



## Covalently cross-linked sulfonated poly(ether ether ketone)/tungstophosphoric acid composite membranes for water electrolysis application

In-Young Jang<sup>a,\*</sup>, Oh-Hwan Kweon<sup>a</sup>, Kyoung-Eon Kim<sup>a</sup>, Gab-Jin Hwang<sup>b</sup>, Sang-Bong Moon<sup>c</sup>, An-Soo Kang<sup>a,\*\*</sup>

<sup>a</sup> Department of Chemical Engineering, Myongji University, San 38-2, Nam-dong, Cheoin-gu, Yongin-si, Gyeonggi-do 449-728, South Korea

<sup>b</sup> Department of Hydrogen & Fuel Cell Research, Korea Institute of Energy Research, 71-2, Jang-dong, Yuseong-gu, Daejeon 305-343, South Korea

<sup>c</sup> Elchem Tech Co., Ltd., New T Castle 1001, Gasandong 429-1, Geumchun-gu, Seoul 153-803, South Korea

### ARTICLE INFO

#### Article history:

Received 8 January 2008

Received in revised form 12 February 2008

Accepted 3 March 2008

Available online 20 March 2008

#### Keywords:

Composite ion-exchange membrane

Cross-linking

Tensile strength–elongation

Membrane electrode assembly

Impregnation–reduction method

Polymer electrolyte membrane electrolysis

### ABSTRACT

Composite polymer electrolyte membranes consisting of covalently cross-linked sulfonated polyether ether ketone (SPEEK) with tungstophosphoric acid (TPA) are prepared and their electrochemical and mechanical properties are investigated with regards to application in water electrolysis. Covalently cross-linked membranes (CL-SPEEK) comprised of sulfochlorinated SPEEK membranes and SPEEK partially lithiated by LiCl, are prepared by reaction with 1,4-diiodobutane, and blended with TPA to avoid excessive water swelling and to reinforce their mechanical properties. These ion-exchange membranes show good electrochemical properties, including proton conductivity, ion exchange capacity (IEC), thermal stability, anti-oxidative stability, and satisfactory mechanical characteristics, such as tensile strength and elongation. In particular, among the TPA-composite membranes, the CL-SPEEK/TPA30 (30 wt.% TPA) membrane displays higher proton conductivity ( $0.128 \text{ S cm}^{-1}$ ) and tensile strength (75.01 MPa) than Nafion<sup>®</sup> 117 at 80 °C. The ion-exchange membranes are used to construct membrane electrode assemblies (MEAs) of use in polymer electrolyte membrane electrolysis (PEME). The MEA are prepared using a non-equilibrium impregnation–reduction (I–R) method. The electrochemical surface area (ESA) and roughness factor of the MEA prepared with CL-SPEEK/TPA30 electrolyte measured by cyclic voltammetry are  $25.11 \text{ m}^2 \text{ g}^{-1}$  and  $321.4 \text{ cm}^2 \text{ Pt cm}^{-2}$ , respectively. The prepared MEAs are used in the water-electrolysis unit cells. The cell voltage is 1.78 V at  $1 \text{ A cm}^{-2}$  and 80 °C, with a platinum loading of  $1.28 \text{ mg cm}^{-2}$ . The results of the present study suggest that the good conductivity and mechanical properties of covalently CL-SPEEK/TPA composite membranes make them well suited for use in PEME.

© 2008 Elsevier B.V. All rights reserved.

### 1. Introduction

Polymer electrolyte membrane electrolysis (PEME) is a clean and highly efficient energy technology for the production of hydrogen from water, which is an abundant resource. Therefore, polymer electrolyte membrane–electrocatalyst assemblies can be designed to generate hydrogen electrochemically from pure water at high pressures, thus eliminating the need for mechanical compression. The advantages of PEME over alkaline electrolysis include lower parasitic energy losses and higher ecological purity hydrogen output [1]. Thus, PEME is a simple, sustainable and cost-effective technology for hydrogen generation.

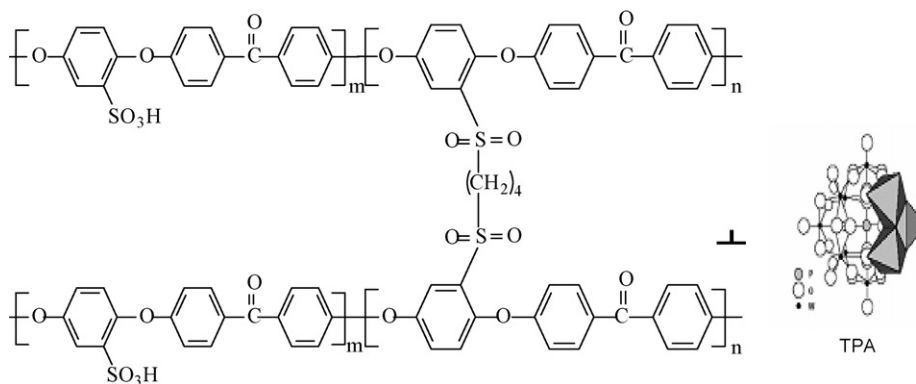
Recently, the commercially available Nafion membrane, which is a perfluorosulfonic acid solid polymer electrolyte membrane produced by the Dupont Co., has been the best-performing polymer electrolyte [2]. However, the current industry standards for perfluorosulfonic polymers have been limited by their high cost and loss of membrane characteristics, such as proton conductivity, at temperatures above 80 °C. Sulfonated aromatic polymers, such as polyether ether ketone (PEEK), polysulfone (PSf) and polybenzimidazoles have satisfactory chemical and electrochemical properties and lower production costs [3].

PEEK polymers cannot be used in PEME applications. The high degree of sulfonation required to achieve sufficient proton conductivity, causes PEEK polymers to become excessively water-swollen or soluble in water, thereby destroying their mechanical properties. To achieve high proton conductivity without these drawbacks, chemically cross-linkable ionomeric systems were proposed and a few such systems have been studied [4,5]. Sulfonated PEEK (SPEEK) can also be cross-linked via thermally activated bridging of the

\* Corresponding author.

\*\* Corresponding author. Tel.: +82 31 330 6386; fax: +82 31 337 1920.

E-mail address: [askang@mju.ac.kr](mailto:askang@mju.ac.kr) (A.-S. Kang).



**Scheme 1.** Structure of covalently cross-linked SPEEK/TPA composite.

polymer chains with polyatomic alcohols, such as ethyleneglycol and glycerine [6].

Membrane electrode assemblies (MEAs) fabricated by means of the conventional hot-pressing method are usually inclined to delamination at both the anode and cathode interfaces after long-term operation that degrades cell performance. The interfacial contact between the electrocatalysts and the polymer electrolyte membrane (PEM) has been improved by synthesizing Pt/PEM MEA using the non-equilibrium impregnation–reduction (I–R) method. A Pt/PEM MEA prepared using this method were a few microns thick, hydrophilic and porous [7]. In addition, Pt/PEM MEA prepared using the non-equilibrium I–R method exhibit excellent adhesion and durability, because the metal clusters are embedded in the membrane surfaces [8].

The purpose of the present study is to investigate the effects of tungstophosphoric acid (TPA) and the concentration of the reductant,  $\text{Na}_2\text{SO}_3$ , on covalently cross-linked CL-SPEEK/TPA composite membranes and on the properties of the resulting materials, such as electrochemical performance in PEME and thermo-mechanical stability. Thus, MEAs are prepared from CL-SPEEK/TPA30 composite membranes using the non-equilibrium I–R method and the Pt-loading content, electrochemical characteristics and current–cell voltage of PEME cells are investigated.

## 2. Experimental

### 2.1. Preparation of covalently cross-linked SPEEK/TPA membranes

Covalently cross-linked SPEEK membranes were prepared via a five-step synthesis as follows: sulfonation–sulfochlorination, partial reduction, lithiation, cross-linking, and addition of TPA. Polyether ether ketone (Victrex 450G,  $M_n=100,000$ ) was sulfonated at room temperature for approximately 150 h, according to a previously reported method [9].

The resulting SPEEK membranes, with an ion-exchange capacity (IEC) of  $2.7 \text{ mequiv. g}^{-1}$  dry membrane, were dissolved in thionyl chloride ( $\text{SO}_2\text{Cl}$ , 90% pure, Samchun), followed by addition of *N,N*-dimethylformamide ( $\text{HCON}(\text{CH}_3)_2$ , 99.8% pure, Junsei) to the solution. As a result of this reaction, SPEEK was transformed into sulfochlorinated PEEK (PEEK– $\text{SO}_2\text{Cl}$ ).

The PEEK– $\text{SO}_2\text{Cl}$  was then added to various concentrations of sodium sulfite ( $\text{Na}_2\text{SO}_3$ , 98% pure, Aldrich) solution with stirring. The resulting mixture was heated at  $70^\circ\text{C}$  overnight to obtain the PEEK– $\text{SO}_2\text{Cl}$ – $\text{SO}_2\text{Na}$  polymer.

The prepared polymer was lithiated using various weight ratios (5–10 wt.%) of a lithium chloride (LiCl, 98% pure, Junsei) solution. The resulting partially lithiated PEEK– $\text{SO}_2\text{Cl}$ – $\text{SO}_2\text{Li}$  was filtered, dialyzed to remove residual LiCl and excess  $\text{Na}_2\text{SO}_3$ , and then dried at  $40^\circ\text{C}$  under vacuum.

The PEEK– $\text{SO}_2\text{Cl}$ – $\text{SO}_2\text{Li}$  polymer was dissolved in 1-methyl-2-pyrrolidinone (NMP, 99% pure, Lancaster) and various weight ratios (0–60 wt.%) of powdered TPA ( $\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot\text{aq}$ , Fluka) were added to the solution, followed by addition of the cross-linker, 1,4-diiodobutane (Lancaster, 99%), to yield the covalently cross-linked SPEEK/TPA solution, as shown in Scheme 1. The resulting mixture was stirred for 16 h and then cast on to a glass plate with a doctor's knife. The cast membrane was dried at room temperature for 12 h, at  $60^\circ\text{C}$  for 4 h and at  $120^\circ\text{C}$  for 12 h. The resulting covalently cross-linked SPEEK and composite SPEEK/TPA membranes are referred to as CL-SPEEK and CL-SPEEK/TPA, respectively.

### 2.2. Characteristics of prepared ion-exchange membrane

#### 2.2.1. FT-IR spectra

Fourier transform infrared (FT-IR) spectra (KBr discs with polymer or attenuated total reflection (ATR) with membrane) were recorded with a Bomem MB104 spectrometer.

#### 2.2.2. Thermal stability

A TGA 2950 thermo-gravimetric analysis (TGA) instrument (TA Company, New Castle, Delaware) was used to study the thermal stability of PEM samples. Each sample was heated in nitrogen from 25 to  $700^\circ\text{C}$  at a scanning rate of  $10^\circ\text{C min}^{-1}$ .

#### 2.2.3. Mechanical properties and anti-oxidative stabilities

Tensile strength–elongation tests were performed according to the standard method (ASTM D 882) using a Lloyd universal testing machine (model LR5K, UK). The test specimens were cut into strips 70 mm long and 25 mm wide, and the thickness of each strip (approximately  $170 \mu\text{m}$ ) was measured with digital vernier calipers. The relative humidity, temperature, gauge length and crosshead speed were set at  $50 \pm 5\%$ ,  $25^\circ\text{C}$ , 30 mm and  $5 \text{ mm min}^{-1}$ , respectively. Eight replicate measurements were performed and the average of the six data points remaining after discarding the maximum and minimum values was calculated. Using the wet method, the membrane was immersed in  $25^\circ\text{C}$ -water for 24 h. The tensile strength and breaking elongation of the prepared ion-exchange membranes were directly obtained from the tensile tests. The energy-to-breaking point, which is the fracture energy per unit volume of the sample and corresponds to the toughness of the membranes, was obtained from the tensile stress–elongation curves for each sample.

A membrane sample ( $5 \text{ cm} \times 5 \text{ cm} \times 170 \mu\text{m}$ ) was weighed and soaked in Fenton's reagent (2 ppm  $\text{FeSO}_4$  in 3%  $\text{H}_2\text{O}_2$ ) at  $80^\circ\text{C}$  with continuous stirring at a speed of 70 rpm. Anti-oxidative stability was quantified by the time that elapsed between immersion in Fenton's reagent and membrane fracture or breakage [10].

### 2.3. Membrane properties of prepared ion-exchange membrane

#### 2.3.1. Water uptake

Water uptake ( $W_u$ ) was determined as the difference in weight ( $W$ ) between the dried and the swollen membranes. The weight of the dried membrane was measured ( $W_{dry}$ ) and then the membrane was soaked in water until the weight remained constant. The membrane was then removed from the water, wiped with blotting paper, and weighed again to obtain the wet weight ( $W_{wet}$ ).  $W_u$  was calculated using formula:

$$W_u = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100 \quad (1)$$

#### 2.3.2. Ion-exchange capacity

After immersion in pure water for 1 day, a membrane sample was immersed for 1 day in a large volume of a 1-M HCl aqueous solution to transform the membrane into the  $H^+$  form. The membrane was then washed with de-ionized water to remove excess HCl, and equilibrated with de-ionized water for an additional 4 h with frequent changes of the water to remove the last traces of acid. The membrane was then equilibrated with exactly 50 ml of a 0.01-M NaOH aqueous solution for 24 h. The ion-exchange capacity was quantified by measuring the reduction in alkalinity by means of back-titration. The IEC of the PEM was calculated as follows:

$$IEC = \frac{N_{NaOH} \times f_{NaOH} \times (V_{NaOH}/1000) - (V_{NaOH}/V_{sample}) \times N_{HCl} \times f_{HCl} \times (V_{HCl}/1000)}{\text{g dry membrane}} \times 1000 \quad (2)$$

where  $f$  is the factor of the solution,  $N$  the normal concentration of the solution, and  $V$  is the volume of the acid–base solution.

#### 2.3.3. Proton conductivity

The proton conductivity of the polymer membranes was measured using a.c. impedance spectroscopy with a Solartron 1260 analyzer across 13-mm diameter samples clamped between two blocking platinum electrodes. The sample discs were hydrated by soaking in water overnight and were wet when placed in the measurement cell. The conductivity,  $\sigma$ , of the samples was calculated from the impedance data, using the relation,  $\sigma = d/RS$ , where  $d$  and  $S$  are the thickness and face area of the sample, respectively, and  $R$  is derived from the low intersect of the high frequency semicircle on a complex impedance plane with the  $Re(Z)$  axis. The impedance data were corrected for contributions from empty and short-circuited cells.

### 2.4. Membrane electrode assembly

Tetraammineplatinum chloride hydrate ( $Pt(NH_3)_4Cl_2$ , Aldrich, 98%) and sodium borohydride ( $NaBH_4$ , Aldrich, 98%) were used as the electrocatalytic material and reducing agent, respectively. The prepared ion-exchange membrane was fixed in the plating cell with the top surface facing the impregnation solution – 5 mM  $Pt(NH_3)_4Cl_2$  in a methanol–water mixture – for 1 h in accordance with non-equilibrium I–R methods [11]. After impregnation, the platinum solution was removed from the plating cell and then replaced with a reducing solution of  $NaBH_4$  that ranged in concentration from 0.3 to 1.0 M. The pH was maintained at 13 by adding NaOH. The other side of the membrane was impregnated and reduced under the conditions described above. After the reduction step was completed, the MEA was soaked in 0.5 M  $H_2SO_4$  for 2 h to exchange  $Na^+$  for  $H^+$  and then were immersed in de-ionized water for 2 h before re-drying at 80 °C and 12 h.

### 2.5. Evaluation of MEA and cell performance

The characteristics and performance of the prepared MEA were analyzed and evaluated by scanning electron microscopy (SEM), cyclic voltammetry (CV) and current–voltage  $I$ – $V$  curves. The cross-sectional morphologies and platinum distribution of the prepared MEA were analyzed using a Hitachi S-3500N SEM. Cyclic voltammetry was performed using an EG&G PAR potentiostat–galvanostat model 273A and a conventional three-electrode cell with the prepared MEA as the working electrode, a saturated calomel reference electrode (SCE) and a Pt counter electrode. The potential ranged from 0 to 1.5 V vs. Standard hydrogen electrode (SHE) and the scan rate was 10  $mV s^{-1}$ . The CVs were measured at the working electrode in nitrogen-purged 0.5 M  $H_2SO_4$  at 25 °C. The electrochemical surface area (ESA) was calculated from the charge passed ( $Q_H = 210 \mu C cm^{-2}$ ) by a full monolayer of adsorbed hydrogen atoms. The prepared MEA was tested using a single cell with an active area of 9  $cm^2$  at 80 °C and under ambient pressure for application in PEMFC.

## 3. Results and discussion

### 3.1. Characteristics of covalently cross-linked SPEEK membranes

#### 3.1.1. FT-IR study

FT-IR spectra of the products resulting from each step in the five-step synthesis of CL-SPEEK are shown in Fig. 1. A peak due to the

$SO_3H$  group resulting from sulfonation of PEEK to produce SPEEK in the first step is evident at 1080  $cm^{-1}$ . After the second step, the asymmetric vibrations of the  $SO_2$  group of PEEK– $SO_2Cl$  are located between 1360 and 1385  $cm^{-1}$ . The S=O symmetrical stretching of the PEEK– $SO_2Cl$ – $SO_2Li$  resulting from partial reduction and lithiation is evident in the range between 960 and 980  $cm^{-1}$ . In the fourth step, the addition of TPA, terminal oxygen interacts with the protonated-water dimer in the secondary structure, resulting in a shift, from 1007 to 980  $cm^{-1}$ , in the vibrational band of the terminal oxygen in the primary structure. The band at 880–890  $cm^{-1}$  corresponds to the symmetric stretching of the corner-shared octahedral, W– $O_c$ –W and the band at 814–895  $cm^{-1}$  corresponds to the symmetric stretching of edge-shared octahedral, W– $O_c$ –W [12].

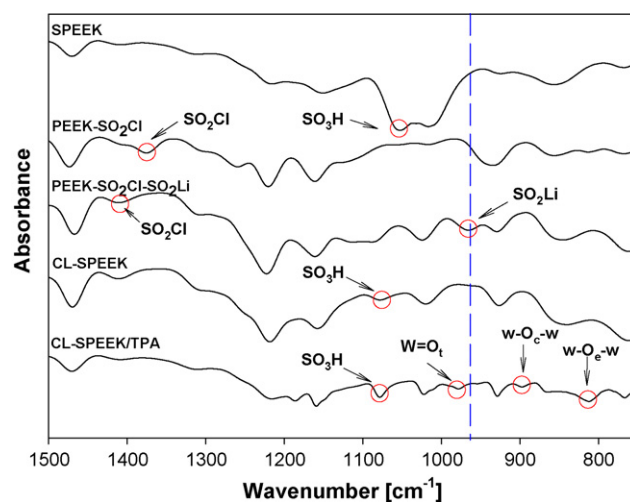


Fig. 1. FT-IR spectra of SPEEK, covalently cross-linked SPEEK and SPEEK/TPA membranes.

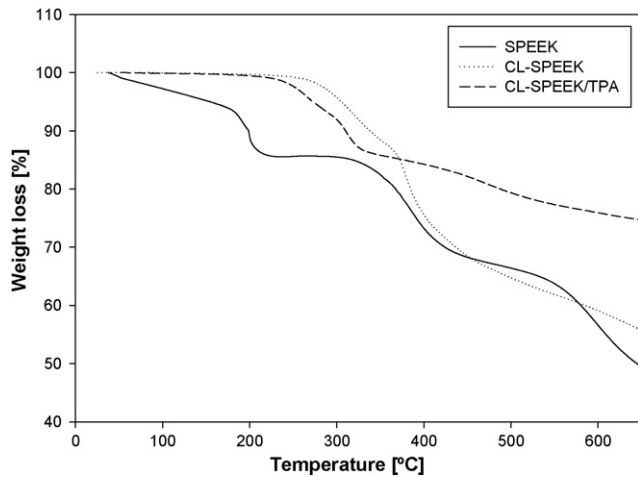


Fig. 2. TGA curves of SPEEK, covalently cross-linked SPEEK and SPEEK/TPA membranes.

These bands are due to the coulombic interaction between the hydroxyl groups of the PEEK donor and the salt of TPA in the hybrid membrane. This finding indicates that the TPA particles interact with the sulfonic acid group as opposed to some other functional unit in the backbone. After performing the final step, the peak resulting from the third step disappears due to the formation of cross-links between the lithium group of PEEK-SO<sub>2</sub>Cl-SO<sub>2</sub>Li and the cross-linking agents in the CL-SPEEK and CL-SPEEK/TPA membranes.

### 3.1.2. Thermal stability

The TGA thermodiagrams of SPEEK, CL-SPEEK and CL-SPEEK/TPA are given in Fig. 2. The TGA traces of the prepared membranes exhibit the typical two-step weight loss of sulfonated PEEK at temperatures of approximately 200 and 400 °C. The first weight loss is due to splitting-off of the sulfonic acid groups. The second thermal degradation, which occurs at 400 °C, arises from decomposition of the main chain [13]. The second weight loss of CL-SPEEK/TPA is lower than that of CL-SPEEK due to the added TPA, which is resistant to thermal decomposition up to 800 °C. The thermal properties of CL-SPEEK and CL-SPEEK/TPA are satisfactory for use in PEME cells.

### 3.1.3. Mechanical properties and anti-oxidative stabilities

The tensile strength–elongation curves of partially reduced CL-SPEEK treated with various concentrations of reductant, Na<sub>2</sub>SO<sub>3</sub>, are shown in Fig. 3(a). The tests were carried out at room temperature and 50 ± 5% relative humidity. As expected, tensile strength increases with increasing Na<sub>2</sub>SO<sub>3</sub> concentrations, whereas elongation shows an opposite trend. The mechanical properties of the partially reduced membranes undergoes a transition from ductile to brittle behaviour with increasing Na<sub>2</sub>SO<sub>3</sub> concentrations due to the greater degree of cross-linking in the membrane.

The tensile strength–elongation traces for the CL-SPEEK/TPA composite matrix at a fixed concentration of 2 M Na<sub>2</sub>SO<sub>3</sub> shown in Fig. 3(b) illustrate the effect of TPA on the tensile strength–elongation curves under dry conditions. In general, elastic ductile polymer films exhibit two characteristic regions of deformation in their stress–elongation curves [14]: below yield points, the stress increases rapidly with increasing elongation and a steep initial slope can be observed in the elastic moduli; above yield points, the stress slowly decreases with elongation until breaking failure occurs, indicating that an increase in TPA concentration induces a transition from brittle to ductile behaviour. As shown in Fig. 3(b) with increasing TPA content in CL-SPEEK/TPA, the stress decreases,

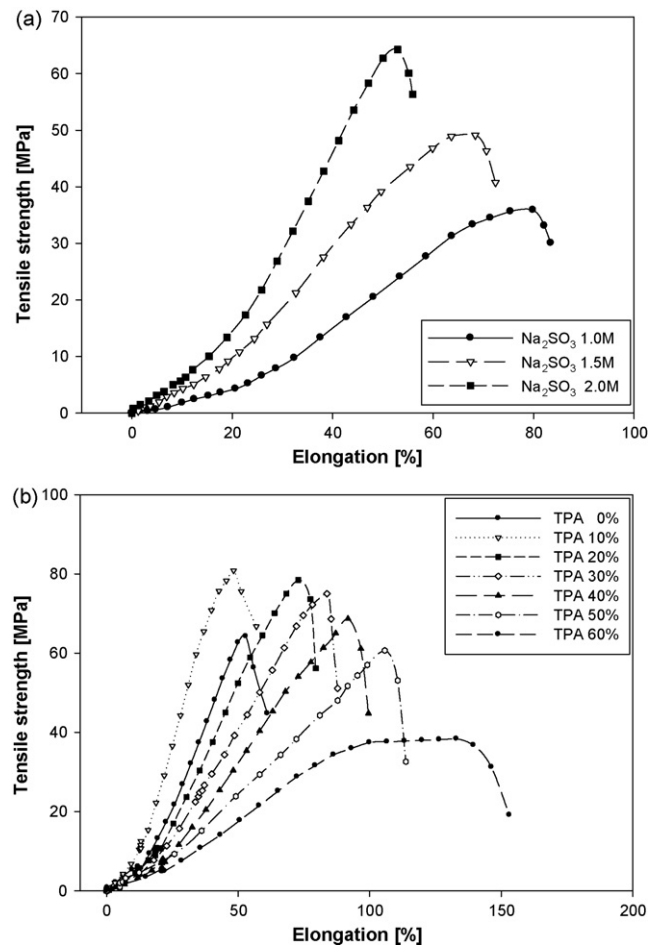


Fig. 3. Tensile strength–elongation curves of covalently cross-linked SPEEK and SPEEK/TPA membranes with variations of (a) Na<sub>2</sub>SO<sub>3</sub> concentration and (b) TPA contents at fixed concentration of 2 M Na<sub>2</sub>SO<sub>3</sub> and 7 wt.% LiCl.

and the elongation at the breakpoint increases. This phenomenon, which is observed in the range of 10–60 wt.% TPA is inconsistent with the general expectation described above [9]. By contrast the CL-SPEEK without TPA added exhibits lower tensile strength values than the polymers blended with TPA. This result can be explained by specific hydrogen-bonding interactions between the TPA and the sulfonated matrix during the initial stage of TPA blending (0–10 wt.% TPA), producing a mechanism for reinforcement [12].

As shown in Fig. 4, the tensile strength of CL-SPEEK/TPA30 with 7 wt.% LiCl and 30 wt.% TPA in dry and wet conditions is 75.01 and 38.15 MPa, respectively, and is higher than the tensile strength of Nafion 117 and of pure sulfonated SPEEK (10.42 MPa) [9]. Comparison between CL-SPEEK/TPA and the pure polymer without cross-linking reveals that cross-linking between the PEEK polymer backbone and the cross-linker (1,4-diiodobutane) increased the mechanical strength sevenfold. When tested under wet conditions, the increased water content induces a transition from brittle to ductile behaviour. Taking into account actual PEME behaviour under wet conditions, the composite membranes met the requirements of PEME cells.

The anti-oxidative stability of the membranes was quantified by measuring the time elapsed between immersion of the membranes in oxidant until they broke into pieces. As can be seen in Table 1, the anti-oxidative stability of CL-SPEEK/TPA is higher than that of pure SPEEK, possibly due to the relatively poor water-solubility and cross-linking of the composite. Moreover, the anti-oxidative stabi-

**Table 1**  
Physical and electrochemical properties of Nafion 117, sulfonated PEEK membrane, and covalently cross-linked SPEEK and SPEEK/TPA composite membranes

Property	Nafion 117	Pure SPEEK	CL-SPEEK <sup>a,b</sup>	CL-SPEEK/TPA30 <sup>b</sup>	Test method
Thickness ( $\mu\text{m}$ )	183	169	170	170	–
Basis weight ( $\text{g m}^{-2}$ )	360	155	160	185	–
Conductivity ( $\text{S cm}^{-1}$ )					
25 °C	0.092	0.027	0.087	0.092	Impedance
80 °C	–	Swelling	0.116	0.128	
I.E.C. ( $\text{mequiv. g}^{-1}$ dry membrane)	0.91	1.71 <sup>c</sup>	1.75	1.81	–
Water uptake (%)	38	42.31	44.6	38.5	ASTM D 570
Tensile strength (MPa)	43	10.42	64.25	75.01	ASTM D 882
Elongation at break (%)	225	316.2	61.11	87.84	ASTM D 882
Thickness change (%) <sup>d</sup>	14	13	13	12	ASTM D 756
Linear expansion (%) <sup>d</sup>	15	14	15	14	ASTM D 756
Oxidative stability (h:min)	–	6:32	29:41	48:32	–

<sup>a</sup> At fixed concentration of 2 M  $\text{Na}_2\text{SO}_3$  and 7 wt.% LiCl.

<sup>b</sup> IEC of starting materials: 2.65  $\text{mequiv. g}^{-1}$  dry membrane (degree of sulfonation: 97%).

<sup>c</sup> Degree of sulfonation: 65%.

<sup>d</sup> After swelling in water.

ties shown in Table 1 are much better than those reported for SPEEK membranes [15].

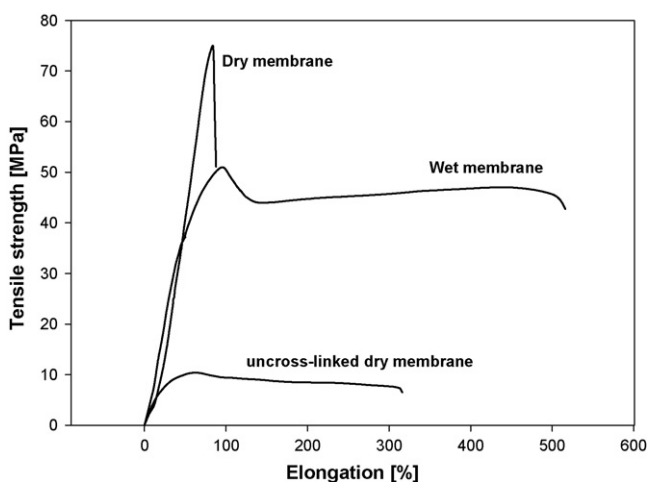
### 3.1.4. Proton conductivity, water uptake and IEC

The important determinants of the suitability of ionomer membranes for PEME are proton conductivity, water uptake, IEC, and mechanical properties. The water content and water state in sulfonated polymers are very important, as they directly affect proton transport across the membranes. Generally, protons can be transported along hydrogen-bonded ionic channels and with cationic mixtures, such as  $\text{H}_3\text{O}^+$ ,  $\text{H}_5\text{O}_2^+$ , and  $\text{H}_9\text{O}_4^+$ , in aqueous media [16]. Free protons move through a localized ionic network within fully water-swollen sulfonated polymer membranes. Therefore, water uptake strongly depends on the sulfonic acid content and also is related to the IEC. Accordingly, a proper water content should be maintained in sulfonated polymer membranes to guarantee high proton conductivity.

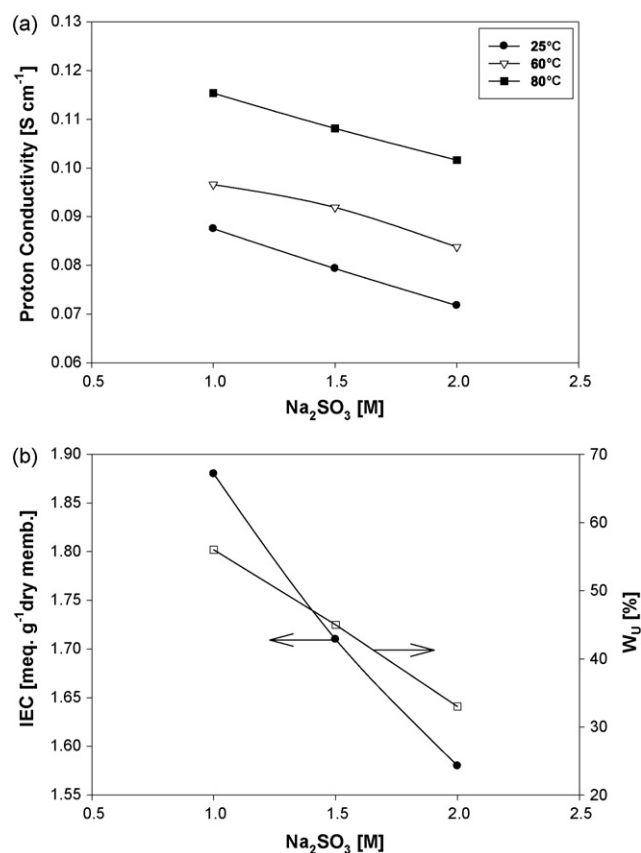
The proton conductivity, water uptake and IEC of partially reduced CL-SPEEK, which are treated with various concentrations of the reductant  $\text{Na}_2\text{SO}_3$  at variable temperatures with a fixed concentration (10 wt.%) of LiCl solution, are shown in Fig. 5. The amount of cross-linking agent, 1,4-diiodobutane, was fixed at 0.005 ml. Addition of >0.01 ml prevents casting of the polymer solution because of gel formation. As shown in Fig. 5(a), the proton conduc-

tivity of CL-SPEEK decreases significantly as the  $\text{Na}_2\text{SO}_3$  content increases due to cross-linking. The CL-SPEEK with 1 M  $\text{Na}_2\text{SO}_3$  has the highest proton conductivity, namely, 0.088 and 0.115  $\text{S cm}^{-1}$  at 25 and 80 °C, respectively. The membrane with an IEC value of 2.7  $\text{mequiv. g}^{-1}$  dry membrane is initially soluble in water. Therefore, its water uptake may be considered to be equal to infinity. After the membrane is cross-linked, however, the conductivity is 0.088  $\text{S cm}^{-1}$  [6].

The use of 1 M  $\text{Na}_2\text{SO}_3$  reduces the number of  $\text{SO}_2\text{Na}$  groups (cross-linkable sites) and this thereby lowers the degree of cross-



**Fig. 4.** Comparison of tensile strength–elongation curves of covalently cross-linked SPEEK/TPA30 of dry and wet and pure uncross-linked membranes at 7 wt.% LiCl.



**Fig. 5.** (a) Proton conductivity and (b) ion-exchange capacity and water uptake of covalently cross-linked SPEEK membranes at fixed concentration of 10 wt.% LiCl in accordance with  $\text{Na}_2\text{SO}_3$  concentration.

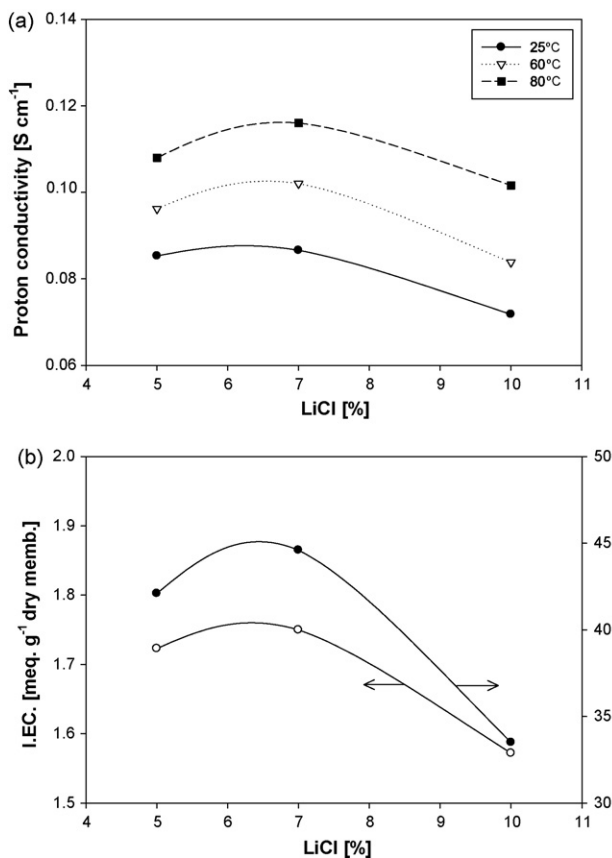


Fig. 6. (a) Proton conductivity and (b) ion-exchange capacity and water uptake of covalently cross-linked SPEEK membranes at fixed 2 M  $Na_2SO_3$  in accordance with LiCl contents.

linking and induces a water-soluble polymer, which prevents the casting of membranes. At concentrations greater than 2 M  $Na_2SO_3$ , proton conductivity is reduced, but membrane properties such as proton conductivity and mechanical strength are considerably enhanced in comparison with uncross-linked SPEEKs (Table 1 and Fig. 3). This result is obtained because partial cross-linking also constrains water uptake to a limited extent, especially at high temperatures [17]. Although cross-linking decreases the number of sulfonic acid groups available for proton transfer, CL-SPEEK has even higher conductivity than that of the uncross-linked membrane [9]. This feature indicates that protons (or hydronium ions) migrate more effectively in the PEM—possibly due to better hydrophilic channel connectivity [18].

As shown in Fig. 5(b), water uptake and IEC exhibit trends similar to that of proton conductivity. Water uptake and IEC decrease with increasing  $Na_2SO_3$  concentration due to cross-linking, whereas the mechanical properties, such as tensile strength (Fig. 3) and swelling in hot water, increase as expected. In the case of CL-SPEEK partially cross-linked with 2 M  $Na_2SO_3$ , the proton conductivity is lower than that of 1 M  $Na_2SO_3$ , but the mechanical properties are optimum, as shown in Fig. 3. Therefore, CL-SPEEK partially cross-linked with 2 M  $Na_2SO_3$  is determined to be the optimum membrane.

Variations in proton conductivity, water uptake and IEC with the LiCl content of the CL-SPEEK are shown in Fig. 6. As shown in Fig. 6(a), the proton conductivity of the membranes increases as the LiCl content is increased up to 7 wt.%; at LiCl contents >7 wt.% LiCl, however, the proton conductivity decreases. Fig. 6(b) shows that the relationships of water uptake and IEC to LiCl content are similar to that observed for proton conductivity. The CL-SPEEKs are all water-insoluble, which is a strong indicator of cross-linking. Therefore,

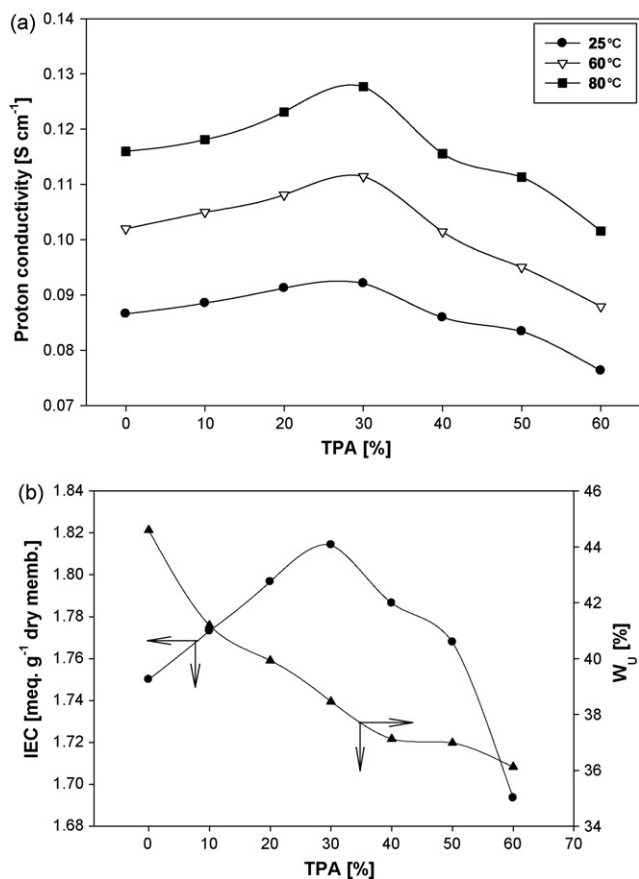
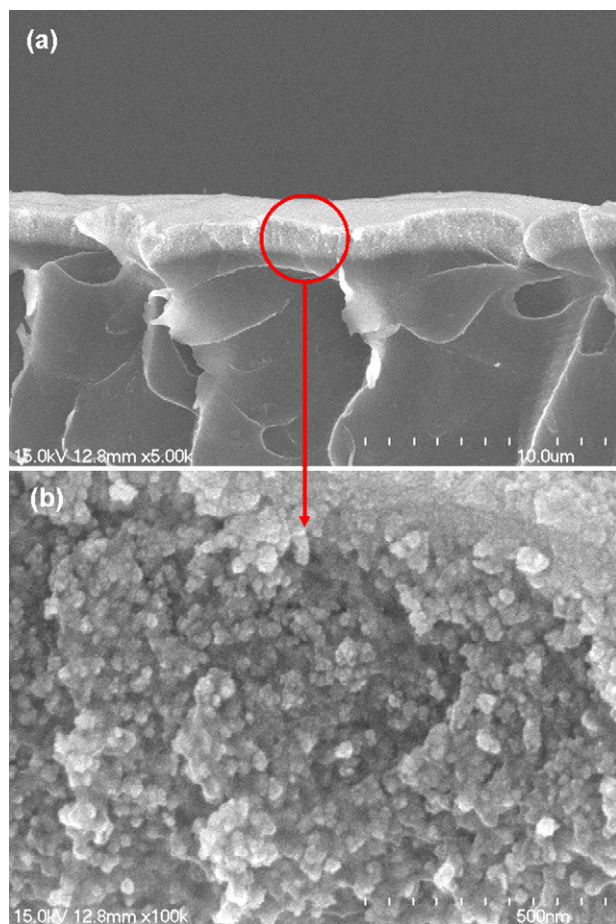


Fig. 7. (a) Proton conductivity and (b) ion-exchange capacity and water uptake of covalently cross-linked SPEEK membranes of 2 M  $Na_2SO_3$  and 7 wt.% LiCl in accordance with TPA contents.

taking all of the data, including mechanical properties, into account, it is concluded that the optimum preparation of CL-SPEEKs uses a 2 M  $Na_2SO_3$  solution and 7 wt.% LiCl.

Fig. 7(a) shows the effects of TPA content on the proton conductivity of the CL-SPEEK/TPA prepared using 2 M  $Na_2SO_3$  and 7 wt.% LiCl at various temperatures. TPAs are one of the most attractive inorganic modifiers because, in crystalline form, these materials form highly conductive and thermally stable Keggin units [12]. Interestingly, the proton conductivity of composite membranes increases slightly as the TPA content is increased up to 30 wt.%; above 30 wt.% TPA, however, the proton conductivity decreases. For example, the proton conductivity at 80 °C is greater than the conductivities at 25 and 60 °C; the highest ion conductivity value –  $0.128\ S\ cm^{-1}$  – is obtained upon addition of 30 wt.% TPA (CL-SPEEK/TPA30). It appears that TPA, being a stronger acid, systematically yields a higher proton conductivity, as well as better water retention, at higher temperatures [4]. On the other hand, the difference in proton conductivity with and without the addition of 30 wt.% TPA,  $9.21 \times 10^{-2}$  and  $8.7 \times 10^{-2}\ S\ cm^{-1}$ , respectively, is insignificant in comparison with the uncross-linked SPEEK/TPA at 25 °C [9]. Thus, it appears that activity of TPA is inhibited by the structure of the cross-linked matrix. The IEC and water uptake shown in Fig. 7(b) exhibits patterns similar to those shown in Fig. 5(b), except for the IEC curve for 0–20 wt.% TPA. Additional physical and electrochemical properties of the prepared ion-exchange and electrochemical membranes are shown in Table 1. Therefore, CL-SPEEK/TPA30 is promising as an alternative membrane in PEM electrolysis cells, due to its satisfactory water uptake, mechanical properties, anti-oxidative stability, and proton conductivity.



**Fig. 8.** SEM images of surface and cross-section of Pt/CL-SPEEK-TPA30/Pt electro-catalysts prepared by non-equilibrium I–R method: (a) cross-section and (b) Pt layer.

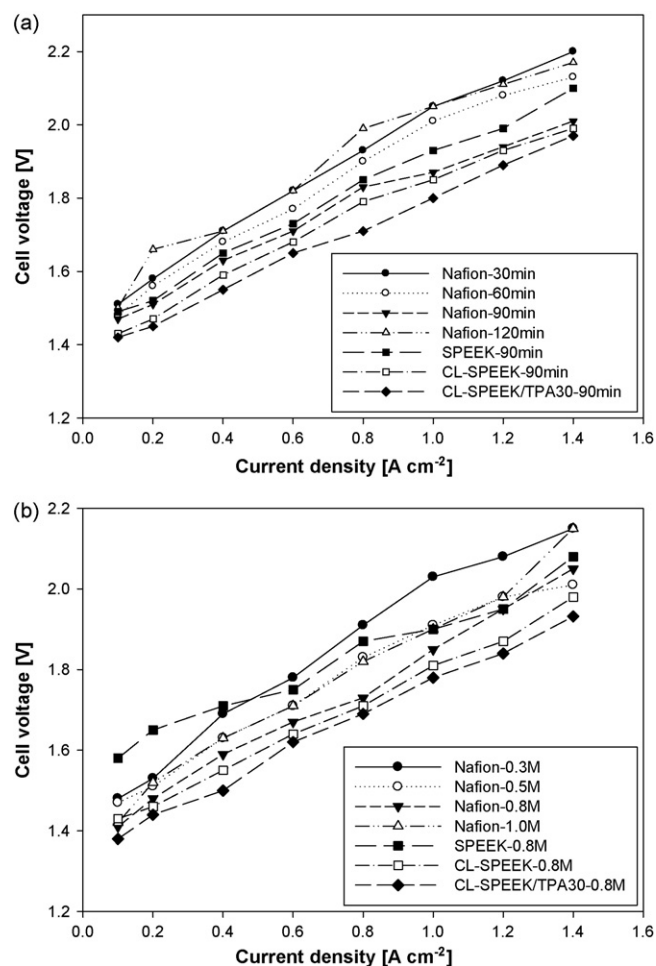
### 3.2. Water electrolysis with MEA

#### 3.2.1. SEM properties

Fig. 8(a) and (b) shows cross-sectional SEM images of a MEA (Pt/CL-SPEEK-TPA30/Pt) prepared by the non-equilibrium I–R method; the images are magnified 5000- and 100,000-times, respectively. The images show a typical cross-section of a MEA and a Pt layer prepared by this procedure [11]. The Pt layer forms extensively on the membrane surface, as in SPEEK/TPA, and shows uniform distribution of the clusters of Pt particles [9,11].

#### 3.2.2. Single-cell performance in polymer electrolyte membrane electrolysis cells (PEMEC)

Fig. 9(a) and (b) shows the cell voltage vs. current density curves of MEA prepared using the non-equilibrium I–R method in relation to the reduction time and the concentration of the reducing agent, respectively. The water electrolysis cell was operated at 80 °C and under atmospheric pressure. Using the non-equilibrium I–R method, Pt clusters form on the interface region where they are accessible to the reactant and are in intimate contact with the polymer electrolyte. Particles deposited deep within the membranes that do not come in contact with the current-collector are useless for electrolysis. To establish good contact with the current collector, it is necessary for a Pt/PEM/Pt MEA to have a Pt layer exposed at the surface. As a result, among Nafion 117, pure SPEEK, SPEEK/TPA, CL-SPEEK, and CL-SPEEK/TPA, the optimum membranes were CL-



**Fig. 9.** Effects of reduction time and reducing agent concentration on performance of single cells using Pt/PEM/Pt electrodes prepared by non-equilibrium I–R method at 80 °C and atmosphere pressure: (a) variations of reduction time and (b) variations of reducing agent concentration.

SPEEK/TPA composites. The optimal conditions for the preparation of MEA are a reduction time of 90 min and a reducing agent concentration of 0.8 M. The cell voltages of the MEA constructed using CL-SPEEK and CL-SPEEK/TPA30 were 1.81 and 1.78 V at 1 A cm<sup>-2</sup> at 80 °C, respectively, with platinum loadings of 1.31 and 1.28 mg cm<sup>-2</sup>.

Table 2 shows the additional cell performance characteristics for the CL-SPEEK/TPA30-based PEME cell. For comparison, the performance of Nafion 117, SPEEK-TPA and CL-SPEEK cells under the same conditions is also presented. Based on these cell performances, the current–voltage curve of the CL-SPEEK/TPA30 in the water electrolysis cell reveal the best performance among the four membranes mentioned above, that is, Pt/Nafion 117/Pt, Pt/SPEEK-TPA/Pt, Pt/CL-SPEEK/Pt and Pt/CL-SPEEK-TPA30/Pt.

**Table 2**

Electrochemical property of Pt/PEM electrodes prepared by non-equilibrium I–R method (Pt(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub> concentration = 5 mM, NaBH<sub>4</sub> = 0.8 M, impregnation time = 60 min, reduction time = 90 min, cell temperature = 80 °C)

	Nafion 117	SPEEK	CL-SPEEK	CL-SPEEK/TPA
Pt loading (mg cm <sup>-2</sup> )	1.21	1.01	1.31	1.28
ESA (m <sup>2</sup> g <sup>-1</sup> )	22.48	10.11	23.46	25.11
Cell voltage (V, at 1 A cm <sup>-2</sup> )	1.85	1.90	1.81	1.78
Cell efficiency (% , ε <sub>ΔH</sub> )	80.0	77.9	81.8	83.1

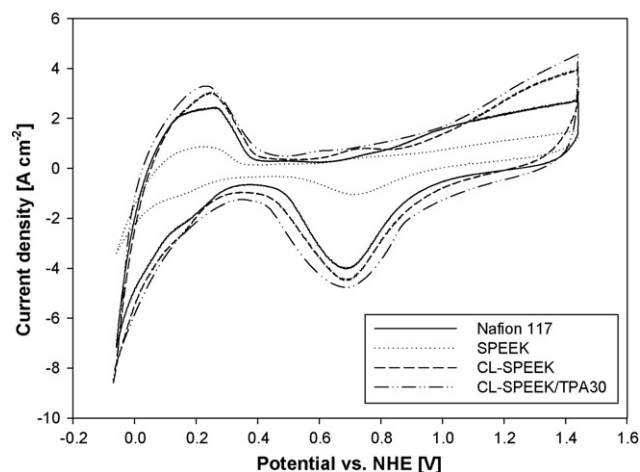


Fig. 10. Cyclic voltammograms of Pt/PEM electrodes prepared by non-equilibrium I-R method; geometrical area:  $1.0 \text{ cm}^2$ ; scan rate:  $10 \text{ mV s}^{-1}$ .

### 3.2.3. Cyclic voltammograms

Fig. 10 shows the cyclic voltammograms of the MEA prepared using the non-equilibrium I-R method with Nafion 117, SPEEK/TPA and CL-SPEEK and CL-SPEEK/TPA30 membranes.

ESA were obtained from the coulombic charge for the oxidation of atomic hydrogen adsorbed on the electrode. The upper potential limit of the integration of the current-potential curve is taken as the point where the double-layer current is no longer constant, approximately at  $E=0.4 \text{ V}$  vs. SHE. The lower potential limit of the integration is determined by the local maximum at  $E=0.05 \text{ V}$  vs. SHE occurring between hydrogen evolution and hydrogen adsorption. The ESA of the CL-SPEEK/TPA30 ( $25.11 \text{ m}^2 \text{ g}^{-1}$ ) is higher than that of Nafion 117 ( $22.48 \text{ m}^2 \text{ g}^{-1}$ ) and CL-SPEEK ( $23.46 \text{ m}^2 \text{ g}^{-1}$ ).

## 4. Conclusions

Covalently cross-linked composite membranes have been successfully prepared from sulfonated-sulfinated PEEK, followed by addition of TPA, and cross-linking with 1,4-diiodobutane. The cross-linking and blending with TPA reactions are verified by FT-IR. Cross-linking greatly increases the mechanical strength of the polymer and reduces swelling in water. Although cross-linking decreases the number of sulfonic acid groups available for proton transfer in the membrane, CL-SPEEK has a conductivity of  $>0.092$  and  $>0.128 \text{ S cm}^{-1}$  at room temperature and  $80^\circ\text{C}$ , respectively. Because of the cross-linked structure, the membrane properties, including proton conductivity, tensile strength, swelling, dimensional stability and anti-oxidative stability are enhanced. Moreover,

addition of TPA significantly improves the electrochemical and mechanical properties of the membrane. The CL-SPEEK/TPA30 with addition of 30 wt.% of TPA exhibits the best membrane property values as follows: proton conductivity of  $0.128 \text{ S cm}^{-1}$  at  $80^\circ\text{C}$ ; water uptake of 38.5%; ion-exchange capacity of  $1.81 \text{ mequiv. g}^{-1}$  dry membrane; tensile strength of 75.01 MPa; elongation of 83.76%.

The optimum conditions for the preparation of MEA using the non-equilibrium I-R method are as follows: 0.5 mM Pt solution, an impregnation time of 1 h, 0.8 M  $\text{NaBH}_4$ , and a reduction time of 90 min. The cell performance values during water electrolysis are: the cell voltage of CL-SPEEK/TPA30 is 1.78 V at  $1 \text{ A cm}^{-2}$  at  $80^\circ\text{C}$ ; the platinum loading is  $1.28 \text{ mg cm}^{-2}$ ; the ESA of CL-SPEEK/TPA30 was  $25.11 \text{ m}^2 \text{ g}^{-1}$ .

In summary, CL-SPEEK and CL-SPEEK/TPA30 are interesting candidates for PEM cells due to their high proton conductivity, low swelling in hot water, good mechanical and anti-oxidative stabilities, and stable PEM cell performance.

## Acknowledgement

This paper was performed for the Hydrogen Energy R&D Center, one of the 21st Century Frontier R&D Program, funded by the Ministry of Science and Technology of Korea.

## References

- [1] W. Vielstich, A. Lamm, H.A. Gasteiger, Handbook of Fuel Cells; Fundamentals Technology and Applications, vol. 2, John Wiley & Sons, Ltd., Chichester, 2003.
- [2] J.M. Bae, I. Honma, Solid state Ionics 147 (2002) 189.
- [3] F. Lufrano, G. Squadrito, A. Patti, E. Passalacqua, J. Appl. Polym. Sci. 77 (2000) 1250–1256.
- [4] J. Kerres, C.M. Tang, C. Graf, Ind. Eng. Chem. Res. 43 (2004) 4571–4579.
- [5] J. Kerres, Fuel Cells 06 (2006) 251–260.
- [6] S.D. Mikhailenko, K. Wang, S. Kaliaguine, P. Xing, G.P. Robertson, M.D. Guiver, J. Membr. Sci. 233 (2004) 93–99.
- [7] N. Fujiwara, K. Yasuda, T. Ioroi, Z. Siroma, Y. Miyazaki, Electrochim. Acta 47 (2002) 4079–4084.
- [8] P. Millet, M. Pineri, R. Durand, J. Appl. Electrochem. 19 (1989) 162–166.
- [9] H.J. Lee, Y.K. Jung, I.Y. Jang, G.J. Hwang, K.I. Bae, S.K. Sim, A.S. Kang, Trans. Kor. Hydrogen New Energy Soc. 16 (2005) 40–48.
- [10] N. Li, Z. Cui, S. Zhang, S. Li, F. Zhang, J. Power Sources 172 (2007) 511–519.
- [11] R. Liu, W.H. Her, P.S. Fedkiw, J. Electrochem. Soc. 139 (1992) 15–23.
- [12] Y.S. Kim, F. Wang, M. Hickner, T.A. Zawodzinski, J.E. McGrath, J. Membr. Sci. 212 (2003) 263–282.
- [13] H.B. Park, H.S. Shin, Y.M. Lee, J.W. Rhim, J. Membr. Sci. 247 (2005) 103–110.
- [14] N.E. Dowling, Mechanical Behaviour of Materials, Prentice-Hall, New Jersey, 1993.
- [15] L. Zhang, S. Mukerjee, J. Electrochem. Soc. 153 (6) (2006) A1062–A1072.
- [16] M. Eikerling, A.A. Kornyshev, A.M. Kuznetsov, J. Ulstrup, S. Walbran, J. Phys. Chem. B 105 (2001) 3646–3662.
- [17] F.C. Ding, S.J. Wang, M. Xiao, X.H. Li, Y.Z. Meng, J. Power Sources 170 (2007) 20–27.
- [18] K. Miyatake, N. Asano, T. Tombe, M. Watanabe, Electrochemistry 75 (2007) 122–125.