

Manganese oxide arrays on carbon fiber paper and its application for PEMFC

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Abstract. C-MnO₂ was synthesized by direct hydrothermal decomposition of KMnO₄. The structure and morphology of C-MnO₂ was characterized by XRD and SEM, electrochemical performances were investigated by cyclic voltammetry. The effects of hydrothermal temperatures, and time were systematically investigated. The XRD pattern can be identified as a α -types space group, and it matches well with Bragg reflection of the standard α -MnO₂, suggesting that a targeted α -MnO₂ has been successfully synthesized. The results show that pure phase MnO₂ nanorods can be obtained in 160 °C. C-MnO₂ composites show a larger current response and C-MnO₂ composite material has improved the efficiency of the large current charge and discharge.

1. Introduction

The proton exchange membrane fuel cell (PEMFC) is a type of generator that converts chemical energy directly into electrical energy by using a sulfonate proton exchange membrane as a solid electrolyte. PEMFCs are considered promising sustainable energy technologies due to their high efficiency, quick startup, relatively low operating temperature, simple construction, good dynamic performance, and environmental benignity. For these reasons, the major application potential has been focused on the transportation sector[1]. At present, the major barrier preventing the successful commercialization of PEMFC is its performance and insufficient durability. The durability is directly related to cost, and a substantial increase in durability can reduce costs directly or indirectly[2].

The ideal electric catalyst carrier must have high ratio surface area, high conductivity, certain pore structure, corrosion resistant and suitable surface group. Currently, PEMFCs USES the American Cabot's Vulcan XC-72 carbon black carrier, which has a large number of defects and unsaturated bonds on its surface. These defects and unsaturated bond on adsorption of Pt nanoparticles is very necessary, but it will also cause the loss of stability of carbon materials itself, induce corrosion of carbon materials[3]. The use of highly graphite-graphite materials such as carbon nanotubes, carbon nanofibers, graphene, and ordered mesoporous carbon can effectively reduce the carbon corrosion problem[4-6]. However, highly graphitized carbon materials have surface inertia, not enough active or adsorbed sites to anchor Pt's precursor or Pt nanoparticles. Using traditional methods, such as impregnation, it is difficult to successfully disperse metal catalysts on the carbon carrier. In order to solve this problem, the surface of the graphite carbon carrier is often treated by the acid oxidation process to introduce polar functional groups to improve the adsorption of the precursor. But the introduction of the polar group is also the origin of electrochemical corrosion damage, leading to corrosion of the graphitized carbon carrier, lower the catalyst stability[7].



Manganese dioxide (MnO_2) has wide application in electrochemical battery materials and catalyst, in recent years the study found that, the surface of the MnO_2 has the ability of oxygen enrichment, has a good application prospect for fuel cell cathode catalyst oxygen reduction[8]. The MnO_2 crystal materials have a good adsorption effect on organic molecules due to their unique orients and layer structures and larger than surface area. The MnO_2 is highly absorbent for many metal ions, and its choice of adsorption capacity depends largely on its crystal structure[9].

2. Experimental section

2.1. Synthesis of MnO_2 nanowhisker arrays on carbon fiber paper.

3.5 mmol/L KMnO_4 solution added to the teflon should kettle (not exceed 2/3 of the reaction kettle volume), 1.5 cm x 4 cm carbon fiber paper immersed in the solution, tighten the kettle cover. Finally, the reaction was kept at 160 °C for 0.5 h, 1h, 2h, 3h, 5h. After the autoclave was cooled to ambient temperature, the sample was removed, washed with distilled water, and dried at 60 °C to obtain C- MnO_2 .

2.2. Scanning electron microscopy (SEM) test.

Cut off a small piece of carbon paper from the test and tape the conductive tape onto the bronze seat, then vacuum 30 min and spray gold 10 min. After the success of the sample, the sample is put into the instrument and the picture is preserved with SEM.

2.3. Electrochemical measurements.

Electrochemical measurements were performed on an Autolab electrochemical workstation (PGSTAT302 N, Ecochemie Co., the Netherlands) using a conventional three-electrode cell. The three electrode cell configuration consisted of Pt as the counter electrode; $\text{Hg}/\text{Hg}_2\text{Cl}_2$ electrode (SCE, saturated KCl) as the reference electrode. The sedimentary samples of 6 mm diameter Glassy Carbon Electrode (GCE) as working electrode, in 0.5 mol/L sulfuric acid aqueous solution as the electrolyte solution, electrochemical test at room temperature.

The preparation of the C powder 5 mg was placed in 2 mL of non-aqueous ethanol, and 50 μL 5% of Nafion was dispersed in a test tube and. Platinum wire as the electrode, SCE as reference electrode, carbon fiber paper as working electrode, 0.5 mol/L H_2SO_4 solution as electrolyte, connecting the electrochemical workstation, experimental technology to choose cyclic voltammetry (CV). CV was conducted between 0-1.0 V (vs. SCE) at 50 mV/s.

3. Results and discussion

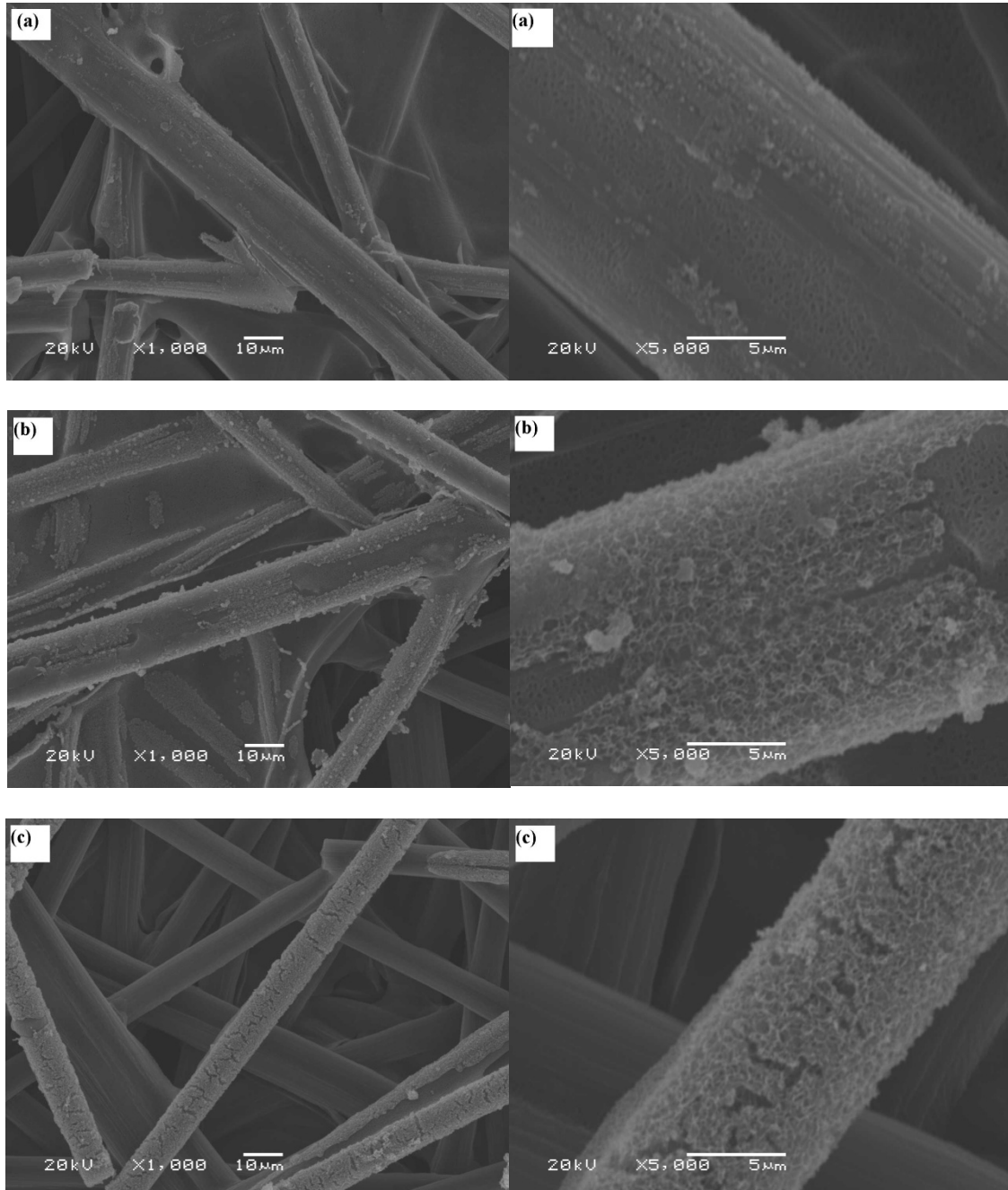
3.1. SEM representation of C- MnO_2 .

When KMnO_4 solution concentration of 3.5 mmol/L, the reaction temperature is 160 °C, observe the SEM (Figure 1), can be seen from the diagram, the initial reaction of 0.5 h, there has been a trace of MnO_2 began to generate; As the reaction time continues, a thin layer of MnO_2 mesh crystals are formed around 1 h, and the individual regions begin to appear in layers of thickening. As the reaction time went through 2 h, the surface of the carbon-fibre paper was covered with thick MnO_2 crystals and slightly cracked in parts. As the reaction time went on, the MnO_2 crystals on the surface of the carbon-fibre paper were visibly reunited, with large clumps and even falling off. When the reaction time was carried out to 5 h, the MnO_2 crystal was crystallized and the crystals fell off in large quantities. It can be explained that 0.5 h to 1.5 h is the best response time.

3.2. XRD of C- MnO_2 .

Can be seen from the diagram (Figure 2), the peaks at 29.0° and 37.8° and 58.0° and 60.0° and 73.5° are associated with the (110), (101), (211), (220) and (301) planes of α - MnO_2 structure, respectively. At the same time, the MnO_2 (110) of the surface of the MnO_2 can be seen through the XRD

characterization, which can be determined that the MnO_2 nanowires are mainly grown along the (110) grain. All the diffraction peaks in the spectra are measured in the four-phase beta MnO_2 (space group: P42/MNM(136)) [10]. In addition, there is no amorphous phase or other type of MnO_2 peak appearing on the X-diffraction spectrum, which also indicates that the final product is highly purified and crystal-clear[11].



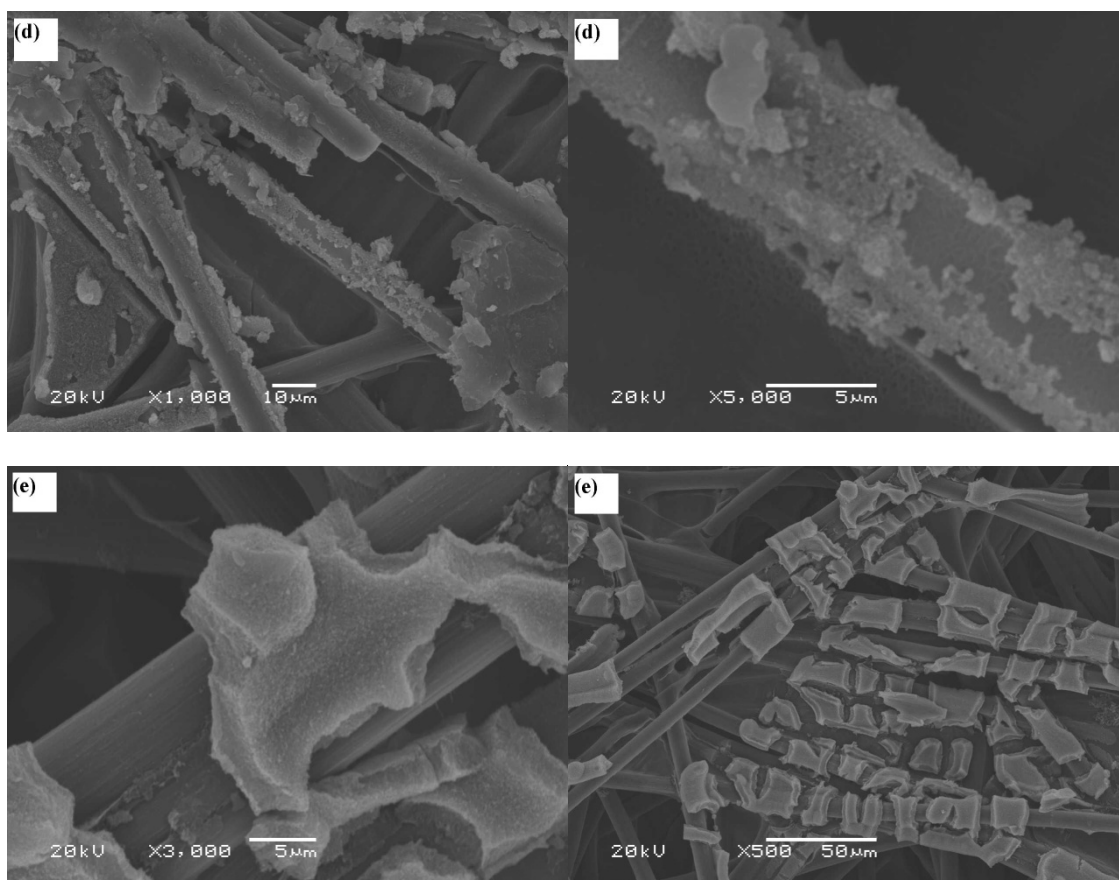


Figure 1. SEM of carbon C-MnO₂. (a) reaction time 0.5 h, (b) reaction time 1h, (c) reaction time 2h, (d) reaction time 3h, (e) the reaction time is 5h.

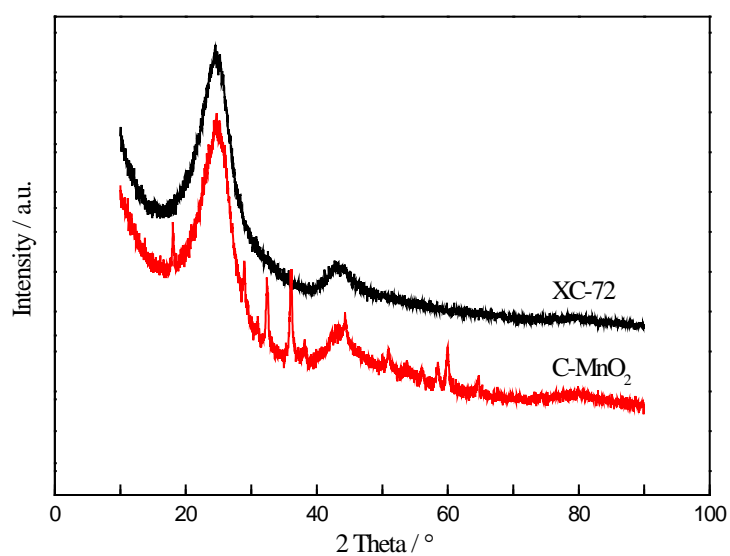


Figure 2. XRD patterns of C and C-MnO₂.

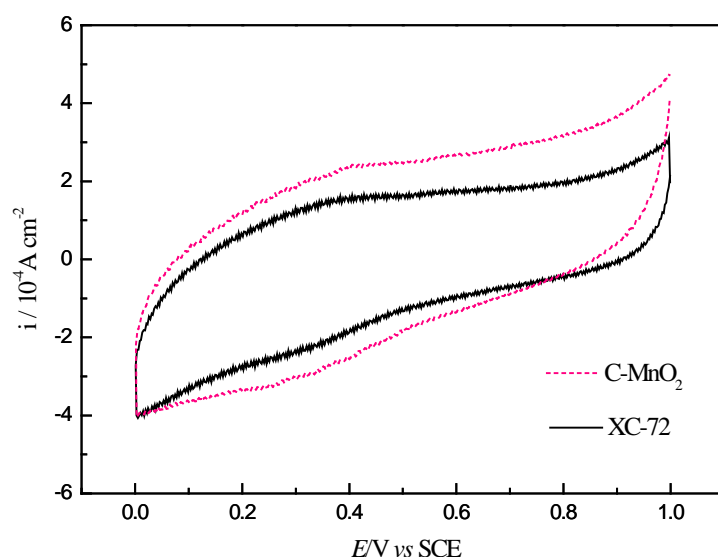


Figure 3. Cyclic voltammetry curves of C and C-MnO₂ after electrochemical oxidation for different time in N₂-saturated 0.5 mol/L H₂SO₄.

3.3. Cyclic voltampere curve of C-MnO₂.

Figure 3 is the cyclic voltampere curve of the XC-72 and C-MnO₂ electrodes in the 0.5 mol/L H₂SO₄ solution, in the 0 V-1.0 V (vs.SCE) scanning potential window. As shown both circular curve showed a good square features, no obvious redox peak, positive and negative scan symmetry, suggests that the kinetics of reversible good charge and discharge process, which shows good electrochemical capacitance characteristics[12]. Excellent properties of C-MnO₂ because of the compound of MnO₂ and C, increased the effective contact area, forming a good conductive network, improve the mass transfer of electrode and load transfer environment. This composite is good for the electronic transmission and diffusion of ions, thus improved the efficiency of the large current charge and discharge.

4. Conclusions

Hydrothermal synthesis was used to prepare C-MnO₂ composite material, the optimum reaction conditions were as follow: 3.5 mmol/L KMnO₄ solution, reaction time 1 h, reaction temperature 160 °C. System with three electrodes respectively to investigate carbon and C-MnO₂ electrochemical performance, system used in the platinum wire as the counter electrode, saturated calomel electrode as reference electrode, 0.5 mol/L H₂SO₄ as electrolyte for testing. Under the scanning rate of 50 mV/s circulation volt-ampere curve, it can be seen that the two have similar shape, but under the same scan rate, C-MnO₂ composites showed a larger current response and C-MnO₂ composite material has improved the efficiency of the large current charge and discharge.

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