Low temperature decal transfer method for hydrocarbon membrane based membrane electrode assemblies in polymer electrolyte membrane fuel cells

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ABSTRACT

Decal transfer is an effective membrane electrode assembly (MEA) fabrication method known for its low interfacial resistance and suitability for mass processing. Previously decal transfer for hydrocarbon membranes was performed at temperatures above $200\,°C$. Here a novel low temperature decal transfer (LTD) method for hydrocarbon membranes is introduced. The new method applies a small amount $(2.2\,\mathrm{mg\,cm^{-2}})$ of liquid (1-pentanol) onto the membrane separator before decal transfer to lower the T_g of the membrane and achieves complete decal transfer at $110\,°C$ and $6\,\mathrm{MPa}$. Nafion binder amount in the catalyst layer and catalyst layer annealing temperature is controlled to optimize the fuel cell performance. Compared to conventional decal transfer (CDT), the novel LTD method shows enhancement in energy efficiency, simplicity in the process scheme, and improvement in fuel cell performance.

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1. Introduction

The ever increasing demand for clean and efficient power sources has brought great interest into developing a non-fossil fuel energy source. In this sense, fuel cells are an attractive power source that emits minimal hazardous waste and operates at high power densities [1–3]. Especially proton exchange membrane fuel cell (PEMFC) is the subject of ongoing research in the field of green vehicles, and has the potential to alter the transportation sector which is one of the largest greenhouse gas emitters [4]. Most research in PEMFC is focused on improving efficiency and reducing cost in the two major components which are the polymer membrane electrolytes and platinum catalysts. Although a clear commercial alternative to platinum has not been developed, possible cost-effective replacement for Dupont's Nafion polymer electrolyte has been developed [5–8]. The most commercially promising membrane electrolytes are hydrocarbon membranes such as sulfonated poly(arylene ether sulfone) (SPAES) [9–11].

Although a new class of polymer electrolytes has been developed, further research into its use in actual fuel cells has been limited. A crucial aspect in fuel cell performance and future commercialization is in the development of membrane electrode assembly (MEA) fabrication schemes suitable for hydrocarbon membrane separators. Among many fabrication methods, decal transfer is known to be best suitable for mass processing of MEAs

as its scheme is continuous [12]. Decal transfer consists of four major steps; catalyst slurry fabrication; drying of the slurry onto a substrate; hot-pressing of the catalyst layer onto a polymer electrolyte membrane; and removal of the substrate. Transfer of the catalyst layer from the substrate to the membrane is performed above the polymer membrane's T_g, at which the softening of the polymer membrane stimulates the interpenetration of polymer strands across the interface [13]. So this scheme is less favorable for hydrocarbon polymers such as SPAES which has a T_g of $220–300\,°C$ (respective to sulfonation degree), compared to Nafion which has a T_g of $100\,°C$ [10,14,15]. In addition to excessive energy needs, high temperature processing brings about complications in the scheme itself, because proton-form sulfonate groups which are the driver for proton transport during fuel cell operation are delinked from the polymer chain at temperatures above $250\,°C$ [10]. Thus additional steps are required in converting the sulfonate groups into its heat resistant sodium-form before hot-pressing and then bringing it back to its operational proton form through acidification afterwards. Furthermore, the acidification process may cause deformation of the MEA due to non-uniform swelling of the polymer membrane. The advantages of low temperature decal transfer (LTD) can rid of this complexity in the process scheme and also eliminate the inevitable loss of sulfonate groups at high temperatures, thus improving performance.

Cho et al. [16] and Krishnan et al. [12] have recently reported a LTD scheme for DMFCs that lowered the hot pressing temperature by adding two extra layers (carbon + Nafion ionomer) to aid in catalyst layer separation from the substrate and adhesion to the membrane. This paper, however, introduces a novel LTD scheme

(110 °C) which undergoes liquid treatment instead of adding multiple layers to the MEA. The liquid can be removed more easily and thus the added liquid has minimal effect on fuel cell performance. Also the novel scheme works well for both PEMFC and DMFC applications. Previous decal transfer schemes that worked well for Pt black catalyst for DMFCs does not necessarily lead to a successful result for Pt/C catalysts used in PEMFCs which have greater catalyst volume.

In this study, PEMFC MEAs are fabricated using a novel LTD scheme. An appropriate liquid is selected for the scheme and its effect on decal transfer is analyzed. The performances of the MEAs, produced using different liquids are compared. For scheme optimization, factors such as Nafion ionomer content and catalyst layer annealing conditions are controlled and analyzed to give the overall optimal performance. Finally, the novel scheme is analyzed and compared with conventional schemes.

2. Experimental

2.1. Preparation of catalyst slurry and catalyst layer on polyimide substrate

A catalyst slurry was prepared by mixing Pt/C (E-tek 40 wt.%), isopropyl alcohol (SK Chemicals Co.), DI water (ELGA Pure Lab Classic), and 5 wt.% Nafion solution (EW1100, Dupont Inc.). The Nafion ionomer content was varied between 10 and 25 wt.% in 5 wt.% increments based on the total solid content in the dried catalyst layer. Homogeneous slurry was produced by using an ultrasonicator (Branson Sonifier 450) for 30 min and was left to stir overnight. The slurry ink was directly coated over a polyimide film (Dupont Inc.) by using a doctor blade system (Auto-Bar Coater GBC-A4). The target loading was 0.4 mg cm^{-2} of platinum. The catalyst coated polyimide film was dried and annealed for 12 h in a convection oven (PHH-101M, ESPEC CORP.) at appropriate temperatures (30 °C, 70 °C, 90 °C, 120 °C, 150 °C). For conventional decal transfer (CDT), sodium hydroxide (98 wt.% bead, Samchun Chemicals Co.) was additionally added to the slurry in molar excess compared to sulfonate groups in the Nafion solution.

2.2. Preparation of polymer electrolyte membrane

Sulfonated poly(arylene ether sulfone) 50 (SPAES50) (degree of sulfonation = 50) membrane was prepared for MEA fabrication [10,11]. Sodium form SPAES50 was dissolved in N-methyl pyrrolidone (NMP) at 140 °C with mechanical stirring for 24 h. The solution was filtered using a membrane filter and casted on a glass plate for 36 h at 80 °C. The casted membrane was acidified in 0.5 M H$_2$SO$_4$ for 2 h and boiled in DI water for 2 h. For CDT, the membrane was acidified and boiled after MEA fabrication. All membranes were approximately 75 ± 5 μm.

2.3. Liquid uptake and Young's modulus

Liquid uptake (LU) by the polymer membrane was measured for 1,2-propanediol (99.5 wt.%, A.C.S. Reagent, Sigma–Aldrich), 1-pentanol (99+ wt.%, A.C.S. Reagent, Sigma–Aldrich), 2-pentanol (98 wt.%, Sigma–Aldrich), decane (98 wt.%, Showa Co.), and dodecane (Cica reagent, Kanto Chemical Co.). After acidification, the membranes were dried on a vacuum plate for 1 h and then further dried in a vacuum oven at 80 °C for 24 h to obtain the dry weight. The dried membranes were immersed in the liquids at room temperature for 24 h before measurement of the wet membrane weight.

Liquid uptake calculation was performed using Eq. (1) where W_{wet} and W_{dry} are the weights of the wet and dry membranes.

$$LU\% = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100\% \qquad (1)$$

Young's modulus was evaluated by UTM (Instron Corporation Series IX Automated Materials Testing System). Each polymer strand was immersed in one of the above liquid for 24 h before actual measurement. The dimension of the polymer strands between the grips was 10 mm in width and 20 mm in length. The crosshead speed was 10 mm min^{-1}.

2.4. Decal transfer and MEA fabrication

Prior to catalyst layer transfer, the hydrocarbon membrane was treated with one of the aforementioned liquids by brushing onto the membrane surface. The liquid content was held constant at 2.2 mg of liquid per cm^2 of polymer membrane by removing excess liquid using a vacuum plate. After treatment, the catalyst coated substrate was hot-pressed onto a hydrocarbon membrane at 110 °C and 6 MPa for 3 min to transfer the catalyst layer from the substrate to the hydrocarbon membrane. SPAES50 was used in all MEA fabrication. For CDT, hot-pressing was performed at 240 °C and 6 MPa for 3 min without liquid treatment.

The residue on the polyimide substrate after LTD was examined with EDX (FE-SEM JEOL JSM-6700F) to verify complete transfer of the catalyst layer. SEM images of the MEA top and cross-section was also taken to verify contact between the MEA layers and to measure catalyst layer thickness and view pore development. The average of three catalyst layer thickness values was recorded for each sample.

2.5. PEMFC performance testing and MEA analysis

MEA performance was measured by assembling single cells with an active area of 5 cm^2. PTFE treated carbon cloth (E-tek) was used as the gas diffusion layer at both anode and cathode. Serpentine type graphite separators with aluminum end plates (Fuel Cell Technologies Inc.) were used. The cell temperature was maintained at 80 °C. Hydrogen and air with 100 R.H.% were used as the inflow gas at the anode and cathode, respectively. PEMFC performance was measured using a commercial test station (Fuel Cell Technologies Inc., FCT-TS300). The IV curve was measured between 0.5 and 1.0 V with a step change of 50 mV per 25 s. MEAs were activated at 0.6 V for 48 h prior to cell performance evaluation. A commercially available electrode layer (40 wt.% Pt/C, 0.4 mg Pt cm^{-2}, Nafion binder, PTFE treated carbon substrate, Fuel Cell Power Inc.) fabricated through the catalyst coated substrate (CCS) method was also tested with SPAES50 as a reference.

Hydrogen fuel crossover was evaluated by utilizing a DC power supply (Agilent N5744A) with the working electrode connected to the cathode and reference electrode to the anode. After extensive purging of the cathode with nitrogen gas, the current produced at the cathode by hydrogen oxidation was measured. The potential range was 0.15–0.5 V and step change was 1 mV per 100 ms.

Electrochemically active surface area (ESA) of the catalyst layer (cathode) was evaluated by cyclic voltammetry (Gamry reference 600). During the measurement hydrogen gas (anode) and nitrogen gas (cathode) were supplied to the fuel cell. In these measurements, the potential was swept from 0.05 V to 1.2 V at a scan rate of 50 mV s^{-1}. Proton adsorption/desorption from platinum catalyst surface was measured at potentials lower than 0.4 V. Double layer charging effects were compensated by subtracting current values at 0.4 V [17].
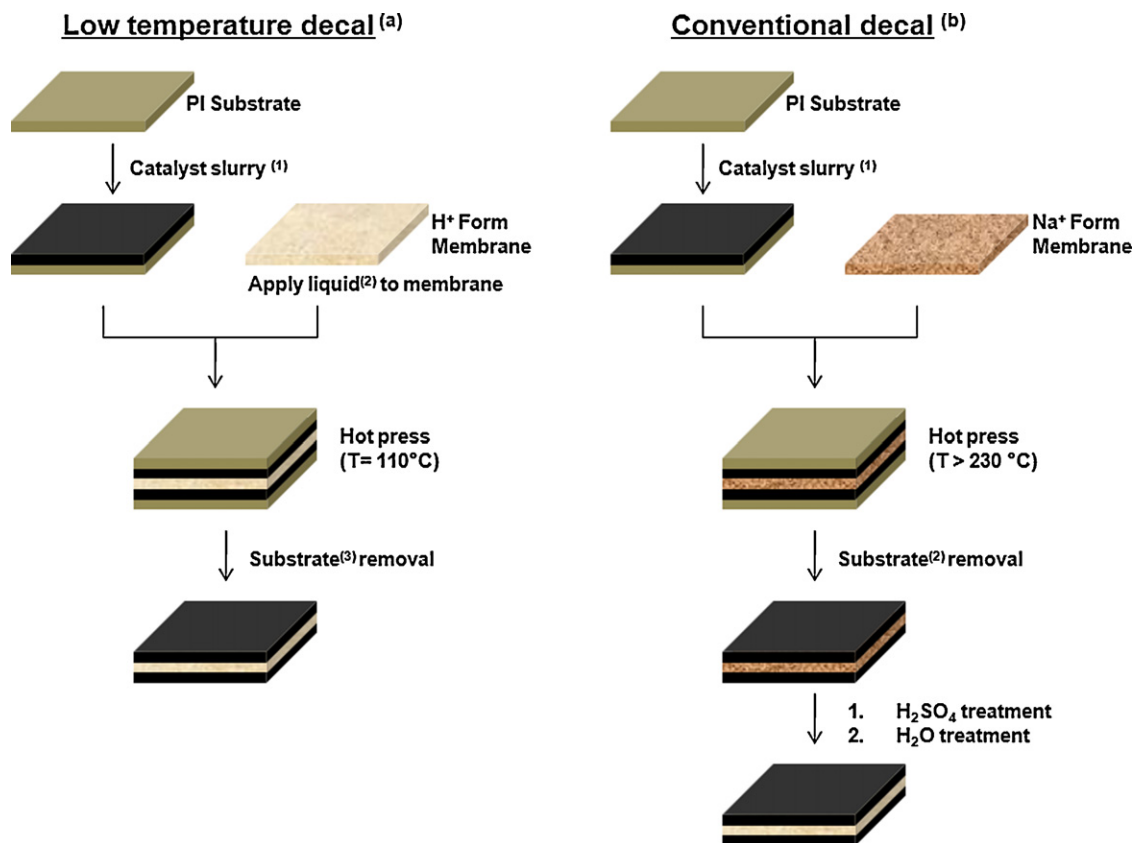
Fig. 1. Schematic diagram of low temperature decal transfer. (a) LTD: (1) catalyst + Nafion ionomer + isopropyl alcohol + H_2O, (2) this study, (3) polyimide film, (b) CDT: (1) catalyst + Nafion ionomer + isopropyl alcohol + H_2O + NaOH, (2) polyimide film.
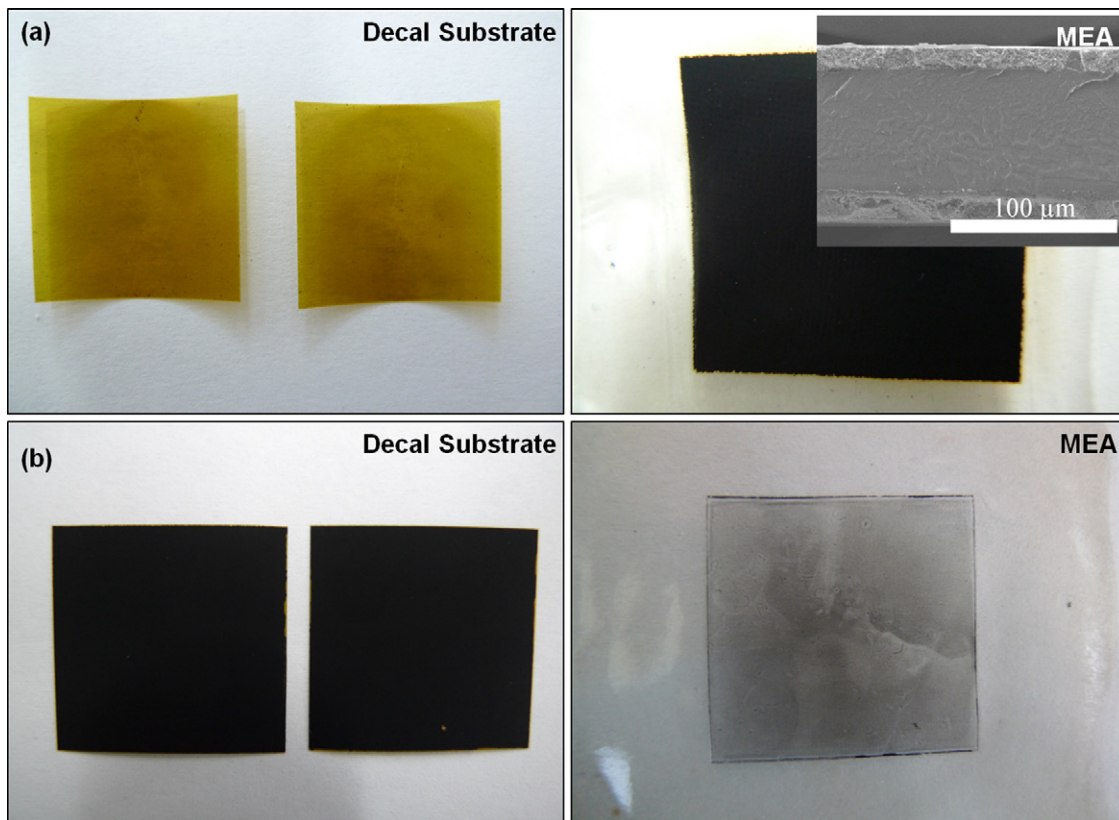

Fig. 2. Effect of liquid use on catalyst layer transfer (inset: cross-section of MEA) (hot pressing conditions: temperature = 110 °C, pressure = 6 MPa, time = 3 min; substrate type: polyimide film; membrane type: SPAES50). (a) 1-Pentanol and (b) no liquid.

Table 1
Characteristic of tested liquids with SPAES50.

Liquid	Boiling point (°C)	Liquid uptake[a] (wt.%)	Young's modulus[b] (MPa)
1-Pentanol	139	158	0.5
2-Pentanol	119	113	1.0
1,2-Propanediol	189	>2000	<0.1
Decane	174	6	830 ± 181
Dodecane	216	6	824 ± 102

[a] Measurements were taken after immersion in liquid for 24 h.
[b] Young's Modulus of SPAES50: 724 ± 129 MPa.

Interfacial contact resistance was also measured by electrochemical impedance spectroscopy (BioLogic SP-300). The measurement was performed at a dc potential of 0.85 V, with an ac frequency range of 1–10 MHz and an ac amplitude of 10 mV. Before each measurement the MEA was stabilized at the dc potential of 0.85 V for 20 min [17].

3. Results and discussion

3.1. Effect of liquid application on decal transfer

A schematic comparison between LTD and CDT is shown in Fig. 1. The advantage of LTD is the substantially lower hot pressing temperature and simplicity in the process scheme. The right utilization of liquid has the effect of lowering the T_g of a polymer by penetrating into the membrane and stimulating easier move-

ment of the polymer strands which is the concept used in polymer welding [13]. This in effect allows complete decal transfer at 110 °C (pressure = 6 MPa, time = 3 min) which is more than 100 °C lower than that required by the conventional scheme. To the best of our knowledge, the novel LTD's hot-pressing temperature is the lowest reported value yet. Krishnan et al. has recently introduced a decal transfer method for DMFCs at 140 °C (pressure = 8 MPa, time = 8 min) [12]. Another advantage of the scheme is that LTD can avoid CDT's post acidification process after MEA fabrication. During this step, hydrocarbon membranes which usually have high water uptake undergo permanent MEA deformation due to uneven swelling. LTD can avoid this problem by acidifying hydrocarbon membranes before MEA fabrication. This is possible because the hot-pressing temperature is lowered below the temperature at which the proton-form sulfonate groups are lost from the polymer chain. To verify the necessity of an additional liquid removal step for the above liquids, performance measurements with and without liquid removal were taken but they had no noticeable difference in performance and fuel crossover. This is because the amount of liquid (2.2 mg cm^{-2}) added is very small in the beginning and the hot-pressing step is operated at temperatures near the liquid boiling point at which most of the liquid is eventually vaporized.

Several liquids are tested to see their effectiveness in improving decal transfer. The criterion in liquid selection is good absorbability by the hydrocarbon electrolyte membrane. Thus the chosen liquids contain a hydroxide group segment for compatibility with the hydrocarbon membrane and a straight hydrocarbon segment
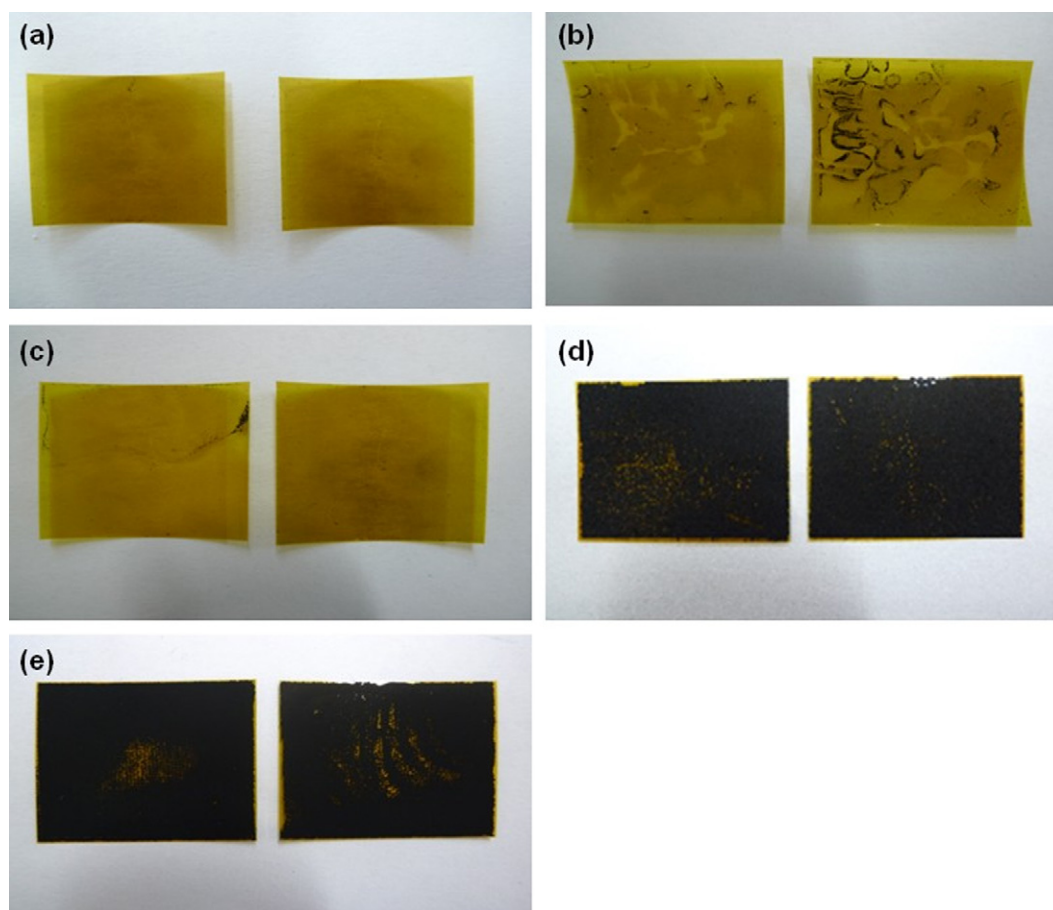

Fig. 3. Residual polyimide substrates after low temperature decal transfer using different liquids (hot pressing conditions: temperature = 110 °C, pressure = 6 MPa, time = 3 min; substrate type: polyimide film). (a) 1-Pentanol, (b) 2-pentanol, (c) 1,2-propanediol, (d) 1-decane and (e) 1-dodecane.
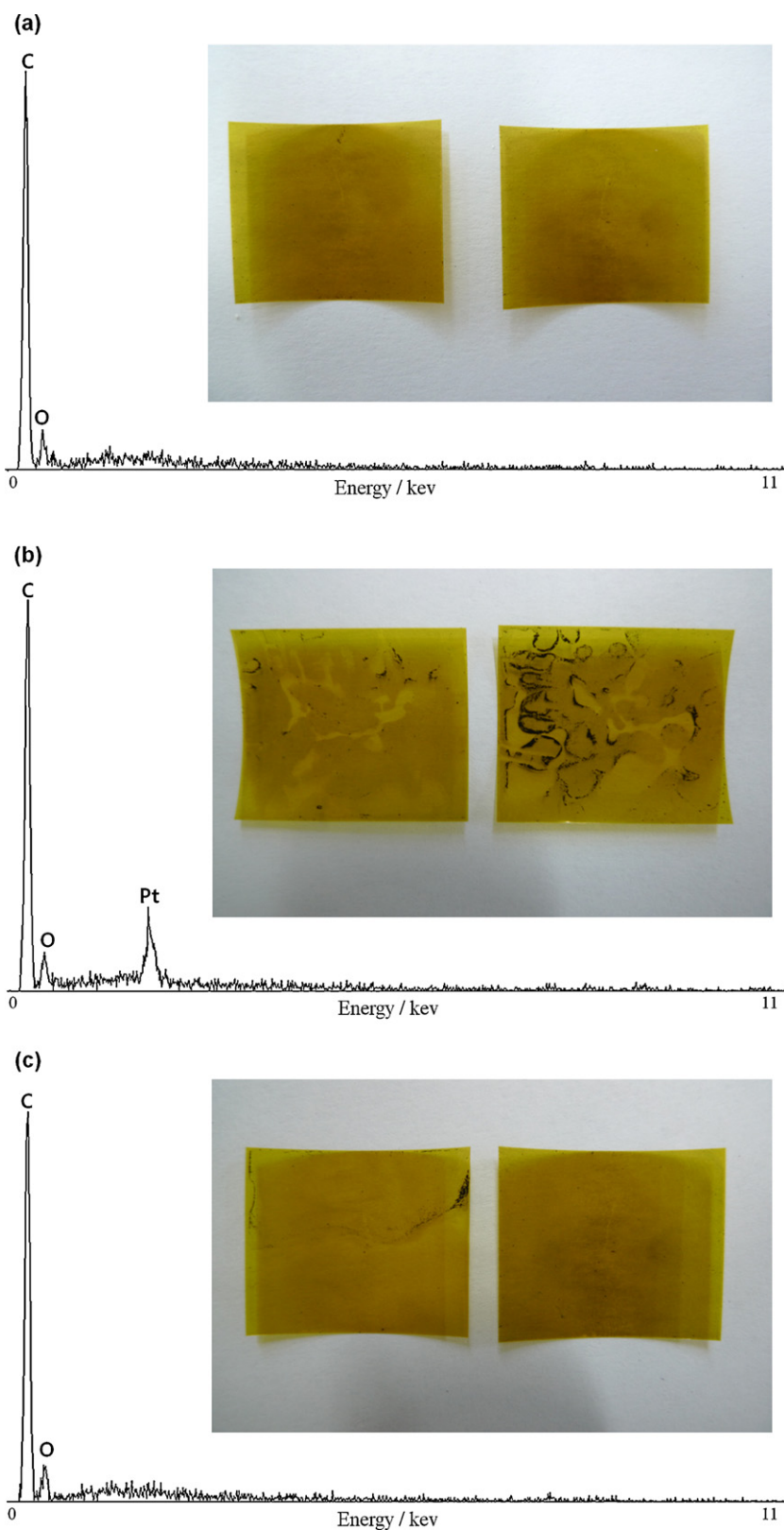
Fig. 4. EDX analysis of residual polyimide substrate after low temperature decal transfer (inset: top-view of polyimide substrate after decal transfer) (hot pressing conditions: temperature = 110 °C, pressure = 6 MPa, time = 3 min; substrate type: polyimide film). (a) 1-Pentanol, (b) 2-pentanol and (c) 1,2-propanediol.

to control the volatility of the liquid. Liquids with an extremely high absorbability by the MEA as well as high boiling point, however, are not favorable as there is a possibility of liquid remaining in the MEA after LTD. But the liquids still need to have a

relatively high boiling point to withstand hot-pressing conditions. Consequently, chemicals from the alcohol group with boiling points between 120 and 200 °C are primarily investigated. The chosen liquids satisfying the described criteria are 1-pentanol, 2-pentanol,
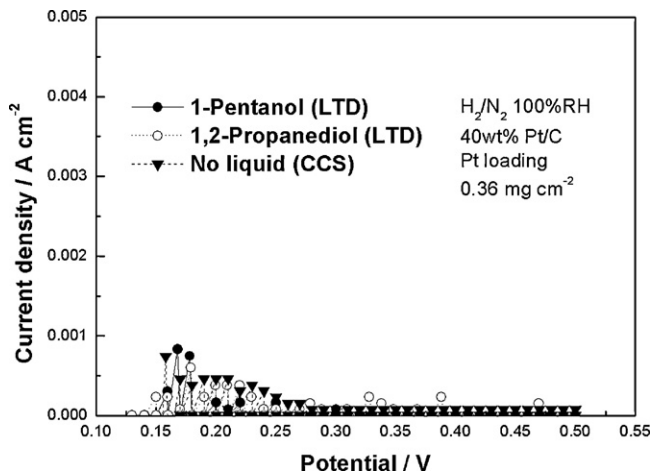
Fig. 5. Effect of liquid application on hydrogen fuel crossover during fuel cell operation (potential range: 0.13–0.50 V; step change: 1 mV per 100 ms; inflow gas: H_2 (anode), N_2 (cathode); membrane type: SPAES50).

and 1,2-propanediol. Decane and dodecane are also tested for comparison as liquids not satisfying the criteria. Basic characteristics of the chosen liquids with the membrane are summarized in Table 1.

The effect of liquid (1-pentanol) use on decal transfer is given in Fig. 2. At the same temperature and pressure it is evident that the use of 1-pentanol greatly improves the degree of catalyst layer transfer. While LTD results in catalyst layer transfer of 100 wt.%, LTD w/o liquid treatment results in a transfer of less than 5 wt.%. The dark layer in the MEA in Fig. 2(b) is the result of pressure alone and will nearly disappear when the pressure is reduced below 6 MPa with all other conditions constant. As for LTD, however, lower pressures of 4 MPa can still result in complete catalyst layer transfer. As application of pressure during decal transfer reduces fuel pathways developed in the catalyst layer, a lower pressure application by LTD may be beneficial in improving mass transfer and thus fuel cell performance.

Decal transfer results of the above mentioned chemicals are shown in Fig. 3. A clear line can be drawn between the relatively hydrophilic alcohols (Fig. 3(a)–(c)) and the relatively hydrophobic simple hydrocarbons (Fig. 3(d) and (e)). The presence of an appro-
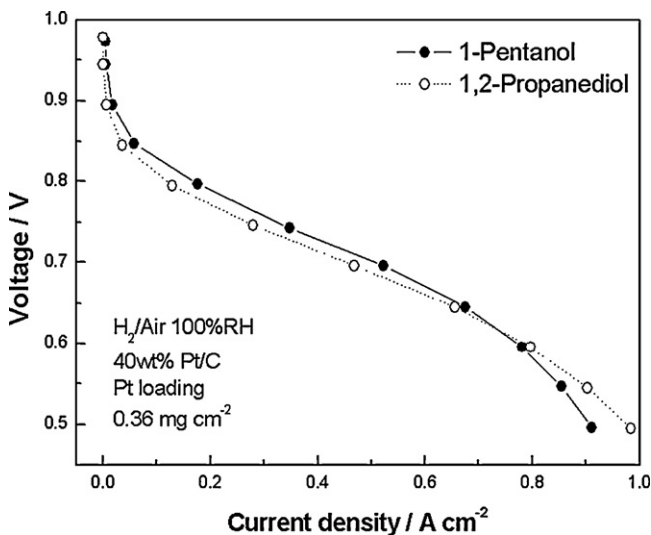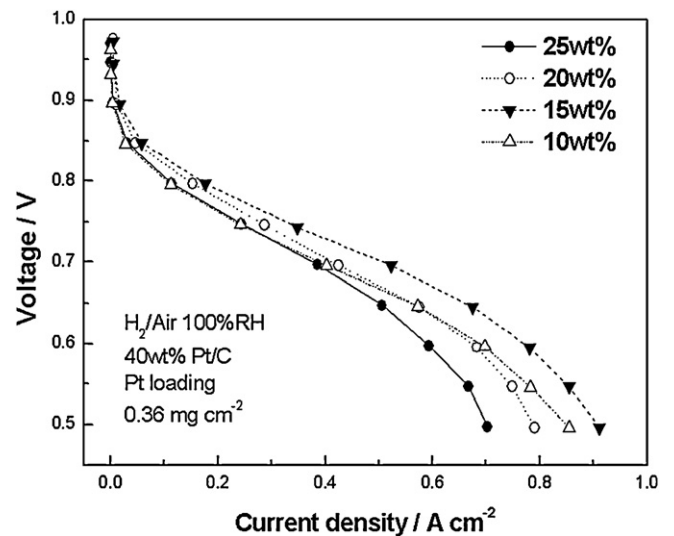

Fig. 7. Effect of Nafion binder content on MEA performance (liquid type: 1-pentanol; hot pressing conditions: temperature = 110 °C, pressure = 6 MPa, time = 3 min; inflow gas: H_2 (anode), air (cathode); membrane type: SPAES50).

priate liquid has a distinct effect on catalyst layer transfer. Even the successful samples, however, still have a thin dark layer covering the substrate surface. The composition of the dark layer is verified through EDX analysis and is shown in Fig. 4. For decal transfer using 1,2-propanediol and 1-pentanol, the remnants are negligible in amount and not detectable. For 2-pentanol, however, a detectable amount of platinum is measured. Relatively unsuccessful transfer when using 2-pentanol is mainly due to its low boiling point around 119 °C, which is very close to the hot pressing temperature. Although the hot-pressing time only spans over 3 min, liquid is lost during the process. In addition to the presence itself, the amount of liquid application also has a significant effect on catalyst layer transfer. Transfer is not improved simply by applying more liquid to the membrane because an overflowing amount of liquid is forced to aggregate under pressure and creates a serpentine transfer pattern.

As for decane and dodecane, the degree of catalyst layer transfer is less than 10 wt.%. The applied liquid formed a thin well spread
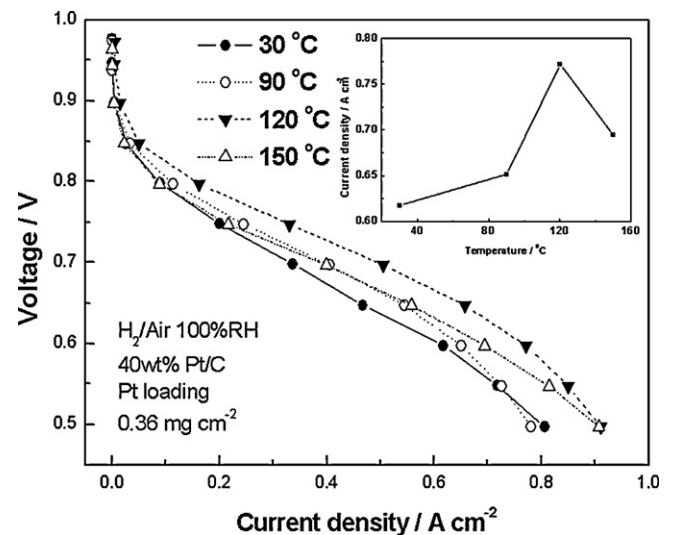

Fig. 6. Effect of liquid type on MEA performance (hot pressing conditions: temperature = 110 °C, pressure = 6 MPa, time = 3 min; inflow gas: H_2 (anode), air (cathode); membrane type: SPAES50).

Fig. 8. Effect of catalyst layer annealing temperature on MEA performance (inset: current density @ 0.6 V) (liquid type: 1-pentanol; hot pressing conditions: temperature = 110 °C, pressure = 6 MPa, time = 3 min; inflow gas: H_2 (anode), air (cathode); membrane type: SPAES50; Nafion binder content: 15 wt.%).
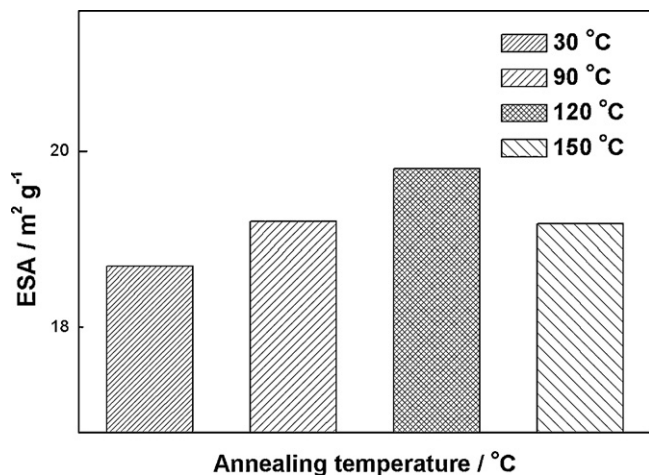
Fig. 9. Effect of catalyst layer annealing temperature on electrochemically active surface area (liquid: 1-pentanol; hot pressing conditions: temperature = 110 °C, pressure = 6 MPa, time = 3 min; membrane type: SPAES50; Nafion binder content: 15 wt.%; potential range: 0.05–1.20 V; scan rate: 50 mV s^{-1}; inflow gas: H$_2$ (anode), N$_2$ (cathode); membrane type: SPAES50).

layer above the membrane as it has low surface tension. Simple straight chain hydrocarbons, however, do not have any functional groups for hydrogen bonding with the sulfonate groups of the hydrocarbon backbone and thus show low absorbability by the membrane. The small amount that is transferred is expected to be due to the compatibility between the hydrophobic liquid and the carbon present in the catalyst layer. Dodecane is tested in addition to decane because the liquid amount can be better controlled and less affected by the hot-pressing temperature and to investigate the effect of a longer carbon chain in improving compatibility with the carbon in the catalyst layer. The two samples, however, show similar results without any noticeable improvement.

The above results show that application of hydrophilic alcohols allows decal transfer to be successfully performed at lower temperature and pressure by the reduction in T_g. The right utilization of liquid and in this case alcohols has the effect of lowering the T_g of a polymer by penetrating into the membrane and stimulating easier movement of the polymer strands which is the concept used in polymer welding [13]. The reduction in T_g and thus softening of the SPAES membrane by water uptake has also been reported by Kim et al. [18]. Alcohols that show successful LTD also show high liquid uptake values compared to decane and dodecane as shown in Table 1. So liquids that show high liquid uptake values are those that can penetrate well into the membrane and cause a reduction in T_g. These liquids that show high liquid uptake by the membrane, decreased the membrane modulus by a large degree (<1 MPa) and thus caused softening of the membrane. The softening of the membrane increased adhesion at the interface through the interpenetration of the polymer strands at the interface. Successful catalyst layer transfer occurs when the increased adhesion at the membrane/catalyst layer interface exceeds that at the catalyst layer/substrate interface. The improved adhesion between the membrane and catalyst layer also coincides with the decrease in interfacial contact resistance of the MEAs fabricated by LTD compared to that fabricated by CDT that is further explained in Section 3.4.

As for 1,2-propanediol and 1-pentanol, the results show 100 wt.% catalyst layer transfer. Although complete transfer is achieved using the two liquids, their effect on the polymer membrane itself needed to be investigated. Fig. 5 shows the amount of fuel crossover during fuel cell operation and is a method for investigating pin-hole formation or polymer disentanglement. This method of fuel crossover evaluation measures the current produced

by the hydrogen at the cathode while input gas is hydrogen and nitrogen at the anode and cathode, respectively. As can be seen, liquid use in decal transfer does not result in permanent damage (pin-hole formation or polymer disentanglement) of the membrane itself as the fuel crossover is nearly identical to the fuel cell produced using the CCS method which does not undergo liquid treatment. MEA fabricated using the CCS method is included as a reference because it does least damage to the membrane during MEA fabrication. Current densities below 1 mA cm^{-2} are significantly low values as it is approximately four times lower than that observed for Nafion 212.

The effect of liquid type on PEMFC performance is also investigated in Fig. 6. The nearly overlapping performance curves shows that liquid type does not have a significant effect on fuel cell performance.

3.2. Effect of Nafion binder content on performance

Further experiments were performed to optimize the parameters affecting fuel cell performance for the novel MEA fabrication method. Nafion which act as proton conductor, binder for mechanical stability, and hydrophilic agent is one of the most important components in the MEA and is discussed as the first variable. Kim et al. [17] and Jeon et al. [19] reported that optimum Nafion content is drastically different for each type of fuel cell as there are numerous types of MEA fabrication parameters (platinum loading amount, catalyst ink composition). Thus the procurement of the optimum Nafion content is crucial for different fabrication schemes and thus the effect of Nafion content on fuel cell performance is shown in Fig. 7. Nafion content is varied in a range between 10 and 25 wt.% of the overall catalyst layer mass in 5 wt.% intervals. For all MEAs tested, the open circuit voltage is above 0.96 V indicating negligible crossover of inlet gas. Overall it is evident that the optimum Nafion content is 15 wt.% of the catalyst layer. Fuel cell performance is basically affected by three factors which are activation overpotential, resistance loss, and concentration overpotential. Activation overpotential is dominant at high voltage regions and is related to the current loss due to the sluggish oxygen reduction reaction (ORR) at the cathode. ORR is largely influenced by the development of pores in the catalyst layer for efficient transfer of oxygen to the catalyst particles as well as the structuring of the Nafion channels for efficient charge transfer [17]. For Nafion content below 15 wt.%, the current density at high voltage region shows a sharper drop than that at 15 wt.% as the Nafion channels for charge transfer is not fully developed due to a shortage in the Nafion amount. But as the Nafion content is raised beyond 15 wt.%, the excess amount of Nafion hinders the transfer of oxygen and thus the current density shows still a sharper drop in the performance curve than that at 15 wt.%. Concentration overpotential is dominant at low voltage regions and is related to the limited gas transfer rate that cannot keep up with the reaction rate. As the Nafion content increases, the slope of the curves shows a steeper drop due to mass transfer hindrance from the increased Nafion content. As for resistance loss, which is dominantly responsible for the mid-voltage region, is related to the resistance of the individual components of the MEA, especially the membrane separator. The slopes of the performance curves are relatively linear to each other. Completely parallel curves, however, are not obtained as activation overpotential, resistance loss, and concentration overpotential simultaneously influence the shape of the entire curve.

3.3. Effect of annealing temperature on performance

To further optimize performance, the catalyst layer annealing temperature is investigated as well. The effect of catalyst layer annealing temperature on overall fuel cell performance is shown
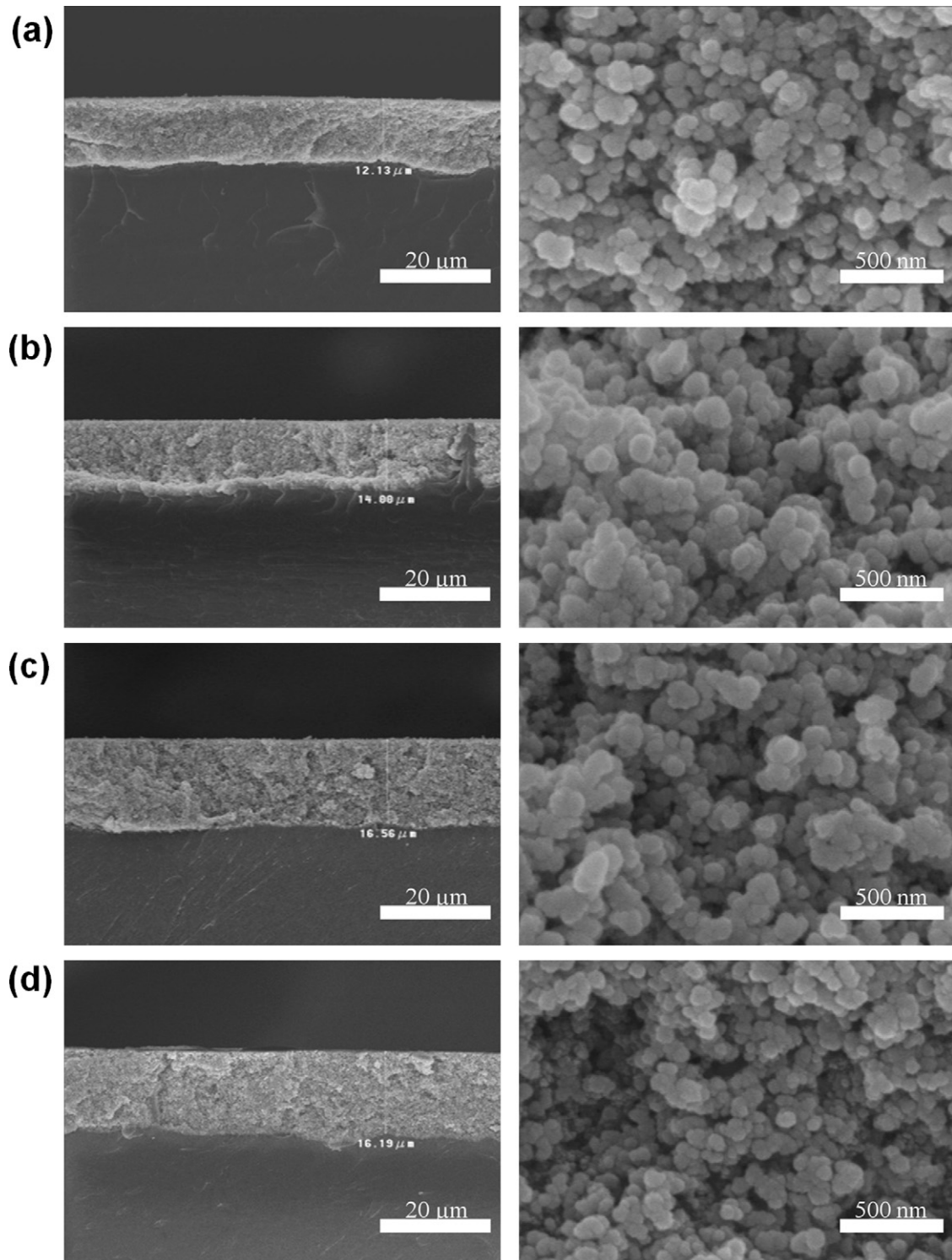
Fig. 10. SEM images of catalyst layers prepared at different annealing temperatures (liquid: 1-pentanol; hot pressing conditions: temperature = 110 °C, pressure = 6 MPa, time = 3 min; membrane type: SPAES50; Nafion binder content: 15 wt.%). (a) 30 °C, (b) 90 °C, (c) 120 °C and (d) 150 °C.

in Fig. 8. Temperatures up to 150 °C are chosen, as Nafion polymer degradation begins at temperatures above 200 °C [20]. The performance increases up to 120 °C which is above the T_g of Nafion binders in the slurry and then decreases with further temperature increase. Optimum performance at 120 °C may be caused by the combination of three factors which are pore development,

ionomer channel formation and catalyst aggregation. There is a distinct difference in performance between those made above the T_g of Nafion and those fabricated below the T_g. Especially at 0.6 V, which is the voltage value in which optimum power is achieved, there is a sharp rise in current density as the temperature is raised above the Nafion binder's T_g. Below the T_g of Nafion, difficulties in
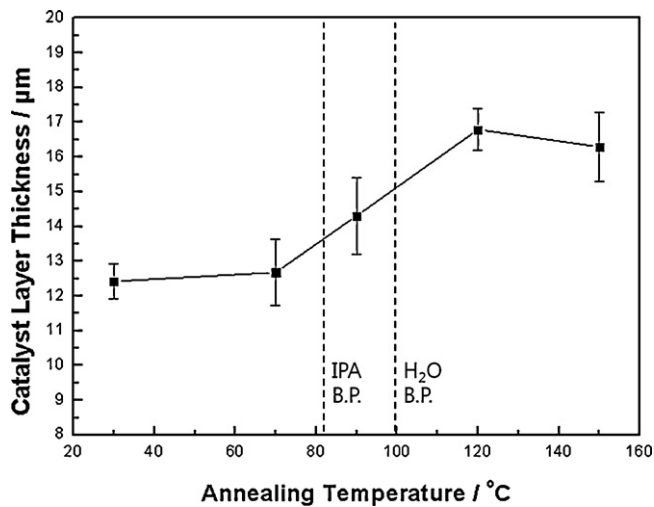
Fig. 11. Effect of catalyst layer annealing temperature on its thickness (liquid: 1-pentanol; hot pressing conditions: temperature = 110 °C, pressure = 6 MPa, time = 3 min; membrane type: SPAES50; Nafion binder content: 15 wt.%).

Fig. 13. Electrochemical impedance spectroscopy of MEAs fabricated by decal transfer method (DC voltage: 0.85 V; AC amplitude: 10 mV; AC frequency range: 1–10 mHz; inflow gas: H_2 (anode), air (cathode); membrane type: SPAES50). (a) Low temperature decal transfer and (b) conventional decal transfer.

polymer chain movement hinders full development of the polymer network which is crucial for proton transport. A further temperature increase to 150 °C, however, leads to a drop in performance. This trend seen in the performance curve is also verified in the ESA measurements in Fig. 9. The drop in performance and ESA at 150 °C may be attributable to the aggregation of catalyst particles at elevated temperatures. Wu et al. also reported that heat treatment of Pt/C inevitably leads to a drop in catalytic performance. Catalytic activity of Pt/C heat treated at 120 °C was 16.4% lower than that heat treated at 70 °C [21].

The general improvement in performance for MEAs fabricated at higher temperatures may be a result of porosity as well. The relationship between porosity and performance can be seen in the high current density region of Fig. 8. As the catalyst annealing temperature increases, the slopes of the curves at this region become flatter. This is because catalyst layers prepared at higher temper-
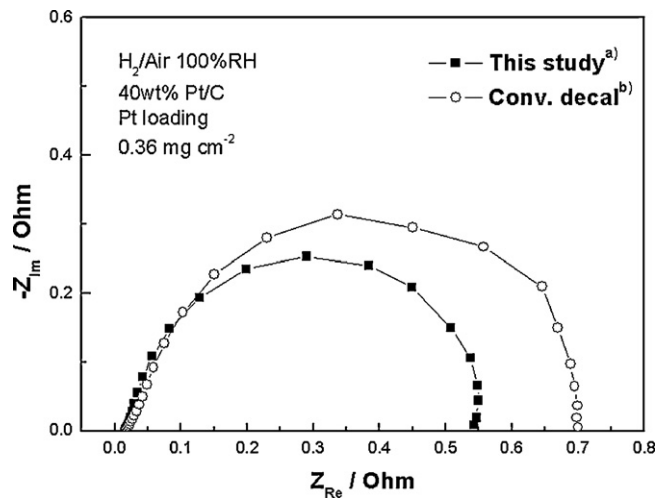

Fig. 12. MEA performance of low temperature decal transfer (liquid type: 1-pentanol; membrane type: SPAES50; Nafion binder content: 15 wt.%; catalyst layer annealing temperature: 120 °C; hot pressing conditions: temperature = 110 °C, pressure = 6 MPa, time = 3 min; inflow gas: H_2 (anode), air (cathode)). (a) Low temperature decal transfer, (b) conventional decal transfer and (c) catalyst coated substrate.

atures have more well developed pores which lead to a smaller mass transfer resistance. Park et al. has previously investigated the effect of catalyst layer annealing temperature up to 90 °C and discovered a distinct rise in performance and pore development [22]. The temperature range, however, was small and below the T_g of Nafion which is non-optimal as indicated by the performance curve in Fig. 8. Furthermore the investigation had been performed using the CCS method which normally does not involve a hot pressing step. The following investigation is performed to see if the trend in pore development observed by Park et al. is still apparent while using LTD as this fabrication method involves a hot-pressing step that may tear down the pore structure.

Fortunately, the trend in pore formation observed by Park et al. is clearly observed in the SEM images in Fig. 10. This is an indication that pore formation during the catalyst layer annealing step is maintained during the hot-pressing step and thus is a factor influencing the performance curve in Fig. 8 [22]. The average catalyst layer thickness values are as follows: 12.4 ± 0.5 μm (30 °C), 14.3 ± 1.1 μm (90 °C), 16.8 ± 0.6 μm (120 °C), 16.3 ± 1.0 μm (150 °C). The catalyst layer thickness shows a 31% increase in thickness as the annealing temperature is increased from 30 °C (12.4 μm) to 150 °C (16.3 μm). The catalyst layer thickness in Fig. 10(c) and (d) overlap, however, showing that an increase in temperature does not increase porosity above a certain point. Especially the boiling point of the solvent used in the catalyst slurry may have strong influence on pore formation. The relationship between catalyst layer thickness and annealing temperature is shown in Fig. 11. As mostly water and isopropyl alcohol are used in the slurry, a noticeable rise in thickness is observed as the annealing temperature is raised above the alcohol's boiling point. This rise continues as it crosses the boiling point of water. A change in temperature beyond 120 °C, however, does not have a distinct effect on porosity development. Still the gradual increase in porosity as the preparation temperature increases is observed in the magnified (50,000×) image of the catalyst layer cross-section up to 150 °C.

3.4. Comparison with conventional methods

A comparison of fuel cell performance for MEAs produced by different fabrication schemes is shown in Fig. 12. Results show
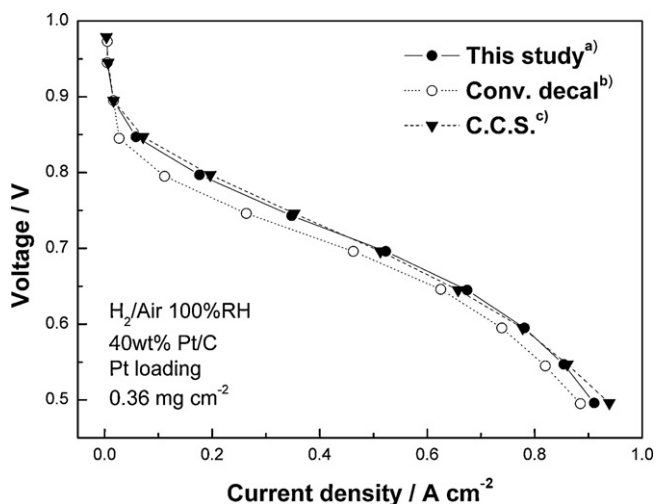
that the optimized fuel cell fabricated using LTD is more effective than that fabricated using CDT and as good as that fabricated using CCS in terms of performance. The overlap between the performance curves (LTD, CCS) shows that liquid application does not inflict permanent damage to the polymer membrane in terms of performance.

EIS spectra of the MEAs fabricated using LTD and CDT is shown in Fig. 13. The intercept of the curve at the real axis in the high frequency region corresponds to the ohmic resistance of the MEA. The overlap of the arcs at this point can be an indication that identical type of membrane and catalyst layer was used in the experiment. The diameter of the arc in the figure represents the charge transfer resistance at the membrane–electrode interface. The arc diameters of the MEAs produced by LTD and CDT are $0.53\,\Omega$ and $0.70\,\Omega$, respectively. LTD thus produces MEAs with lower interfacial contact resistance than that produced by CDT. This result may be one of the possible causes for the improvement in PEMFC performance in Fig. 12.

4. Conclusion

In this study, a novel low temperature decal transfer (LTD) method has been developed for fabricating MEAs that use hydrocarbon membranes for PEMFCs. Among several types of liquids, those with hydroxide groups show good compatibility with the sulfonated hydrocarbon membrane and thus display good transfer. Complete decal transfer is achieved at temperature and pressure as low as $110\,^{\circ}$C and 6 MPa using 1-pentanol. Liquid treatment greatly improves the degree of catalyst layer transfer while causing no decay to fuel cell performance. Optimum fuel cell performance is reached at a Nafion ionomer content of 15 wt.%. The catalyst layer shows the best performance when the layer is dried and annealed at a temperature of $120\,^{\circ}$C. Compared to conventional decal transfer (CDT), the novel LTD method shows an improvement in performance while achieving energy efficiency and simplification in the process scheme.

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