Synthesis of Bipolar Plates for Fuel Cells based on Exfoliated Graphene Nanoplatelets filled Polymeric Nanocomposites

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Abstract

The objective of this research is to investigate the potential of using exfoliated graphene nanoplatelets (GNP) as the conductive filler to construct highly conductive polymeric nanocomposites to substitute for conventional metallic and graphite bipolar plates in the polymer electrolyte membrane (PEM) fuel cells. High density polyethylene (HDPE) was selected as the polymer matrix and solid state ball milling (SSBM) followed by compression molding was applied to fabricate HDPE/GNP nanocomposites. Results showed that HDPE/GNP nanocomposites made by this method exhibited excellent flexural properties and low gas permeability with GNP loadings up to 60wt%, which successfully meet the DOE requirements for bipolar plates. However, it was found that using GNP alone as a single conductive filler was insufficient to achieve the required electrical conductivity (>100 S/cm). Combining GNP with a minor second conductive filler such as carbon black (CB) and carbon nano-tubes (CNT) could substantially enhance the electrical conductivity of the resulting nanocomposites. At the same time, the processing time of SSBM is considered as a crucial parameter in optimizing the various properties of the final nanocomposites. It is believed that the bipolar plates made from HDPE/GNP nanocomposites will allow lighter weight of PEM fuel cells with enhanced performance which is particularly suited for automotive applications.

1. Introduction

Polymer electrolyte membrane (PEM) fuel cell is considered to be one of the most promising power sources for stationary and transportation application in the future due to its high efficiency, high-power density, convenient fuel supply, and long-life time [1, 2]. Fuel cells produce electrical energy by converting the chemical energy stored in certain fuels like hydrogen and methanol through oxidation and reduction reactions. Among all the components in PEM fuel cells, bipolar plates are one of most important parts which account for approximately 80% of the fuel cell volume, 70% of the fuel cell weight and as much as 60% of the entire stack cost [3]. The manifold functions of bipolar plates include connecting and separating the individual fuel cells in series to form a fuel cell stack with required voltage, aiding a uniform fuel gas and oxygen flow in and out (gas channels), conducting current from one cell to another, facilitating water management within the cells, and supporting thin membranes and electrodes from the clamping forces [4]. In this case, bipolar plates must exhibit excellent electrical and thermal conductivity, adequate mechanical strength, good chemical corrosion resistance, and low gas permeability [5, 6]. Moreover, good processability and low manufacturing cost are generally required if bipolar plates are to be widely used in the automotive industry [7, 8].
The conventional materials for producing bipolar plates are metal and graphite. Metallic materials like iron and copper have the attributes of excellent electrical and thermal conductivity, low cost, good mechanical strength and ease to fabricate but their oxidation and chemical corrosion resistance is very low [9]. Additional coatings are therefore needed to prevent the oxidation and corrosion under the fuel cell operation environment [10]. However, due to the different thermal expansion coefficient between the coating layer and the metal plate, micro-pores and micro-cracks are usually created after certain time of fuel operation, which deteriorate the protection from the coating and cause the extra ohmic losses [2]. Bipolar plates made from graphite exhibit high corrosion resistance, excellent electrical and thermal conductivity. But the gas distribution channels are very difficult to be machined on the plates due to the brittleness of graphite. In this case, graphite plates have to be fabricated with a thickness in the order of several millimeters, making the fuel cell stacks to be massive and voluminous [11]. These drawbacks of conventional materials have motivated researchers to develop alternative products for bipolar plates. Polymeric composites filled with conductive fillers have now gained more and more research attention which offer the advantages such as lower cost, higher processability, and lighter in weight when compares to the metallic and graphite bipolar plates [12-14]. Besides, the gas flow channels can be easily molded into the surfaces of the plates without the costly secondary machining step. However, polymeric composites are associated with the problem of balancing the electrical and thermal conductivity with the mechanical strength. Recently, carbon fiber, carbon black, and natural or synthetic graphite have been extensively explored as the conductive fillers to fabricate polymeric composites for bipolar plates. To meet the minimum requirement of electrical conductivity, it is found that excessive conductive fillers (usually > 70wt%) have to be incorporated into the polymeric composites, which substantially reduce their mechanical strength and ductility [15].

Exfoliated graphene nanoplatelets, GNP, is receiving steadily increasing attention as a viable and inexpensive conductive filler in composite materials [16-18]. Research in Dr. Drzal group has shown that GNP possesses excellent mechanical and structural properties, superior electrical and thermal conductivity, and extremely low gas permeability [19-21] due to its extended networks of \( \text{sp}^2 \)-hybridized carbons (i.e., large sheets benzene rings) in the graphitic basal plane. All these excellent properties of GNP make it attainable in many engineering applications such as electromagnetic interference (EMI) shielding devices, rechargeable batteries, electronic devices, light emitting diodes (LEDs), gas sensors, super capacitors and photovoltaic cells [22]. In this case, GNP-based polymeric nanocomposites are considered to have the potential to satisfy the various requirements for bipolar plates while maintaining the GNP content at relatively low levels (\( \leq 60\text{wt\%} \)). To prove this concept, HDPE/GNP nanocomposites made by Solid State Ball Milling (SSBM) and compression molding were developed and evaluated in this report. The reason of selecting solid state ball milling to be the compounding method is because of its capability of achieving high electrical conductivity in GNP nanocomposites as described in a previous study [23]. In the SSBM process, polymer particles are uniformly coated with GNP platelets which facilitate the formation of conductive pathways during the following injection molding or compression molding steps. The electrical and thermal conductivity of the resulting nanocomposites are thus excellent, offering the potential to meet the DOE targets with less GNP content.
2. Experimental

2.1 Materials

In this research, HDPE pellets with the trade name Marlex® HXM 50100 (Density 0.948 g/cm³, Flow index 10.0 g/10 min, MW~ 230,000) were purchased from Chevron Phillips Chemical Company. GNP nanoplatelets with the diameter around 25μm (GNP-25) were obtained from XG Science, Inc [24]. Multi-wall carbon nano-tubes, MWCNT, were obtained from Bayer Material Science Company with the diameter of individual MWCNT being around 15nm and the length between 1 to 10μm. ‘High Structure’ carbon black (CB, KETJENBLACK EC-600 JD), was from Akzo Novel Polymer Chemicals LLC.

2.2 Processing: Solid State Ball Milling (SSBM) and Compression Molding

The starting material for SSBM is a mixture of GNP-25 and HDPE powder (diameter ~ 100μm) which was obtained from the cryogenic milling of as-received HDPE pellets. SSBM process was carried out in a SPEX SamplePrep 8000D Dual Mixer/Mill® system which is shown in the Figure 1. The mixture of GNP-25 and HDPE powder at selected weight ratios (10 wt%, 20 wt%, 30 wt%, 40 wt% and 50 wt% GNP loading) was added into a stainless steel vial where six steel balls (2 large balls: 1/4 inch in diameter and 4 small balls: 1/8 inch in diameter) were used as the milling medium. SSBM time was first kept at 200 minutes and then the SSBM time was adjusted accordingly to optimize the various properties of HDPE/GNP nanocomposites which will be discussed in the following chapter. Based on a previous study, SSBM could produce a HDPE and GNP powder mixture with each HDPE particle uniformly coated with GNP platelets [23]. Then the GNP coated HDPE powder was compression molded at 190°C into flexural coupons for mechanical properties and electrical conductivity test, round disks (thickness: ~1.5mm, diameter: 25mm) for thermal conductivity test, and thin film (thickness: ~300 micros) for oxygen permeability measurement.

![Figure 1 SPEX SamplePrep 8000D Dual Mixer/Mill® system and its steel vial set](image)

2.3 Experimental characterization

A UTS SFM-20 machine (United Calibration Corp.) was used to measure the flexural properties. Flexural coupons were tested under 3-point bending mode at a flexural rate of 0.05 in/min by following the ASTM D790 standard.
Electrical conductivity measurements were done on the composite flexural coupons by a four point method. Thermal diffusivity ($\alpha$, m$^2$/s) of GNP nanocomposites (round disks) was measured by a LFA Nanoflash 447 Light flash system. To calculate the thermal conductivity, the bulk density of the samples ($\rho$, kg/m$^3$) was obtained by dividing the mass over the volume, and the specific heat capacity ($C_p$, J/(kg·K)) was measured through the Dynamic Scanning Calorimetry (DSC Q2000, TA instrument). The thermal conductivity ($\kappa$, W/(m·K)) of GNP samples was then calculated by the following equation: $\kappa = \alpha \times \rho \times C_p$.

The O$_2$ permeability of GNP nanocomposite films was measured based on the ASTM D3985 standard by using a MOCON ® Ox-Tran 2/20 instrument at room temperature. The testing pressure was set as around 0.21 MPa. The thickness of the composite films was kept at 0.3mm.

The dispersion of GNP in HDPE matrix was observed with an environmental scanning electron microscopy (ESEM Carl Zeiss EVO) at an accelerating voltage of 15 kV. The preparation of SEM samples in this study included epoxy mounting, grinding, polishing and etching steps. First, nanocomposite specimens were mounted with epoxy in cylindrical sample holders to maintain a flat surface over the entire grinding and polishing area. After the epoxy was fully cured, samples were carefully ground and polished. O$_2$ plasma etching (25mins, 375W) was then applied at the last step to remove the polymer in top surface allowing the GNP platelets to stand out under SEM observation.

### 3. Results and discussion

The flexural properties of HDPE/GNP-25 nanocomposites fabricated by SSBM and compression molding are presented in the Figure 2. From this figure, it is noted that both the flexural strength and the flexural modulus exhibit a monotonic increase with the increasing GNP content up to 50wt%. At a 20wt% GNP loading, the flexural strength of the nanocomposites is around 28MPa, which has exceeded the DOE target (>25 MPa) for bipolar plates. The highest flexural strength (~ 50 MPa) occurs at the sample incorporated with 50wt% GNP platelets, which is almost twice as much as the DOE target. A decrease in the flexural strength is observed at the sample with 60wt% GNP loading, indicating the insufficient of HDPE to wet all the GNP platelets at this high GNP content. However, the flexural strength remains at a high value of 45 MPa.
The oxygen permeability of these nanocomposite films as a function of GNP loading is shown in the Figure 3. It is seen that from the neat HDPE to the HDPE/GNP-25 sample with 60wt% GNP, the $O_2$ permeability is reduced by almost two orders of magnitude. And it is also found that the thin film made by neat HDPE already exhibits a low gas permeability that could successfully satisfy the DOE target for bipolar plates.

Figure 4 displays the in-plane electrical conductivity of SSBM HDPE/GNP-25 nanocomposites. Unfortunately, it is concluded that the electrical conductivity does not meet the DOE target (>100 S/cm) even at the GNP loading of 60wt%, which implies that using GNP alone as a single conductive filler may not be sufficient to provide enough electrical conductive paths for a desired electrical conductivity.
Figure 4 In-plane electrical conductivity of HDPE/GNP-25 nanocomposites made by SSBM and compression molding

The morphology of HDPE/GNP-25 nanocomposites made by SSBM and compression molding is shown in the Figure 5, which helps to explain why these composites exhibit excellent mechanical and gas barrier properties but unsatisfactory electrical conductivity.

As seen from these ESEM images, the GNP density in the polymer matrix significantly increases with the increasing GNP content. At 60wt% GNP loading, a good coverage of GNP platelets throughout the composite is observed. Increased GNP density greatly contributes to the enhanced mechanical, electrical and gas barrier properties of the resulting GNP nanocomposites. However, there are still numerous micro-pores and micro-gaps between GNP nanoplatelets that are clearly detected in the sample even at 60wt% GNP loading. It is thus believed that the presence of these micro-pores and micro-gaps dramatically inhibits the interconnection between GNP
platelets and reduces the electron transportation pathways within the polymer matrix resulting in a low electrical conductivity.

In order to enhance the electrical conductivity of HDPE/GNP-25 nanocomposites to meet the DOE requirement for bipolar plates, combination of GNP with a second conductive filler of different geometry was considered for a synergistic effect. In this study, MWCNT and CB were applied for this purpose. The hybridized HDPE/GNP nanocomposites with MWCNT or CB were also fabricated by the same SSBM and compression molding process as described in the experimental section. The total filler loading was kept at 60wt% and the weight ratio between GNP and MWCNT or CB was changing from 50:10 to 30:30 wt%. The electrical and mechanical properties of these hybridized nanocomposites are shown in the Figure 6 and Figure 7 respectively.

From the results of the electrical conductivity measurement (Figure 6), it is seen that a sharp increase in electrical conductivity is observed when 10wt% of GNP is substituted with CB. As the CB to GNP ratio further increases, the electrical conductivity goes to a maximum of 48 S/cm at around 40/20 GNP to CB ratio. Significant increased electrical conductivity indicates the positive synergistic effect between GNP platelets and CB particles in enhancing electron transportation throughout the composites. And for the GNP/MWCNT hybridized nanocomposites, an increased electrical conductivity is also detected and the highest electrical conductivity also occurs at 40/20 GNP to CNT weight ratio. However, the enhancement is found to be much lower than the GNP/CB hybridized ones. Based on a previous study, MWCNT tends to agglomerate in HDPE matrix without special surface treatments [25], which may explain the lower improvement in electrical conductivity for GNP/MWCNT hybridized nanocomposites.

And based on the flexural properties of these hybrid nanocomposites displayed in the Figure 7, it is found that combination of GNP platelets with MWCNT lowers the flexural strength and flexural modulus of the resulting nanocomposites while GNP/CB hybridized samples exhibit even higher flexural properties than the control sample (HDPE/GNP-25 60 wt%) if the GNP/CB weight ratio is not lower than 40/20.

Therefore, it is concluded that GNP/CB hybridized nanocomposite offers better enhancement in electrical and mechanical properties. For the composite with 40/20 GNP to CB weight ratio, the electrical conductivity is increased by more than one order of magnitude and the flexural strength and modulus are enhanced by 8% and 4% respectively.
Although the combination of GNP with CB substantially increases the electrical conductivity of the resulting nanocomposites, the best conductivity (~48 S/cm) in GNP/CB hybridized nanocomposites still does not meet the DOE target. In this case, the GNP size effect was taken into consideration. Based on previous research, it is known that smaller size of GNP in the polymer matrix offers better mechanical properties while larger size of GNP leads to higher electrical conductivity [26]. Combination of smaller size of GNP platelets with larger ones was thus investigated to fabricate HDPE/GNP nanocomposites for bipolar plates with the SSBM process. Importantly, the size of GNP platelets can be easily controlled by the SSBM time. Take the composition of HDPE/CB/GNP25(s)/GNP25(l) (40:20:20:20 wt%) for example, GNP25(s) means the smaller size of GNP which is SSBM processed for 200 mins. And the GNP25 (l) represents the larger size of GNP which is SSBM processed only for 30 mins.

The synergistic effect of combining smaller size of GNP platelets with larger ones on the electrical, thermal, and mechanical properties of the resulting nanocomposites is shown in the Figures 8, 9, and 10 respectively. From the Figure 8 and Figure 9, it is concluded that both the electrical conductivity and the thermal conductivity are tremendously increased with the increasing fraction of the larger size GNP-25 (l).
composition of HDPE/CB/GNP-25(s)/GNP-25(l) (40:20:10:30wt%), the in-plane electrical conductivity reaches 132 S/cm and the in-plane thermal conductivity is 11.3 W/mK. Both of them have exceeded the DOE target for bipolar plates. And for the mechanical properties as displayed in the Figure 10, although the flexural strength is reduced as expected when the fraction of larger GNP platelets increases, it remains at around 38MPa which is 53% higher than the DOE requirement for the bipolar plates (25 MPa).

Figure 8 Synergistic effect on electrical conductivity of combining small size of GNP with large ones

Figure 9 Synergistic effect on thermal conductivity of combining small size of GNP with large ones
Conclusions

This study has explored the potential of using HDPE/GNP nanocomposite as a novel polymeric bipolar plate in fuel cells. HDPE/GNP nanocomposites were fabricated by the SSBM and compression molding process and the effectiveness of GNP platelets in enhancing the mechanical properties and lowering the gas permeability of the composites was investigated.

To enhance the electrical conductivity, synergistic effects between GNP and other conductive fillers such as MWCNT and CB was discussed. It was found that the binary blends of GNP with CB resulted in a better enhancement in electrical and mechanical properties of the hybridized nanocomposites. Meanwhile, the combination of smaller size of GNP platelets with larger ones was discovered to be another crucial parameter in determining the various properties of the resulting nanocomposites. These synergistic effects allow the optimization of processing characteristics and mechanical properties for highly electrical and thermal conductive nanocomposites aimed for bipolar plates in automotive applications.

References


24. GNP is an exfoliated graphene nanoplatelet material obtained from XG Sciences, Inc., East Lansing, MI (www.xgsciences.com).