

Study on the electrical and mechanical properties of polyvinylidene fluoroide/titanium silicon carbide composite bipolar plates

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Abstract

A new composite bipolar plate was fabricated by compression molding technique using polyvinylidene fluoride (PVDF) as binder and titanium silicon carbide (Ti_3SiC_2) as conductive filler. The effects of Ti_3SiC_2 content, the particle size of Ti_3SiC_2 , the mould pressure and mould pressing time on the electrical conductivity and the flexural strength of the conductive composite are discussed. The electrical conductivity and flexural strength of the composite bipolar plate with 80 wt.% Ti_3SiC_2 content, prepared with a mould pressure of 10 MPa for 10 min, was 28.83 S cm^{-1} and 24.92 MPa, respectively, and can be improved by optimizing the Ti_3SiC_2 content and Ti_3SiC_2 particle size. The electrical conductivity of the composite can also be improved by improving the mould pressure and prolonging the mould pressing time.
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1. Introduction

The polymer electrolyte membrane fuel cell is a very promising power source for residential and mobile applications [1]. Until recently, the wide commercialization of the technology has not been made possible mainly due to high cost of the fuel cell system. One of the most expensive components in PEMFC, the bipolar plates, which electrically connect successive cells in a fuel cell stack, require high surface and bulk electric conductivity, sufficient mechanical strength, chemical stability in the PEMFC environment, gas tightness, and light weight in addition to low manufacturing cost [2]. The most commonly used bipolar plate material is graphite, which has excellent electrical conductivity and corrosion resistance, but the difficulty in machining and its brittleness adds considerable costs and causes the fuel-cell stack to be heavy and voluminous. They can represent as much as 60% of the stack cost, and nearly 80% of weight of the fuel cell stack. Metal is also a good material for bipolar plate, but it is unable to resist corrosion in fuel cells

[3–5]. Therefore, for wide commercialization of PEMFC, investigation on developing low manufacturing cost new materials is urgent.

Polymer matrix composite, which has the advantages of low cost, lightweight, and easier manufacturing over the other materials [6], is a less expensive and lighter-weight alternative to graphite and metal. Currently, carbon composite bipolar plate has been developed extensively, however, little research has been conducted to fabricate metal compound composite bipolar plate. LaConti report fabrication of titanium carbide bipolar plate by compression molding technique in the US Patent 6,083,641, the plate exhibits good electrical conductivity as well as long-term mechanical and thermodynamic stability in the fuel cell environment [7]. Except for the titanium carbide bipolar plate, there is little information available in literature about fabrication of metal compound composite bipolar plate.

Ti_3SiC_2 , a ternary-layered metallic carbide that combines the merit of metals and ceramics, has electrical conductivity greater than many pure metals, excellent corrosion and oxidation resistance, moderate strength [8]. In this paper, we aim to fabricate metal compound composite bipolar plate for PEMFC using Ti_3SiC_2 as conductive filler and PVDF as binder, main factors affecting the electrical and mechanical properties of bipolar plate are investigated.

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2. Experimental

2.1. Materials

PVDF, with density of 1.78 g cm^{-3} , was purchased from the San Ai Fu Co. of Shanghai, PR China. The conductive filler, Ti_3SiC_2 was self-prepared by pressureless sintering the mixture of elemental Ti, Si, C powders with a stoichiometric molar ratio of 3:1:2 on 1400°C for 2 h under argon atmosphere, the crystal phase component of the sintered powders was shown in Fig. 8.

2.2. Composite preparation

Various sizes of Ti_3SiC_2 particle was prepared by screen mesh method, the mixture of PVDF and Ti_3SiC_2 powder was first dry-mixed evenly in a mechanical mixer for 24 h, and then spread in a metal picture-frame mold. The mold was placed on flat plate sulfuration bed and heated to 200°C . A pressure of 5–30 MPa was applied and held for 5–90 min to fabricate the composite. After the mold was cooled naturally in the air, the sample was pulled off from the mold.

2.3. Measurements of performance

The electrical resistivity of the samples was measured at room temperature using four-point probe detector. The average resistivity of each sample was obtained from ten repeated measurements at different locations on the sample. The resistivity (ρ) was calculated as: $\rho = 2\pi SV / (2 - 1.414)I$ and the conductivity (σ) was calculated as: $\sigma = 1/\rho$, where S , V and I are distance between two probes (2 mm), the numerical reading voltage (mV) and the applied current (100 mA), respectively.

The flextural strength of composite samples was investigated using an Instron 5548 micro tester. The width and thickness of the sample were 6 and 4 mm, respectively. The supporting span was 25 mm and the rate of displacement was 0.5 mm min^{-1} .

The section morphology of composite samples was analyzed by a JSM-5610LV type scanning electron microscope (SEM). The crystal phase component of pressureless sintering Ti_3SiC_2 powder was investigated using a rotating anode X-ray diffractometer.

3. Results and discussion

3.1. The effect of Ti_3SiC_2 content on the electrical conductivity of the composite

The samples with different Ti_3SiC_2 content were prepared by compression molding the mixture under pressure of 10 MPa for 10 min, and their bulk conductivities were measured (Fig. 1). It can be seen from Fig. 1 that the bulk conductivity increase linearly from 21.42 to 63.3 S cm^{-1} with increasing Ti_3SiC_2 content from 60 to 90 wt.%. With Ti_3SiC_2 content in the range of 60–90 wt.%, the bulk conductivities of the composite were all over 10 S cm^{-1} , which can meet the lowest electrical requirement for PEMFC bipolar plates [9]. However, the bulk conductivities of the composite were much lower than that of PocoTM

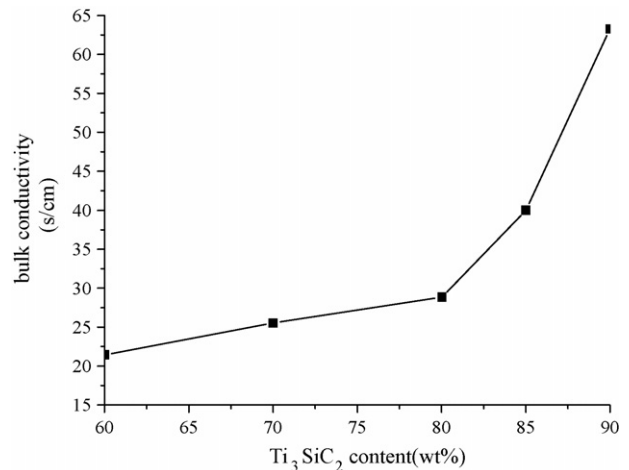


Fig. 1. Bulk conductivity of composite with different Ti_3SiC_2 content.

graphite (680 S cm^{-1}) and needed to be further improved in future experiment.

The electrical mechanism of the composite materials involves mutual contact of the conductive filler particles in the materials resulting in the formation of electrical channels [10], when Ti_3SiC_2 content increased, the current carrier concentration increased and the scattering process of grain boundary weakened, hence the bulk conductivity increased.

The sectional morphology of a composite containing 80 wt.% Ti_3SiC_2 was investigated by SEM (Fig. 2). It can be seen from Fig. 2 that the fiber-like PVDF spread uniformly between Ti_3SiC_2 particles and bind each other to prevent Ti_3SiC_2 particles from contacting each other, which is unfavorable for the improvement of electrical conductivity.

3.2. The effect of Ti_3SiC_2 content on the flexural strength of the composite

The composites were prepared with a mould pressure of 10 MPa and mould pressing time of 10 min, and the effect of

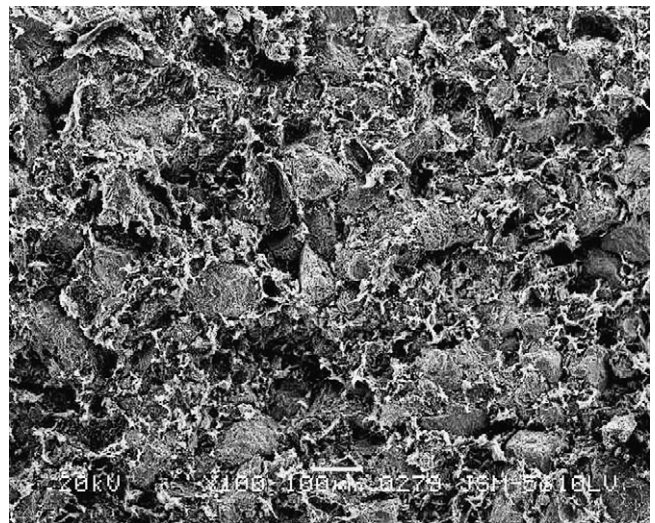


Fig. 2. SEM photograph of PVDF/ Ti_3SiC_2 composite.

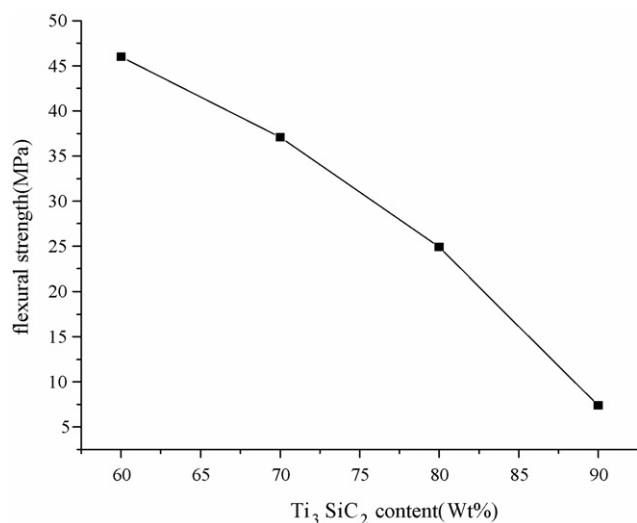


Fig. 3. Effect of Ti₃SiC₂ content on flexural strength.

Ti₃SiC₂ content on the flexural strength of the composite was investigated (Fig. 3). It can be seen from Fig. 3 that the flexural strength of the composite decreases with increase in Ti₃SiC₂ content. On one hand, as Ti₃SiC₂ content increased, the adhesion between PVDF and Ti₃SiC₂ become weaker. On the other hand, increasing Ti₃SiC₂ content increased the number of voids, these all make the flexural strength decrease. The flexural strength was 24.92 MPa when Ti₃SiC₂ content was 80 wt.%, while the flexural strength of Poco™ graphite bipolar plate can attain 45 MPa. However, this conductive plate should not broke under normal cell assembling and operating conditions of PEMFC.

3.3. The effect of Ti₃SiC₂ particle size on the conductivity of the composite

For Ti₃SiC₂ 80 wt.% and a mould pressure of 10 MPa for 10 min, the effect of Ti₃SiC₂ particle size on the conductivity of the composite was investigated (Fig. 4). It can be seen from Fig. 4 that when the content of the Ti₃SiC₂ particle is certain,

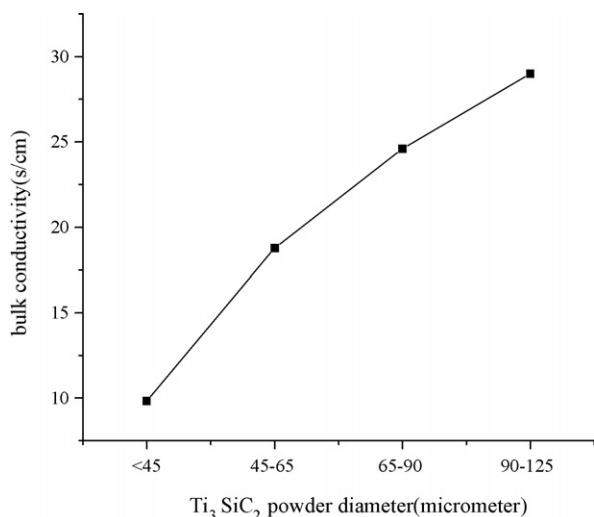


Fig. 4. Bulk conductivity of composite with different Ti₃SiC₂ particle size.

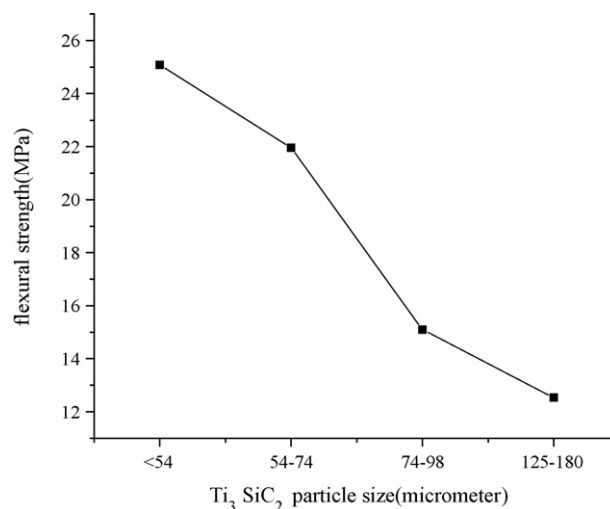


Fig. 5. Effect of Ti₃SiC₂ particle size on flexural strength.

the larger the particle diameter is, the higher the conductivity is. This is because for composites containing a large quantity of conductive fillers, the contact resistance between conductive fillers greatly influences the conductivity of composite. As Ti₃SiC₂ particle size increased, the quantity of Ti₃SiC₂ particles decreased, whereas the contact area between Ti₃SiC₂ particles increased, thus making the contact resistance decreased and the conductivity increased.

3.4. The effect of Ti₃SiC₂ particle size on the flexural strength of the composite

For a content of Ti₃SiC₂ of 80 wt.%, prepared with a mould pressure of 10 MPa and mould pressing time of 10 min, the effect of Ti₃SiC₂ particle size on the flexural strength of the composite was investigated (Fig. 5). It can be seen from Fig. 5 that the flexural strength of the composite decreases with increase in Ti₃SiC₂ particle size. On one hand, small size Ti₃SiC₂ particle possesses more surface area than longer Ti₃SiC₂ particle, hence it has a stronger absorbing ability than longer Ti₃SiC₂ powder, the adhesion between PVDF and Ti₃SiC₂ become stronger. On the other hand, the number of voids increases with increasing Ti₃SiC₂ particle size. Consequently, the flexural strength of the composite decreases with increase in Ti₃SiC₂ particle size.

3.5. The effect of mould pressure on the conductivity of the composite

When Ti₃SiC₂ content was 80 wt.% and mould pressing time was 10 min, the effect of mould pressure on the conductivity of the composite was investigated. The experimental result was shown in Fig. 6, under the pressure of 5–30 MPa, the conductivity increased linearly with increase in mould pressure. On one hand, with the increase of pressure, the adhesion between PVDF and Ti₃SiC₂ was intensified, thus the quantity of the pores in the composite decreased; On the other hand, the contact resistance between Ti₃SiC₂ particles also decreased. Therefore, the conductivity increased as the pressure increased.

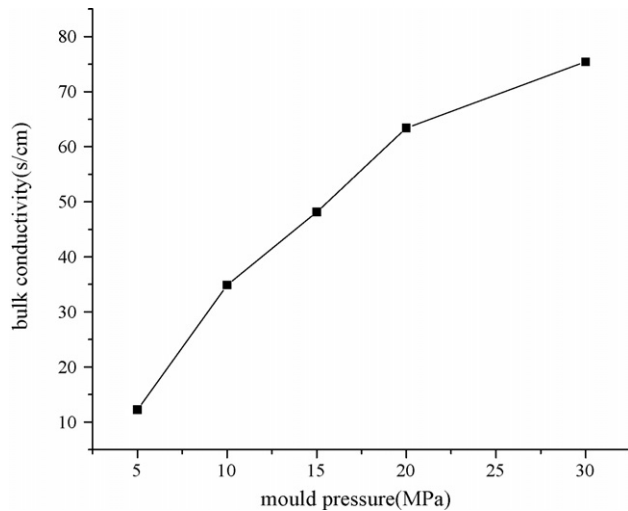


Fig. 6. Effect of mould pressure on conductivity.

3.6. The effect of mould pressing time on the conductivity of the composite

For Ti_3SiC_2 80 wt.% and mould pressure of 10 MPa, the effect of mould pressing time on the conductivity of the composite was investigated. The experimental result was shown in Fig. 7, during a mould pressing time of 5–90 min, the conductivity increased linearly with increase in mould pressing time. On one hand, when prolonging the mould pressing time under a certain pressure, the quantity of the pores in the composite will decrease and the compactness of composite improved; On the other hand, it was favorable for the direct contact of Ti_3SiC_2 particles, thus make the conductivity of the composite increase.

It also can be seen from Figs. 6 and 7 that for the composite with a 80 wt.% Ti_3SiC_2 content under the preparation conditions of mould pressure of 10 MPa and mould pressing time of 10 min, increasing the mould pressure increases the conductivity of the composite more than prolonging the mould pressing time. The conductivity of the composite can increase 116% by increasing

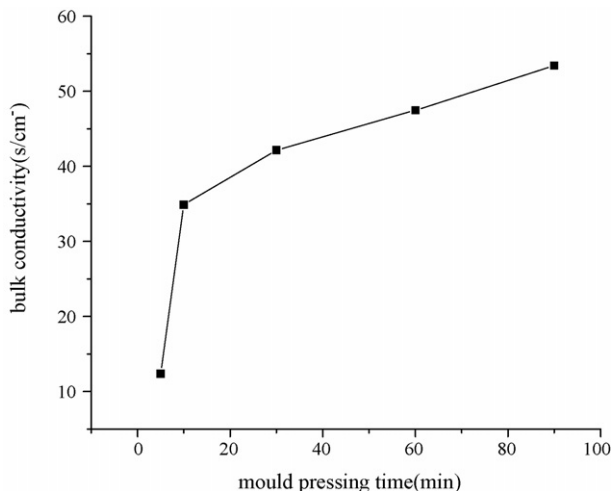


Fig. 7. Effect of mould pressing time on conductivity.

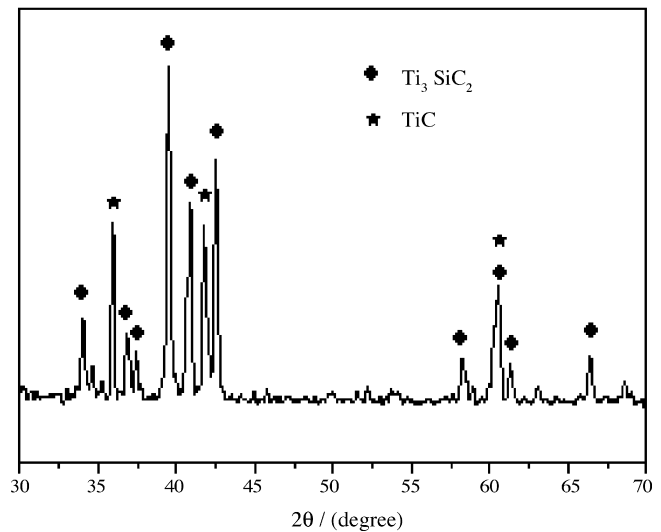


Fig. 8. The XRD pattern of the pressureless sintering Ti_3SiC_2 powder.

the mould pressure and an increase of 53% was obtained by prolonging the mould pressing time.

3.7. The XRD analysis of Ti_3SiC_2 powder

Fig. 8 was the XRD pattern of the pressureless sintering Ti_3SiC_2 powder, mainly two phases (Ti_3SiC_2 and TiC) are found in the sample, other phases almost do not exist. The weight percentages of Ti_3SiC_2 and TiC were calculated according to the equations: $W_{\text{TSC}} = 1.80 / (1.80 + I_{\text{TC}} / I_{\text{TSC}})$, $W_{\text{TC}} = (I_{\text{TC}} / I_{\text{TSC}}) / (1.80 + I_{\text{TC}} / I_{\text{TSC}})$ where W_{TSC} , W_{TC} are weight percentages of Ti_3SiC_2 and TiC phases, $I_{\text{TC}} / I_{\text{TSC}}$ is the integrated diffraction intensity ratio of TiC to Ti_3SiC_2 main peaks [11]. Consequently, the weight percentages of Ti_3SiC_2 and TiC were calculated to be 76.6 and 23.4%, respectively. As the literature shows, the conductivity of high purity Ti_3SiC_2 is $4.3 \times 10^4 \text{ S cm}^{-1}$, the specific conductivity of TiC is $1.90 \times 10^4 \text{ S cm}^{-1}$ which is in the same order of magnitude with the conductivity of Ti_3SiC_2 [12,13]. Therefore, a small quantity of TiC shows little effect on the conductivity of the composite, and the effect of TiC on the other properties of the composite need to be further studied in future experiment.

4. Conclusion

With PVDF as the adhesive and Ti_3SiC_2 as the conductive filler, PVDF/ Ti_3SiC_2 composite bipolar plates were prepared by compression molding technique. The conductivity and flexural strength of the composite bipolar plates with 80 wt.% Ti_3SiC_2 , prepared by a mould pressure of 10 MPa for 10 min, were 28.83 S cm^{-1} and 24.92 MPa respectively, which can meet the requirements of PEMFC bipolar plates with regard to electrical and physical properties. As a result, the PVDF/ Ti_3SiC_2 composite bipolar plates appear to be a good candidate for PEMFC bipolar plates. The electrical conductivity and flexural strength of this composite bipolar plate can be all improved by optimizing

the Ti_3SiC_2 content, Ti_3SiC_2 particle size and the compression molding conditions, especially the mould pressure.

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