A study on the manufacturing of graphite bipolar plates for proton-exchange membrane fuel cell

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1. Introduction

Polymer electrolyte fuel cells are use polymer membranes with a hydrogen ion exchange property and they are called proton-exchange membrane fuel cell (PEMFC). Compared to other forms of fuel cells, polymer electrolyte fuel cells show lower operation temperatures, higher current densities and output densities, shorter starting time and faster responses to load changes. Especially, since they use polymer membranes as electrolyte, there is no loss of electrolyte, methanol reformers which are an existing established technology can be applied and they are less sensitive to reaction gas pressure changes. Also, since they have advantages including simple designs, easy production and diverse ranges of outputs; they can be applied to various areas. Currently, they are intensively studied and developed as power sources of fuel cell cars, home power generation and portable devices. And various kinds of prototypes are being released and some are under trial runs. It can be said that the commercialization of these polymer electrolyte fuel cells will be determined by the degree of reduction of stack prices which is several thousand dollars per KW at this moment [1]. Of fuel cell components, the bipolar plates serve the role of securing flow paths and conducting electric currents to the outside in addition to the role of separating the gases and air supplied to fuel cells and thus low gas permeability is required in operation environments in addition to high electric conductivity, corrosion resistance and heat conductivity [2]. Most of the bipolar plates currently used are made by machine processing with high density graphite and the cost is high since the processing is difficult and takes a long time as high density graphite is easily broken. Therefore the composite bipolar plates to be made with carbon materials with resins are being actively studied. However these composite bipolar plates still have many technical problems such as the problem that their heat and electric conductivities will decrease as the content of binder increases.

In this study the bipolar plates were manufactured from natural graphite mixed with coal-tar pitch. The coal-tar pitch is used as a binder to produce high density graphite. Green plates from the mixtures were formed through compression molding and heated the plates up to their carbonization temperature. Then tar was impregnated to the plate and reheated. The plate and measure basic physical properties of the plates required for bipolar plates and examine the possibility to apply the plates to products.

2. Experiments

The crystalline flake graphite used in this study was HC-198(Hyundai Coma Industrial Co.) and coal-tar pitch was used as a binder and tar was used as an impregnation material. The crystalline flake graphite and coal-tar pitch were mixed by mechanical stirrer. And the mixture was ball milled for 10 hours for uniform mixing and compression molded with a load of 76MPa. The plate was heated to 1000℃ in a nitrogen atmosphere and temperature rising speed was 5℃/min. And then tar was impregnated into the heat treated specimen before re-heating. The coal-tar pitch was analyzed by TGA to measure its decomposition beginning temperature and weight change. The changes of degrees of crystallization between before and after the heat treatment were measured by Raman spectroscopy. The microstructure of the manufactured graphite specimen was observed by optical microscope and the density was measured by Archimedean method.

3. Results and discussions

1. Thermal analysis

The equipment used in the thermal analysis was Q600 SDT (Simultaneous DSC-TGA) of TA instruments Co. Fig. 1 shows the results of the thermal analysis of coal-tar pitch with the thermal analyzer. Coal-tar pitch was heated to 1000℃ under a nitrogen atmosphere at a temperature rising speed of 10℃/min. At this time the thermal decomposition of coal-tar pitch began at around 200℃ and the reaction continued until the temperature became around 550℃. The amount of weight decrease was around 67% finally. This is considered to be a result of thermal decomposition and polycondensation reactions of organic matters occurred simultaneously as the coal-tar pitch consisting of mixtures of aromatic organic compounds.

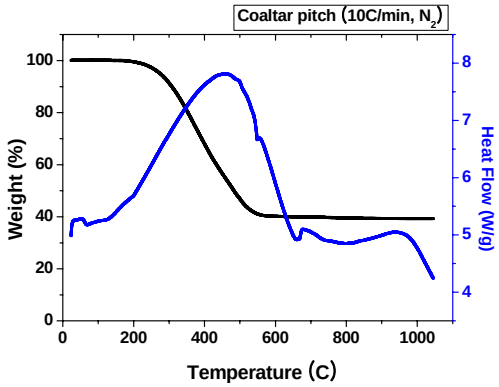

Fig. 1. Results of thermal analysis of coal-tar pitch

2. Degree of crystallinity

Table 1 shows the results of the degree of crystallinity of coal-tar pitch in relation to heat treatment using Raman spectroscopy. The 1360cm^{-1} and 1580cm^{-1} peaks of the Raman spectra become the scales of D-peak and G-peak respectively. Therefore, I_{1360}/I_{1580} becomes a scale to show crystallinity, the degree of crystallinity of the coal-tar pitch used in this study decreased as the heat treatment temperature increased while its intensity ratio (Id/Ig)

increased gradually to 0.61, 0.79 and 0.90. The reason why the degree of crystallinity decreases as heat treatment temperature increases is reported to be the development of fine grain mosaics [3].

Table 1. Results of measurement of the degree of crystallization of the coal-tar pitch

crystalline	25℃	500℃	1000℃
Id/Ig	0.61	0.79	0.90

3. Density measurement

The specimens used in the density measurement were heat treated at 1000℃ using the coal-tar pitch as a binder and specimens heat treated again after impregnated with tar once. The densities were measured with the Archimedean method and the measured values of density are shown in Table 2. The density of the specimens heat treated at 1000℃ was 1.58g/㎤ and their porosity was 26.3%. The density of the specimens heat treated again after impregnated with tar once after the heat treated again 1.60g/㎤, and its porosity was 23.5%. Thus changes in density between before and after the impregnation were minimal and the porosity decreased by around 3%.

Table 2. Results of densities and porosities of the specimen before and after impregnation

1000℃	Porosity (%)	Density (g/㎤)
After heat treatment	26.3	1.58
Heat treatment again after impregnation	23.5	1.60

4. Microstructure observations

Fig. 2 shows the microstructures of the specimen after the heat treatment and the specimen heat treated again after impregnation.

The microstructures were observed with x50 and x100 magnifications using an optical microscope after fine grinding of the section of each specimen. The specimen heat treated again after impregnation seems to have fewer pores and to be denser than the specimen after heat treatment. These pores are considered to be residual spaces after the volatilization of tar and it is considered to be possible to fill up the pores with repeated impregnations of tar.

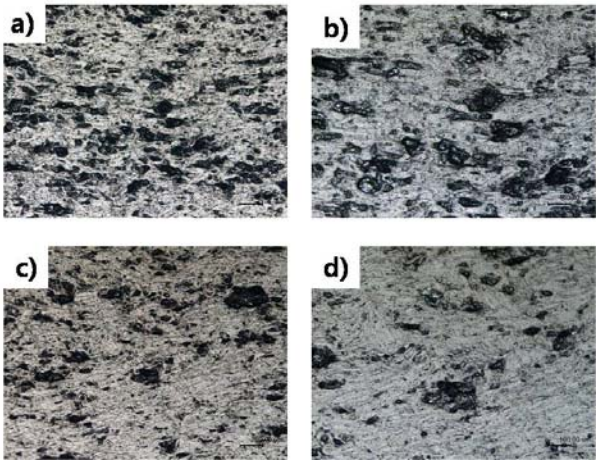

Fig. 2. Results of microstructures observation; a) x50 image after the heat treatment, b) x100 image after the heat treatment, c) x50 image of the specimen heat treated again after impregnation, d) x100 image of the specimen heat treated again after impregnation

4. Conclusion

Natural graphite and coal-tar pitch were mixed to form specimen. The specimens were heated to their carbonization temperature, impregnated with tar and heat treated again. And their microstructures, degree of crystallization, densities, and porosity were measured.

The heat treated specimen and the impregnated specimen did not showed large differences in densities and porosities although the microstructures of the impregnated specimen were denser than those of the heat treated specimen. However since the porosity is high as 25% or higher, additional studies to repeat impregnations 2~3 times in order to reduce the porosity are necessary.

In addition the control of pores created by the gas outs resulting from the thermal decomposition reaction of coal-tar pitch with a carbonization yield of around 40% is considered to be a very important factor. Therefore, it is considered that additional studies about pitch binders and heat treatment conditions will be necessary.

5. Reference

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