Macromolecules*, 1998, **31**, 3385-3387.

[10] A. Saxena, R. Sadhana, V. L. Rao, P. V. Ravindran and K. N. Ninan, *J Appl Polym Sci*, 2005, **97**, 1987–1994.

[11] M. J. Sumner, W. L. Harrison, R. M. Weyers, Y. S. Kim, J. E. McGrath, J. S. Riffle, A. Brink and M. H. Brink, *J Membr Sci*, 2004, **239**, 199–211.

[12] Z. J. Pu, L. Chen, Y. Long, L. F. Tong, X. Huang, and X. B. Liu, *J Polym Res*, 2013, **20**, 281-289.

[13] M. N. Feng, X. Huang, Z. J. Pu and X. B. Liu, *J Mater Sci: Mater Electron*, 2014, **25**, 1393–1399.

[14] Y. H. Liu, B. L. Yi, Z. G. Shao, D. M. Xing and H. M. Zhang, *Electrochem Solid St*, 2006, **9**, A356-A359.

[15] S. H. Joo, C. Pak, E. A. Kim, Y. H. Lee, H. Chang, D. Seung, Y. S. Choi, J. B. Park, and T. K. Kim, *J power sources*, 2008, **180**, 63-70.

[16] R. Kannan, B. A. Kakade, and V. K. Pillai, *Angew Chem In. Ed*, 2008, **47**, 2653-2656.

[17] Z. Q. Xu, Z. G. Qi, and A. Kaufman, *Electrochem Solid S*t, 2005, **8**, A313-A315.

[18] H. Dogan, E. Yildiz, M. KAYA and T. Yinan, 2013, *Bull Mater Sci*, **36**, 563-573.

[19] W. L. Harrison, F. Wang, J. B. Mecham, V. A. Bhanu, M. Hill, Y. S. Kim and J. E. McGrath, *J Polym Sci Part A: Polym Chem*, 2003, **41**, 2264–2276.

[20] L. Chen, Z. J. Pu, J. Yang, X. L. Yang and X. B. Liu, *J Polym Res*, 2013, **20**, 45-53.

[21] Y. Sone, P. Ekdunge, and D. Simonsson, *J Electrochem Soc*, 1996, **143**, 1254-1259.