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Surface modification of carbon fiber phenolic bipolar plate for the HT-PEMFC with nano-carbon black and carbon felts

Minkook Kim [1], Jun Woo Lim [1], Dai Gil Lee *,[1]

School of Mechanical Aerospace and Systems Engineering, Korea Advanced Institute of Science and Technology, ME3221, 291 Daehak-ro, Yuseong-gu, Daejeon-shi 305-701, Republic of Korea

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A B S T R A C T

The high temperature proton exchange membrane fuel cell (HT-PEMFC) operating from 120 °C to 220 °C is able to overcome many technical issues related to the low-temperature PEMFC (LT-PEMFC), such as their complex water/thermal management to prevent flooding/drying out of the membrane and their low tolerance to carbon monoxide. In a PEMFC stack, the bipolar plates are a major component, contributing 50% of the total cost and 80% of the total weight.

In this study, a composite bipolar plate was developed using resole type phenolic and continuous carbon fiber to improve the high-temperature performance (~220 °C) for use in HT-PEMFC applications. To improve the mechanical and electrical properties, the nano-size carbon black was mixed with phenolic resin. A pre-cure process using hot rolling was developed to achieve partial wetting of the carbon fiber felt on the carbon/phenol composite bipolar plate surface. The randomly oriented carbon fiber felt was co-cure bonded with the pre-cure process to modify the surface of the composite bipolar plates by exposing the bare carbon fibers on the outer surface, which reduced the ASR (areal specific resistance). The developed composite bipolar plate satisfied the DOE technical targets.

1. Introduction

The proton exchange membrane fuel cell (PEMFC) is a promising source of alternative energy due to its high efficiency and low emissions. The PEMFC stack is a layered structure of unit cells, which are composed of bipolar plates, a gas diffusion layer (GDL), and a membrane electrode assembly (MEA) layer and endplates, as shown in Fig. 1. It generates electricity from the electrochemical reaction of hydrogen and oxygen and produces only water and heat without pollution [1,2]. Specifically, there have been rapid advances in low-temperature (60~80 °C) proton exchange membrane fuel cells (LT-PEMFCs) for transportation applications, because of their high power density and rapid start up due to low operating temperatures [3]. For these reasons, the LT-PEMFC technology has been developed and studied globally as a next generation energy source. However, there are still many technical challenges to be surmounted, such as its complex water/thermal management to prevent flooding/drying out of the membrane and its low tolerance to carbon monoxide (CO) less than 10 ppm [4,5].

A high-temperature PEMFC (HT-PEMFC) operating in the range of temperatures from 120 °C to 220 °C is able to overcome many of these technical issues by elevating the operating temperature. The proton conduction mechanism of HT-PEMFCs is dependent on the phosphoric acid content [6,7] and not on the humidity of the membrane [8]. Therefore, water management is not required, which simplifies the balance of plant (BOP) of the system. In addition, because of the high operating temperature, it is possible to recover the waste heat, leading to improved heat integration [9] and improved resistance to CO poisoning [10]. Table 1 shows the comparison of characteristics between LT-PEMFCs and HT-PEMFCs.

In a PEMFC stack, the bipolar plates are a major component, contributing 50% of the total cost and 80% of the total weight [11]. The bipolar plates mechanically support and clamp other components for assembly and provide an electrical passage from cell to cell. For these functions, bipolar plates must have good electrical conductivity and high mechanical strengths. The bipolar plates provide flow channels for reactants such as hydrogen and oxygen and also separate them. To verity the performance of the bipolar plate, the United States Department of Energy (DOE) has proposed technical targets of bipolar plates for LT-PEMFCs, as shown in Table 2.

Because of its good electrical conductivity, graphite is the most commonly used material for bipolar plates. However, the lacks of

* Corresponding author. Tel.: +82 42 350 3221; fax: +82 42 350 5221.
E-mail address: dglee@kaist.ac.kr (D.G. Lee).
[1] http://www.scs.kaist.ac.kr

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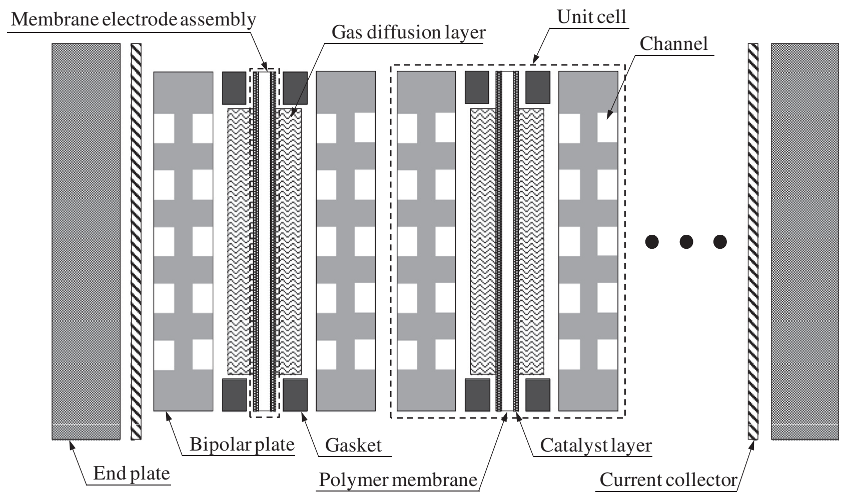

Fig. 1. Schematic diagram of a PEMFC stack.

Table 1
Comparisons of characteristics between the LT-PEMFC and the HT-PEMFC.

Features	LT-PEMFC	HT-PEMFC
Operating temperature (°C)	70–80 °C	125–220 °C
Membrane	Nafion	Polybenzimidazole (PBI)
Ion transport mechanism	Water channel	Phosphoric acid
Humidification	RH 50–100%	No humidifier
Durability against CO	10 ppm	10,000 ppm

Table 2
Technical target values of US-DOE for bipolar plate.

Characteristic	DOE target
Flexural strength	>25 MPa
Areal specific resistance	<30 mΩ cm^2
Gas permeability	N/A
Corrosion resistance	<1 μA/cm^2
Electrical conductivity (in plane)	>100 S/cm

mechanical strength and the brittleness of graphite are problems for mass production and for full-scale commercialization [12]. Metals such as stainless steel and aluminum are also possible materials for bipolar plates due to their good electrical conductivity, excellent gas impermeability and ease of fabrication. However, metals are unable to resist corrosion and require an expensive coating because inside of the PEMFC is a strong acid environment [13]. Composite bipolar plates that use continuous carbon fibers and epoxy resin have been recently developed. Carbon composites are considered to be potentially useful materials due to their good mechanical properties and high electrical conductivity resulting from their high fiber volume fraction [14–16].

Few studies about the composite bipolar plate for HT-PEMFCs have been conducted; commercial graphite bipolar plates for LT-PEMFCs are simply adapted and used without verification for high-temperature application. Most of the developed composite bipolar plates cannot be used for HT-PEMFCs because of their poor high-temperature performance. For example, the continuous-use temperature of DGEBA (diglycidyl ether of bisphenol-A)-based epoxies is 150 °C due to its low glass transition temperature [17].

In this study, a composite bipolar plate was developed using resole type phenolic and continuous carbon fibers to improve the high-temperature performance up to 220 °C for use in HT-PEMFC applications. Phenolic resins are inexpensive, have excellent chemical and thermal properties and cure much faster than epoxy resin; moreover, the glass transition temperature (T_g) of phenolic molding compounds ranges between 200 °C ~ 350 °C depending on the curing temperature [18]. However, since the phenolic is inherently brittle, nano size carbon black was mixed with a resole-type phenolic resin to improve both the mechanical and electrical properties. The electrical resistance and tensile strength of the composites were measured with respect to temperature (20~220 °C) and mixed carbon black wt.%. Finally, the surface of the bipolar plates was modified using a pre-cure process and using randomly oriented carbon felt. The bare carbon fibers of the felt were exposed on the surface of the carbon composite bipolar plate to reduce the contact resistance with the GDL.

2. Experimental

2.1. Materials and fabrication process of composite bipolar plate

The composite bipolar plates were molded with a resole-type phenolic resin (KC-4703, Kangnam Chemical, Korea) and with a continuous carbon fiber. The properties of the resole-type phenolic resin are shown in Table 3. The reinforcement was a 1 k plain-weave carbon fiber (CF 1114, Hankuk Carbon, Korea) with the thickness of 140 μm, a thread count of 0.69 × 0.69 per mm (17.5 × 17.5 thread count per inch) and an areal density of 95 g/m^2. To improve the mechanical and electrical properties as well as the high-temperature performance of the composite bipolar plate, the nano-size carbon black (Ketjen black 600JD, Mitsubishi Chemical, Japan) whose material characteristics are shown Table 4, was mixed with the phenolic resin. To accomplish a uniform dispersion of the carbon black in the phenolic resin, the pre-mixed carbon black and the phenolic resin were post-mixed using a 3-roll milling method. The weight (wt.)% of carbon black was varied

Table 3
Properties of the resole type phenolic resin.

Properties	KC-4703 (Kangnam Chemical, Korea)
Appearance	Liquid
Solids	60%
Solvent	Methanol
Curing temperature	120 °C
Viscosity (@ 25 °C)	0.25 Pa s
Gel time (@ 120 °C)	15 min