Original article

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Metal-insert technique for polypropylene composite bipolar plate manufacturing

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Abstract: A single cell of direct methanol fuel cell (DMFC) typically delivers an electrical potential between 0.5 and 1 V; thus DMFCs are assembled in parallel to meet power demands (1–5 kW). Bipolar plates (BPs) are the primary components connecting a single cell to the adjacent cells so that they provide optimum electrical conductivity. The objective of this research is to reduce the volume resistance of BPs made from a polypropylene/carbon composite by utilizing a metal insert technique. A major obstacle when it comes to molding composite plates inserted by a thin metal sheet is the delamination of material layers after the cooling process. The delamination issue is due to different surface polarities between metal and polypropylene-composite surfaces. One of the strategies to solve this issue is to modify the surface of one layer for creating similarity of the surface polarity. A metal sheet surface was coated with graphene using a cold spraying technique to enhance adhesion ability. The suitable spraying conditions were determined by experimenting with varying temperature, pressure, graphene quantity and graphene types. The effectiveness of surface modification by the graphene spraying technique was assessed by a surface morphology observation, an electrical conductivity measurement and DMFC performance tests. Results were interesting, they indicated that when DMFC was assembled with silver sheet, inserted BPs provided 25.13 mW/cm² of power density, 3,350.7 mWh of generated energy and 67% of efficiency. This highlights that the performance of a BP

prototype is superior to the performance of a commercial composite bipolar plate.

Keywords: bipolar plates; cold spray; direct methanol fuel cell; metal insert technique; polypropylene composite.

1 Introduction

To achieve the desired voltage and current, single fuel cells are typically connected in combination (Figure 1A). A direct methanol fuel cell stack with a large number of single cells require bipolar plates (BPs) with manifolds to provide a uniform flow distribution in every single cell [1]. The manifold transfers the reactant gases to the active areas while also gathering the unreacted reactants and products of the redox reactions. In this type of DMFC stack system, electrons must transfer through BPs to complete an electrical circuit. Therefore one critical fuel cell performance factor is the electrical conductivity of the BPs. The better the transfer efficiency of the electricity of the BPs, the fewer plates are required to produce the desired power output. In order to meet their functionality requirements, material selection and BP design related to their features and properties under realistic operating condition should be considered. Common BP materials are metallic alloys, graphite and polymer composites [2]. Most of the polymer composite BPs are carbon–polymer composites that are created by incorporating a carbonaceous material into a polymer binder. Both thermoplastic and thermosetting have been used to fabricate BPs [3]. Among the thermosetting resins, such as phenolics, epoxies, polyester, and vinyl ester, etc., the epoxy resin is a popular choice for carbon–polymer BP production [4]. During the molding process, the thermosetting resin allows for molding of intricate details. Moreover, the resins can be highly cross-linked through a proper curing process, and the cross-linked structure provides good chemical resistance. Thermoplastic, such as polypropylene (PP), polyethylene (PE), poly (vinylidene fluoride) (PVDF), liquid crystalline polymer (LCP), poly (phenylene sulfide) (PPS), and fluoropolymer [5], have been used less in BP fabrication than

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Figure 1: Schematic of electron transport through DMFC stack (A); electron transport on a BP surface (B).

thermosetting resins regarding to chemical resistance and mechanical strength. On the other hand, they can be injection-molded and are therefore more beneficial in automated manufacturing. This process is suitable for a mass production for future markets. However, high filler loadings limit possibilities for the injection molding process because of the higher viscosity of the composite material. The electrically conductive fillers ordinarily are expanded graphite, carbon fibers, carbon black, carbon nanotubes and graphene [6]. The combinations of these carbon fillers are frequently used to gain the synergistic effect on electrical conductivity [7].

The volume resistivity is a measurement of how strongly a material opposes the flow of electric current. The following Eq. (1) is used to calculate BP resistance and conductivity from the average resistivity measurements [8]. In the case of surface resistance [9], the resistance is determined by the ratio of DC voltage drop per unit length to

the surface current per unit width. The surface electrical resistivity measurement as described in Figure 1B.

$$\text{Resistivity} = \frac{V}{I} \times \frac{\text{Contact area (cm}^2\text{)}}{\text{Sample thickness (cm)}} = \Omega \cdot \text{cm} \quad (1)$$

In Eq. (1), V is voltage (V) and I is current (A). To improve the electrical conductivity, both the process of materials selection and forming techniques were investigated. Polymer composite BPs are superior to both graphite and metal BPs in terms of size and weight, allowing for the production of smaller, lighter fuel cells via an uncomplicated process, which are key features for wide market acceptance. The polymer composite BPs can be applied to DMFC at operating conditions ($\text{pH} = 3\text{--}6$) [10] since they are not prone to the corrosion problem. Regardless of that, the electrical conductivity of the polymer composite BPs must be of great concern. Many methodologies, such as sol-gel [11], hot rolling process [12], and material insertion used to enhance the volume conductivity of polymer composites have gained serious attention from researchers. The improvements in the volume conductivity of BPs were emphasized in this paper. The metal insertion technique was addressed in this work for improving the volume conductivity of BPs, since it can be developed to be an over-molding process that is suitable for realistic mass production in industries. The possible types of metals with great potential selected for the over-molding technique may be a graphite sheet, carbon fabric layer, metal sheet and metal grid [13–18]. Regardless of that, the technique and material options heavily depend on the requirement of the volume resistance for a fuel cell application which should be lower than $30.0 \text{ m}\Omega \text{ cm}^2$ (a requirement set by the US department of energy) [13]. The results from previous researches made via materials insertion for enhancing volume conductivity or reducing volume resistance were around 38.0 S/cm of volume conductivity and $21.0 \text{ m}\Omega \text{ cm}^2$ of volume resistance [14]. The thickness of inserted composite BPs is also important because it allows for a faster transfer of electrons to the external circuit [14]. Therefore, the thickness of created bipolar plates in this research work was strictly controlled not to exceed 3.00 mm .

One of the questions being pointed out often is about interface adhesion, and practical solutions, such as chemical surface modification, and plasma or corona treatment, for this issue were also examined [19]. The plasma treatments reduced the volume resistance to $18.0 \text{ m}\Omega \text{ cm}^2$ [19]. The metal insertion was also subjected to experimentation where several types of metals were used to study the prospect of using this method to increase electrical conductivity. Copper [16], thin aluminum foil [17]

and metal mesh [18] are interesting metals that were studied for this technique. The main focus of this work was on using copper and silver sheets to insert in the middle of BP due to their higher electrical conductivity (5.90×10^7 S/cm for copper and 6.30×10^7 S/cm for silver) and lower corrosion [20]. The final goal of this BP development is to create a molded metal insert BP suitable for mass production which can be done via injection molding, compression molding, or thermoforming. It is worth noting that sub-techniques used in all mentioned processes for molding metal insert BP may be either over-molding or in-mold labeling [21, 22]. To achieve an improvement of interface adhesion in this research, graphene spraying technique was utilized, since this technique is best suited for industrial manufacturing, along with that very few information about the usage of this technique in BP production was reported. BPs used for the experimental activities in this work cannot be mass-produced; therefore, metal insert BPs were fabricated via a compression molding process instead of using an over-molding technique via injection molding process. Plain plaques of polypropylene/three-carbon filler composites were injection-molded and two composite plaques were over-molded on a thin copper or silver sheet in a sandwich form utilizing a compression mold (Figure 2). The final product was a metal insert BP with reactant flow channels. Before placing the copper or silver sheet on a composite plate, the metal sheet was treated by graphene spraying on its surface. The selection of graphene for the cold spraying process was determined due to its excellent electrical conductivity (7.00×10^4 S/cm) [23]. In addition to that the cold spraying can be done in a room-temperature environment at ambient pressure. Since graphene consists of solid nanoparticles that cannot flow through the tip of a spray gun, colloidal or suspension form should be prepared. This kind of graphene suspension is an effective way to avoid graphene agglomeration during the spraying process [24] when the conductive network is broken by the insulation gap between the metal sheet and PP composite.

Figure 2 illustrates an electrically conductive path through interfaces of all the components. Graphene layer interacts with fillers (carbon black, carbon fiber and graphite) in polypropylene matrix by Van der Waals force [25]; the graphene layers can act as electron transfer paths across insulating gaps between the metal sheet and polypropylene composite plates. The cold spraying process includes three imperative factors, a droplet velocity on support; droplet dispersion on a support; and solvent evaporation [26]. A surface morphological study using scanning by electron microscope (SEM) was performed to prove the ability of interfacial adhesion. Both volume, as well as surface conductivity were measured to validate a level of success in the metal insert technique in a BP application. The invented BPs were used in real DMFC for testing meaning the DMFC performance in terms of power density, energy production and efficiency.

2 Materials and methods

2.1 Metal sheet surface polishing

Metal sheets used in this research were copper and silver since they possess higher electrical conductivity. The metal sheets were initially polished using metallurgical grinder polisher (Struers Als Denmark, LaboPol-5, No.5200307) at 300 rpm for 5 min to provide a rugged surface for better mechanical adhesion. After this procedure, surfaces of metal sheets were cleaned in an ultrasonic bath (Elma D-78224 Singen/Htw No.690) containing acetone (LabGrade, J.T. Baker) for 10 min. The cleaned sheets were dried in an oven, following that the sheets were weighed. This data along with the initial weights were recorded.

2.2 Graphene types

Three types of graphene nanoplatelets, purchased from XG Science, utilized for these experimental activities: GnP-C-750 (Grade C), GnP-M-5 (Grade M), and GnP-H-100 (Grade H) were used to investigate the effects of graphene thicknesses and areas on surface adhesion performance. Their characteristics as follows: GnP-C-750 possesses black

Figure 2: Perspective of creating polypropylene composite BP.

granule shape, a few of thickness, 1 μm of agglomeration diameter, and 500–700 m^2/g of surface area; GnP-M-5 provides black granule shape, 6–8 nm of thickness, 5 μm of agglomeration diameter, and 120–150 m^2/g of surface area; and GnP-H-100 acquires black granule shape, 15 nm of thickness, 200 μm of agglomeration diameter, and 50–80 m^2/g of surface area.

2.3 Graphene preparation using solvent dispersion

Before spraying graphene nanoplatelets on metal sheets, the graphene nanoplatelets were deagglomerated in a solvent to enhance the dispersibility of graphene particles. Graphite nanoplatelets (0.05 g) were sonicated gently in various organic solvents, acetone (J.T. Baker), ethanol (Merck KGaA), and dimethylformamide (DMF) (Asia Pacific Specialty Chemical Limited) for 3 h. The graphene suspension possessed 2.5%vol of concentration. Suspension behavior of graphene particles and solvent evaporation characteristics was observed. The graphene morphology was observed by the optical microscope (Olympus, No.BH2-UMA) to observe the graphene agglomeration and dispersion.

2.4 Graphene spraying onto metal sheet surfaces

Metal sheets (1.50 $\times$ 8.00 cm of sheet dimension) were heated on a hotplate to expand the metal surface resulting in better adhesion between graphene particles and metal surface. To study the impact of metal surface heating on adhesion capability, metal sheets were heated to a temperature of 120, 140 and 160 $^{\circ}\text{C}$ respectively. Graphene suspension was sprayed onto metal sheet surfaces using an air blush (HKX HB3G, no.HM2200). Spraying pressure (20, 30, and 40 psi) and suspension quantities (2.0, 3.0, and 4.0 ml) were cogitated to find an optimal condition for graphene spraying. The spraying pressure is required to accelerate the velocity of graphene particles in attacking metal surfaces and to allow for a decrease in graphene agglomeration. The suspension quantities used for the spraying procedure affected the thickness of the graphene layer and adhesion ability. Note that GnP-C-750 was applied to survey the proper factors for graphene spraying. The suspension formulas consisted of 5.00 mg of

GnP-C-750 suspended in various ethanol volumes (2.0, 3.0, and 4.0 ml).

2.5 The bipolar plate forming process

Injected composite bipolar plates with a thickness of 3.00 cm were fabricated through an over-molding technique using a compression molding machine (Cometech, G6010-01-024). The composite was made from polypropylene (Equistar® PP35FU01) and a three-carbon filler system consisting of carbon black (CB: VULCAN® XC72 by Cabot Corporation), PAN-based milled carbon fiber (AGM-99) (Asbury Graphite Mills Inc.), and synthetic graphite (Asbury Graphite Mills Inc). The polypropylene composite contained 55%wt of filler loaded with 1:1:1 of a filler ratio. For the over-molding procedure, a metal sheet was placed between two injected composite plates located in a compression mold. The sample-set was preheated at 180 $^{\circ}\text{C}$ for 5 min and then heated at the same temperature under 1,500 psi for 10 min. After the heating stage was completed, under pressure cooling step followed for 10 min.

2.6 Bipolar plate characterizations

Thickness and weight were recorded after the insertion to observe feasibility in using the bipolar plates for DMFC in a single cell. Either surface or volume electrical conductivity was measured using electrometer (Keithley, 6517A). Optical microscope (Olympus; BH2-UMA), stereo microscope (Nikon SMZ800) and scanning electron microscope (EDS, JEOL, JSM 5410 LV) were used to investigate surface and cross-section morphology concerning electrical conductivity values and surface adhesion. A single cell of DMFC was assembled with commercial membrane electrode assembly (MEA), SGL gas diffusion layer made out of woven carbon fiber cloth, and created BPs.

The MEA with 183 μm of membrane thickness used in the single-cell was produced from Nafion 117 coated by 4.0 mg/cm^2 of platinum ruthenium at an anode side, 4.0 mg/cm^2 of platinum black at a cathode side. To operate the DMFC, the test system was constructed, as depicted in Figure 3. Methanol (1 M) was injected into the cell through an anode BP at a flow rate of 5 ml/min, while air zero was fed with 10 ml/min of flow rate to a cathode side. The operating temperature

Figure 3: The schematic of DMFC in-house test station.

varied from 30 to 80 °C to determine the effect of operating temperature on single-cell performance. The performance of the single-cell was validated by monitoring polarization curves.

2.7 Methanol and sulfuric acid absorption test

Methanol and sulfuric acid absorption tests were performed at room temperature on all composite samples to make sure that polypropylene composites can be used in real DMFC circumstances. Polypropylene composite specimens with the dimensions $1.00 \times 3.00 \text{ cm} \times 3.00 \text{ mm}$ were independently immersed in 1 M methanol solution and 1 M sulfuric acid solution. The specimens were transposed from and to the solutions every 24 h, dried and weighted to analyze absorption of the solutions as a function of time. The test had been performed for 1,400 h. Final and initial weights were compared for the explanation of methanol and sulfuric acid uptakes in the composites.

3 Results and discussion

3.1 Graphene cold spraying on the metal surface

A metal insert technique is based on the concept that electrons can easily transfer through the copper sheet to form an electric circuit, thus by improving bipolar plates, electrical conductivity can also be improved. However, this technique will not provide any advantage if there is not a proper interface contact between metal and a polypropylene composite. The surface energies of a copper sheet surface and polypropylene composite surface typically differ; thus, a polypropylene composite cannot perfectly coat a copper sheet, leading to an increase in interfacial contact resistance. Graphene has attracted tremendous attention trying to solve this issue due to its extraordinary surface properties and electrical conductivity. Surface properties of graphene with regards to its surface energy and surface roughness are important when it comes to adhering ability [27]. To obtain the desired effect of the spraying process, the imperative subjects should be discussed as follows.

3.1.1 Metal sheet heating

A metal sheet was heated to initiate heat expansion of the surface, since the expansion increased contact areas. Moreover, the accumulated heat on the metal surface also contributed to solvent evaporation from the surface. The heating temperature had a meaningful influence on the contact areas of a metal sheet. Figure 4 displayed the copper surface change during the heating procedure. Heating copper sheet with a higher temperature than 120 °C damaged

Figure 4: Heated copper surface observation at 120 (A), 140 (B), and 160 (C) of surface temperature.

passive film ordinarily coated on the copper resulting in oxidation reaction on the copper surface. Cuprous oxide was produced at 140 °C of surface temperature, whereas cupric oxide formed at a surface temperature of 160 °C. The oxidation occurrence can be physically observed by a change of surface color since various oxidation numbers of copper ions brought about color differentiation. In the case of a silver sheet, an oxide film on silver surface decomposed when the silver surface is heated in the air above 200 °C [28]. Whereupon, copper or silver sheet was heated until its surface temperature reached 120 °C before spraying.

3.1.2 Remedy for graphene agglomeration

Graphene was dispersed in solvent with the assistance of ultrasonication for 3 h to acquire dispersive uniformity. A suitable solvent for graphene suspension was determined by testing various types of solvent (acetone, ethanol, and dimethylformamide).

Images from an optical microscope observed indicated that the ultrasonication provided a positive effect on graphene dispersion in every case (Figure 5). It is important to note that the images were taken 24 h after the ultrasonication. Graphene particles were deagglomerated and became better distributed compared to a scenario without the ultrasonication. Agglomerated graphene nanoplatelets were progressively fragmented and dispersed by actions of shockwaves and shear force generated from ultrasonic cavitation [29]. By comparing different solvents, it was clear that graphene acquired the best dispersion stability in dimethylformamide, since its solubility parameters, surface tension and dipole moments are about the same as the values of graphene [30, 31].

However, the optical micrographs showed graphene dispersion in dimethylformamide and ethanol had been affected in a similar way. Dispersed graphene in all three solvent systems was prepared for actual spraying via a spray gun to observe the actual spraying ability. Results showed that graphene suspensions using acetone and dimethylformamide as solvents were not able to be ejected from a nozzle of the spray gun because nozzle occlusion by agglomerated graphene existed from the beginning of a spraying process. That is why ethanol was used for the

Figure 5: Monitoring graphene suspension in different solvents: acetone (A, B); ethanol (C, D); and dimethylformamide (E, F).

preparation of graphene suspension. A rational explanation of using graphene was for it to be a tie for a layer that corresponds with hydrophobic film and microscale surface roughness. Sprayed graphene nanoplatelets were able to form hydrophobic corolla-like films with microscale surface roughness on a flat metal surface. The residual oxygen-containing groups on graphene surfaces interacted with polar metal surfaces.

3.1.3 Metal surface polishing

Metal sheets were polished and cleaned before beginning heating and spraying processes. When it comes to the consideration of surface polishing, properly polished metal surface contributes to a better adhesion performance due to mechanical adhesion. The mechanical adhesion occurs when of graphene nanoplatelets penetrate the craggy sites of a polished metal surface. The mechanical interlocking contributes to adhesive bonds between graphene films, containing microscale surface roughness, and surface roughness of the copper surface (Figure 6A and 6B) [32, 33]. The velocity, related to injecting pressure of the graphite suspension moving from a nozzle to a metal surface, is one of the key contributing factors for desired graphene coating [34].

3.1.4 Spraying stage

The graphene solution was fed into a hopper on the top of a spray gun, then the graphene suspension moved downward according to the gravitational force. If injection pressure is applied to the spraying system, the graphene suspension would be sprayed by drag flow [35].

Figure 6: Images of copper sheet surface: cross-section (A) and surface roughness (B) were taken by optical microscope. Images of graphene-coated copper sheets: cross-section of GnP-C-750 coated copper sheet (C); surface of GnP-C-750 coated copper sheet (D); cross-section of GnP-M-5 coated copper sheet (E); surface of GnP-M-5 coated copper sheet (F); cross-section of GnP-H-100 coated copper sheet (G); and surface of GnP-H-100 coated copper sheet (H) were captured by stereo microscope.

If suspension flows close to the nozzle wall, the flow velocity will be lower than in the middle area due to friction force. The applied injection pressure brings about a shear force that can break cohesive force between graphene clusters resulting in better graphene film formation. On the other hand, spraying graphene suspension onto the metal surface under high pressure causes undesirable flow velocity. Due to that, the graphene layer thinning and spreading appearance leads to graphene losses. Thus after careful consideration, an injection pressure of 20 psi was chosen for graphene spraying. A key advantage of applying graphene spraying is an increase in electrical conductivity of BPs; so it is imperative to control graphene quantities. The graphene quantities however, cannot be imposed directly during the spraying stage because it was a graphene solution that was injected, not the actual solid graphene particles. The volumes of graphene suspension were varied during the experiment (2.0, 3.0 and 4.0 ml per one side of a metal sheet) to endorse the desired graphene quantity depending on the electrical conductivity of the coated surface. It is important to note that only one type of graphene (GnP-C-750) was utilized to study the effect of graphene suspension volume used in the spraying stage. Thicknesses of graphene layers on metal surface rose from 0.22 to 0.35 mm with an increase in graphene suspension volumes. An increase in the graphene layer thickness indicated an increase in a number of graphene layers. This, in theory, should increase the electrical conductivity, but experimental results were the opposite of what was expected. When the thickness of graphene layers went up, it lead to a decrease of electrical conductivity on a surface from 6,339 to 1,827 S/cm. This can be explained by the connection with graphene clusters or agglomeration. Graphene nanoplatelets tend to agglomerate and stick to each other, forming microparticles because graphene acquires Van der Waals forces, and π - π stacking between the graphene lamellae [36]. The weak bonding strength between the graphene and metal sheet principally resulted from the low surface activity of graphene, presenting the difficulty for graphene to properly bond with the metal interface. This expression is asserted by the wider standard deviations of higher thicknesses (Figure 7). Nonuniformity of graphene layer thickness and dispersion decreased the effectiveness of conductive electrical network causing a direct effect on electrical conductivity.

3.1.5 Graphene types

Special consideration in the usage of various graphene types is necessary. Different graphene types possess

Figure 7: The relation among surface electrical conductivity of metal sheets with a varying volume of graphene suspension and graphene layer thickness.

different properties when it comes to surface areas, agglomeration diameter and thickness, all of which are crucial for graphene coating performance. Graphene coating results were directly affected by graphene types; GnP-C-750, GnP-M-5, and GnP-H-100 were investigated in this part. Stereo microimages present surface and cross-section characteristics of copper surfaces coated by three types of graphene.

The layer of GnP-C-750 looked uniformly occupied, smooth surface, and with consistent thickness. GnP-M-5 and GnP-H-100 layers presented uneven surfaces with varied thicknesses which were confirmed by a wider range of thickness compared to standard deviations (Figure 6). The results were in accordance with electrical conductivity tendency (Figure 8A). GnP-C-750 coated on a copper sheet provided the highest surface electrical conductivity (5,893.06 S/cm). The uneven surfaces may come from graphene removal affected by weaker interaction between the graphene layer and copper surface. The GnP-C-750 has the highest surface area (750 m²/g), a thin layer, and the smallest agglomeration size (1 μ m). These properties promote the adhesion capability between interfaces.

3.2 The metal insertion technique for fabricating BPs

3.2.1 Success in metal insertion

A metal insert BP comprises of two injected composite plates made from polypropylene/three-carbon filler composite and a GnP-C-750 coated metal sheet located in the middle of BP. The copper and silver sheets are 0.10 and 0.05 mm of thicknesses.

Figure 8: The surface electrical conductivity of metal sheet coated with different types of graphene (A); the electrical conductivity of metal (copper and silver) insert BPs (B).

SEM micrographs illustrate cross-sections of copper insert BPs (Figure 9). A sample preparation which is not adequate may cause incorrect bonding assessment, thus the sample cutting method was carefully concerned. Cross-section cut of metal insert BPs was performed using a laser cutting machine. The edge, which was SEM photographed, was not the cut side, but it was the real edge of molded BP. Poor interfacial interaction between the injected composite plate and copper sheet is shown in Figure 9A. Gaps throughout the interfaces between those surfaces were observed to determine an adhesion efficiency. For finding of the adhesion efficiency along interface between a metallic plate and composite surfaces, a random sampling of 57 grid squares ($68.97 \mu\text{m}^2$ for each square) were designed and calculated via direct visualization. Results indicated that uncoated GnP-C-750 on the copper sheet presented unsatisfied interfacial interaction (gaps between interfaces) with lowest adhesion efficiency (0%), while the coated GnP-C-750 on the copper sheet, uncoated GnP-C-750 on the silver sheet, coated GnP-C-750 on the silver sheet possessed 68, 73, and 88%, respectively. The gaps between interfaces decreased electrical conductivity. The mentioned conductive paths can be explained in the schematic drawing in Figure 2. Gaps may occur from shrinkage or stress relaxation of polypropylene composite plates, especially when there is a weak interfacial attraction between polypropylene composite and metal surfaces.

Figure 9: SEM images show the effect of GnP-C-750 on metal sheet interface feature inside metal insert BP: uncoated GnP-C-750 on the copper sheet (A); coated GnP-C-750 on the copper sheet (B); uncoated GnP-C-750 on the silver sheet (C); coated GnP-C-750 on the silver sheet (D).

The shrinkage phenomenon is related to the microstructure of polypropylene and its crystallization. Polypropylene is cooled in mold below its transition temperature, the polymer chains arrange itself in a more orderly pattern, creating crystallization. Polymer chain orientation makes more significant difference in specific volume between their melt phase and crystalline phase. Most shrinkage occurs in the mold during the cooling stage, but some shrinkage arises after the ejection of the composite plate, as it continues to cool. Afterward, composite plates continue to shrink slightly for several hours or even days until the temperature and moisture content stabilizes. Coating GnP-C-750 onto the copper surface magnificently enhances the interfacial interaction between polypropylene composite and copper surfaces, as indicated in Figure 9B. In the scenario of silver insert BP, what happened at interfaces almost identical to what happened with the copper case, but interfacial adhesion between polypropylene composite and silver surfaces was superior to the adhesion between the polypropylene composite and silver surfaces (Figure 9C and 9D). The significant empirical information of surface adhesion is about the discrepancy of surface energies between two material surfaces. The adhesion force between two surfaces is high if two surfaces occupy similar surface energies and low when there is a large differentiation between those two surfaces. Typically, the surface energies of copper, silver, and polypropylene composite are around 1.83, 1.50, and 0.03 J/m², respectively [37, 38]. It implies that the adhesion between silver/composite plates is stronger than the adhesion between copper/composite plates. This description accords with a result from a literature [39] which stated that adhesion force between silver and acrylonitrile butadiene styrene (ABS) was about 133 nN, while the adhesion force between copper and ABS was 104 nN. Note, surface energy of ABS is 0.042 J/m² [40].

When it comes to the electrical conductivity of both the surface or volume conductivity, obvious concordance to the interfacial characteristics in both cases (copper and silver cases) cannot be seen. Examining the GnP-C-750 coated silver sheet, it can be seen that it made no significant difference in both electrical conductivities compared with the uncoated silver sheet case.

This is mainly because the interfacial adhesion performance of the GnP-C-750 coated or uncoated silver surface is correlated. On the other hand, the BP containing GnP-C-750 coated copper sheet offered a higher volume conductivity (0.44×10^{-7} S/cm) than the original value of BP including uncoated copper sheet (0.29×10^{-7} S/cm) (Figure 8B) due to the improvement of the interfacial interaction. Electrons travel through BP from the front side to the backside (Figure 2). It implies that the volume

conductivity is related to surface electrical conductivity. If no surface treatment was applied, then the surface electrical conductivity does not change, it will show by a slight increase in the volume of electrical conductivity. The unwanted electrical resistance of the surface takes place on the polypropylene-rich layer on the BP surface occurring throughout a BP production.

3.2.2 Fabricated BP performance validation

The DMFC testing facility in the KMUTNB laboratory was established to support developments in bipolar plates through the validation of DMFC operation to assess the performance of a DMFC single cell. The cell was operated at 80 °C since preliminary results showed that operating DMFC at 80 °C provided the highest power density (27.19 mW/cm²). Every DMFC was, therefore, operated at 80 °C during this part of the research. The reason for that being the influence of operating temperature on the kinetic rate of the redox reaction. Furthermore, all DMFCs were run with 5 ml/min of methanol flow rate, and 10 ml/min of air zero flow rate.

Results of DMFC performance diagnoses (Figure 10) stated that the DMFC assembled with silver insert BPs generated 25.13 mW/cm² of maximum power density, 3,350.7 mWh of maximum energy, and 67% of efficiency. The performance of the DMFC assembled with silver insert BPs was superior to the performance of the DMFC assembled with commercial epoxy composite BPs, but it was still inferior compared to the performance of a cell that utilized commercial graphite BPs. Results assure us that a metal insert technique can in fact enhance DMFC performance. A comparison among DMFC assembled with different BPs,

Figure 10: Polarization curve and power density curves of DMFCs assembled using various BPs.

commercial BPs and research-scale BPs, with similar active areas, indicate that silver insert BPs are promising in DMFC application (Figure 10), as it satisfied generated power density requirement. It is a well-known fact that increasing the number of DMFC single cells in a DMFC stack increases generated power density while increasing the surface area of the cells increases the current. A fuel cell stack is made to produce and meet demand in power, voltage, and current for desired applications in cameras (3 W), mobile phones (3 W), and laptop computers (25 W). The simulation results indicated that eight silver inserted BPs in seven cells were needed for operating a camera or mobile phone, while a laptop computer required 63 silver inserted BPs in 62 cells. In comparison to other BPs, nine epoxy composite BPs and 15 PP composite BPs were assembled for 8 and 14 DMFCs to operate a camera or mobile phone. A laptop computer requested 68 DMFCs including 67 epoxy composite BPs or 111 DMFCs consisting of 112 PP composite BPs to be a power supply. Calculations of BP amount requirement for stack making were based on the assumption that the same specification of a DMFC stack was used in all cases, and the DMFC stack operation acquired the same losses. The DMFC stack including silver insert BPs, requires less BP quantity in every application compared to the requirement of other stacks. It can be stated that the created silver insert BPs provide the desired performance and has the potential to be developed for commercial use.

3.3 Methanol and sulfuric acid absorption behaviors

The methanol and sulfuric acid uptakes were investigated, in which absorption of both solutions is gravimetrically determined. The intermittent DMFC operation results in continuous absorption which eventually leads to BP and fuel cell voltage degradations. Results show that composite plates rapidly absorbed methanol and sulfuric acid solutions in the period between 0 and 1,128 h. This is due to the presence of porosity in polypropylene composites. Subsequently, the values of weight change achieved a plateau, at 4% of weight change for methanol absorption and at 5% of weight change for sulfuric acid absorption, implying saturated absorption. When comparing methanol absorption of other BPs from the literature review, the polypropylene composite BPs are promising in the DMFC application. Examples of methanol absorption analyses are presented as follows: a polyvinylidene fluoride BP reached saturated absorption at 2% of weight change and the saturated absorption of an epoxy BP appeared at 4% of weight change [41].

4 Conclusions

The enhancement of volume conductivity of BPs using metal sheet insertion method was investigated, and experimental results show the feasibility of using metal sheet insertion technique for BP modification. Inserting a thin sheet of copper or silver in the middle of a BP by over-molding is conceivable and produced BPs offer desirable performance for the DMFC operation. However, graphene coating via cold spraying technique is required to improve interfacial interaction between composite plates and a metal sheet. To do that, GnP-C-750 graphene is selected for spraying with the optimal condition being 2.0 ml/side of graphene volume, 20 psi of injection pressure, and 120 °C of metal surface temperature. The surface treatment of metal sheet performed before the over-molding to provide a boost to surface adhesion efficiency. The volume conductivity of metal insert BPs with metal sheet coated with graphene provide only slight increase compare to the BP with an uncoated metal sheet. The ambiguous change of the volume of electrical conductivity corresponds to higher surface resistance which comes from polymer rich-layer on the BP surface. The desirable DMFC performance affirms the achievement of using silver insert BPs in fuel cell application. BP surface treatment is recommended to be carried out in parallel with metal sheet insertion to exalt an overall electrical conductivity of BPs.

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