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Development of Open-Pore Copper Foams to Use as Bipolar Plates in Polymer Electrolyte Membrane Fuel Cell Stacks

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Abstract: Polymer electrolyte membrane fuel cell stacks contain fluid flow plates, generally known as bipolar plates; which are traditionally made from graphite based materials. Brittleness of graphite enforces manufacturers to fabricate bipolar plates in great thicknesses which severely reduce the stack's power to weight ratio. Therefore, recently the use of low permeability open-pore metallic foams has been attended. This survey is focused on development of powder metallurgy method to manufacture copper foams for use as bipolar plates. After three-point flexural tests and air permeability measurements, it was shown that powder metallurgy method based on using space holder agent has high capability to produce functionally graded foams in order to substitute conventional stack fluid field plates.

Key words: Metal foam · Polymer electrolyte membrane fuel cell · Bipolar plates · Powder metallurgy · Permeability

INTRODUCTION

Renewable energy sources like fuel cells have increasingly been used during recent years because of some serious difficulties like shortcomings and also pollution nature of fossil fuels. Fuel cell as a kind of direct electrochemical system is used to convert hydrogen chemical energy to electrical one which consists from anode, cathode and electrolyte. Depending on the type of electrolyte, these cells are classified to: polymer, alkaline, phosphoric acid, molten carbonate and solid oxide fuel cells. Polymer electrolyte membrane fuel cells (PEMFCs) have been studied in this work; which are mostly applied in transport and portable devices. PEMFC mono cells could be connected together, in form of stacks, through some graphite based bipolar plates (BPs) to achieve higher electrical efficiency. The BPs are multi-functional components in which provide reactants for the contiguous cells, connect them electrically and remove heat and water from stack. As graphite is brittle and fragile, these plates should be manufactured in high thicknesses that results in about 80 percent of the total stack weight. On the other hand, 45 percent of total stack costs are dedicated to the machining of BPs in order to make them efficient fluid field plates (FFPs). Therefore, use of metallic foams as an alternative for BPs has been introduced recently. Indeed, porous metals with high strength to weight ratio would increase stack's power to density ratio and also could eliminate the machining costs. Additionally, heat and electrical conductivity of metallic materials are several orders of magnitudes higher than graphite. In this regard, Kumar *et al*. [1] used 316L stainless steel foam as FFPs and found that decrease in porous medium permeability lower than 10^{-8} m^2 could enhance forced convection [1, 2] and thus increases fuel cell power density. Arisetty *et al*. [3] reported the effect of microstructure on mass transfer properties and also electrical conductivity of metal foams as BP and gas diffusion layer (GDL) of direct methanol fuel cells. In a research work done by Shudo *et al*. [4] it was found that decreasing diffusion polarization, especially in cathode and at low temperatures, plays an important role on cell efficiency as a result of applying 90% porous stainless steel was compared to machined electrode from the same material.

The only main issue about using metallic material in the acidic environment of PEMFC stacks (pH<5) might be its corrosion. Several investigations performed in this area have presented chemical stability improvements of porous metal foams by using metallic or non-metallic coatings

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[5-7]. On the other side, cost effective routes to produce metallic foams with open interconnected pores are inconsiderable. The aim of this study is the development of metallic foams produced by powder metallurgy (PM) method based on use of space holder materials for BP applications. So, open-pore copper foams, because of its high heat and electrical conductivity, have been synthesized and characterized in the aspects of mechanical behavior and permeability properties.

MATERIALS AND METHODS

Lost carbonate sintering (LCS) method developed by Zhao *et al*. [8] was selected to synthesize Cu foams. This route consists of four different steps: (i) blending of metal and space holder powders with a binder; (ii) compaction; (iii) sintering and (iv) space holder removal. Merck (Germany) copper powder with particle size below 63 μm and also commercial pure potassium carbonate, K_2CO_3, as space holder material was used as raw materials. K_2CO_3 powder was sieved and classified into three distinctive ASTM mesh numbers. As carbonate powder in LCS method plays the role of pore forming agent, its volume fraction (f_c) and also particle size (s_c) are the controlling factors for respectively porosity percent (ε) and cell size (d_{cell}) of the foam product. After blending of Cu powder with different f_c and s_c of K_2CO_3 and ethanol as binder, the green compacts were obtained under 250 MPa compaction pressure. Drying of green compacts was done in a laboratory oven at 150°C for about 1 hour. Subsequently, samples were sintered in an electric furnace heated to 850°C for about 4 hours. In the last step, K_2CO_3 particles were decomposed from the structure with an additional heating at 1000°C (2 hours) and then porous specimens were cooled naturally to the ambient temperature. All the samples were coded using M followed by four digits; in which first two digits are the f_c and the others are s_c of K_2CO_3 used for synthesis. As mentioned before, both f_c and s_c could determine the ε and d_{cell} of the final foam product. In the following, the flexural strength properties of copper foams with different ε and d_{cell} were characterized through three-point bending tests according to the ASTM E290-97a using Hounsefield setup model H50KS at 1mm.min^{-1} loading rate. The flexural strength of the foam product (σ_f) is the maximum tolerated stress by specimen before any failure occurs, as shown in equation Error! Reference source not found.. In this equation, F is the maximum load. L, b and d are also the span length between two lower supports, width and thickness of the sample, respectively.

$$\sigma_f = \frac{3FL}{2bd^2} \quad (1)$$

The samples fracture surfaces were investigated through scanning electron microscopy (SEM) by Seron Technology model 550i setup and thus d_{cell} of each specimen was calculated by image analysis of micrographs. Each foams porosity percent, ε, was also measured according to the ASTM C20.

Finally in order to characterize the permeability properties of Cu foams, compressible air permeability analysis was performed based on the method A of ASTM F778-88 standard by Shirley air permeability tester model M021S at temperature of 300K, relative humidity of 35% and also standard ambient pressure. All the foam samples were sealed by an insulated apparent mounted in all aspects except perpendicular to the thickness just for fluid passing. These samples were fixed between two flanges with 10mm diameter and the pressure loss during fluid flow was measured to determine the fluid conductivity of the foam product.

RESULTS AND DISCUSSION

Table 1 summarizes the ε and d_{cell} of copper foam samples produced in this study. An optical image of copper foams with same ε and three distinct pores per linear inches (ppi) associated with three different K_2CO_3 particle sizes used through synthesis process are also presented in Fig. 1.

Fig. 1: Copper foams with the same ε and different d_{cell} (40, 50 and 65 ppi respectively from top to bottom)

Table 1: ε and d_{cell} of open-pore copper foam specimens

Sample code	ε (%)	d_{cell} (ppi)
M6030	62.9	40
M6040	62.3	50
M6050	63.8	65
M7050	65.7	65
M8050	77.2	65

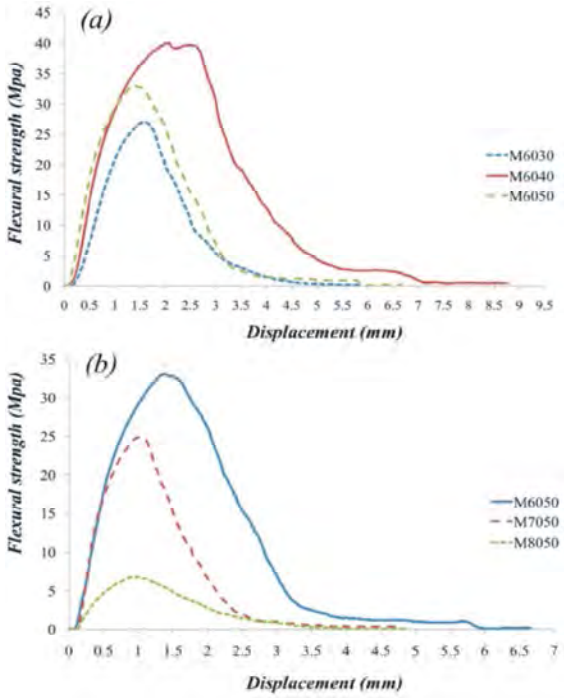

Fig. 2: Stress-displacement curves for Cu foams, (a) $\varepsilon \sim 60\%$ and different d_{cell}; (b) d_{cell} = 400µm and different ε.

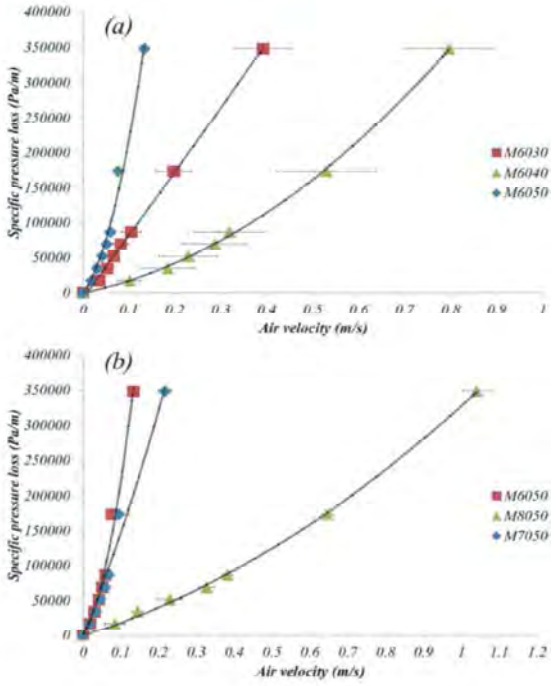

Fig. 3: Specific pressure loss vs. air velocity for Cu foams with (a) $\varepsilon \sim 60\%$ and different d_{cell}; (b) d_{cell} = 400µm and different ε.

Stress-displacement figures of Cu foams are illustrated for samples of f_c = 60 ($\varepsilon \sim 60\%$) with different d_{cell} (Fig. 2a) and also d_{cell} of 65 ppi with different f_c or ε (Fig. 2b). Average d_{cell} of each sample has been measured by image analysis of SEM micrographs from specimen's fracture surfaces. Based on SEM results, cell diameters of about 400, 500 and 620 µm were calculated for ASTM mesh numbers equal to 50, 40 and 30, respectively. The maximum stress value of these curves states the flexural strength of each foam sample. As Fig. 2a represents, it seems that d_{cell} is not much more effective on the mechanical properties of foam products. This could be due to the non-isotropic nature of the foams produced by PM method in which space holder particles usually rearrange during compaction step and thus would result in non-homogeneous distribution of Cu particles across the thickness. Consequently, loading on this anisotropic structure may cause an imminent failure in any region. On the other side, as seen from Fig. 2b, increasing f_c from 60 to 80 which almost causes a similar variation on ε, would reduce the foam's flexural strength.

Generally mechanical deformation in porous media with porosities higher than 0.3 would mainly occur in cell wall regions [9]. So, increasing ε and thus decreasing relative density of these porous materials results in low mechanical integrity of cell walls which could reduce the sample strength under any form of loading. This result is in good agreement with other similar works [10, 11]. As the flexural strength needed for BPs in PEMFC stacks is about 30 MPa [12], the metallic foams with about 60% porosity and average d_{cell} of 400-500 µm would be suitable for this application.

In the following, fluid conductivity properties of foam samples were characterized. The velocity of fluid passing through porous specimen is the ratio of volume flow rate to the flow cross-sectional area. The permeability analysis results for foams with $\varepsilon \sim 60\%$ and different d_{cell} as curves of specific pressure loss versus air velocity (V_o) are illustrated in Fig. 3a. Also for Cu foams with d_{cell} = 400 and different ε is shown in Fig. 3b. Several tests were performed on the same sample to check for the repeatability. The slop of these kinds of curves could lead one to the fluid conductivity or permeability of foam samples.

Obviously from Fig. 3, the pressure drop across the foams has a quadratic relation with superficial fluid velocity. These non-linear variations could be approximated using Hazen-Depuit-Darcy model which is widely accepted by several researchers [13-15] stated as follows:

Table 2: K and C permeabilities besides each copper foam sample besides their flexural strength

Sample code	K × 10^{10}[m^2]	C × 10^{-5}[m^{-1}]	σ_f [MPa]
M6030	4.18	64.74	26.93
M6040	11.7	6.8	39.97
M6050	2.2	223.31	33.16
M7050	2.05	181.62	24.86
M8050	9.77	7.2	6.81

$$\frac{dp_o}{dx}=\frac{P_i^2-P_o^2}{2PoL}=avo+ßv_o^2 \quad (1)$$

where P_i and P_o are the inlet and outlet pressure values and L is the sample thickness. The α and β coefficients in Equation 1 could be calculated from the slopes of the linear and non-linear portions of Fig. 3 using:

$$a=\frac{\mu}{K},ß=C? \quad (2)$$

In the recent equation, K is the Darcy and C is the non-Darcy permeability coefficient. In experimental conditions, the dynamic viscosity, μ and air density, ρ, were measured as1.983×10^{-5} Pa.s and 1.265 Kgm^{-3}, respectively.

Table 2 summarizes the permeability and mechanical test data of copper foam specimens. Obviously, increasing ε would increase K and decrease C. Actually the linear term in equation 1 is related to the viscosity drag force while the non-linear term is responsible for the drag force of porous medium solid walls. As shown in this table, increasing void space volume fraction reduces the impact of solid walls drag force against air flow. On the other side, the variation of d_{cell} does not show any significant effect on the fluid conductivity of porous samples.

A similar study conducted by Medraj *et al*. [14] on two groups of metal foams with different microstructures revealed that pressure gradient through PM foams, called complex foams in that survey, is much more dependent on various parameters like the homogeneity degree of raw powder materials and also pressing conditions. So, fluid conductivity may differ from one sample to another independent of open interconnected porosity percent. So, it's inevitable to check the microstructure and permeability characteristics of PM foam products before any usage. The materials used as FFPs in fuel cell stacks should have maximum viscous drag force against reactant gases[12] which requires minimum K permeability value. As mentioned before, research works [1, 2, 16] carried out on the use of metallic foams in FFPs report an impressive effect of the permeability of these materials in which lowering than a value about 10^{-8} m^2 could enhance the overall stack power density. Data summarized in Table 2, one can conclude that permeability coefficients of Cu foams produced by PM method could satisfy the mass transfer conditions needed in PEMFC stack. Generally, two permeability modes could be considered to use open pore copper foams synthesized in this work: in-plane and through-plane. Actually increasing though-plane permeability results in an increment of mass flux and thus more effective gas transport to the catalyst layer. Subsequently, increasing number of electrochemical reactions per unit time results in higher power efficiency. This mainly requires decreasing of in-plane permeability. Arisetty *et al*. [3] found that foam microstructure could severely affect its mass transfer and electrical conductivity properties. Based on their results, more operative transport of reactant gases could be reached with an efficient CO_2 bubble detachment which requires increment of pore sizes. As another result, they found that when pore size grows, it needs more distance for an electron to get into the nearest rib which implies a higher electrical resistance. On the other side, increasing of ε improves wetting angle and results in better gas and water management; but it necessitates noticeable depletion of flexural properties (Table 2). So, by considering mechanical strength, permeability, electrical conductivity in one side and gas-water management on the other side, copper foams with ε ~ 60% and d_{cell} of about 400 to 500μm could be suitable to use as BPs in PEMFC stacks. Metallic foams have many advantages for using in FFPs provided that they are made corrosion resistant. So, research and development on the coating of synthesized copper foams and its corrosion resistance evaluations are the future scopes of authors.

CONCLUSION

Synthesis and development of open-pore copper foams produced by LCS method for using in FFPs of PEMFC stack was done in this work. Conclusions of this research are as follows:

- Measurement of foams flexural properties, as a criterion of their mechanical behavior, showed a considerable increment of bending strength with decreasing of ε.
- d_{cell} did not reveal any significant effect on foams mechanical properties. This might be due to the anisotropic nature of the foams produced by LCS method.

- The permeability analysis of Cu foams proved PM process based on using space holder materials for synthesizing metal foams with appropriate permeability values, below 10^{-8} m^2, to use as FFPs in fuel cell industry.
- With a tradeoff between characteristics evaluated in this study and the results achieved by other researchers on the BP usages of these kinds of materials, it could be concluded that copper foams with $\varepsilon \sim 60\%$ and d_{cell} of about 400 to 500μm is applicable to use as conventional BPs in order to enhance stack power density.

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