

Preparation of catalyst coated membrane by modified decal transfer method for proton exchange membrane fuel cell

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Abstract. A new catalyst coated membrane (CCM) was prepared by modified decal transfer method. A structure of ionomer/catalyst/carbon/substrate was used to facilitate the transfer of catalyst layer from decal substrate to the membrane at quite low hot-pressing temperature (120 °C) for 8 min. Several decal substrates were tested to select a proper substrate, namely PTFE cloth, PTFE film, aluminium foil, and OHP transparent sheet. The transfer degree of catalyst layer was estimated. Elemental analysis and SEM-mapping were performed to evaluate the residue, whereas contact angle measurement was conducted to characterize the hydrophobicity of decal substrates. The results showed that PTFE cloth and PTFE film transferred approximately 90% of catalyst layer onto the membrane, while the other two substrates were around 70%. Furthermore, the elemental analysis of the residue on the substrate revealed that it was mainly composed of carbon and fluorine for PTFE cloth and PTFE film. This result supports other findings that PTFE cloth and PTFE film are suitable as decal substrate at low temperature hot pressing for fabricating CCM.

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) have been already commercialized for stationary application and become one of potential candidates for automobile applications. PEMFCs show high energy efficiency and low temperature operation compared to conventional combustion engine. As the heart of PEMFC, preparation of membrane electrode assembly (MEA) directly influences the cell performance. Many studies have been made to improve MEA preparation [1-4]. Typically, there are two categories of MEA fabrication, namely catalyst-coated on electrode (CCE) and catalyst coated on membrane (CCM). The performance and durability of CCM are usually higher than that of MEA prepared by the CCE method due to better interfacial contact between membrane and catalyst and better catalyst utilization [5-7].

Instead of direct coating the catalyst onto the membrane that might undergo swelling, catalyst layer can be deposited onto the membrane by decal method. Catalyst inks are coated over a substrate to form a catalyst layer, and then transferred onto the membrane by hot pressing under certain temperature and pressure condition [7,8]. Low Pt loading and low catalyst losses during MEA fabrication can be obtained by this way [9]. Furthermore, to facilitate the transfer of catalyst layer



from the decal substrate to a membrane, Park *et al.*, (2008) [10] introduced a layer composed of carbon powder and Nafion ionomer prior to coating the catalyst.

Conventionally, decal transfer is performed by hot pressing at 150-200°C [7,11,12]. As a consequence, the H⁺ form of Nafion membrane should be converted to other cationic forms such as Na⁺ or K⁺ to give more mechanical strength. Subsequence re-protonation by boiling the MEA in sulfuric acid solution is also required. This process seems to be more complex and the temperature of hot pressing is too high. Recently, Cho *et al.*, (2009) [4] have reported low temperature decal transfer for direct methanol fuel cell (DMFC) by adding carbon layer and Nafion ionomer layer prior to hot pressing at 140 °C.

Among many aspects that has been studied regarding decal technique, a choice of the materials as a decal substrate have been a challenging task to get a complete transfer of catalyst layer onto membrane [4,8,13]. The choice of decal substrate depends on several parameters, such as chemical and mechanical stability, hydrophobicity, adhesive strength with catalyst layers [14] as well as hot press condition. Cho *et al.*, (2009) [4] have chosen Teflon film as decal substrate, while Xie *et al.*, (2004) [8] preferred Kapton film than Teflon film to avoid the problem of ionomer segregation.

In this work, the catalyst layer was transferred onto the membrane by decal method as previously report [4], but at lower temperature. Various substrates such as Teflon cloth, PTFE film, Al foil and OHP transparency sheet were studied by measuring the degree of catalyst transfer in order to find the best substrate for hot pressing at 120 °C for 8 min. SEM and elemental analysis were performed on the residue remained on the substrate to investigate whether it is catalyst particles or carbon powder.

2. Experiment

In all methods, Nafion® 117 membrane (DuPont Inc.) and 5wt.% Nafion ionomer solution (DuPont Inc.) were used. Catalyst Pt/C (20wt.% Platinum on Vulcan XC 72) and Carbon Vulcan XC 72 for carbon layer were purchased from Fuel Cell Earth LLC. All chemicals such as hydrogen peroxide (H₂O₂), sulfuric acid (H₂SO₄), ethanol, and isopropyl alcohol (IPA) were in analytical grade and purchased from Merck. Four substrates were used, such as virgin electrical grade film of Teflon PTFE purchased from Fuel Cell Earth LLC (denoted as PTFE film), commercial grade of woven glass fiber coated with PTFE (denoted as PTFE cloth), commercial grade of aluminium foil (denoted as Al foil), and commercial grade of OHP transparency sheet (denoted as OHP sheet).

The membranes were pre-treated to eliminate any organic or inorganic impurities prior to use in MEA preparation. The treatment process was accomplished by successively soaking the membranes in 3% H₂O₂, deionized water, 0.5M H₂SO₄, and then deionized water again at 70-80 °C for 1 h each step

[15]. Carbon ink was made of carbon Vulcan XC-72 and ethanol, while catalyst ink was prepared by mixing Pt/C, Nafion ionomer solution, and IPA ultrasonically for 60 min. The weight ratio between Pt and Nafion in catalyst ink was set at 65:35.

The detail procedure of the catalyst coated membrane prepared through the decal transfer method is schematically represented in Figure 1. Firstly, a thin carbon layer was applied over each substrate, and this was followed by addition of catalyst layer. An additional layer of Nafion ionomer was then sprayed on the coated catalyst layer. The prepared multi-layer substrates (outer ionomer/catalyst/carbon/substrate) were then hot pressed on both sides of the membrane at 120 °C for 8 min to form CCM. The hot-pressing conditions used for this work have been optimized in our lab. The geometric active area of all the MEAs was 3 cm x 3 cm.

The residue remained on the substrate after decal transfer was examined using SEM-EDS (Hitachi SU 3500) to verify a complete transfer of the catalyst. SEM images obtained by BSE detector was done at 15 kV accelerating voltage. Prior to measurement, the samples were coated using gold sputtering. For evaluating the hydrophobic properties of the substrates, contact angles between water and the substrates were measured using sessile drop method. For each measurement, a water droplet was placed onto the surface of the substrate and images were captured with a digital camera. Furthermore, the contact angles were estimated by measuring the angle between water drop and the substrate regarding to drop shape analysis.

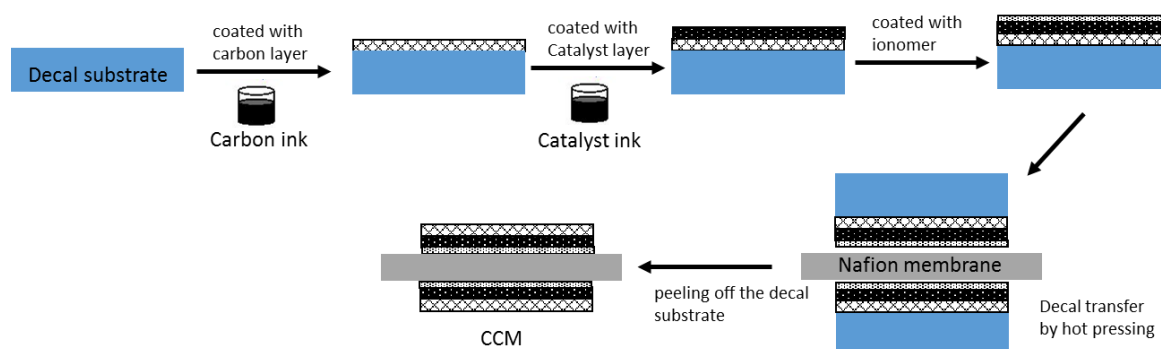


Figure 1. Schematic Diagram of Low-Temperature Decal Method.

3. Results and Discussion

A schematic procedure of low temperature decal transfer is shown in Figure 1. The advantage of this method is significantly lower hot pressing temperature, even if it is compared with previously report by Cho *et al.*, (2009) [4]. By using this low temperature for decal process, H⁺ membrane can be used instead of Na⁺ membrane, which is used for high temperature decal process [16]. Therefore, re-protonation of membrane by boiling MEA in sulfuric acid solution is not necessary, hence it shortened the process. This is another advantage of this method, which is the simplicity in the process scheme.

To facilitate a good transfer of catalyst layer from a decal substrate to a membrane, carbon layer was applied onto the substrates prior to depositing catalyst layer as previously report [4]. The composition of materials in this carbon layer is equated to that used in microporous layer (MPL) deposited on the gas diffusion layer (GDL). Thereby, it is expected that no negative effect on MEA performance.



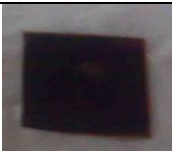

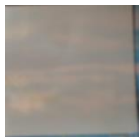


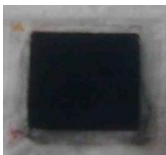








Substrates	After transfer			Decal transfer (Approx. %)
	Anode	Cathode	MEA	
 PTFE cloth				90
 PTFE film				90
 Al foil				70
 OHP sheet				70

Figure 2. Photograph of Decal Substrates before Coating Process and After Catalyst Layers were Transferred to The Membranes with Active Area of 3 cm x 3 cm

Photographs of decal substrates after hot-pressing are given in Figure 2. It is obvious that the transfer degree of the catalyst layer depends on the type of substrate. As shown in figure 2, PTFE cloth and PTFE film have a fairly good transfer, even though the surface of PTFE cloth and PTFE film appears slightly dark after being peeled off from the catalyst layer. A black residue also remained on the surface of OHP sheet and Al foil, but they appear thicker than that of on PTFE cloth and PTFE film. It is assumed that the black residue was carbon layer, and it will be checked by EDS and described in the later session. Furthermore, Al foil shows not suitable as a substrate for hot pressing condition at 120 °C for 8 min. This is probably due to low mechanical stability of Al foil, which is too thin for this hot pressing condition. OHP transparent is also demonstrated to be inadequate as a substrate for this decal transfer method, since it underwent dimensional changes of MEA. This could

be explained that hot pressing temperature of 120°C is above glass transition temperature (T_g) of OHP film, which is made of polyethylene terephthalate (PET) (T_g between 65-80 °C). Above its glass transition temperature, the film becomes soft and changes the dimension due to pressing. Mehmood and Ha [9] also experienced changes in geometric dimension of MEA when using Teflon film as decal substrate after flat-press at 150°C under pressure of 8 MPa for 8 min.

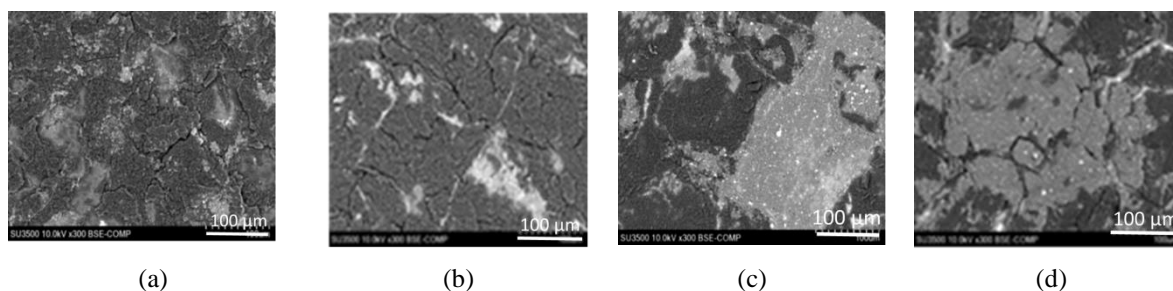


Figure 3. SEM Images of Residual Surface of (a) PTFE cloth, (b) PTFE film, (c) Al foil, and (d) OHP sheet.

Table 1. Elemental Analysis of Residue on the Substrate Surface in Atomic Percentage.

Element	PTFE cloth	PTFE Film	Al foil	OHP Sheet
C	78.34	85.84	87.22	80.49
O	2.57	3.05	3.90	8.48
F	18.78	10.77	8.05	10.47
S	0.26	0.30	0.41	0.32
Pt	0.06	0.04	0.42	0.25

In order to identify the dark material (residue), small pieces were cut from the middle of the substrates that experienced hot-pressing at 120°C and then were subjected to SEM-EDS analysis. Figure 3 presents SEM images of the residue remains on the substrates obtained by BSE detector. BSE is beam electron that is reflected from the samples by elastic scattering. BSE images can provide information about the distribution of different elements in the sample because BSE signal is strongly related to the atomic number (Z) of the specimen. In Figure 3, bright contrast represent the present of Pt particles. Analyzing the residue using EDS (Table 1) reveals that the residues are composed of carbon and fluorine. Only small amount of Pt left on the PTFE cloth and PTFE film. This indicates that catalyst layers are completely transferred for the case of PTFE cloth and PTFE film. On the other hand, the residue on Al foil and OHP sheet contained quite high Pt. This can be explained that the residue was not only carbon layer, but also catalyst layer which is contained 0.45 mg/cm² of Pt. In term of measuring the hydrophobicity of substrates, the sessile drop method was used to measure static contact angles. The sessile drop method requires a flat surface upon which a liquid drop can be placed and those substrates fulfill this requirement. As can be seen in Figure 4, all substrate exhibit

almost the same contact angle with Al foil and OHP sheet were slightly lower than the others. This result indicates that high degree of catalyst transfer onto PTFE cloth and PTFE film was not because those substrates have slightly higher hydrophobicity, but because they have good mechanical stability for press process at 120°C. Mechanical stability of materials at high temperature is closely related to thermal properties especially with glass transition temperature. It should be ensured that hot pressing temperature is below the glass transition temperature of the substrates.

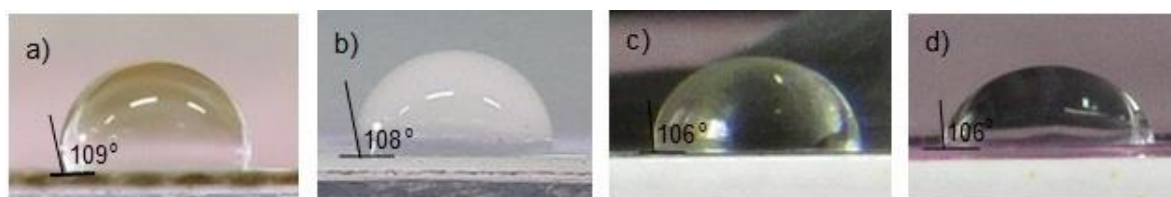


Figure 4. Photograph of a Drop of Aquades on Surface of a) PTFE Cloth, b) PTFE Film, c) Al Foil, and d) OHP Sheet.

4. Conclusion

The MEA prepared by decal transfer method has been developed at low temperature hot pressing of 120 °C. By using this low temperature, this method can provide shorter process because it is not necessary to re-protonation of Nafion membrane since the H⁺ form of Nafion membrane can be directly used instead of using Na⁺ form of membrane as in conventional decal method. Among several types of substrates, PTFE cloth and PTFE film showed the most suitable substrates for this method. OHP sheet was not strong enough to be processed at temperature of 120°C due to low glass transition temperature. Moreover, evaluation on residue left on the substrates proved a complete catalyst transfer to the membrane for PTFE cloth and PTFE film, while there were some Pt catalyst remained on the surface of Al foil and OHP sheet based on elemental analysis. Based on the results, mechanical stability at this hot pressing condition was the main reason for different degree of transfer rather than hydrophobicity of substrates.

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References

- [1]. Towne S *et al* 2007 *J. Power Sources* **171** 575-84.
- [2]. Prasanna M *et al* 2008 *Electrochim. Acta* **53** 5434-41.
- [3]. Sun L *et al* 2008 *Solid State Ionics* **179** 960-5.
- [4]. Cho JH *et al* 2009 *J. Power Sources* **187** 378-86.
- [5]. Lindermeir A *et al* 2004 *J. Power Sources* **129** 180-7.
- [6]. Tang H *et al* 2007 *Electrochim. Acta* **52** 3714-8.
- [7]. Song SQ *et al* 2005 *J. Power Sources* **145** 495-501.
- [8]. Xie J *et al* 2004 *J. Electrochem. Soc.* **151** A1084-93.
- [9]. Mehmood A and Ha HY 2012 *Int. J. Hydrogen Energy* **37** 18463-70.
- [10]. Park HS *et al* 2008 *J. Electrochem. Soc.* **155** B455-60.
- [11]. Wilson MS *et al* 1995 *Electrochim. Acta* **40** 355-63.
- [12]. Song S *et al* 2005 *J. Power Sources* **140** 103-10.
- [13]. Yoon YJ *et al* 2011 *J. Power Sources* **196** 9800-9.
- [14]. Mehmood A and Ha HY 2013 *Int. J. Hydrogen Energy* **38** 12427-37.
- [15]. Scott K *et al* 1999 *J. Power Sources* **79** 43-59.
- [16]. Saha MS *et al* 2010 *Electrochem. Comm.* **12** 410-3.