Short communication

Poly(vinylidene fluoride) based anion conductive ionomer as a catalyst binder for application in anion exchange membrane fuel cell

Fengxiang Zhang*, Huamin Zhang**, Chao Qu, Junxia Ren

Lab of Fuel Cell Key Materials and Components, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, China

ABSTRACT

An anion conductive polymeric ionomer incorporated into the electrodes of an anion exchange membrane fuel cell (AEMFC) can help to enhance anion transport in the catalyst layer of electrode, and thus improve the catalyst efficiency and performance of AEMFC. In this work, we report the synthesis and properties of a new type of anion conductive ionomer, which is synthesized by grafting of poly(vinylidene fluoride), or PVDF with poly(vinylbenzyltrimethylammonium chloride) via atom transfer radical polymerization. The ionomer obtained shows improved hydrophilicity relative to pristine PVDF, and exhibits an ion exchange capacity of 1.59 mmol g^{-1}. When used in a direct hydrazine hydrate fuel cell (DHFC) as a catalyst binder, the synthesized ionomer imparts the DHFC a significantly improved power density, which is 5–10 fold as much as that of the cells without using such ionomer. The method developed here for anion exchange ionomer synthesis is facile, green and does not involve the use of carcinogenic chemicals such as chloromethylmethylether and trimethylamine, which are often used for conventional anion exchange membrane or ionomer synthesis.

1. Introduction

Fuel cells are electrochemical devices that can convert chemical energies stored in fuels (such as hydrogen, alcohol, hydrazine and sodium borohydride) into electrical energy through catalyzed electrochemical reactions. Among the various types of fuel cells reported so far, anion exchange membrane fuel cells (AEMFCs) are advantageous in kinetics of anodic fuel oxidation and cathodic oxygen reduction reactions [1,2]. This type of fuel cell, therefore, allows the use of non-noble metals such as nickel, cobalt and silver as electro-catalysts, which can translate into reduced cost of fuel cell as compared with proton exchange membrane fuel cells. Another striking feature of AEMFC is that its solid membrane electrolyte, as opposed to the metal-ion-containing liquid electrolyte in conventional alkaline fuel cells, makes the cell free of electrode clogging issue and benefits mass transfer in the electrodes. With the above advantages, AEMFC has received intensive interests and attention from the community of new energy research during the past few years.

To insure effective electrochemical reactions in the catalyst layer of an AEMFC electrode and to improve the catalyst utiliza-

tion efficiency, an anion conductive polymer ionomer is needed to bind the catalyst particles and form a porous architecture that can simultaneously facilitate transport of anions, electrons, and reactants/products as schematically shown in Fig. 1. Such an anion conductive ionomer is exactly the analogy of Nafion used in proton exchange membrane fuel cells (PEMFCs) as a catalyst binder. Also as in PEMFC, for incorporation into the catalyst layer, the anion conductive ionomer is first dissolved in a low-boiling-point solvent, and then mixed with catalyst to make a paste for coating onto a carbon paper; lastly the resulting electrode is heated to remove the solvent. While there are different types of AEMs reported in the literature, a suitable catalyst binder for AEMFC is not easily available at present although some groups [3,4] have reported aminosilane-based, chloride conductive layer incorporated into the electrodes for CuCl/HCl electrolyzers. One reason for this situation lies in the fact that most of the AEMs reported so far are fabricated via a post amination route where a chloromethylated polymer is cast into a membrane, or (irradiation) grafted onto a preformed polymer matrix (such as polytetrafluoroethylene, or PTFE), which is then treated with a trimethylamine solution (aq.) and a NaOH or KOH solution for quaternary amination and alkalization, respectively. Such a fabrication route, according to our own experience and other researchers' findings [5], often results in the AEM insoluble in either ethanol/isopropanol or polar solvents like N-methyl-2-pyrrolidone (NMP), N,N-dimethylacetamide (DMAc), dimethylsulfone (DMSO) and N,N-dimethylformamide (DMF), and thus unable to be made into a solution for catalyst binding purpose.
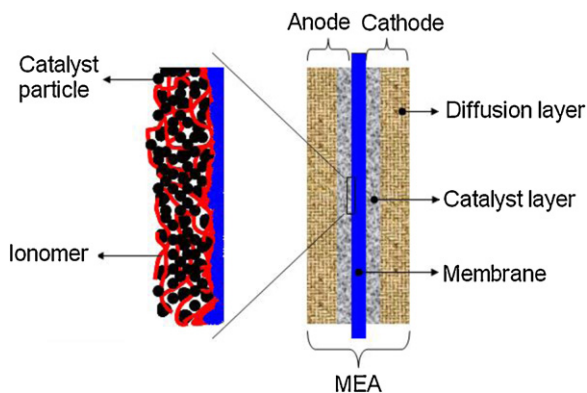
Fig. 1. Schematic for the architecture of ionomer-containing electrode membrane assembly (MEA). The ionomer may or may not be of the same material with the membrane.

Due to the limited availability of suitable ionomers, many AEMFCs rely on KOH or NaOH addition in the anolyte [6–10] to render the catalyst exposed to hydroxide ions; in such cases, PTFE or Nafion are often used as the catalyst binder although they are not anion conductive. In recent years, some advancement has been achieved in addressing the above mentioned difficulty. For example, Valade et al. synthesized ionomers of fluorinated poly(diallyldimethylammonium chloride)s [poly(DADMAC)] or poly(chlorotrifluoroethylene-co-DADMAC) copolymers [11]. Gu et al. [12] prepared a phosphonium type, alcohol soluble anion conductive ionomer, and the AEMFC with such ionomer exhibited remarkably high power output (200 mW cm^{-2}). Varcoe et al. incorporated polyvinylbenzylchloride into the catalyst layer and treated it with tetramethylethylenediamine to accomplish simultaneous quaternary amination and crosslinking [13,14]. Despite these progresses, efforts are still needed to synthesize more efficient ionomer for use in AEMFC, and to develop easier and greener way of synthesizing such ionomer.

In this work, we report our preliminary but promising results on synthesis and properties of a new type of anion conductive ionomer. It is synthesized by grafting of poly(vinylidene fluoride), or PVDF with poly(vinylbenzyltrimethylammonium chloride) via atom transfer radical polymerization (ATRP). Apart from being a high-performance material, PVDF has been reported to be able to function as a macroinitiator for ATRP utilizing its secondary fluorine atoms although the C–F bond is stronger than C–Cl or C–Br. Good examples include syntheses of copolymers of PVDF with poly(oxyethylene methacrylate) [15] and 3-trimethoxysilylpropyl methacrylate [16], as well as growth of poly (ethylene glycol) monomethacrylate brush from the PVDF surface [17]. Inspired by these examples, we herein explore on synthesis of VBTAC grafted PVDF via ATRP, and the application of the synthesized copolymer as an electrode ionomer for direct hydrazine fuel cell (DHFC). Our results show that the synthesized ionomer can improve DHFC performance significantly (5–10 fold increase of power density). Our method of making electrode ionomer is facile, inexpensive and avoids the use of chloromethylmethylether and trimethylamine, both of which are strongly toxic and carcinogenic. To the best of our knowledge, this method has not been reported for synthesis of anion conductive ionomer prior to the present study.

2. Experiment

2.1. Synthesis of PVDF-g-PVBTAC (PgP) ionomer

0.75 g of PVDF, 0.08 g of CuCl (catalyst) and 0.025 g of 4,4′-bipyridine (coordinating agent) were added to a three-necked round bottom flask equipped with a vacuum line and a drop funnel. The flask then underwent three cycles of evacuation and nitrogen purge. Subsequently 25 ml N-methyl-2-pyrrolidone (NMP) was added and stirred; when a homogeneous and clear solution resulted, 0.75 g vinylbenzyltrimethylammonium chloride (VBTAC) was added and the flask underwent another three cycles of evacuation and nitrogen purge. The reaction mixture was stirred at 30 °C for 24 h, and then transferred to copious amount of vigorously stirred methanol/water mixture (1/1 by volume). The resultant precipitate was stirred 12 h to remove catalyst, coordinating agent, unconsumed monomer and PVBTAC homopolymer (if any). Finally the product was filtered and washed with methanol, and vacuum dried at 50 °C overnight. All the chemicals are of analytical grade and used as received.

2.2. Characterization of the synthesized PgP ionomer

PgP was dissolved in dimethylformamide (DMF) and cast on a glass slide; after the solvent was evaporated by thermal treatment, the resulting membrane was studied by ATR-FTIR on a JASCO FT-IR 4100 spectrometer with an ATR accessory containing a Ge crystal. For comparison, a pure PVDF membrane was also studied by FTIR. Both spectra were recorded in the wave number range from 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1}.

The ion exchange capacity (IEC) of the synthesized PgP ionomer was determined by titration method. A known amount of dried PgP powder was soaked in 0.01 M aqueous solution of NaOH for 48 h; the NaOH solution was then titrated with 0.01 M HCl with phenolphthalein as the indicator. The IEC was calculated from the following equation: IEC = $(M_1V_1 - M_2V_2)/m$, where m is the mass of dried PgP; M_1 and V_1 are, respectively, the concentration and volume of NaOH solution before titration; M_2 and V_2 represent, respectively, the concentration and volume of HCl solution consumed in titration.

2.3. Linear sweep voltammetry (LSV)

LSV was performed to study the oxygen reduction behavior of the catalyst layer with the synthesized PgP ionomer as binder. A mixture containing 1 ml ethanol, 20.00 mg in-house prepared catalyst CoNx/C (synthesis and characterization to be reported separately) and 50 μl PgP solution (2%, w/v) was sonicated for 30 min; 5 μl of such mixture was cast onto a clean glassy carbon electrode (GCE) (4 mm in diameter) surface and dried in air (co loading 0.105 mg cm^{-2}). For comparison, a pure CoNx/C layer was also made on GCE surface following the above procedure except the inclusion of PgP, and then fixed with a top layer of Nafion (4 μl, 1% ethanol solution) to prevent fall-off the catalyst particles during tests. LSV measurements were carried out in a standard three-electrode cell consisting of a GCE working electrode (coated with the catalyst layer described above), a Pt foil counter electrode and an Hg/HgO reference electrode. All the measurements were conducted using a CHI 660 electrochemical station (CH Corp., USA) with 1.0 M KOH solution (O$_2$ saturated) as electrolyte. The sweep rate was 5 mV s^{-1}.

2.4. Electrode fabrication and fuel cell tests

In-house synthesized Co and CoNx/C were used as the anode and cathode catalysts, respectively. For electrode preparation, catalyst was blended with a calculated amount of PgP solution (2% by weight in DMF) to make a catalyst ink and sprayed onto carbon cloth with an air brush; catalyst loadings are 2 mg cm^{-2} of Co for the anode and 0.4 mg cm^{-2} of CoNx/C for the cathode. A commercial AEM (obtained from Tokuyama Co. Japan) was sandwiched between the above-obtained anode and cathode; the resultant "sandwich" was
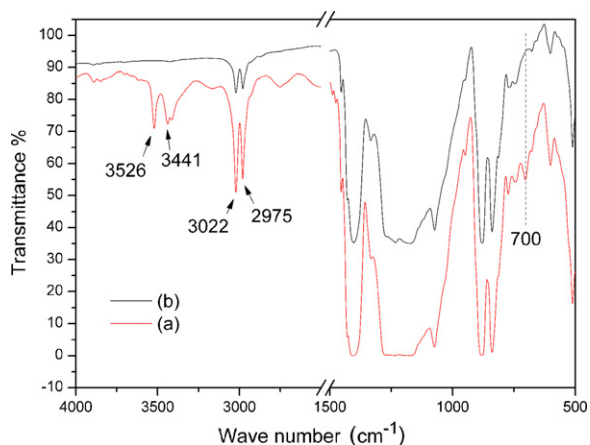
Fig. 2. FTIR of PgP (curve a) in comparison with PVDF (curve b).

then mounted in a $5 \times 5 \, cm^2$ test fixture containing graphite blocks with serpentine flow channels. The test fixture was assembled with a torque of 5 N m. To avoid damage of the membrane's quaternary ammonium groups at elevated temperatures, no hot pressing was conducted, which is similar to the practice of Varcoe et al. [18], although this may affect, to some extent, fuel cell performance due to presumably higher contact resistance between membrane and electrodes. For operation of DHFC, its anode was supplied with an aqueous fuel solution of 4 M hydrazine hydrate containing 1 M NaOH at a flow rate of 5 ml min^{-1}, and its cathode was fed with 0.04 MPa oxygen (100% humidified). Fuel cell test was conducted 70 °C with an Arbin Instruments (College Station, TX) Fuel Cell Test Station (FCTS).

3. Results and discussion

Fig. 2 shows the FTIR spectrum of the synthesized PgP (curve a); it displays all the characteristic absorption bands that are present in pure PVDF (curve b). In addition, a new band at 700 cm^{-1} appears in curve (a), which is attributed to the bending vibration of methyl group (–CH$_3$) in VBTAC. The absorption bands at 3022 and 2975 cm^{-1} exist in both spectra, and are assignable to the methylene (–CH$_2$–) moieties. These two bands, however, are much stronger in the spectrum for PgP than in PVDF; this further evidences the successful grafting of VBTAC, whose methylene group contributes to the higher intensity of the two bands at 3022 and 2975 cm^{-1}. The bands at 3526 and 3441 cm^{-1} are due to water that is bound with the quaternary ammonium moieties in PgP ionomer, though the possibility may not be ruled out that trace amount of ligand remain in the final product.

There is a solubility difference between the synthesized ionomer and pure PVDF: the former can make a solution of maximum 3%

with aprotic polar solvents like NMP, DMAc, DMSO and DMF while the latter is fully soluble in all the above solvents. This change in solubility constitutes another piece of evidence, in addition to the spectroscopic result shown in Fig. 2, for the successful grafting of VBTAC, and can be explained by the likelihood that cross-linking has taken place to some degree during ATRP. Such cross-link is believed to form between two propagating radicals (initiated by PVDF) coupled together, resulting in two PVDF chains linked to each other with a PVBTAC chain. This is different from small-molecule alkyl halide initiated ATRP, where coupling termination is also inevitable [19,20] but the resulting coupled macromolecule is a linear chain, instead of being cross-linked. Note that the above mentioned cross-linking did not occur to a high degree, and the synthesized PgP ionomer can make a dilute solution (2 wt%) using DMF as solvent, which can satisfy the need for preparing anion conductive catalyst layer. Although not so volatile as ethanol or isopropanol, which are typical solvents for making Nafion solutions in preparation of PEMFC electrodes, DMF has a relatively high vapor pressure (0.49 kPa, 25 °C) compared with NMP (0.066 kPa, 25 °C), DMAc (0.33 kPa, 20 °C) and DMSO (0.05 kPa, 20 °C), and is suitable for making an ionomer solution that can be used to prepare a catalyst ink.

Water affinity is an important property determining the performance of an electrode ionomer/binder; the grafting of VBTAC has created a change in this property of PVDF. For comparison, the PgP ionomer and pure PVDF were each made into a membrane, whose water contact angles (WCA) were measured and shown in Fig. 3: PgP exhibits a WCA of 74°, while PVDF 87. Evidently, the PgP ionomer is more hydrophilic than PVDF, and this is attributed to the grafting of VBTAC, which is a highly hydrophilic and water soluble salt. In addition, the hydrophilicity of PgP is close to that of some commercial AEMs reported in the earlier studies. For example, Tokuyama membranes AM-1 and AFN display WCA of 78.8 and 78.7° respectively [21]. Proper hydrophilicity is an essential property for an electrode ionomer, which must be able to provide an interface with catalyst particles that is favorable for water-involved hydroxide ion transport. It is important to note that the WCA measurement for the PgP membrane was made on its chloride form, instead of having been alkalized by NaOH or KOH treatment; this makes sure that the WCA change is solely attributed to grafted side chains instead of to other factors such as alkali caused defluorination of PVDF.

Anion exchange is the targeted core function of the PgP ionomer synthesized. This property was characterized by the ionomer's ion exchange capacity (IEC) relative to hydroxide ions. Based on the titration method, IEC value of PgP was measured to be 1.59 mmol g^{-1} at room temperature. This value is comparable to those reported in the literature for anion conductive membranes or ionomers. For example, an irradiation derived, quaternary ammonium functionalized FEP anion exchange membrane shows an IEC of 1.08 mmol g^{-1} [22], while an AEM of poly(methyl methacrylate-
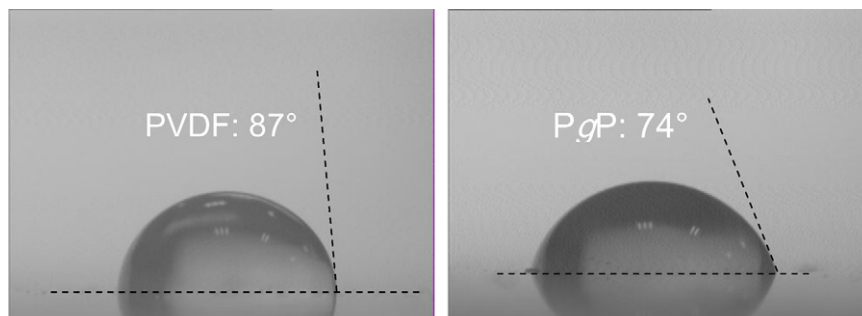

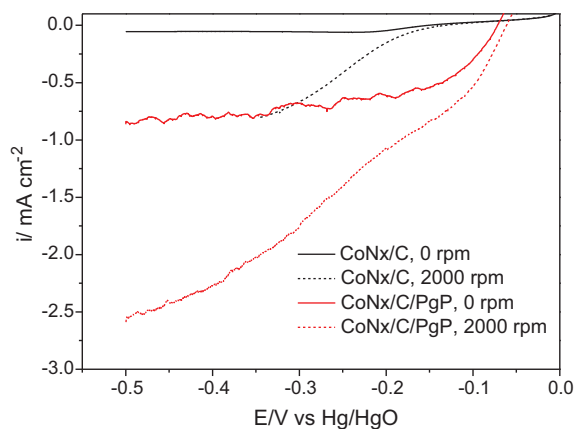**Fig. 3.** Water contact angles of PgP and PVDF membranes.

Fig. 4. Linear sweep voltagrams of the CoNx/C catalyst layer incorporating the synthesized PgP ionomer (CoNx/C/PgP) and that without such ionomer (CoNx/C).
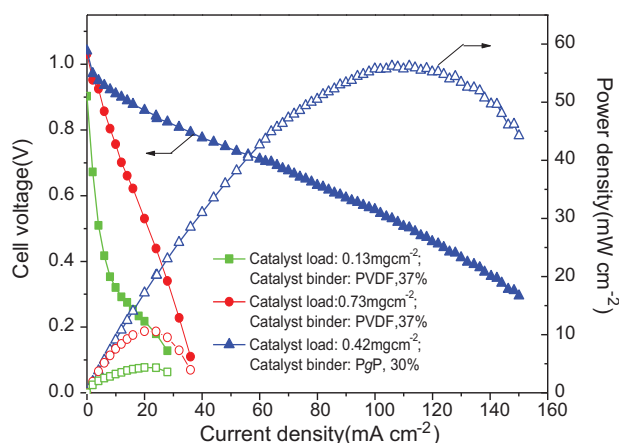

Fig. 5. Polarization (solid symbols) and power density (open symbols) curves of DHFC with PgP or PVDF as the catalyst binder. Fuel: 4 M hydrazine hydrate containing 1 M NaOH at a flow rate of 5 ml min^{-1}; oxidant: 0.04 MPa oxygen (100% humidified); cell temperature: 70 °C.

co-butyl acrylate-*co*-vinylbenzyl chloride) (also ammonium type) has an IEC value of 1.25 mmol g^{-1} [23]; in other cases, IEC of 1.3 mmol g^{-1} was reported for anionic membrane based on polyepichlorhydrin matrix (functionalized with a cyclic diamine DABCO) [24], and 1.14 mmol g^{-1} reported for an hydroxide conductive ionomer of poly(vinylbenzyl chloride) cross-linked with a diamine [13]. Poly (arylene ether sulfone) ionomers with pendant quaternary ammonium exhibits high IEC ranging from 1.58 to 3.02 mmol g^{-1} (corresponding to substitution degree of 40–90%) [5]. It should be clarified that in our work, the IEC value for PgP was measured in its powder form, instead of membrane. When cast into a membrane, its IEC dropped to 1.02 mmol g^{-1}, and the conductivity of the cast membrane was low (on the order of 10^{-3} S cm^{-1}). This is because the membrane has a more compact structure than the powder, and exerts a higher resistance for ion exchange.

Next, an electrochemical study (linear sweep voltammetry, Fig. 4) was performed to investigate the oxygen reduction reaction (ORR) occurring on the catalyst layer with the synthesized PgP ionomer as binder (CoNx/C/PgP) and that without PgP ionomer (CoNx/C). It can be seen that the ORR onset potential for CoNx/C/PgP is ca. 0.06 V higher than that of CoNx/C, indicating a smaller polarization of the former compared with the latter. Meanwhile, the current density at −0.5 V (disc electrode rotating speed 2000 revolution per min or rpm) for CoNx/C/PgP is ca. 1.7 mA cm^{-2} higher than that for CoNx/C, which can be attributed to the enhanced hydroxide ion transport between the catalyst particles. These observations clearly reveal that the catalyst layer incorporating PgP ionomer outperforms that without such ionomer.

For its application as a catalyst binder in AEMFC, the synthesized PgP ionomer, dissolved in DMF (a 2% solution), was blended with catalyst (Co for anode and CoNx for cathode) to make a paste, which was then coated on carbon paper and dried for solvent removal. The resultant electrodes and a commercial AEM were assembled into a fuel cell, whose anolyte was hydrazine hydrate containing 1 M NaOH and oxidant was humidified oxygen (the cell is named DHFC). Fig. 5 shows the voltage–current polarization and power density of such DHFC and the results of the cells without using PgP as the catalyst binder. It can be seen that the polarization curve for the cell with PgP catalyst binder (30% relative to catalyst loading) shows a much smaller slope than that with PVDF binder (37% relative to catalyst loading), indicating a lower electrochemical polarization on the electrodes. Meanwhile, the cell with the PgP binder shows a peak power density of ca. 55 mW cm^{-2} at a catalyst load of 0.42 mg cm^{-2}; this is ca. 5–10 fold as much as the power densities of the cells with PVDF binder, depending on the catalyst loadings (0.73 or 0.13 mg cm^{-2}). The above differences are

attributed to the enhanced anion transport in the catalyst layer to facilitate electrode reactions, i.e., improved catalyst efficiency. Without such ionomer, even if the catalyst loading was nearly doubled (0.73 versus 0.42 mg cm^{-2}), the power density of the cell is about 80% lower (10 versus 55 mW cm^{-2}). It should be mentioned that the use of commercial AEMs is to guarantee a reliable comparison of cell performance, because the commercial AEM is more uniform in thickness and more conductive than our cast PgP membrane, thus making sure that the variation of cell performance is mainly due to the catalyst ionomer instead of other factors such as membrane thickness and conductivity.

Note that the fuel cells involved in the above comparisons were all supplied with hydrazine hydrate containing 1 M NaOH. Definitely, NaOH can contribute to the anion transport in the catalyst layer since the electrodes were fully exposed to the alkaline environment during cell operation. Even with such a contribution, the effect of ionomer for improving fuel cell performance is clear as shown in Fig. 5. In fact, the addition of NaOH in the anolyte is for the purpose of suppressing the hydrazine hydrolysis [25], which proceeds following the equation $N_2H_4 + H_2O = N_2H_5^+ + OH^-$. A previous study by Asazawa et al. [26] reveals that the addition of KOH improved the cell performance remarkably; the cell performance was very poor in the absence of KOH and for 0.1 M KOH, and the cell exhibited a very low open circuit voltage of 0.282 V in the absence of KOH.

One more point concerning NaOH addition in the anolyte is that it can cause de-fluorination of PVDF following the mechanism shown below [27]: $-[CH_2-CF_2]_n- + NaOH \rightarrow -[CH_2-C(OH)_2]_n-$. In this context, we treated a PVDF membrane by soaking it in 3 M NaOH solution (aq.) at 60 °C for 3 days, and found it still an intact membrane (no cracking or decomposition observed). We further performed a stress–strain analysis on the treated membrane in comparison with a pristine PVDF membrane (as shown in Fig. 6), finding that the treated PVDF membrane had a higher modulus and a lower elongation at break than the un-treated one, i.e., it became brittle. This is believed to be associated with the possible double bond formation accompanying the above defluorination, which proceeds as follows [28]: $-(CH_2-CF_2)_n- + NaOH \rightarrow -(CH=CF)_n- + NaF + H_2O$. The above observations and analyses suggest that NaOH exposure did create chemical changes to PVDF membrane, but did not lead to molecular chain scission or decomposition of the material. This provides feasibility for PVDF based ionomer to function as a catalyst binder (not in membrane form) in an AEMFC.
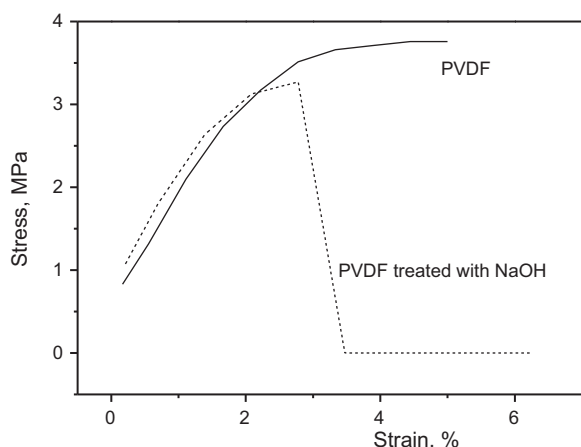
Fig. 6. Stress–strain curves for a PVDF membrane treated in NaOH solution (aq.) at 60 °C for 3 days and an un-treated PVDF membrane.

4. Conclusion

Grafting of PVDF with VBTAC via ATRP technique has afforded the formation of quaternary ammonium functionalized, anion conductive ionomer that can be dissolved in DMF and used as the catalyst binder for AEMFC electrodes. Chemistry, water affinity and ion exchange property of the ionomer synthesized have been characterized by FTIR, contact angle measurement and ion exchange capacity, respectively. Effectiveness of the ionomer as a conductive catalyst binder is demonstrated with improved performance of DHFC. This work opens an alternative to the existing method for synthesis of anion conductive polymer ionomer that can function as an effective catalyst binder applicable in AEMFC. Further work will be done to optimize the ionomer synthesis and its loading in the catalyst layer.

Acknowledgements

References

[1] J.S. Spendelow, A. Wieckowski, Phys. Chem. Chem. Phys. 9 (2007) 2654–2675.
[2] A.V. Tripkovic, K.D. Popovic, B.N. Grgur, B. Blizanac, P.N. Ross, N.M. Markovic, Electrochim. Acta 47 (2002) 3707–3714.
[3] S. Ranganathan, E.B. Easton, Int. J. Hydrogen Energy 35 (2010) 1001–1007.
[4] S. Ranganathan, E.B. Easton, Int. J. Hydrogen Energy 35 (2010) 4871–4876.
[5] J. Wang, Z. Zhao, F. Gong, S. Li, S. Zhang, Macromolecules 42 (2009) 8711–8717.
[6] E. Agel, J. Bouet, J.F. Fauvarque, J. Power Sources 101 (2001) 267–274.
[7] Y.S. Li, T.S. Zhao, Z.X. Liang, J. Power Sources 187 (2009) 387–392.
[8] H. Hou, G. Sun, R. He, B. Sun, W. Jin, H. Liu, Q. Xin, Int. J. Hydrogen Energy 33 (2008) 7172–7176.
[9] E.H. Yu, K. Scott, J. Power Sources 137 (2004) 248–256.
[10] J.H. Wang, S.H. Li, S.B. Zhang, Macromolecules 43 (2010) 3890–3896.
[11] D. Valade, F. Boschet, S. Rouäldès, B. Ameduri, J. Polym. Sci. Part A: Polym. Chem. 47 (2009) 2043–2058.
[12] S. Gu, R. Cai, T. Luo, Z.W. Chen, M.W. Sun, Y. Liu, G.H. He, Y.S. Yan, Angew. Chem. Int. Ed. 48 (2009) 6499–6502.
[13] J.R. Varcoe, R.C.T. Slade, E.L.H. Yee, Chem. Commun. (2006) 1428–1429.
[14] S.D. Poynton, J.P. Kizewski, R.C.T. Slade, J.R. Varcoe, Solid State Ionics 181 (2010) 219–222.
[15] J.F. Hester, P. Banerjee, Y.Y. Won, A. Akthakul, M.H. Acar, A.M. Mayes, Macromolecules 35 (2002) 7652–7661.
[16] Y. Chen, H. Kim, React. Funct. Polym. 68 (2008) 1499–1506.
[17] Y. Chen, D. Liu, Q. Deng, X. He, X. Wang, J. Polym. Sci. Part A: Polym. Chem. 44 (2006) 3434–3443.
[18] J.R. Varcoe, R.C.T. Slade, E. Lam How Yee, S.D. Poynton, D.J. Driscoll, D.C. Apperley, Chem. Mater. 19 (2007) 2686–2693.
[19] S.M. Jo, W.S. Lee, B.S. Ahn, K.Y. Park, K.A. Kim, I.S.R. Paeng, Polym. Bull. 44 (2000) 1–8.
[20] R. Sharma, A. Goyal, J.M. Caruthers, Y.Y. Won, Macromolecules 39 (2006) 4680–4689.
[21] M.S. Kang, Y.J. Choi, S.H. Moon, AIChE J. 49 (2003) 3213–3220.
[22] H. Herman, R.C.T. Slade, J.R. Varcoe, J. Membr. Sci. 218 (2003) 147–163.
[23] Y. Luo, J. Guo, C. Wang, D. Chu, J. Power Sources 195 (2010) 3765–3771.
[24] D. Stoica, L. Ogier, L. Akrour, F. Alloin, J.F. Fauvarque, Electrochim. Acta 53 (2007) 1596–1603.
[25] W.X. Yin, Z.P. Li, J.K. Zhu, H.Y. Qin, J. Power Sources 182 (2008) 520–523.
[26] K. Asazawa, T. Sakamoto, S. Yamaguchi, K. Yamada, H. Fujikawa, H. Tanaka, K. Oguro, J. Electrochem. Soc. 156 (2009) B509–B512.
[27] Q. Zhang, J. Lu, F. Saito, M. Baron, J. Appl. Polym. Sci. 81 (2001) 2249–2252.
[28] G.J. Ross, N.P. Barradas, M.P. Hill, C. Jeynes, P. Morrissey, J.F. Watts, J. Mater. Sci. 36 (2001) 4731–4738.