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Constructing polymeric proton donor and proton acceptor in layer-by-layer structure for efficient proton transfer in PEMFC

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ABSTRACT

Heterocyclic compounds are known as proton transfer species for anhydrous polymer electrolyte membrane (PEM), for which efficient proton conductivity at high operating temperature has yet to be found. The present work proposes an approach to enhance the proton transfer of the membrane by combining the concept of proton donor and acceptor with an ordered structure, i.e. layer-by-layer (LbL). By simply applying poly(acrylic acid) (PAA) as a polymeric proton donor and benzimidazole (BIm) conjugated on branching poly(ethyleneimine) as a polymeric proton acceptor and alternately coating the sulfonated poly(ether ether ketone) (SPEEK), a LbL membrane can be obtained. The proton transfer can be fine-tuned by the number of bilayers, and at that time, the 20-bilayered SPEEK/BIm-PEI/PAA is an optimal condition, which achieves a balance between the hydrogen bond and chain mobility under LbL packing that allows a 1.5 higher order of magnitude conductivity than an as-prepared SPEEK membrane even at a high operating temperature range (90–170 °C). The present work, for the first time, shows how a simple LbL technique is practical for constructing high-ordered structure of proton donor and acceptor species on the membrane surface for the efficient proton transfer in a PEM.

Introduction

The polymer electrolyte membrane fuel cell (PEMFC) is accepted as one of the most promising green power generators due to the use of unlimited hydrogen as a resource, simple but highly efficient electrochemical energy and zero emission as well as other attractive features such as low noise and low maintenance cost [1–4]. Commercial perfluorosulfonated membrane such as Nafion® has been known for its efficient proton conductivity (as high as 10^{-2} S/cm) [5] via water molecules in forms of hydronium ion (H_3O^+) attached on sulfonated groups as proton transfer species. The biggest limitation of perfluorosulfonated membrane is the decrease of its proton conductivity when the temperature of the cell becomes higher than the water evaporation temperature as a consequence of accumulated heat from energy loss in the cell [1]. In fact, this also leads to a need for a thermally stable membrane of which perfluorosulfonated membrane and sulfonated polyether ether ketone (SPEEK®) are suitable.

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To overcome water dehydration at a high operating temperature (above water evaporation temperature) as mentioned above, the anhydrous membrane, based on the use of nitrogen containing heterocyclic derivatives, e.g. imidazole, benzimidazole and pyrazole etc., is accepted as a thermally stable proton acceptor up to 200 °C [6–8]. Considering the incorporation of the heterocycles in the PEM, the possibilities are, for example, homopolymers, copolymers, blends and grafting. Kim et al. proposed the Nafion® – benzimidazole blend membrane to maintain proton conductivity up to 200 °C [9]. Shen et al. synthesized polymer containing benzimidazole which provides conductivity 10^{-2} S cm^{-1} at 160 °C [10]. Although those cases offer certain proton conductivity at high operating temperature, the most effective and efficient proton transfer system has yet to be found.

For a proton transfer mechanism, it is known that not only a hydrogen bond network, but also a proton source in the membrane is needed to initiate proton transfer. In other words, the sulfonyl groups in Nafion® and SPEEK® together with doping with strong acids, such as phosphoric acids, play the role of proton donors at that time the water molecules act as proton acceptors in the form of an hydronium ion, which encourages the idea of incorporating the proton donor in the membrane as well as the proton acceptor. Previously, it was reported that the use of PAA as a proton donor in copolymers [11] led to improvement of proton transfer conductivity in the membrane. In fact, these studies on model compounds using X-ray single crystal analysis [12] insist that the balance of the hydrogen bond network between proton transfer species and molecular mobility plays an important role for the Grotthus mechanism and Vogel–Tamman–Fulcher (VTF), or vehicle mechanism.

As a hydrogen bond is essential for proton transfer, the ordering of proton donors and acceptors by aligning both functional groups in a regular manner might favor the hydrogen bond network in the polymer matrices so that proton transfer becomes significantly efficient.

A Layer-by-layer (LbL) technique between two polymers under interactions such as electrostatic, van der Waals and hydrogen bonds, is accepted as a simple and efficient way to form a polymer complex [13–15]. This technique, therefore, is recognized as a way to fabricate a regular nanostructure under molecular alignment in the form of polymer thin layers and films. In the field of PEM, Deligöz and coworkers reported on LbL deposition of poly(allylamine hydrochloride) and polyvinylsulfonic acid on Nafion® membrane [16] to obtain LbL composite membrane with low methanol crossing over for a direct methanol fuel cell. Jiang and coworkers applied oppositely charged polycations, i.e. poly(diallyldimethylammonium chloride) and poly(allylamine hydrochloride) with polyanions, i.e. poly(2-acrylamido-2-methyl-1-propanesulfonic acid), poly(1-(4-(3-carboxy-4-hydroxyphenylazo) benzene sulfonamido)-1,2-ethanediyl, sodium salt), poly(sodium styrene sulfonate) and poly(acrylic acid) [17] and showed a successful methanol cross over reduction in a direct methanol fuel cell (DMFC).

It appears the LbL consisting of a proton donor such as a polymer with acidic pendant group, and proton acceptor, such as a polymer with heterocycles, not only creates regular packing due to polymer complexation, but also a hydrogen bond network where the proton transfer is possible. In fact, previous studies have clarified that efficient proton transfer is related to the balance between the hydrogen bond among heterocycles and mobility of heterocyclic chains [12,18]. Taking this into account, this work focuses on the use of poly(acrylic acid) as the proton donor and branching heterocycles as the proton acceptor so that the LbL is satisfied with a hydrogen bond network as well as molecular mobility initiated by the branching heterocycles. The sulfonated poly(ether ether ketone) is applied as the substrate where the LbL is constructed on the surface. This work also extends to clarify the optimal number of layers and membrane performance under temperature variation.

Experiment

Materials

Poly(ether ether ketone) powder was a gift from JJ-Degussa Chemicals (Thailand) Ltd. Branching polyethylene imine (bPEI) (MW 25,000 g mol^{-1}), 2-(chloromethyl)benzimidazole (MBz), poly(acrylic acid) (PAA) (MW 450,000), and deuterated dimethyl sulfoxide (DMSO-d6) were purchased from Aldrich Co., Germany. Dimethyl sulfoxide and potassium hydroxide were bought from Acros Co. Germany. All chemicals were used as-received except bPEI, which was dried under vacuum at 80 °C for 48 h before use.

Synthesis and preparation of SPEEK membrane

SPEEK was prepared by dissolving dry poly(ether ether ketone) (PEEK) (2 g) in 200 mL concentrated (98%w/v) sulfuric acid. The solution was stirred vigorously for 8 h before precipitating in an ice-cooled deionized water (DI water) bath followed by DI water washing until the precipitate became neutral. The precipitate was dried at 80 °C to obtain SPEEK. The SPEEK obtained was dissolved in DMSO to achieve 5%w/v and was cast in a 3 × 3 × 0.5 cm mold to obtain the membrane.

Synthesis and preparation of BIm-PEI

The modification of bPEI with BIm was carried out as reported previously. In brief, to DMSO solution (10 mL) containing bPEI (2 g, 46.5 mmol), an amount of KOH (0.36 g, 6.4 mmol) was added and allowed to heat at 90 °C for 30 min. A DMSO solution (20 mL) containing MBz (1.07 g, 6.4 mmol, or 0.2 equivalent of the primary and secondary amine contents in bPEI) was added drop-wise, and the reaction was carried out under N_2 atmosphere overnight. The solution obtained was neutralized by 1 M HCl and dialyzed against DI water several times before freeze-drying to obtain BIm-PEI.

Layer-by-layer membrane preparation

The LbL membrane was prepared as follows. The solutions of BIm-PEI 3.01×10^{-5} mmol/mL (7.00 g in 100 mL DI water containing 2.93 g NaCl), and of PAA 1.11×10^{-6} mmol/mL (0.048 g in 100 mL DI water containing 2.93 g NaCl) were prepared. The SPEEK membrane (3 × 3 cm) was alternatively

soaked in BIm-PEI solution and PAA solution for 2 min. Before soaking in another solution, the membrane was rinsed thoroughly by deionized water. Alternate soaking was carried out for 5, 10, 20 and 40 times to obtain the LbL SPEEK membrane with the pairs of proton donor and acceptor layers on both sides, so-called bilayers. All the membranes were dried at 80 °C for 15 h and kept in a desiccator until used. Fig. 1 shows the schematic and chemical structure of LbL SPEEK membrane.

Membrane characterization

The contact angle was evaluated by using a Drop Shape Analysis System DSA 10 Mk. 100 μl of 0.05%w/v SPEEK in DMSO was cast under 70 °C on a glass slide to form a substrate layer before alternate soaking into BIm-PEI and PAA solutions for 2 min, rinsing with DI water and drying after each soaking. After deposition, the water contact angle measurement was carried out. The deposition of the BIm-PEI and PAA was quantitatively and qualitatively analyzed by using a Molecular Interaction Analyzer AFFINIXQ8. The gold probes were heated under 70 °C for 4 h to cast 2 μl of 0.05%w/v SPEEK on the surfaces. The probes were treated with 2 μl of BIm-PEI solution for 2 min and were rinsed with 10 μl of DI water after 2 min followed by drying and measuring the frequency change (Δf) and converting into the mass change (Δm) using Sauerbrey relation [19]. The alternate soaking with PAA to form layer by layer on the probe was also carried out similarly.

Proton conductive measurement

Proton conductivity was measured by using a Cole–Cole plot obtained from a μAUTOLAB Type III impedance spectrometerin frequency range of 500 kHz–1 Hz with an a.c. signal amplitude of 50 mV. The sample was cut into a circle of 1 cm diameter and assembled in a sealed-off Teflon cell equipped with copper electrodes. The conductivity (σ) was calculated according to:

$$\sigma = L/RA$$

where L is the sample thickness; A is the cross-sectional area between membrane and electrode (0.4418 cm^{-2}) and R is the resistance determined from an impedance spectra.

Results and discussion

Formation of BIm-PEI and PAA as LbL SPEEKPEM

The conjugation of BIm on to b-PEI was confirmed by FTIR, ^1H NMR and elemental analysis as reported previously [18]. It was found that BIm was introduced on to primary amine and secondary amine for 17%DS, which was calculated by the method in the report [18,20] (Supporting Information Figs. S1 (FTIR) and S2 (NMR)).

In order to confirm the BIm-PEI and PAA depositing on SPEEK membrane in LbL structure, structural analysis of the

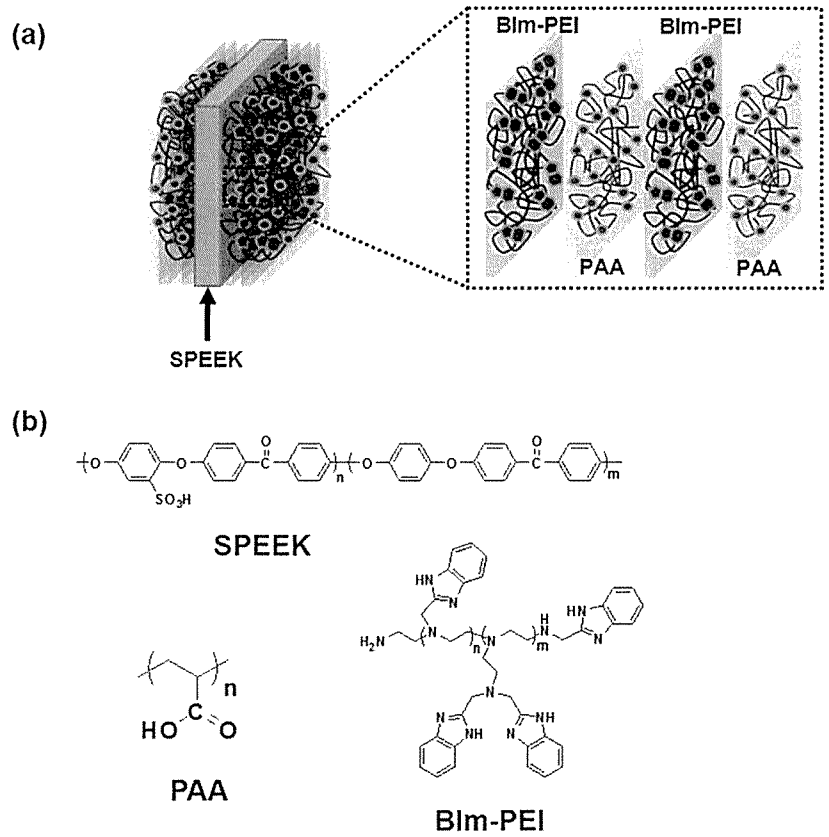

Fig. 1 – Schematic of Proton LbL SPEEKPEM with 2 bilayers (a) and structure of SPEEK, PAA and BIm-PEI (b).

membrane by ATR-FTIR was carried out. Fig. 2 shows the sulfonate (O=S=O) group of SPEEK at 1216 cm^{-1}, 1074 cm^{-1} and 1012 cm^{-1} [21,22]. After the SPEEK membrane was treated with PAA, the peak at 1723 cm^{-1} and 1655 cm^{-1}, referring to the –C=O of the carboxylic acid and the –NH– belonging to imidazole group, respectively, could be identified. The broad absorption band from 2400 cm^{-1}–3600 cm^{-1} indicates the hydrogen bond in the membrane.

Contact angle measurement was applied to follow the change of the surface (Fig. 3). It is important to note that the water contact angle of SPEEK, PAA and BIm-PEI were at 54°, 78°, and 14°, respectively. When the SPEEK was treated with BIm-PEI, the contact angle was shifted from 54° to 14°, implying that the layer of BIm-PEI was stabilized on the SPEEK. After alternate soaking with PAA, the membrane showed the surface contact angle at 78°. Thus, the contact angle of the membrane shifted according to the PAA and BIm-PEI. In other words, the zig-zag pattern of the contact angle plot confirms the successful layer by layer of BIm-PEI and PAA on SPEEK.

The amount of BIm-PEI and PAA deposited on SPEEK was quantitatively analyzed by using quartz crystal microbalance (QCM). The SPEEK cast on the gold probe of QCM was used as the membrane to observe how much the amount of BIm-PEI and PAA could be stabilized on the membrane in each soaking process. Fig. 4 shows an increase of the mass with an average amount of 1500–1800 ng/cm^{-2} when the number of layers on SPEEK increased. Although the plots lead us to see a drastic change from layer 2 to layer 3, the correlation suggested the increase of mass development is related to the number of layer under linear relationship as seen in the R value (0.98413).

Proton conductivity evaluation

Basically, the proton conductivity of the PEM relied on several factors, especially the proton transfer species and its mechanism. The present work focused on the anhydrous membrane, as the proton transfer relied on the heterocycles. Here, the LbL of PAA and BIm-PEI was expected to show high efficiency

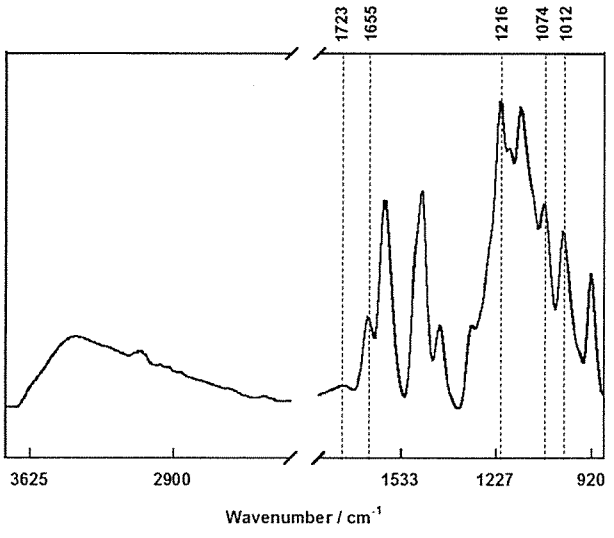

Fig. 2 – FTIR spectrum of SPEEK/BIm-PEI/PAA-20.

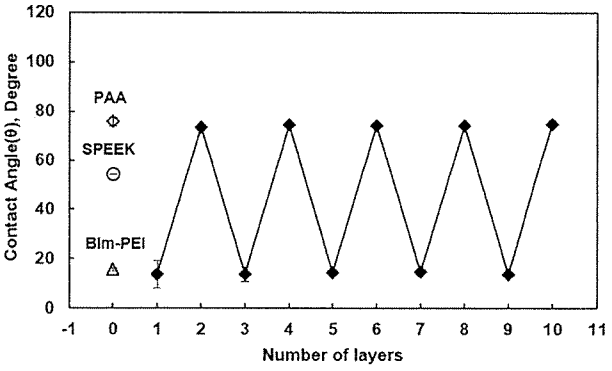

Fig. 3 – Contact angle measurement of each assembled layer.

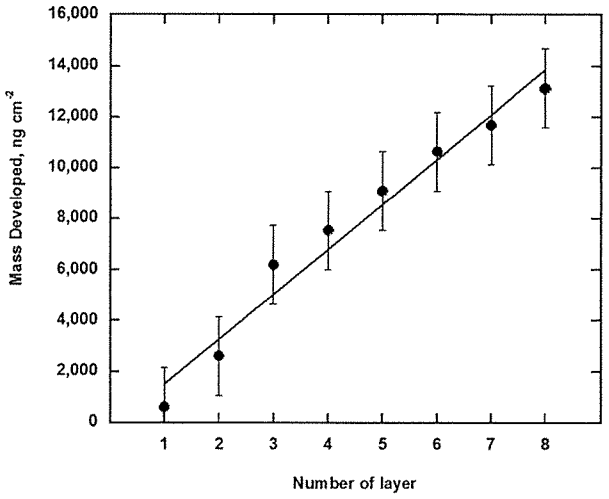

Fig. 4 – Mass developed on SPEEK membrane casted on gold sensor calculated from QCM data.

related to not only the proton donor and acceptor, but also the LbL ordered structure.

A comparative study between the neat SPEEK membrane, the SPEEK membrane containing BIm-PEI and PAA in random form and the SPEEK membrane with BIm-PEI and PAA in LbL form leads to the answers (i) how the proton donor and acceptor in SPEEK membrane enhances proton conductivity, and (ii) how the LbL ordered structure further favors proton conductivity in a SPEEK membrane. Fig. 5 shows the proton conductivity of all membranes without any acid doping. The proton conductivity of the neat SPEEK relied on the temperature. At 90 °C–100 °C, the membrane showed the conductivity for 10^{-6} S/cm^{-1}. Chen et al. [23] reported that the SPEEK membrane contains traces of water, and this functions in proton transfer. The decline of conductivity at the temperature above water evaporation indicates the loss of water molecules in SPEEK. For the SPEEK containing BIm-PEI and PAA, the conductivity is almost an order of magnitude increase, and this suggests the role of proton donor and acceptor. In the cases of SPEEK with LbL of BIm-PEI/PAA, proton conductivity increased for one to two orders of

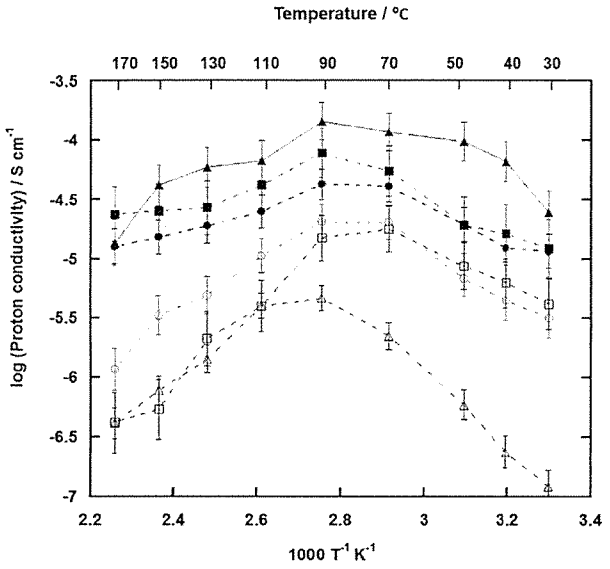

Fig. 5 – Proton conductivity of SPEEK/BIm-PEI/PAA-5 (-●-), SPEEK/BIm-PEI/PAA-10 (-■-), SPEEK/BIm-PEI/PAA-20 (-▲-), SPEEK/BIm-PEI/PAA-40 (-○-), SPEEK/BIm-PEI/PAA-mix (-□-) and pure SPEEK membrane (-Δ-), under 30–170 °C temperature range.

magnitude. This reflects how the ordered structure of proton donor and acceptor significantly enhances proton conductivity. Especially for SPEEK/BIm-PEI/PAA-20, the membrane shows its proton conductivity for as high as 0.144 mS/cm at 90 °C (Fig. 5). Moreover, at a temperature as high as 100–170 °C where water molecules no longer exist to favor the proton transfer, all the LbL SPEEK/BIm-PEI/PAA membranes exhibit higher proton conductivity than SPEEK and maintain the σ value above 10^{-6} S/cm due to proton transfer under hydrogen bond network among $-SO_3H$, –COOH, and –BIm groups belonging to SPEEK, PAA, and BIm-PEI in LbL structure instead of using water as in traditional perfluorosulfonated membrane such as SPEEK or Nafion® (σ of Nafion® = 10^{-5}–10^{-6} Scm^{-1} in 80–140 °C) [24]. This implies how the ordered structure plays an important role in proton conductivity [25–27]. The increase of proton conductivity when the number of bilayers increases from 5 to 20 bilayers might be due to the increase in the amount of proton transfer species.

It is important to note that when the bilayer number was as high as 40 bilayers, the σ value of SPEEK/BIm-PEI/PAA-40 decreased 5 times as compared to that of SPEEK/BIm-PEI/PAA-20. In other words, Fig. 5 shows the optimal bilayer numbers at about 20. This then leads to the question of what is the main factor to control the optimal number of bilayers. In order to clarify this, the proton transfer mechanism was considered. It is known that in the case of anhydrous polymer electrolyte membrane, proton transfer depends on the proton hopping via the hydrogen bond between the heterocycles under the resonance structure. As proton transfer along benzimidazole can be evaluated from the N–H–N, the investigation of this type of intermolecular hydrogen bond enables comparison of the favorable proton transfer condition of each membrane. Here, the temperature dependence FTIR in the range of 3200 cm^{-1}–2800 cm^{-1} was carried out to identify the isosbestic point, which reflects the equilibrium of the covalent bonded N–H and intermolecular hydrogen bonded H–N. Fig. 6 shows the lowest isosbestic point for SPEEK/BIm-PEI/PAA-20.

This indicates that this membrane exhibits more favorable intermolecular hydrogen bond formation as compared to the other membranes. Fig. 7 shows the plot of the isosbestic point related to the number of bilayers. It is clear that when the number of bilayers is as high as 40, the isosbestic point is at a high wavenumber in the FTIR pattern. This shows that the covalent NH bond of SPEEK/BIm-PEI/PAA-40 is quite strong and that it is difficult to transfer this covalent bonded proton to the intermolecular hydrogen bond. In other words, the significantly high number of layers restricts the molecular motion and retains the covalent bond. The results show the balance between molecular mobility and hydrogen bond as a key of the efficient proton transfer system, which has been previously reported [11,12,18,28].

Proton transfer mechanism evaluation

As mentioned above, the mechanism of proton transfer can be generally classified into two types, i.e. Grotthuss mechanism and vehicle mechanism [12,28]. Grotthuss mechanism refers to proton hopping to another, for example, through the resonance structure and hydrogen bond network of heterocycles, while vehicle mechanism refers to the proton transfer via molecular mobility, for example, the benzimidazole groups or chains movement. Therefore, the Arrhenius plot was applied to observe the activation energy.

The Arrhenius plot is based on Eq. (1) [28]

$$\mathrm{Log}(\sigma) = \mathrm{Log}(\sigma_0) - E_a/RT \quad (1)$$

where σ is proton conductivity at various temperature (S/cm), E_a is an activation energy (KJ/mol), R is the gas constant (8.134 J/K•mol) and T is an absolute temperature (K).

The non-linear trend in the Arrenius plot (Fig. 5) shows clearly that the proton mechanism of the membranes does not rely on the Grotthuss mechanism. Instead, the convex trend in the range of 30–90 °C indicates that the proton probably transfers via vehicle mechanism. The E_a value can be calculated using the negative slope of the plots. In the case of the VTF mechanism, the proton can be transferred directly by the thermally active molecules as its vehicles. The corresponding equation is given in Eq. (2).

$$\mathrm{Log}(\sigma) = \mathrm{Log}(\sigma_0) - E_a/R(T - T_0) \quad (2)$$

where σ is proton conductivity at various temperature (S/cm), E_a is an activation energy (KJ/mol), R is a gas constant (8.134 J/K•mol) and T is an absolute temperature (K). T_0 is the Vogel temperature which is the point when there is no configurational change of entropy in the polymer [28].

Proton transfer efficiency can be evaluated using activation energy as a guideline. In other words, the lower the E_a value, the easier the proton transfer. The σ data from 30 to 90 °C in Fig. 5 are in accordance to Eq. (2). The E_a values were calculated and plotted in Fig. 8. The VTF parameters were calculated (see Supporting Information) and are summarized in

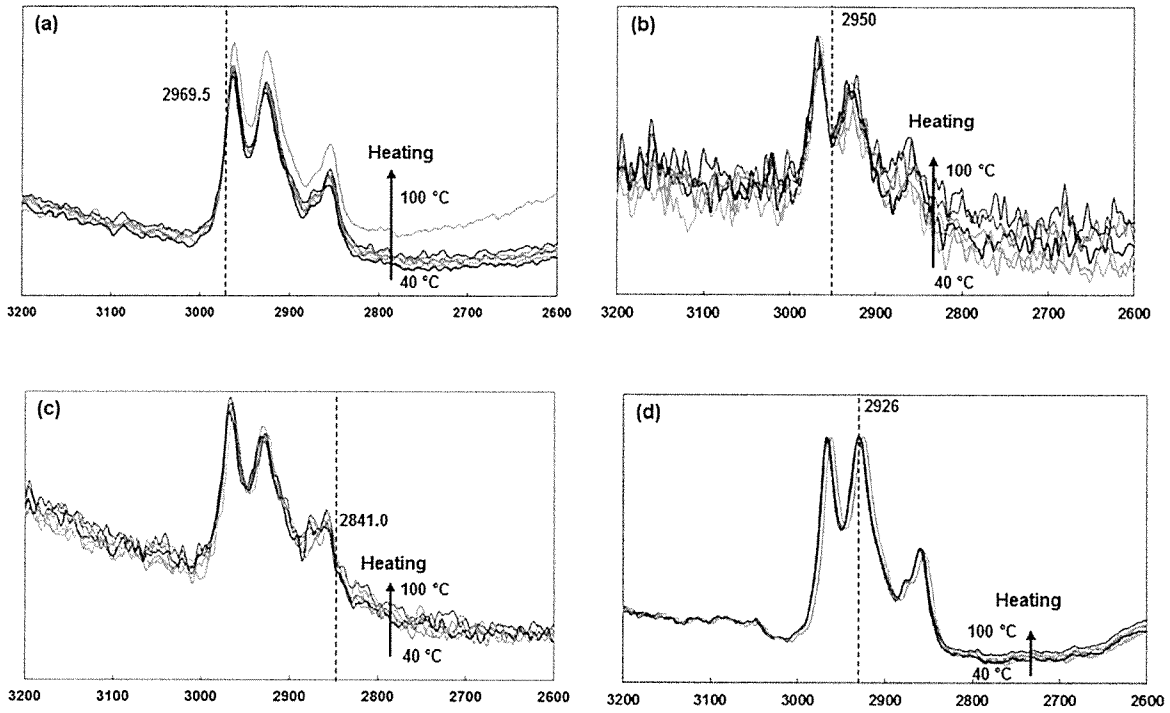

Fig. 6 – Temperature dependence FTIR spectra in 40–100 °C and Isobestic Position of SPEEK/BIm-PEI/PAA-5 (a), SPEEK/BIm-PEI/PAA-10 (b), SPEEK/BIm-PEI/PAA-20 (c) and SPEEK/BIm-PEI/PAA-40 (d).

Table 1 (Supporting Information). Fig. 8 and Table 1 indicate that proton transfer proceeds via vehicle process or VTF mechanism. The LbL membranes with proton donor and acceptor show significantly lower E_a values than SPEEK (Fig. 8). This might be due to both proton donor and acceptor facilitating proton transfer through the membranes. It is clear that an increase of donor-acceptor bilayer, i.e. from 5, 10 to 20 bilayers, leads to a decrease in E_a value. This implies the ease of proton movement. It should be noted that when the number

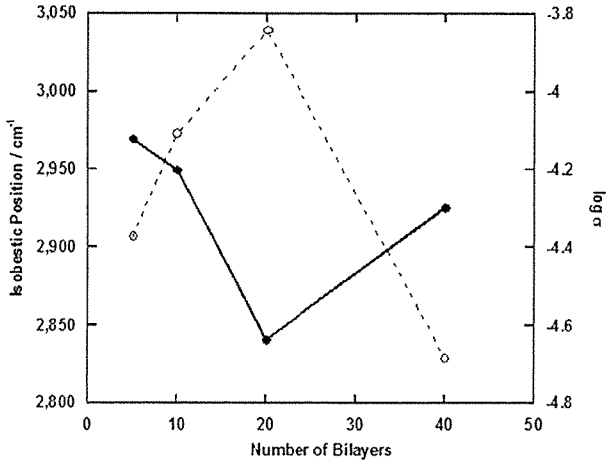

Fig. 7 – Proton conductivity at 90 °C (–○–) and Isobestic Position (—●—) of LbL SPEEK/BIm-PEI/PAA related to number of bilayers.

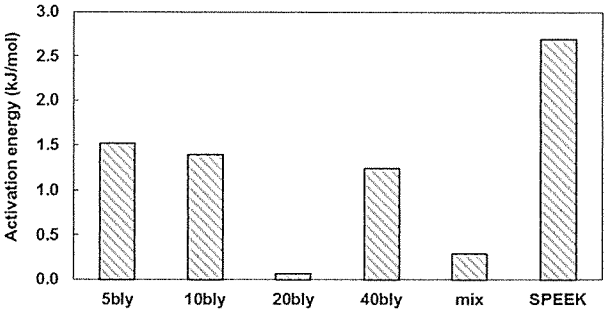

Fig. 8 – Activation energy, E_a of SPEEK/BIm-PEI/PAA-5 (5bly), SPEEK/BIm-PEI/PAA-10 (10bly), SPEEK/BIm-PEI/PAA-20 (20bly), SPEEK/BIm-PEI/PAA-40 (40bly), SPEEK/BIm-PEI/PAA-mix (mix) and SPEEK membrane under 30–90 °C temperature range.

Table 1 – Parameters obtained from curve fitting of temperature dependence proton conductivity with VTF equation (30–90 °C).

Samples	VTF parameters		
	σ_0 (S/cm)	T_0 (K)	R^2
SPEEK/BIm-PEI/PAA-5	0.00048	190	0.9986
SPEEK/BIm-PEI/PAA-10	0.00118	220	0.9888
SPEEK/BIm-PEI/PAA-20	0.00018	293	0.9966
SPEEK/BIm-PEI/PAA-40	0.00024	225	0.9905
SPEEK/BIm-PEI/PAA-mix	0.00003	265	0.9988
SPEEK	0.00088	220	0.9945

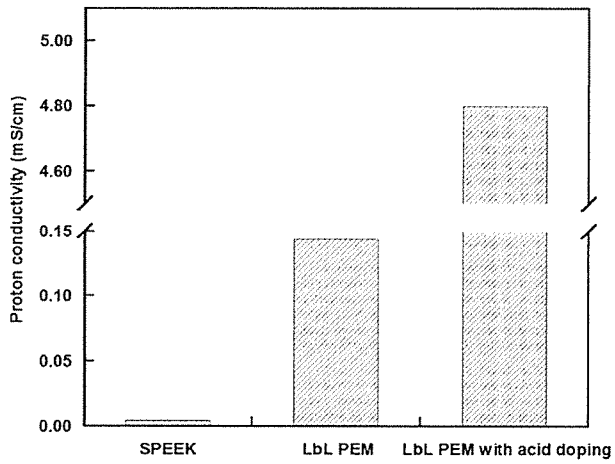

Fig. 9 – Proton conductivity of SPEEK, LbL PEM (SPEEK/BIm-PEI/PAA-20), LbL PEM with acid doping.

of bilayers becomes as high as 40 bilayers. The result reflects that the effective proton transfer relies on the balance of molecular mobility and hydrogen bond network as mentioned in section "Proton conductivity evaluation".

Acid doping of SPEEK/BIm-PEI/PAA-20

According to Fig. 9, the optimum condition for LbL membrane is SPEEK/BIm-PEI/PAA-20. As it is known that the doping with acid enhances proton conductivity due to an increase in the number of the proton in the system, the membrane was doped with 1 M of H_2SO_4 for 24 h at room temperature to facilitate the protonation for all heterocyclic units in the membrane. The LbL PEM SPEEK/BIm-PEI/PAA-20 with acid doping shows a significant increase of proton conductivity for 33 times as compared to that of SPEEK/BIm-PEI/PAA-20 membrane. This shows a successful protonation of heterocyclic molecules even in the form of LbL structure.

Conclusions

A simple layer-by-layer self-assembly technique was applied to construct a high ordered structure of proton donor and proton acceptor. The polymeric proton acceptor was prepared using bPEI substituted with BIm, which led to the successful LbL with polymeric proton donor, i.e. poly(acrylic acid). The LbL was qualitatively and quantitatively analyzed by FTIR, QCM and AFM. The LbL membrane showed the highest proton conductivity at 20 bilayers for 0.144 mS/cm at 90 °C when the temperature was above water evaporation. The Arhenius plot concluded that the proton transfer was under vehicle mechanism and, at that time, the isosbestic point obtained from FTIR spectra suggested the balance of the heterocycles mobility and hydrogen bond belonging to the acrylic acid and imidazole groups. This work showed that proton transfer could be enhanced by (i) incorporating proton donors together with proton acceptors in the system, and (ii) constructing a high-ordered structure of proton donor and proton acceptor.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.ijhydene.2016.01.069.

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