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Developing high performance magnesium phosphate cement composite bipolar plates for fuel cells

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Abstract

In this work, we report a comprehensive study on developing high performance magnesium phosphate cement (MPC) composite bipolar plates for fuel cells. The MPC composite bipolar plates composed of MPC with partial replacement of fly ash as the binding matrix phase and multiple carbon-based materials (including graphite, carbon fiber and multi-walled carbon nanotubes) as the conductive phase. A simple hot-press process was applied to produce the MPC composite. After the optimization on the formula and the structure of the MPC composite and the processing parameters, all the US DOE 2015 technical targets, including electrical conductivity, flexural strength, corrosion resistance were achieved as well as low cost. Finally, the performance of the as-prepared MPC composite bipolar plates was investigated via a three-single-cell stack of passive-type direct methanol fuel cells. The performance test results indicated that the MPC composite bipolar plates were capable of fuel cell applications.

Keywords: magnesium phosphate cement (MPC); bipolar plates (BPs); fuel cells (FCs); direct methanol fuel cells (DMFCs)

1. Introduction

Fuel cells, especially proton exchange membrane fuel cells (PEMFCs), are one of the most promising alternative power generation technologies owing to the merits of high cleanliness and high efficiency. Usually, to implement a

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scalable power supply at a stationary level (>10 kW) requires at least hundreds or thousands of single cells assembled in series or parallel as fuel cell stacks. Bipolar plates (BPs), as one of the key components to compose these fuel cell stacks, account for nearly 80 % of the cell volume and around 50 % of the stack cost [1~3].

Up to now, the typical materials to compose BPs include metals/metal alloys, polymeric composites, and graphite [4]. Though the metals/metal alloys based BPs present excellent electrical and thermal conductivity, mechanical properties as well as low fabrication cost, they are quite easily corroded in the acidic environment of fuel cell anode [5]. As for the polymeric composite based BPs, the main drawback is poor electrical conductivity [6]. Graphite is a promising material to fabricate BPs with ultrahigh electrical conductivity, light weight, and relatively low cost, except for its brittleness. So far, many studies have been conducted to resolve the brittle problem of graphite based BPs. For instance, the researchers in Wuhan University of Technology developed an aluminate cement-graphite composite BP with high-strength and highly conductive properties [7]. However, the structure of aluminate cement becomes unstable in acidic environment (<4 pH), accompanied by the dissolution of metallic ions (such as Ca^{2+}, Al^{3+}, etc.), which will contaminate the membrane electrodes of PEMFCs. Nowadays, researchers financially supported by US department of energy (DOE) are yet struggling to achieve the US DOE 2015 technical and cost targets of the BPs. The main targets of US DOE 2015 include the electrical conductivity (>100 S/cm), the flexural strength (>25 MPa), the corrosion resistance (<1 μA/cm^2), and the cost (<5 $/kW) [8].

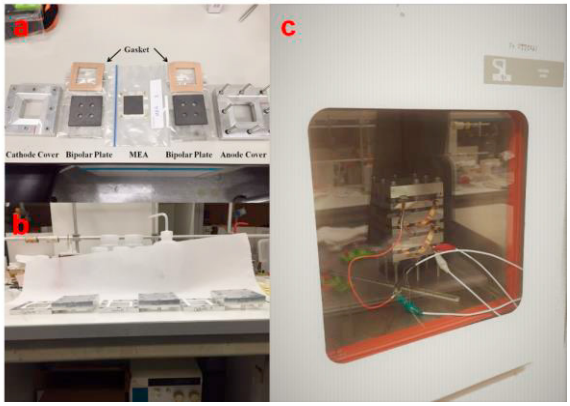

Fig. 1 the pictures of fuel cell stack: a) the disassembled single cell unit; b) the stack covers; c) the three-single-cell stack during the performance test

Magnesium phosphate cement (MPC) is a kind of low-pH cement, which can keep stable under acidic environment [9, 10]. When using MPC as the binder and carbon materials (graphite powder, carbon fiber, CNTs, etc.) as fillers, it is possible to produce high performance BP that fulfills all technical targets of US DOE 2015 and simultaneously achieves low cost [11, 12]. In this work, we report a comprehensive study on developing high performance magnesium phosphate cement (MPC) composite BPs for fuel cells. The MPC bipolar plates composed of MPC with partial replacement of fly ash as the binding matrix phase and multiple carbon-based materials as the electrical conductive phase. A simple hot-press process was applied to produce the MPC composite. After optimization on the formula and the structure of the MPC composite and the processing procedures, all the US DOE 2015 technical and cost targets were achieved simultaneously. Finally, a performance test of passive-type direct methanol fuel cells (DMFCs) was employed to investigate the as-prepared MPC composite BPs. The performance results indicated that MPC composite BPs were capable of fuel cell applications.

2. Experimental

2.1. Fabrication of MPC composite

The method to fabricate the MPC composite has been illustrated in our previous work [8]. In a typical process, the dead burnt magnesia, KDP powder and certain amounts of FA and carbon fillers were dry mixed at room temperature (RT). The M/P ratio was fixed to be 8.0. The volume replacements of 0-50 % in the solid phases with

FA and/or graphite were investigated and the volume replacements of 0-8 % CF and 0-4 % MW-CNTs in addition to graphite were applied. After dry mixing of the solids, deionized water was added to initiate the hydration reaction. The water/cement ratio was fixed to be 0.25. The wet cement paste was stirred vigorously at RT for 30 min. The acquired paste was put in the die mold, and pre-pressed under 2 ton loads in the hot-press machine at 60 ^{o}C for 10 min. Then, the load was increased to 30 ton (72 MPa) and the paste was hot-pressed at 100 ^{o}C for another 20 min. After that, the load was reduced to 2 ton again and the machine temperature was decreased to RT through air cooler. Finally, the MPC composite was obtained after releasing from the mold.

2.2. Characterization of MPC composite

The characterization of MPC composite include microstructure analysis and measurements of electrical conductivity, flexural strength, and corrosion resistance. The micro-morphology of the MPC composite was investigated via JEOL 6390 (JEOL Ltd., Japan) and the elemental distributions of the MPC composite were also explored via EDAX. The electrical resistivity was measured using a four-point conductivity probe (SX1944, Shanghai Yanhua Ltd., China). The electrical conductivity was the reciprocal of the electrical resistivity. To measure the flexural strength, a three-point bending test was conducted following the procedure prescribed by ASTM C78/C78 M-10 (MTS 858 Universal Testing Machine, MTS, MN, USA). For each formula, three specimens with width of 50 mm and thickness of 3 mm were measured using a span of 80 mm and a stroke control at a loading rate of 0.1 mm/min. Two linear variable differential transformers (LVDTs) were set up on each side of the specimen to measure the midpoint deflection. The corrosion resistance of the MPC composite was determined by measuring the Tafel plots via an electrochemical working station equipped with a current amplifier (CHI 660E&680, Shanghai CHI, China). The typical three-electrode system was employed during the measurements, in which a MPC composite specimen as the working electrode, a standard Ag/AgCl electrode as the reference electrode, and a platinum sheet as the counter electrode.

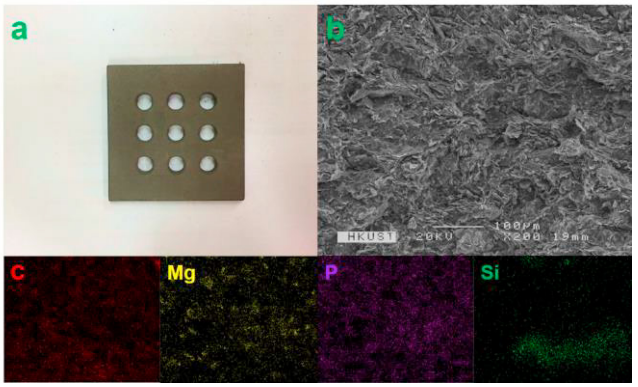

Fig. 2 the picture of the MPC composite BP and SEM image of the MPC composite BP with EXAD mapping images

2.3. Fuel cell stack assembly

After the optimization on the formula and the structure of the MPC composite and the processing procedures, the final formula of the MPC composite was [M/P=8, W/C=0.25, G 40 %, CF 1 %, MW-CNTs 2 %, FA replacement 40 %]. Then, a three-single-cell stack of passive-type DMFCs was assembled to test the performance of the MPC composite BPs. As shown in Fig. 1, the single cell unit composed of two covers, two four-hole MPC composite BPs, two gaskets and a membrane electrode assembly (MEA). The anode cover was sealed on one side by a polymethyl methacrylate (PMMA) plate to form the fuel container, while the cathode cover was opened on both sides. The methanol fuel can be directly injected into the fuel container through the fuel inlet which was drilled across the anode cover. The stack was manually assembled in series by tightening the coupling bolts located at the cover edges. Copper foil was used as the current collector and the interconnectors between each two single cells. The active area of the stack was ~3.14 cm^2 equal to the total area of four-hole on the BPs.

2.4. Performance test

The performance tests of stack were conducted in a passive mode at ambient pressure through an electrochemical working station equipped with a current amplifier (CHI 660E & 680, Shanghai CHI, China). For each test, the whole stack was horizontally set in an oven at 80 ºC. Then, 2.0 ml 5.0 M methanol aqueous solution was injected in each single-cell's fuel container and the static air was used as the oxidant agent. Two-electrode method was applied to investigate the performance, including the open circuit potential (OCP), the polarization curve (PC), and the electrical impedance spectroscopy (EIS). The working electrode and the counter electrode was connected to the anode and the cathode of the stack, respectively. The voltage range was 3.0 V to -3.0 V for the OCP and PC measurements. In EIS measurement, an alternative current impedance (ACI) method was used with a voltage bias of 5.0 mV and the measured frequency range was 100.0 kHz to 1.0 Hz.

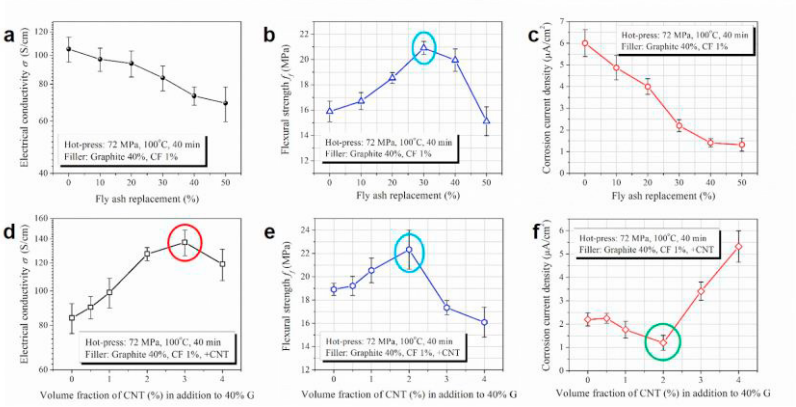

Fig. 3 The influence of fly ash replacement: a) electrical conductivity; b) flexural strength; c) corrosion current density and carbon nanotubes: d) electrical conductivity; e) flexural strength; f) corrosion current density

3. Results and discussions

3.1. Characterization of MPC composite

The SEM and EDAX elemental distribution images of the optimized MPC based composite (formula is [M/P=8, W/C=0.25, G 40 %, CF 1 %, MW-CNTs 2 %, FA replacement 40 %]) are shown in Fig. 2. A dense morphology of the MPC based composite was observed, which might provide low gas permeability through the material. It could be seen in the figure that the binder matrix phase-the MPC hydration product was well formed to connect all the components. And the size of such products were about 50 μm. This was confirmed by the EDAX mapping images. It could been seen magnesium and phosphorous (represent MPC phase) were well distributed in the composite. So was carbon, which indicated carbon-based materials, such as graphite, CF and MW-CNTs were also well distributed among the composite. While FA particles seemed aggregated according to the silicon distribution in the EDAX mapping image. The micro-morphology investigation indicated that the carbon-based materials as the conductive phase were well connected and percolated through the MPC binder matrix phase continuously, suggesting the formation of the electrical conductive network. Meanwhile, the dense morphology ensured the low gas permeability through the MPC composite.

The optimal amount of graphite in the MPC composite was determined to be 40 % in volume fraction, which had been discussed elsewhere [8]. At this point, the electrical conductivity and flexural strength could be well balanced with the assistance of the FA replacement. Then, it was found that the volume fraction of fly ash replacement and the amount of MW-CNTs in addition to the graphite were the two key factors that affected the properties of the MPC composite. Fig. 3 shows the influence of these two factors on the properties of the MPC composite. It could be examined in the figure that both the electrical conductivity and the corrosion current density of the MPC composite decreased along the increment of the FA replacement, which indicated the corrosion resistance displayed an

opposite trend since it was the reciprocal of the corrosion current. As for the flexural strength, the addition of the FA replacement up to 30 % could improve the flexural strength of the MPC composite. However, this improvement was limited when the amount of the FA replacement was higher than 30 %. This could be due to the aggregation problem of the FA. As shown in Fig. 1, even at the optimized formula, the aggregation of FA particles already appeared. Thus, more amount of the FA replacement (higher than 30 %) would aggravate this aggregation and suppress the hydration reaction among the MPC binder matrix phase, which resulted in the decrease of the flexural strength [13, 14].

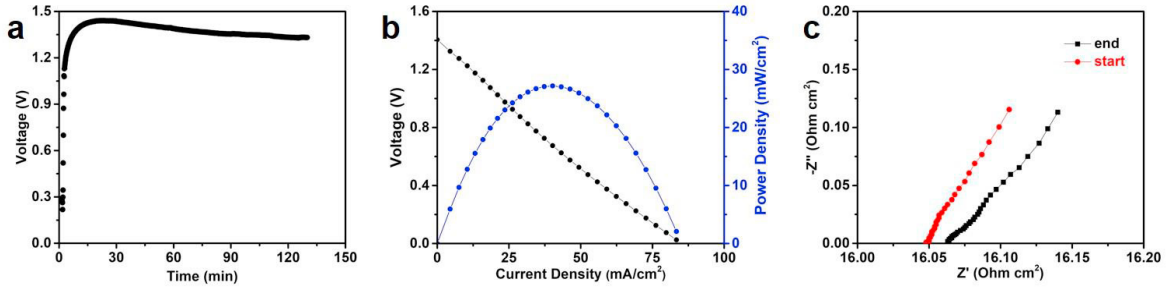

Fig. 4 the electrochemical characterization results of the stack equipped with the MPC composite BPs: a) open circuit potential; b) current density-stack voltage-power density plot; c) electrical impedance spectroscopy

At the beginning of this work, CF, as a kind of large aspect ratio material was selected in the formula to bridge the graphite particles for a well-connected conductive phase as well as to bundle the MPC hydration products for a strength binder matrix phase. Then, it was found that MW-CNTs were more suitable to improve the targeted properties of the MPC composite and there were collaborative promotion between the two carbon-based materials. As shown in Fig. 3d-f, all the figures showed a turning point on the plot, at a MW-CNTs volume fraction of around 2 % (3 % for electrical conductivity plot). Before the turning point, all the properties increased following the increasing CNT volume fractions, while beyond that the increasing MW-CNTs dosages showed a negative effect on those properties. The negative effect of MW-CNTs at relatively higher amounts could be attributed to the following proposed mechanisms. Similar to carbon fiber, CNT is also a kind of large aspect ratio material which can act as bridges between graphite particles. Like FA, when the volume fraction is relatively high, MW-CNTs would be tend to agglomerate, which suppressed their effective dispersion. This conglomeration of MW-CNTs could even disturb the effectiveness binding between the conductive phase and binder matrix phase, and lead to loose material structure, which is unfavorable to the three targeted properties (electrical conductivity, flexural strength, and corrosion resistance) of the MPC composite. In such a case, the incorporation of MW-CNT would break the interconnections between conductive phase and binder matrix phase rather than bridging them.

3.2. Performance analysis of the fuel cell stack

BPs made of the optimized formula of the MPC composite were tested in a three-single-cell stack of passive-type DMFCs. The results of the electrochemical characterization were plotted in Fig. 4. It could be seen in Fig. 4a that the OCP of the stack quickly reached the peak value of 1.42 V at the beginning of the test, then voltage value slowly creeped down and finally became stable at around 1.36 V. The average OCP of a single-cell was ~0.45 V, which was consistent with the literature reports [15]. The peak power density of the stack was 27.15 mW/cm^2 at the current density of 40.22 mA/cm^2, which was quite high among the passive-type DMFCs [16]. The EIS of the stack were measured at the beginning and the end of the test as shown in Fig. 4c. It was found that the impedance slightly increased after the performance test. This increase was mainly attributed to the increase of the resistance of the stack as the imaginary part of the impedance seemed unchanged and such slight increase could be neglected. The electrochemical characterization of the stack indicated the MPC composite BPs were capable of applications in DMFCs.

4. Conclusions

A comprehensive study on developing high performance magnesium phosphate cement (MPC) composite bipolar plates of fuel cells was reported in this work. A simple hot-press process was applied to produce the MPC composite. The MPC composite composed of MPC with partial replacement of fly ash as the binding matrix phase and multiple carbon-based materials (including graphite, carbon fiber and multi-walled carbon nanotubes) as the conductive phase. The optimized formula was [M/P=8, W/C=0.25, G 40 %, CF 1 %, MW-CNTs 2 %, FA replacement 40 %]. All the US DOE 2015 technical targets, including electrical conductivity, flexural strength, and corrosion resistance were achieved by this MPC composite BPs as well as low cost. Then, a three-single-cell stack of passive-type direct methanol fuel cells was tested to examine the performance of the MPC composite bipolar plates. In conclusion, the MPC composite bipolar plates were capable of fuel cell applications.

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