Article

A High Conductive Composite Bipolar Plate with Conductive Network Constructed by Chemical Vapor Deposition

Wenkai Li 1, Haodong Zeng 1, Tao Peng 1, Ziteng Gao 2 and Zhiyong Xie 1,2,*

1 Carbon-Carbon Composite Materials Research Institute, Powder Metallurgy Research Institute, Central South University, Changsha 410017, China; 203306055@csu.edu.cn (W.L.); 193312151@csu.edu.cn (H.Z.); 203312077@csu.edu.cn (T.P.)
2 Guangdong Hydrogen Development New Material Technology Co., Ltd., A1 (Block 2), No. 28, Xingsheng East Road, Hecheng Street, Gaoming District, Foshan 528500, China; gaoziteng1995@outlook.com
* Correspondence: xzy507@csu.edu.cn

Abstract: In this study, a highly conductive composite bipolar plate with an embedded conductive carbon nanofiber network was prepared by chemical vapor deposition, and a conductive network was constructed inside the composite bipolar plate. The latter network was then compared with a conductive network formed by directly adding carbon nanotubes more evenly distributed. The optimum preparation methods of vapor-grown carbon fibers and the fiber content were analyzed, and the specific surface area and porosity of the bipolar plates were measured and analyzed using a BET test. The results show that the carbon nanofibers prepared under the conditions of 700 °C and a content of 2% exhibited the best effect on improving the performance of the bipolar plates. The conductivity of the prepared bipolar plates could reach 255.2 S/cm, which is 22.1% higher than treatment with multi-walled carbon nanotubes. The bending strength of the prepared bipolar plates was 47.92 MPa, and the interface contact resistance was 6.24 mΩ·cm². In conclusion, the bipolar plates modified with vapor-grown carbon fibers were a promising kind of material for proton exchange membrane fuel cells.

Keywords: composite bipolar plates; carbon nanotube; chemical vapor deposition; vapor-grown carbon fibers; proton exchange membrane fuel cell

1. Introduction

The proton exchange membrane fuel cell (PEMFC) is considered to be one of the most prized potential energy conversion devices in the 21st century due to its unique advantages, such as its high rate of energy conversion, pollution-free emissions, and noise-free operation [1–3]; however, owing to the high preparation cost of PEMFCs, its application is limited [4]. Bipolar plates (BPs) are key components of PEMFCs, and they are responsible for energy conduction, material transportation, structural support, etc. [5,6]. BPs also play a vital role in the comprehensive performance of PEMFCs. The quality and manufacturing cost of bipolar plates can account for more than 50% of the mass and more than 30% of the total cost of PEMFC stacks, so the development of BPs with an improved performance can thereby effectively improve the performance of fuel cells [7].

According to the different material classifications, BPs can be divided into graphite BPs, metal BPs, and resin/graphite composite BPs. Graphite BPs have good electrical conductivity, thermal conductivity, and corrosion resistance [8]; however, their mechanical properties are poor, and the graphite BPs with flow channels are costly. In addition, graphite BPs have a low gas transmission rate [9]. Metal BPs have a higher mechanical strength, good air permeability, electrical conductivity, and are easier to process than graphite BPs; however, in order to prevent metal BPs from corroding in the operating environment of a PEMFC, a more expensive surface treatment and modification is required [10,11]. Resin/graphite composite BPs have many advantages such as their light weight, easy
fabricability, corrosion resistance, inexpensiveness, etc., but their electrical conductivity and contact resistance are lower than graphite BPs [12–14]. Recently, the composite BPs have aroused extensive research interest because of their higher corrosion resistance and easier fabricability.

At present, the main processing techniques of composite BPs are compression molding [15], injection molding [16], and extrusion molding [17]. To solve the shortcomings of the insufficient conductivity and inferior bending strength of composite BPs, many methods have been deeply researched to improve their performance. B. Dhungana [18] et al. studied the relationship between the fluidity of the composite BPs’ material and the performance of the BPs during the compression molding process, and optimized the relevant process parameters. Jiang [19] used extrusion molding and compression molding methods to prepare composite BPs with multiple fillers for comparison and added a plasticizer to improve the insufficient fluidity of the conductive fillers and the performance of the BPs. To improve the preparation process, the third type of conductive filler is also an important means to solve the insufficient conductivity of the composite BPs. Carbon nanofibers, carbon nanotubes, conductive carbon black, and graphene [20–22] have been shown to improve compatibility between resins and graphite, increase the internal conductive paths of the composite BPs, and the comprehensive performance of the composite BPs. However, Nanoscale fillers are difficult to disperse during the preparation process of the composite BPs, and the agglomeration is severe, so the improvement effect is often unsatisfactory.

The chemical vapor deposition method allows carbon nanofibers to grow in situ on the surface and pores of graphite. During the process, the uniformity and dispersion of the grown carbon nanofibers can be controlled by controlling the catalyst content and the deposition temperature. Therefore, the in situ preparation of carbon nanofibers by chemical vapor deposition has shown a great potential application for PEMFC in the field of the performance improvement of composite BPs.

Herein, novel composite BPs modified with nanoscale vapor-grown carbon fibers (VGCFs) are reported. The synthesis of the VGCFs was optimized and the amount of the VGCFs was researched. The results show that composite BPs modified with VGCFs had a better conductivity, high flexure strength, low corrosion current, and an outstanding interface contact resistance. Compared with the direct addition of MWCNTs to enhance the conduction and enhancement of bipolar plates, the addition of VGCFs by the CVD method can more effectively improve the electrical conductivity and mechanical properties of composite bipolar plates. At the same time, the VGCFs prepared by CVD can also overcome the difficulty of dispersing nano-fillers such as MWCNTs and can form integral conductive networks inside the composite bipolar plate.

2. Materials and Methods

2.1. Materials

The materials that were used in this work were: expanded graphite (EG, 99.9% purity, Qingdao Runda Chemical Co., Ltd., Qingdao, China), Polyether ether ketone resin (poly-ether-ether-ketone (PEEK), 99.9% purity, Zhejiang Xiangyang Chemical Industry, MW = 200,000, China), and multi-walled carbon nanotubes (MWCNTs, 99.5% pure, length 3–12 µm). Ni(NO₃)₂·6H₂O (aladin Co., Ltd., Shanghai, China).

2.2. The Preparation of VGCFs with CVD

Ni(NO₃)₂·6H₂O was dissolved in alcohol to prepare a solution (0.025 mol/L, 100 mL), the expanded graphite (16 g) was soaked in the prepared solution, and after ultrasonic dispersion, suction filtration and drying were carried out to disperse a small amount of catalyst particles on the surface of the expanded graphite. Subsequently, VGCFs were prepared on the expanded graphite particles in situ in a quartz tube furnace. As shown in the deposition temperature in Supplementary Materials, Ni catalyst-loaded expanded graphite particles were subjected to CVD after catalyst reduction under a hydrogen atmosphere inside a quartz tube furnace, and the distribution of the catalyst after reduction is as shown
in the TEM image of Figure S2. Hydrogen (400 sccm), Argon (2000 sccm), and Acetylene (100 sccm) were fed into the quartz tube furnace. The deposition time was 20 min, and the chemical vapor deposition was carried out at different temperatures (600, 700 and 800 °C).

2.3. The Preparation of Composite BPs with Compression Molding

The difference in the quality of the powder before and after the deposition could be calculated by weighing the amount of deposited VGCFs, and the deposited VGCFs were added to the mixed powder of PEEK and EG according to different mass fractions (0.5~2.5%) as shown in Scheme 1, and the addition amount was adjusted so that the mass fraction ratio satisfied PEEK:(VGCFs + EG) = 4:6. After mixing using a ball mill for 2 h, the powder was hot-pressed and molded. During the compression molding, the mold size used was 10 × 40 × 40 mm³, pressed at 270 °C for 10 min under a pressure of 15 MPa and a piece of PTFE membrane was added to the inside of the mold to absorb the overflowing resin, thereby reducing the resin accumulation on the surface of the bipolar plate.

Scheme 1. Schematic illustration of preparation of VGCF-modified composite BPs.

2.4. Characterization of VGCFs and Prepared Composite BPs

A scanning electron microscope (SEM, JSM–7600F) was used to observe the micro-morphology of the VGCFs and the surface of the BPs. Transmission electron microscope (TEM, JEOL ARM–200) was used to characterize the fiber size of different morphologies and the distribution of fibers on the surface of EG particles. Raman spectroscopy was performed on the surface of EG particles deposited with VGCFs using Oxford MAX20 Raman Spectrometer, and the scanning range was 500–4000 nm. The Rigaku X-ray Diffractometer Miniflex 600 was used to test X-ray diffraction patterns of VGCFs, and the scanning range was 5–90°.

The Instron 3369 Universal Mechanical Tester was used to test the bending strength. The sample was shaped into a long strip with a size of 40 × 10 mm² and measured by the three-point bending method, with a bending moment of 20 mm, and the bending strength was calculated from the maximum bending stress.

The ST2258C four-probe tester (Zhejiang Jingwei Instrument Co., Ltd., Jiaxing, China) was used to test the inplane conductivity of the BPs, as shown in Scheme 2. The sample size was 10 × 40 × 40 mm³, and thickness was 0.6 mm. The conductivity of the composite bipolar plate can be calculated by Equation (1).

\[
\sigma = \frac{1}{\pi d v} \ln \left( \frac{l_{13}}{l_{12}} \frac{l_{24}}{l_{34}} \right),
\]

where \( I \) is the current, \( v \) is the voltage between point 2 and point 3, and \( d \) is the thickness of the BPs.
The schematic diagram is shown in Scheme 2c. The test process is as follows: First place the composite bipolar plate sample to be tested between the upper and lower chambers and fix it; then, vacuumize the lower chamber, and then also vacuumize the whole test device. After reaching the set vacuum, inject the required gas into the upper chamber to maintain the pressure difference of the sample to be tested. Under the action of the gas pressure difference, the gas in the upper chamber will penetrate into the lower chamber in the vacuum state. The gas permeability of the composite bipolar plate was characterized by the pressure test of the gas in the lower chamber.

Scheme 2. Schematic illustration of test method: (a) four-probe tester; (b) ICR tester; (c) self-made gas permeability tester.

JC2000A contact angle tester was used to test the contact angle of the BPs. The surface of sample was cleaned, deionized water droplets were placed on the sample surface and photographed immediately, and then the contact angle of the sample surface was calculated by a droplet shape fitting algorithm.

The interface contact resistance (ICR) measurement adopts the test standards in the DOE standard, and the FT361SB contact resistance tester was used for testing as Scheme 2b shows. By measuring the resistance of copper plates and carbon papers, the contact resistance between them, the resistance of the BPs, and the total resistance after series connection, the contact resistance between bipolar plate and carbon paper can be calculated through the following formula:

\[ R = \frac{VA_s}{I} \]  

\[ R_{\text{total}} = 2R_{\text{GDL}} + 2R_{\text{GDL/Cu}} + 2R_{\text{GDL/ICR}} + R_b \]  

\[ R_{\text{sys}} = 2R_{\text{GDL}} + 2R_{\text{GDL/Cu}} + R_{\text{GDL/GDL}} \]  

\[ R_{\text{GDL/ICR}} = \left( R_{\text{total}} - R_{\text{sys}} - R_b \right) / 2 \]

where \( R \) is the total contact resistance, \( V \) is the voltage drop through the setting, \( I \) is the applied current, and \( A_s \) represents the contact area of the sample. Since \( R_{\text{GDL/GDL}} \) is very small, it can be omitted, and ICR can be obtained by Equations (2)–(5). \( R_{\text{total}} \) is the tested resistance with the BPs and the \( R_{\text{sys}} \) is the tested resistance without BPs. \( R_{\text{GDL/Cu}} \) is the interface resistance between copper plates and carbon papers and \( R_{\text{GDL/ICR}} \) is the ICR.

According to DOE standard, self-made equipment was used to test the hydrogen permeability. The schematic diagram is shown in Scheme 2c. The test process is as follows: First place the composite bipolar plate sample to be tested between the upper and lower chambers and fix it; then, vacuumize the lower chamber, and then also vacuumize the whole test device. After reaching the set vacuum, inject the required gas into the upper chamber to maintain the pressure difference of the sample to be tested. Under the action of the gas pressure difference, the gas in the upper chamber will penetrate into the lower chamber in the vacuum state. The gas permeability of the composite bipolar plate was characterized by the pressure test of the gas in the lower chamber.
The Wavedriver100 electrochemical workstation of PINE was used to perform the Tafel polarization curves of the composite BPs. The specific test method employed: the Tafel curve test on the sample under the conditions of 80 °C, 0.5 M H2SO4, and 2 × 10^{-6} M HF solution; the scanning range was from −0.5 V to 0.9 V; and the scan rate was 0.2 mV/s. The working electrode was a wax-sealed composite BP sample per unit area, the counter electrode was a platinum electrode, and the reference electrode was a calomel electrode.

The Mike ASAP2460 Automatic Specific Surface and Porosity Analyzer BET was used to measure the porosity and pore size distribution of composite bipolar plates. The test was carried out at 100 °C under a nitrogen atmosphere, and the degassing time was 8 h.

The thermogravimetric test was carried out with Hitachi ST7200, in a nitrogen atmosphere, at a heating rate of 20 degrees Celsius per minute, and the temperature range was room temperature. The behavior of MWCNTs was 600 degrees Celsius. The results of the thermogravimetric test will be presented in Figure S3.

3. Results

3.1. Morphology of VGCFs and Expanded Graphite

TEM and SEM were used to further characterize the VGCFs and the expanded graphite morphology to better understand their microscopic morphologies. The results are illustrated in Figures 1–3.

Figure 1. SEM image of expanded graphite: (a) Overall morphology of expanded graphite; (b) Partial magnification of expanded graphite.

Figure 1 shows the morphology of the EG. It is evident that the EG was a loose structure with many defects and cracks on the surface, and the contact between the expanded graphite particles was also very loose.

Figure 2a,e and Figure 3a show that the VGCFs synthesized at 600 °C were sparse on the graphite’s surface where many areas of the particles’ surfaces were exposed, and that the VGCFs prepared at 600 °C didn’t fill the defects on the expanded graphite particles’ surfaces; it is also evident from the TEM image in Figure 3b that their diameters were smaller.

Figure 2b,f show the morphology of the VGCFs at 700 °C, and Figure 3d shows the diameter of the VGCFs. The surface of the expanded graphite particles was discovered to be covered with a thicker layer of carbon nanofibers as depicted in Figure 3c, and the VGCFs on the surface of EG that connected the pores of the expanded graphite to form an electrical conductivity path. It was also discovered that the extended VGCFs grew into the gaps of the particles and filled the graphite gaps, as shown in Figure S4.
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The morphology of the deposition products at 800 °C is shown in Figures 2c,g and Figure 3e. The Figure 2c SEM image shows that many thick and short VGCFs agglomerated and entangled the layered structure on the surface of the expanded graphite particles, with diameters ranging from 70 nm to 100 nm. The VGCFs’ coating layer was uneven, and they curled up to form carbon nanoparticles on the surface, as shown in Figure 2g’s TEM image.

From Figure 3f, it can also be found that the deposition products are not uniform fibrous but coarse lumps.

The behavior of the MWCNTs was similar to that of the VGCFs prepared at 800 °C. As shown in Figures 2d and 3e, they agglomerated into one-by-one particles, which were difficult to disperse. This was because the MWCNTs have a smaller diameter and a higher surface energy, as shown in Figure 3h.

### 3.2. XRD and Raman Spectra of EG Modified with VGCFs

Figure 4a shows the XRD spectra of the VGCFs prepared at different temperatures. It is evident that although the morphologies of the VGCFs prepared at different temperatures are different, their crystal forms are all typical Graphite-2H. The peaks in the spectrum are the diffraction peaks of the (002) crystal plane (2θ = 26.381) and the (004) crystal plane (2θ = 54.542) of graphite.
Figure 3. SEM images of MWCNTs and VGCFs prepared at different temperatures dispersed on the surface of expanded graphite and TEM images of individual fibers: (a,b) − 600 °C VGCFs; (c,d) − 700 °C VGCFs; (e,f) − 800 °C VGCFs; (g,h) − 800 °C MWCNTs.

Figure 4b shows the Raman spectra of the VGCFs. The graphitization degree of the VGCFs prepared at different temperatures can be calculated by area integration of the Raman spectra’s D and G bands and the results is showed in Table 1. The graphitization degree of the VGCFs prepared at 600 °C and 700 °C was higher, while the graphitization degree of the VGCFs prepared at 800 °C was lower.

Table 1. The ratio of the integrated value of the D-band and the integrated value of the G-band of carbon fiber at different deposition temperatures: $I_D/I_G$.

|       | 600 °C | 700 °C | 800 °C |
|-------|--------|--------|--------|
| $I_D/I_G$ | 0.154  | 0.113  | 0.379  |

3.3. The Results of Adding VGCFs on the Performance of Composite BPs

Figure 5a shows the compaction density of the BPs. It is evident that the improvement of the compaction density by the excess MWCNTs and VGCFs prepared at 800 °C was relatively limited. The effect of the VGCFs prepared at 600 °C on the improvement of the compaction density was not as good as that prepared at 700 °C. At 700 °C, the compaction density of the VGCFs with 2% mass content was the highest, reaching 1.706 g/cm³, which is increased by 3.8% compared with 1.642 g/cm³ of unloaded VGCFs and MWCNTs.
Figure 4. (a) XRD spectra of VGCF prepared at different temperature. (b) Raman spectra of VGCF prepared at different temperature.

To further study the effect of the addition of VGCFs and MWCNTs on the porosity of the composite bipolar plate, the adsorption–desorption curve of the composite bipolar plate under a nitrogen atmosphere was tested, as shown in Figure S5, and its pore size distribution and the pore size distribution of the composite bipolar plate were obtained from the curve. The porosity was calculated using the DFT method. The results are shown in Figure 6 and Table 2. It is evident that the addition of the VGCFs effectively reduced the porosity, and the VGCFs prepared at 700 °C reduced the porosity at all pore sizes. The VGCFs prepared at 800 °C and MWCNTs were able to fill larger pore sizes but were powerless for smaller pore sizes.

Table 2. The specific surface area, pore volume, porosity and average pore diameter of BPs with different components.

| Sample                        | BET Surface Area m²/g | Volume of Pores g/cm³ | Porosity % | Average Pore Diameter/nm |
|-------------------------------|------------------------|-----------------------|------------|--------------------------|
| No loading of VGCFs and MWCNTs | 10.5139                | 0.06974               | 4.050      | 23.4636                  |
| 2% MWCNTs                     | 12.1030                | 0.06173               | 3.657      | 22.1203                  |
| 2% VGCF prepared at 800 °C    | 10.9146                | 0.06264               | 3.576      | 22.9578                  |
| 2% VGCF prepared at 700 °C    | 4.0991                 | 0.03446               | 2.003      | 33.6280                  |
To further study the effect of the addition of VGCFs and MWCNTs on the porosity of the composite bipolar plate, the adsorption–desorption curve of the composite bipolar plate under a nitrogen atmosphere was tested, as shown in Figure S5, and its pore size distribution and the pore size distribution of the composite bipolar plate were obtained from the curve. The porosity was calculated using the DFT method. The results are shown in Figure 6 and Table 2. It is evident that the addition of the VGCFs effectively reduced the porosity, and the VGCFs prepared at 700 °C reduced the porosity at all pore sizes. The VGCFs prepared at 800 °C and MWCNTs were able to fill larger pore sizes but powerless for smaller pore sizes.

The effect of adding VGCFs and MWCNTs on the flexural strength of the composite bipolar plate is shown in Figure 5b. The VGCFs prepared at 700 °C have the best enhancement effect on the bending strength. The composite BPs’ flexural strength increased from 34.43 MPa without any MWCNT and VGCF loading to 49.74 MPa, meeting the DOE requirements for 2025 (>45 MPa). As the content of the VGCFs increased over 2%, the flexural strength was reduced.

Figure 5c and Table 3 shows the conductivity test results. It is evident that when VGCFs prepared at 700 °C were added to the composite BPs, the conductivities of the composite BPs were best improved when the content of the VGCFs was 2%, which was
better than the conductivity of the composite BPs without any VGCF loading or with MWCNT loading. The conductivity was increased from 188.72 to 255.25 S/cm.

Table 3. Comprehensive performance comparison of BPs.

| Sample                              | Density g/cm³ | Bending Strength /MPa | Contact Angle° | ICR /mΩ·cm² | Conductivity S/cm |
|-------------------------------------|---------------|-----------------------|----------------|-------------|------------------|
| No loading of VGCFs and MWCNTs      | 1.652         | 34.43                 | 95.52          | 7.56        | 188.72           |
| S1 (2% VGCF prepared at 600 °C)     | 1.699         | 42.13                 | 104.45         | 6.68        | 224.36           |
| S2 (2% VGCF prepared at 700 °C)     | 1.718         | 49.14                 | 106.04         | 6.24        | 255.27           |
| S3 (0.5% VGCF prepared at 800 °C)   | 1.689         | 33.27                 | 82.07          | 7.04        | 193.54           |
| S4 (1% MWCNTs)                      | 1.688         | 36.53                 | 95.53          | 6.59        | 204.43           |
| S5 (2% MWCNTs)                      | 1.643         | 33.56                 | 93.07          | 6.67        | 193.27           |

According to the experimental results, an appropriate content of the VGCFs improved the hydrophobicity of the BPs. The results showed that VGCFs with a content of 2% and a temperature of 700 °C have the best improvement effect with a contact angle of 107.6 degrees, as shown in Figure 5d.

To further investigate the effect of the VGCFs on the surface structure of the composite BPs, the interface contact resistance (ICR) between the composite BPs modified with VGCFs and carbon papers was measured and compared. Figure 5e shows the experimental outcomes. The VGCF modified BPs prepared at 700 °C with a 2% content have the smallest ICR according to the DOE test standard (under 1.5 MPa pressure). It increased by more than 10% when compared to the 7.02 mΩ·cm² of the group without VGCFs, and the VGCFs prepared at 600 °C also has a better improvement effect. Nonetheless, because the material itself has good electrical conductivity, and PEEK resin has a good compatibility with expanded graphite, all the samples’ contact resistances can meet the DOE requirements for 2025 (less than 10 mΩ·cm², 1.5 MPa).

VGCFs and MWCNTs can improve the gas permeability of the composite bipolar plate at lower load, but with the increase of the loading, the VGCFs and MWCNTs prepared at 800 °C increased the gas permeability of the bipolar plate. As Figure 5f shows, the VGCFs prepared at 700 °C improved the gas permeability of the bipolar plate to $1.67 \times 10^{-7}$ cm³ (cm²·s)⁻¹, which can be increased by more than 30% compared with $2.61 \times 10^{-7}$ cm³ (cm²·s)⁻¹ without any load.

A Tafel curve in a simulated fuel cell operating environment is shown in Figure 7. Controlling the deposition temperature and the content of the VGCFs can effectively improve the corrosion resistance of the composite BPs. Without any additives, the maximum corrosion current density of the PEEK/EG composite BPs is 13.242 μA/cm². Its corrosion resistance can be significantly improved by adding VGCFs.

![Figure 7. Tafel curves of PEEK/EG and PEEK/EG/VGCFs Composite Plates.](image-url)
4. Discussions

4.1. Influence and Analysis of Different Temperatures on the Morphology of VGCFs and EG Deposed with VGCFs

According to the theory of chemical vapor deposition, generally speaking, the higher the deposition temperature, the faster the growth rate of the VGCFs. It can also be seen from Figures 2 and 3 that as the temperature increases from 600 to 700 °C, the VGCFs gradually thicken and the network structure gradually becomes dense. However, VGCFs prepared at 800 °C formed an uneven coating layer on the surface of EG. Moreover, there was no overall network structure between the defects. This was caused by the excessively high temperature during the deposition process and the excessively fast nucleation speed. Excessively fast nucleation speeds resulted in the catalyst being completely covered in a very short time, preventing the VGCFs from growing any longer. Furthermore, the surface of the carbon nanofiber coating layer was not flat, and the length was insufficient to fill the pores of the expanded graphite. As a result, it was difficult to improve the BP's electrical conductivity and bending strength. The MWCNTs have a higher tendency to agglomerate due to their smaller diameters and higher surface energy.

From the results of the XRD test, there was no obvious difference in the microscopic crystal structure of the VGCFs synthesized at the three temperatures, all of which were Graphite-2H; at the same time, the diffraction peaks were also close, indicating that there is no obvious difference in the crystal structure of the synthesized VGCFs. The graphitization degree of the VGCFs prepared at 600 °C and 700 °C was higher, while the graphitization degree of the VGCFs prepared at 800 °C was lower. This was because the nucleation was too fast at 800 °C during the deposition process, and the catalyst was fully covered early on by the deposited product; thus, the subsequent deposition reaction was carried out with an insufficient catalyst, and the pyrolytic carbon component in the deposited product increased, resulting in a decrease in the degree of graphitization of the product. The graphitization degree was higher at 700 °C than at 600 °C because the pyrolysis of acetylene gas was more sufficient at 700 °C, so the reaction rate was faster, and the degree of the reaction was higher. The Raman spectroscopy results demonstrated that the VGCFs generated in situ on the expanded graphite improved the material’s graphitization degree, reduced flaws and cracks, and boosted crystallinity, all of which contributed to improving the material’s performance. As for the 2D peak at 2500–3000 cm⁻¹, their peak shape and peak width are often used to indicate the stacking method and number of layers of carbon atoms and there were no significant effects on the performance of the VGCFs and the performance of the bipolar plates; the 2D peaks of the as-prepared VGCFs are typical multi-layer graphite peaks.

4.2. Effects of Deposition Temperature and Loading of VGCFs on the Properties of Composite Bipolar Plates

From the BET test results, shown in Figure 6, it is evident that only the VGCFs prepared at 700 °C filled the small-diameter pores well, although the tested three groups can fill the large-diameter pores. This was because the agglomerated particles formed by the MWCNTs and VGCFs prepared at 800 °C can better fill the macropores in the expanded graphite since the volume of the agglomerated particles themselves was also smaller. The particle size of the significantly agglomerated particles was about 1–2 microns, and such large particles are obviously unable to fill the mesopores and micropores with a diameter of less than 50 nm. Combining the previous SEM Figures 2b and 3c and the Raman spectroscopy and BET test results, it is evident that the VGCFs prepared at 700 degrees can fill the tiny pores and defects of expanded graphite.

The conduction mechanism of polymer composites can be explained by the percolation theory and tunnel theory as Equations (6) and (7) [23] show:

\[
\sigma = \sigma_p (v - v_c)^s
\]

\[
i = AV_n \exp(-B/V)
\]
where $\sigma$ and $\sigma_p$ are the electrical conductivity of the composite material and filler, respectively, $v$ is the volume fraction occupied by the filler, $v_c$ is the critical volume fraction of the filler, $x$ is a parameter related to the system dimension [24], $I$ is the current density, $V$ is the field strength, $A$ is the tunneling frequency, and $n$ and $B$ are the properties of the composite constant, where $n$ is 1~3 [25]. In general, the conductive mechanism of filled polymer composites can be considered to be caused by the tunnel effect. There is no conductive medium between the particles, but when the distance is less than 10 nm, the strong electric field between the particles can induce a new electric field, and then a current is formed [26]. For the composite bipolar plates, the distance between the conductive particles was reduced, so the conductivity was improved. The reduction in the distance between the conductive particles can be attributed to the following two reasons: On the one hand, the VGCFs filled the defects and voids inside the graphite particles, decreasing the porosity. On the other hand, the VGCFs created conductive paths between the graphite particles, as shown in Figure 8a,b. However, with the increase of content, the conductivity of the composite bipolar plate decreased. This was due to too many of the carbon nanofibers being ineffectively wetted by the resin [27], and because the agglomeration effect increased the porosity within the BPs, resulting in a low electrical conductivity. As seen in the SEM image of Figure 8c, the excessively added VGCFs may not be effectively wetted by the resin particles, resulting in accumulation and agglomeration at the interface. It is also evident that the MWCNTs agglomerated on the surface of EG, as shown in Figure 8e.

To further study the effect of the VGCFs on the conductive paths between particles, we performed an EDS mapping analysis using PI/PEEK for their similar performance and properties in BPs. Since PI contains nitrogen, the resin and graphite particles can be well distinguished in EDX mapping, and the results are shown in Figure 9a–d. It is evident from the Figure that under the same C content, the distribution of carbon elements added to the VGCFs was more dispersed, and many places without N elements also contained a large amount of C elements, which indicated that the VGCFs formed a uniform conductive network among the particles.

As previously demonstrated by the BET test, due to the agglomeration and increased porosity, the improvement in the compaction density was relatively limited. Although the tendency of the VGCFs to agglomerate at the interface was weaker than the MWCNTs, the experimental results show that excess VGCFs still agglomerated to form carbon nanoparticles at the interface, resulting in a decrease in the compaction density, as is shown in Figure 5a.

However, as the content of the VGCFs increased, agglomeration and entanglement at the interface occurred, which also resulted in a reduction in the flexural strength, as shown in Figure 5b. The improvement effect of the VGCFs prepared at 600 °C was slightly lower than that of the VGCFs prepared at 700 °C, owing to the finer diameter of the nanofibers and thinner covering layer. The VGCFs prepared at 800 °C that did not effectively fill the pores and interfaces of EG and the reduction of porosity was limited, so the effect of improving the bending strength was poor.

The contact angle is an important indicator of the BPs’ hydrophobicity. According to the experimental results, an appropriate content of the VGCFs improved the hydrophobicity of the BPs. The mechanism for the addition of the VGCFs to enhance the hydrophobicity of the composite BPs is, on the one hand, the VGCFs filled the defects in the graphite particles, improving the surface structure, increasing the density of the BPs, and decreasing water permeability; on the other hand, the VGCFs on the surface of the graphite particles built fluffy carbon nanowires on this surface, as shown in Figure 8d, which increased the water adsorption on the surface of the composite BPs, thereby improving its hydrophobicity [28].
Figure 8. (a) VGCFs form conductive paths between particles; (b) VGCFs forming a network structure on the surface of graphite; (c) agglomeration of excessively added VGCFs at the interface; (d) VGCFs form a fluffy shape on the surface of expanded graphite particles; (e) Agglomeration of MWCNTs in composite bipolar plates; (f) schematic diagram of VGCFs forming structure inside BP.

This is due to the very complex multiple nano- and micro-scale ultrastructures on the surface of the bipolar plate, which after water droplets much larger than this structure land on the surface of the bipolar plate, separated by a very thin layer of air, only make contact with the “mountain” bumps on the surface.

However, as shown in Figure 9e,f, the excessive content of the VGCFs destroyed the resin enrichment layer on the surface of the composite BPs and formed pores and cracks, resulting in a decrease in its hydrophobicity.

The results of the experiments show that the loading of the VGCFs significantly improved the interface contact resistance of the BPs. This is primarily because the VGCFs formed a conductive path along the thickness of the BPs and destroyed the resin-rich layer on the surface of the composite BPs, as shown in Figures 8f and 9f. The surface of the BPs with the added VGCFs was not as complete as the surface of the BPs without added VGCFs, and there were only a few cracks. Many VGCFs were dispersed inside the cracks, and a small amount of the VGCF particles were also dispersed on the surface. This might be because during the compression molding process a small amount of the VGCFs flowed to the surface of the bipolar plate with the resin, and the VGCFs had a high aspect ratio and a poor compatibility with the resin, causing many pores and cracks in the resin enrichment layer. This results in few conductive paths and holes on the surface of the resin-rich bipolar plate. As shown in Figure 5e, the ICR was reduced effectively.
Figure 9. (a,b) 40% PI BPs EDX mapping; (c,d) 40%PI/2% VGCFs BPs EDX mapping; (e) Bipolar plate surface morphology (no VGCFs added); (f) Bipolar plate surface morphology (with 2.5% content of VGCFs added).

For the VGCFs prepared at 600 °C and 700 °C, the gas permeability of the composite BPs was effectively reduced due to their ability to fill the pores of the bipolar plate and the defects of graphite. However, for a higher content of MWCNTs, due to their agglomeration, the gas permeability of the composite BPs was reduced. For the VGCFs prepared at 800 °C, due to their uneven layered structure, the porosity between the particles was increased, which has an adverse effect on the gas permeability.

By appropriately adding VGCFs, the corrosion current density can be reduced to 0.826 µA/cm², which can meet the DOE requirements for 2025 (<1 µA/cm²), and the corrosion potential can also be improved, compared with that without any loadings, from −0.014 V to 0.107 V. This is primarily because the addition of the VGCFs resulted in fewer defects and pores on the surface of the composite BPs, a more complete structure, and fewer actual areas in contact with the corrosive liquid, lowering the corrosion rate. Moreover, VGCFs covered the surface of the particles, they protected the covered particles, and reduced the corrosion current density to some extent.

5. Conclusions

Using a chemical vapor deposition method, vapor-grown carbon fibers were introduced into PEEK/EG composite BPs in this paper. The in situ growth of the vapor-phase chemical deposition method was used to create a carbon nanofiber network with a uniform dispersion and less agglomeration in the BPs. Compared with the traditional method of
adding MWCNTs to improve the performance of composite bipolar plates, adding VGCFs using the CVD method can effectively avoid the agglomeration, further improve the performance of BPs, and lower the production cost. The results show that the conductivity of the prepared composite BPs can reach 255.2 S/cm and a bending strength of 47.92 Mpa, a contact resistance 6.24 mΩ·cm², a maximum corrosion current density of 0.826 µA/cm², and a gas permeability of $1.67 \times 10^{-7}$ cm³/(cm²·s), and all the tested performances can meet 2025’s DOE requirements.

**Supplementary Materials:** The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/en15144979/s1, Figure S1. Pretreatment of CVD experiments. Figure S2. Distribution of catalyst on graphite matrix (TEM). Figure S3. TG of composite bipolar plates. Figure S4. Carbon nanofibers connect graphite particles. Figure S5. Nitrogen adsorption and desorption curves: (a) No VGCFs Content; (b) 2% 800 ºC prepared VGCFs; (c) 2% 800 ºC prepared VGCFs; (d) 2% MWCNTs.

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The data presented in this study are available on request from the corresponding author.

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**References**

1. Xiong, K.; Wu, W.; Wang, S.; Zhang, L. A global integral terminal sliding mode control based on a novel reaching law for a proton exchange membrane fuel cell system. Appl. Energy 2021, 301, 117473.
2. Jeong, K.I.; Oh, J.; Song, S.A.; Lee, D.; Kim, S.S. A review of composite bipolar plates in proton exchange membrane fuel cells: Electrical properties and gas permeability. Compos. Struct. 2021, 262, 113617. [CrossRef]
3. Kendall, M. Fuel cell development for New Energy Vehicles (NEVs) and clean air in China. Prog. Nat. Sci. Mater. Int. 2018, 28, 113–120. [CrossRef]
4. Kumar, N.; Shaik, G.P.; Pandurangan, S.; Khalkho, B.; Neelakantan, L.; Chetty, R. Corrosion characteristics and fuel cell performance of a cost-effective high Mn–Low Ni austenitic stainless steel as an alternative to SS 316L bipolar plate. Int. J. Hydrogen Energy 2020, 45, 11092–11473. [CrossRef] [PubMed]
5. Xu, Z.; Li, Z.; Zhang, R.; Jiang, T.; Peng, L.F. Fabrication of micro channels for titanium PEMFC bipolar plates by multistage forming process. Int. J. Hydrogen Energy 2020, 46, 11909–11203. [CrossRef]
6. André, J.; Claude, E.; Sirac, D.; Gastaldin, D.; Rossinot, E. PEMFC Flow-field Design, Channel/land Width Ratio Optimization. Fuel Cells 2020, 20, 231–235. [CrossRef]
7. Kakati, B.K.; Mohan, V. Development of low cost advanced bipolar plates for proton exchange membrane fuel cells. Fuel Cells 2010, 8, 45–51. [CrossRef]
8. Wodarczyk, R. Corrosion analysis of graphite sinter as bipolar plates in the low-temperature PEM fuel cell simulated environments. J. Solid State Electrochem. 2021, 1–9. [CrossRef]
9. Hu, B.; Chang, F.L.; Xiang, L.Y.; He, G.J.; Cao, X.W.; Yin, X.C. High performance polyvinylidene fluoride/graphite/multi-walled carbon nanotubes composite bipolar plate for PEMFC with segregated conductive networks. Int. J. Hydrogen Energy 2021, 46, 25666–25676. [CrossRef]
10. Neto, D.M.; Oliveira, M.C.; Alves, J.L.; Menezes, L.F. Numerical study on the formability of metallic bipolar plates for proton exchange membrane (PEM) fuel cells. Metals 2019, 9, 810. [CrossRef]
11. Jia, Q.; Mu, Z.; Zhang, X.; Zhang, B.; Liu, R.; Gao, K.; Yu, Y.; Lai, Z.; Zhang, J. Electronic conductive and corrosion mechanisms of dual nanostructure CuCr-doped hydrogenated carbon films for SS316L bipolar plates. Mater. Today Chem. 2021, 21, 100521. [CrossRef]
12. Wu, S.D.; Chiou, A.H. The study on a new method of preparing PMMA forming composite bipolar plate. Sci. Rep. 2021, 11, 8753. [CrossRef] [PubMed]
13. Daniel, S.; Gheorghe, O.C. Influence of the Surface Microstructure of Conductive Polymer Composite Bipolar Plate on the Fuel Cell Performance. Macromol. Symp. 2021, 396, 2000324. [CrossRef]
14. Jiang, F.; Liao, W.; Ayukawa, T.; Yoon, S.H.; Nakabayashi, K.; Miyawaki, J. Enhanced performance and durability of composite bipolar plate with surface modification of cactus-like carbon nanofibers. J. Power Sources 2021, 482, 228903. [CrossRef]
15. Akhtar, M.N.; Sulong, A.B.; Umer, A.B.; Yousaf, A.B.; Khan, M.A. Multi-Component MWCNT/NG/EP-based Bipolar Plates with Enhanced Mechanical and Electrical Characteristics Fabricated by Compression Moulding. Ceram. Int. 2018, 44, 11457–11464. [CrossRef]
16. Scott, P.E.; Calay, R.K. Experimental investigation of a novel design of proton exchange membrane fuel cell stack. Heat Transf. Eng. 2013, 34, 925–937. [CrossRef]
17. Radzuan, N.M.; Sulong, A.B.; Somalu, M.R.; Abdullah, A.T.; Husaini, T.; Rosli, R.E.; Majlan, E.H.; Rosli, M.I. Fibre orientation effect on polypropylene/milled carbon fiber composites in the presence of carbon nanotubes or graphene as a secondary filler: Application on PEM fuel cell bipolar plate. Int. J. Hydrogen Energy 2019, 44, 30618–30626. [CrossRef]
18. Dhungana, B.; Son, Y. Fluidity, Physical Properties and Electrical Conductivity of PC/Graphite Interlaced Compound Composite for a Bipolar Plate in the Polymer Electrolyte Membrane Fuel Cell. Polym. Korea 2019, 43, 188–195. [CrossRef]
19. Jang, W.I.; Lee, J.W.; Baek, Y.M.; Park, O.O. Development of a PP/carbon/CNT composite electrode for the zinc/bromine redox flow battery. Macromol. Res. 2016, 24, 276–281. [CrossRef]
20. Hua, Y.Z.; Xiao, D.Y.; Xiao, J.L.; Wang, T. Preparation of CF Reinforced PPS/Graphite Conductive Composite for Bipolar Plate. Adv. Mater. Res. 2014, 2949, 1425–1429.
21. Anas, A.; Yutaro, U.; Yoshiyuki, S. Nylon 6/CB polymeric conductive plastic bipolar plates for PEM fuel cells. J. Nanomater. 2015, 101, 3415–3421. [CrossRef]
22. Ramírez-Herrera, C.A.; Tellez-Cruz, M.M.; Pérez-González, J.; Solorza-Feria, O.; Flores-Vela, A.; Cabañas-Moreno, J.G. Enhanced mechanical properties and corrosion behavior of polypropylene/multi-walled carbon nanotubes/carbon nanofibers nanocomposites for application in bipolar plates of proton exchange membrane fuel cells. Int. J. Hydrogen Energy 2021, 46, 26110–26125. [CrossRef]
23. Kirkpatrick, S. Percolation and Conduction. Rev. Mod. Phys. 1973, 45, 574–588. [CrossRef]
24. Bauhofer, W.; Kovacs, J.Z. A review and analysis of electrical percolation in carbon nanotube polymer composites. Compos. Sci. Technol. 2009, 69, 1486–1498. [CrossRef]
25. Shklovskii, B.I.; Efros, A.L. Electronic Properties of Doped Semiconductors; Springer: Berlin/Heidelberg, Germany, 1984.
26. van Beek, L.K.H.; van Pul, B.I.C.F. Internal field emission in carbon black-loaded natural rubber vulcanizates. J. Appl. Polym. Sci. 1963, 6, 651–655. [CrossRef]
27. Zakaria, M.Y.; Sulong, A.B.; Sahari, J.; Suherman, H. Effect of the addition of milled carbon fiber as a secondary filler on the electrical conductivity of graphite/epoxy composites for electrical conductive material. Compos. Part B 2015, 83, 75–80. [CrossRef]
28. Zhao, X.; Meng, G.; Wang, P.; Pan, Q.; Chen, B.; Zhang, H. Copper-assisted growth of high-purity carbon nanofiber networks with controllably tunable wettabilities. J. Mater. Chem. A 2021, 9, 22039–22047. [CrossRef]