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RESEARCH PAPER

Effects of graphitization of PAN-based carbon fiber cloth on its use as gas diffusion layers in proton exchange membrane fuel cells

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Abstract: Gas diffusion layers (GDL) in proton exchange membrane fuel cells were prepared by graphitization of polyacrylonitrile carbon fiber cloths, to enhance their properties, such as, electrical conductivity, which was examined by electrical tests, X-ray diffraction, and elemental analysis. The results indicated that electrical resistivity declined, L_c increased, and d_{002} decreased with an increase in the heat-treatment temperature. Carbon fiber cloths with a higher heat-treatment temperature performed better as GDLs in terms of current density and power density.

Key Words: Fuel cell; Gas diffusion layer; Graphitization

1 Introduction

The proton exchange membrane fuel cell (PEMFC) comprises of an anode to which hydrogen is supplied, a cathode to which oxygen is supplied, and two gas diffusion layers (GDLs), fabricated by carbon fiber cloth or carbon fiber paper to conduct hydrogen/oxygen-water and electrons, a perfluorosulfonic acid membrane, normally Nafion membrane to conduct protons, two catalytic layers made by spraying platinum on the porous carbon as support, and two bipolar plates fabricated from graphite [1]. The assembly of the anode, the cathode. and the Nafion membrane, is called the membrane electrode assembly (MEA). The usual method for fabricating the MEA is to combine GDLs and proton exchange membrane uniformly, spray-coated with catalyst slurry, by hot pressing [2,3].

Various studies have been carried out for the components of PEMFC, especially for proton exchange membrane [4]. In recent years, remarkable advances have been made in catalysts, coated substrates, and microlayers. The microlayer consists of porous carbon powders and hydrophobic polymers, and is located between the catalyst layer and a GDL to improve the hydrophobic and electrical characteristics. In all investigations, the studies of GDLs are more than that of the others. Of late, a new technique for fabricating GDLs using carbon fiber cloths has been established [5]. According to past studies, temperature of graphitization strongly affects the microstructure and properties. The conductivity of the carbon fiber increases with graphitization temperature, but the hydrophobicity of the surface functional group declines [6,7].

2 Experimental

2.1 Preparation of GDLs

Studies were performed using 1001 and 1007 PAN-based carbon fiber cloths (Taiwan Carbon Technology Co. Ltd.) as the GDLs. Various carbon fiber cloths were cut into appropriate sizes, washed with deionized water to remove the remaining impurities and dried at 120 °C. The resulting samples were subsequently graphitized under a helium atmosphere at 1000, 1300, 1500, 1700, 2000 and 2500 °C in a high-temperature furnace (Astro, U.S.A). The heat-treated samples were cut into 25 cm^2 and washed with deionized water to purify the GDLs.

2.2 Characterization of GDLs

The real densities of the carbon fiber cloths were tested using Accupyc 1330 Pycnometer in helium. The surface electrical resistivity of the carbon fiber cloths was measured using a Loresta GP model MCP-T600. The surface resistivity was measured in the planar direction of the carbon fiber cloths. Measurements were made of at least 30 samples and the mean value was calculated. Elemental analysis was performed using an Elemental Vario ELⅢ. The samples after heat-treatment process were analyzed to determine carbon, hydrogen, and nitrogen content. An MXP-3 X-ray diffraction meter, providing Ni-filtered CuK_α radiation, was applied to determine the crystalline-related characteristic properties of the samples. The step-scanning procedure was used to determine the d_{002} and L_c, stacking height of layer planes. The step-interval was set at 0.02°. Bragg equation and Scherrer equation were applied to

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calculate the d_{002} and L_c.

2.3 Fabrication of PEMFCs

Before fabricating MEA, the carbon fiber cloths were washed in various solutions to remove particles, and was then dried at 120 °C for one day. The catalyst-coated membrane (3-Layer MEA, Dupont) was adopted to test the cell performance. The catalyst-coated membrane and carbon fiber cloths combined to produce the MEA, and the active area was 25cm^2. Oxygen and hydrogen were employed as fuel in the cell; the pressure was set at 1 kg/cm^2 and the gas flow rate was 200mL/min.

3 Results and discussion

The knitting processes of 1001 and 1007 PAN-based carbon fiber cloth is different, leading to the cloth's difference in thickness, warp density, and weft density, designated as CF1001 and CF1007. Fig.1 plots the variation of thickness of the cloths with graphitization temperature. The thicknesses of CF1001 and CF1007 were 0.7 and 0.4 mm, respectively, which are dependent on the diameter of the yarns. Fig.2 shows the warp and weft density of the carbon fiber cloths, as functions of graphitization temperature. A significant weight loss was found during graphitization and large volumes of volatile gases were generated. During graphitization, the diameter of the carbon fiber decreased as the temperature increased [8]. The volume shrinkage of carbon fibers caused the threads to become compact. The thread count of CF1001 increased from 36.6/27.3 to 40.3/28.2 and that of CF1007 increased from 42.9/29.3 to 46.0/30.2, as the temperature was increased from 1000 to 2500 °C. The variation in thickness was not apparent. The thickness of the carbon fiber cloths was determined by the diameter of the yarns and the braiding method. The stress in the yarns and the braid did not increase during the graphitization process. Although the diameter of the fiber decreased, the thickness of carbon fiber cloth was maintained at an approximately constant value.

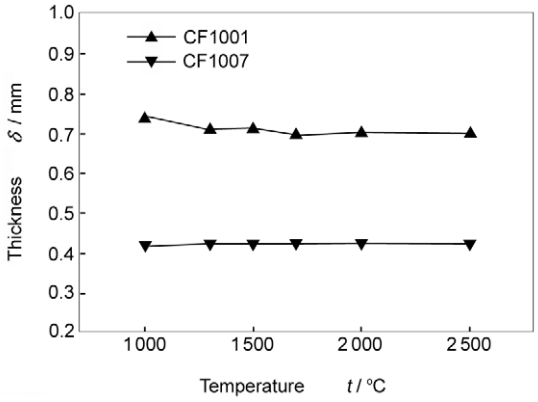

Fig.1 Relationship between thickness and graphitization temperature: (▲) CW1001 carbon fiber cloths; (▼) CW1007 carbon fiber cloths

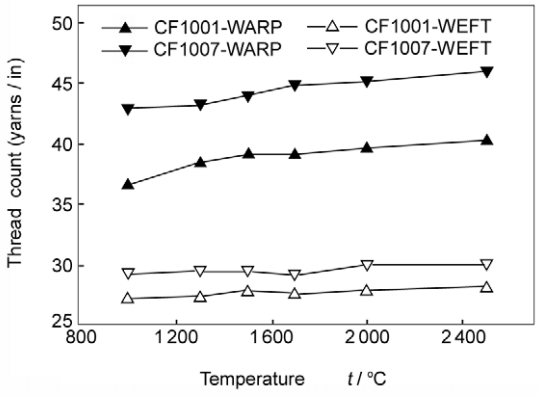

Fig.2 Thread count of carbon fiber cloths as a function of graphitization temperature: (▲) CW1001 carbon fiber cloths in warp; (▼) CW1007 carbon fiber cloths in warp; (△) CW1001 carbon fiber cloths in weft; (▽) CW1007 carbon fiber cloths in weft

Fig.3 plots the density of the carbon fiber cloths against graphitization temperature. The densities of CF1001 and CF1007 were observed to drop rapidly, with that of CF1001 declining from 1.90 to 1.55g/cm^3 and that of CF1007 declining from 1.92 to 1.57g/cm^3, when the temperature was increased from 1000 °C to 1300 °C. Thereafter, the densities increased with temperature to 1.77 g/cm^3 and 1.76 g/cm^3 at 2500 °C, respectively. The sudden decline in density with the graphitization temperature between 1000 °C and 1300 °C was caused by the slow transformation of the open pores in the fibers into closed pores. The formation of the closed pores in the carbon fibers reduced the density [9]. The microstructural changes were probably caused by the increase in the width of the microcrystallites, which were present as elongated ribbons in the graphitization temperature from 1300 to 2500 °C. Fig.4 plots the relationship between the graphitization temperature and the surface electrical resistivity. It could be seen that, as the graphitization temperature decreased, the surface electrical resistivity of CF1001 and CF1007 gradually decreased, especially in the temperature from 1300 to 2500 °C. At temperatures below 1300 °C, the resistivity of CF1001 was 2.85 Ω/sq and that of CF1007 was 4.59 Ω/sq at 1000 °C. It rapidly fell to 0.4 Ω/sq for CF1001 and 0.7 Ω/sq for CF1007 at 1300 °C.

The carbon bonding between graphene layers is weak. The carbon bonding within each graphene layer via sp^2 is strong, which is π and σ bond. The resonance vibration effect of the π bond within the graphene layer causes the movement of the π electrons in the carbon layer, producing electrical conductivity. As the carbon layer stacking increases, the number of π electrons present there also increase, reducing the electrical resistivity or improving the conductivity [10]. CF1001 was fabricated from thick yarns, and the distance between yarns in this is shorter than that in CF1007. A thicker carbon fiber cloth has more intersections among yarns, through which the electrons can conduct, reducing the surface electrical resistivity. From 1300 to 2500 °C, the carbon graphene layer grows steadily and slowly, and the electrical resistivity shows stable values of 0.32 Ω/sq and 0.59 Ω/sq.