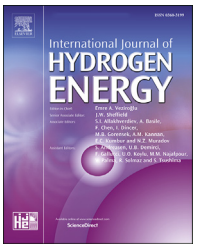
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Metal foams as a gas diffusion layer in direct borohydride fuel cells



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HIGHLIGHTS

- This article reports a comparative performance of various metal foams in DBHYPs.
- Nickel foam with high production cost in DBHYPs used in today's energy technology.
- The use of low-cost open-cell aluminum foams produced by the space holder method.
- The use of Al foams in DBHYPs is restricted due to the reaction in the system.
- Aluminum foams can play a consumable fuel role that provides high current density.

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ABSTRACT

Renewable energy sources have become an important issue due to global warming and the diminishing of fossil fuel resources that have become a major problem for the world. Fuel cells are one of the most important renewable energy systems. The use of metal foams within the scope of commercialization and cost reduction of fuel cells attracts attention today. Metal foams are a material that provides excellent performance in many engineering applications, especially in fuel cells, thanks to the high permeability provided by the porous structure, narrow flow channels, large specific surface area, capillary, and diffusive forces. Among the metallic foams, the focus is on the use of aluminum foam, due to its low cost, superior strength, and thermal conductivity performance properties as well as ease of production. As an alternative to gas diffusion layers, the use of different metallic foam materials in fuel cell systems and performance improvements were analyzed. The use of aluminum foams as flow distributors and electrodes in the anode diffusion layer, which is one of the DBHYP components, provides significant increases in cell performance, cell weight, and volume. It has been found that open-cell metallic foams used in fuel cell systems cause an increase in performance due to their positive effects on the amount of catalyst coating, flow characteristics, and electrical properties.

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Introduction

Throughout the history of humanity, it is tried to produce new structures by imitating the structures found in nature. One of them is porous structures. The use of porous structures has increased due to their unique features such as bone, bark, and wood. Metallic foams are one of the most important porous materials used in the technique. Metallic foams have extraordinary properties in terms of acoustics, impact energy absorption, liquid and gas permeability, thermal and electrical aspects [1,2]. Metallic foams are structurally characterized according to their cell topology, whether they are closed or open-celled, their specific densities, cell size, cell shape, and anisotropy structures. Its main areas of use are shock and impact absorption, thermal insulation, catalyst support, flow-dispersing structure, liquid or gas filtration, and sealing elements [3,4].

Studies on fuel cell systems that convert the chemical energy of hydrogen directly into electricity have increased. It is possible to obtain continuous energy as long as a fuel supplement is provided with fuel cell systems. Fuel storage and transportation problems occur in fuel cell systems where pure hydrogen is used as fuel, due to the flammable and explosive nature of hydrogen. Because of these disadvantages of pure hydrogen, it is more advantageous to work with fuel cell systems in which hydrogen carrier liquid fuels are used. Commercialization of direct boron hydride fuel cells (DBHYP) can be achieved by increasing cell performance while reducing cell volume and cost. The use of metal foams in fuel cells also provides significant improvements in cell performance in fuel cell systems.

In terms of geometry, the major goal is to increase the specific surface area of the hydrogen evolution electrode by increasing its surface roughness and porosity, thereby lowering the electrode's energy consumption during the hydrogen evolution process. In the research, nickel foams are commonly used in liquid fuel batteries [5–7]. The researchers created multiporous and highly active nanocomposite particles, which were then employed as a template to make a highly active electrocatalytic hydrogen evolution electrode [8,9]. The hydrogen evolution overpotential and exchange current density were considerably lowered due to the huge specific surface area and interconnected electron transport skeleton of the multi-level pores, which provide a large number of electrocatalytic active sites [10,11]. Guo et al. [12] fabricated a CoB anode that was directly formed on a Ni-foam substrate for DBHYP. They reported that electrooxidation of $NaBH_4$ with a low CoB loading amount resulted in high electrocatalytic activity for the anode. Celik et al. [13] demonstrated a DBHYP with Ni foam as a substrate for an anode electrode. They investigated the effects of nickel foam on fuel cell performance under steady-state/steady-flow and uniform state/uniform-flow systems. Cao et al. [14] constructed a direct borohydride-hydrogen peroxide fuel cell with an Au deposited Ni foam anode electrode to improve the mass transport properties and obtain high catalytic properties. They reported that a high reaction rate and a significant increase in cell performance had been achieved. Yang et al. [15] prepared an Au nanosheet on Ni foam (Au NS/Ni substrate with one-step electrodeposition and Ni foam supported Au particles (Au NP/Ni) same method for comparison. Characterization showed Au NSs uniformly deposited on Ni and it has a unique open structure that allows maximum use of Au active sites on the surface. They found that the catalytic activity of the Au NSs/Ni foam electrode was 278% higher than that of the Au NPs/Ni foam electrode.

In this study, the use of low-cost open-cell aluminum foams produced by the space holder method instead of nickel-based foams with high production costs in DBHYPs used in today's energy technology is investigated. Efforts have been made to improve the performance of conventional fuel cell systems currently available. The usability and performance of open-cell aluminum foams produced under laboratory conditions and some other commercial metal foams as a gas diffusion layer in DBHYPs have been tested.

Experimental procedure

Metallic foam manufacturing and characterization

Open-cell foams were produced by the space holder method, which is an economical and fast method, and their morphology, structure, chemical, and mechanical properties were examined. The performance of open-cell aluminum foams produced by the space holder method in fuel cells was investigated. NaCl was used as a space holder material. To control the size and shape of the pores, NaCl particles were mechanically divided into parts and separated into different sizes with a Retsch AS 200 sieving machine. To reduce the humidity value of the environment and the salt particles used, a drying process was applied at 85 °C for 1 h. In addition, the same process was carried out for the furnace environment (Fig. 1). NaCl moved away from the precursor structure with the final cleaning process in an ultrasonic washing machine.

Densities of open-cell aluminum foams are measured according to the Archimedes principle. Dry weights of open-cell metallic foams and their weights in pure water were measured and their densities were calculated using Eqs. (1) and (2). The porosity of open-cell metallic foams is calculated by Eq. (3). The masses of the metal foams were measured with a scale with a precision of 0.001 g. The number of pores per unit (PPI) area was calculated by Eq. (4). The diameters of the pores were taken from the average size value of the placeholder particles [6,7].

$$\rho^* = \frac{w_1 \rho_w}{w_2 - w_1} \tag{1}$$

$$\rho_w = 1.0017 - 0.0002315T \tag{2}$$

$$P_{foam} = \left[1 - \frac{\rho_{foam}}{\rho_{bulk}}\right].100 \tag{3}$$

$$\text{ppi} = \frac{300}{D}\sqrt{\frac{(1-\in)^2}{\in \pi}} \tag{4}$$

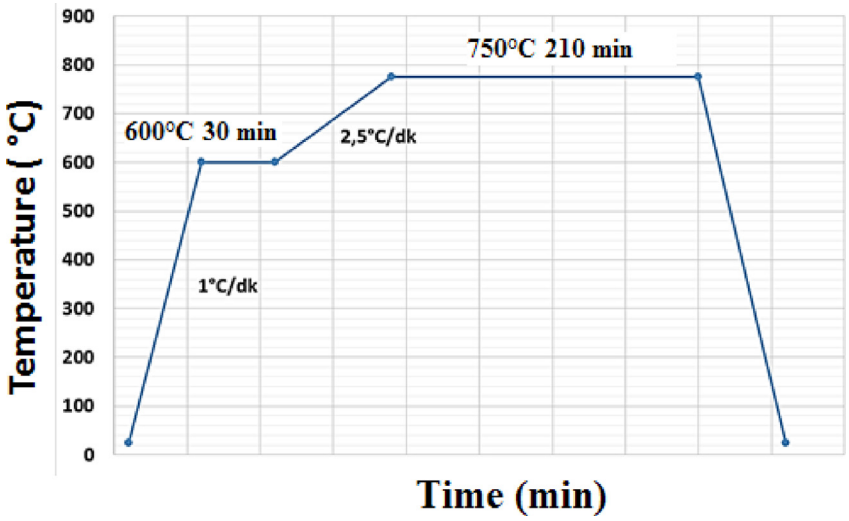


Fig. 1 – Temperatures and times applied in the experiments.

Single-cell testing system

The use of metallic foams as an anode component in DBFCs results in increased electrical efficiency due to increased contact area. Open-celled metallic foams are attractive candidates for catalyst supports in fuel cells with their specific structural properties. Aluminum, copper, and nickel-based metallic foams with different elemental structures are expected to contribute to the system efficiency by taking the role of catalyst carrier in fuel cells (see Table 1). Also, Metal Foams can be used as a catalyst carrier or as the catalyst itself. The foam structure causes a low-pressure drop and turbulent flow which increases the interaction between the catalyst and the reagent. Fuel cells consist of 5 main components. These components consist of the electrolytic membrane, anode and cathode gas diffusion layer, an anode, and cathode flow distributors (Table 2) (see Fig. 2). The single-cell testing system test system is shown in Fig. 3.

In this study, the results of the production technique of open-cell aluminum foams with the space holder method under laboratory conditions were evaluated in terms of energy density in a 25 cm^2 DBFC. To investigate innovations and improvements in the application areas of metal foams, the operating performance of DBFC is examined.

Cathode gas diffusion electrodes (GDE) were prepared by an ultrasonic coating method using a commercial Pt/C (%70) electrocatalyst. Catalyst loading and active area of GDE's were 1 mg/cm^2 and 25 cm^2 respectively. Before the preparation of MEA, the membrane pre-treatment procedure is applied. This procedure was described as follows (i) Membrane was cleaned by boiling it in 3% H_2O_2 for 1 h, (ii) was kept in deionized water for 2 h and 1 h in 0.5 M H_2SO_4, (iii) then flushed with deionized water for 3–4 times. After these steps, the Nafion 117® membrane was conditioned by immersing in a 6 M NaOH aqueous solution for 6 h to transform it into Na^+ form. The MEA was prepared by using Pt/C cathode, Nafion® 117 membrane, and various metallic foams. The fuel solution consisting 4% $NaBH_4$ + 12% NaOH by weight was fed to DBFC. Pure oxygen was used as the oxidant. Time-dependent current data were obtained for 1 h after the test system was filled with fuel.

Results

Macro and microstructure analysis

Cellular materials made of metal, ceramic, polymer, or carbon have a wide range of applications due to their high surface area, low relative density, and complex interface geometries. Cellular materials are used for heat exchangers, energy absorbers, high-temperature filters, electron emitters, fuel cell electrodes, and catalytic supports. There are two types of cellular foam structures: the closed cell structure in which the cells are isolated and the open cell structure in which the cells are openly connected. The properties and capabilities of open-celled foams can be improved and

Table 2 – Components used in single-cell tests.

Component	Property/Trade name
Flow channel	3-channel serpentine flow channel
Gas diffusion layer	Sigraget 34 BC
Membrane	Nafion 117
Electrocatalyst	Pt/C
Current collection plate	gold plated copper

Table 1 – Elemental compositions of aluminum alloy used in the experiment.

	Fe	Si	Cu	Mn	Mg	Pb	Bi	Zn	Cr	Zr	Ti
2011	0.5	0.3	5.0–6.0	–	–	0.2–0.6	0.2–0.6	–	–	–	–



Fig. 2 – Atmosphere controlled oven, b production mold of metal foam.

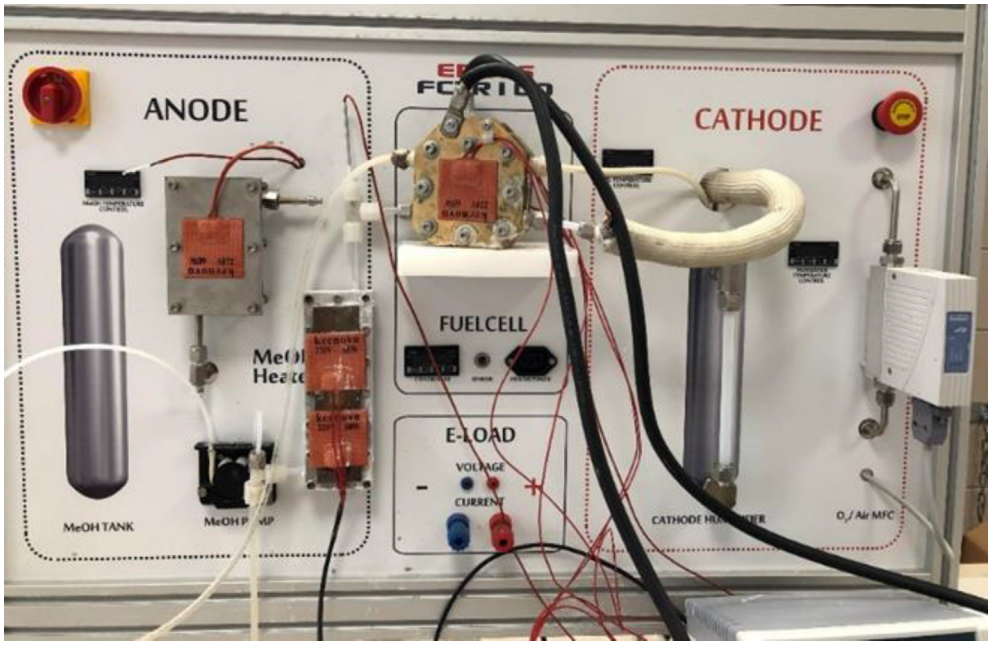


Fig. 3 – Single-cell testing system.

modified by adding a coating to their intra-porous surfaces. In today's liquid fuel cells, porous structures with different properties are used [16–18]. Nickel-based foams are generally preferred in these applications. In this study, the production of aluminum, copper, and nickel foams and their behavior in the liquid fuel cell have been examined. Different and unique techniques are used according to the application areas of metallic foam production. In the production of open-cell metallic foams, space-holding, investment casting, sintering of hollow powders, electroplating, vapor deposition, spray forming and sludge foaming methods are used [8]. The cell size in the foam changes in parallel according to the space holder particle size used during the production. While the cell wall thickness of produced aluminum foams compared to commercial aluminum foams is higher, the cell width is also wider. The cell walls, cell spaces, and nodal points of the aluminum foams produced by the space-holder method were examined with a stereomicroscope. The foams are characterized by the number of pores per inch (PPI). Table 3 shows the cell wall width and cell width values of

Table 3 – Geometric dimensions of aluminum foams.

		Cell wall thickness (μm)	Cell width (μm)
1–2 mm	a)	513.6	1117
Space-holder sample (Al-1)	b)	366.4	812.5
	c)	443	584.2
Commercial	a)	51.16	492
Aluminum Foam	b)	56.55	196.8
	c)	48.04	150.9

Table 4 – Characteristic properties of the metal foam samples.

Foam Samples	Density (g/cm^3)	Porosity (%)	PPI
Al-1 produced	0,95	0,65	24
Al-2 commercial	0,78	0,71	38
Cu-1 commercial	0,74	0,72	37
Cu-2 commercial	0,97	0,64	25
Ni-1 commercial	1,36	0,50	30
Ni-2 commercial	0,88	0,67	23

aluminum foams. Aluminum foam values with 80% porosity and 100 PPI commercially available from Xiamen Tob are also included. The porosity and density of the produced open-celled aluminum foams were calculated. Table 4 shows the characteristic properties (density, porosity, PPI) of all types of metal foam samples.

Microstructural properties were examined by JEOL 50 A SEM-EDS. Fig. 4 shows the scanning electron microscopy image of the samples taken from the aluminum foams after serial sanding up to 2400 grit and subsequently 1-μm colloidal polishing. A regular precipitate structure is observed both on the cell wall surface and on the inner surface of the pore. In

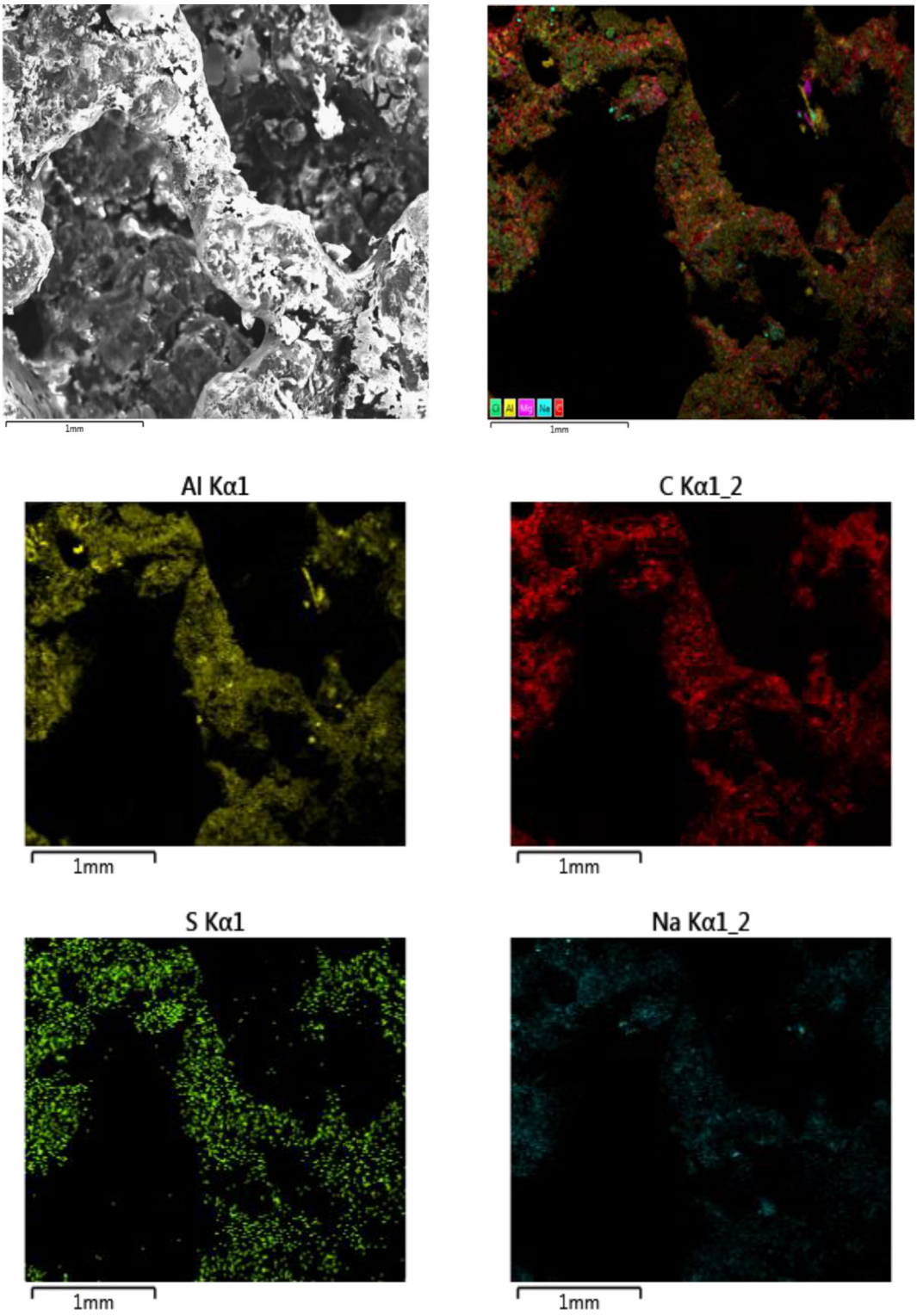


Fig. 4 – SEM and EDS analysis of the A-1 sample.

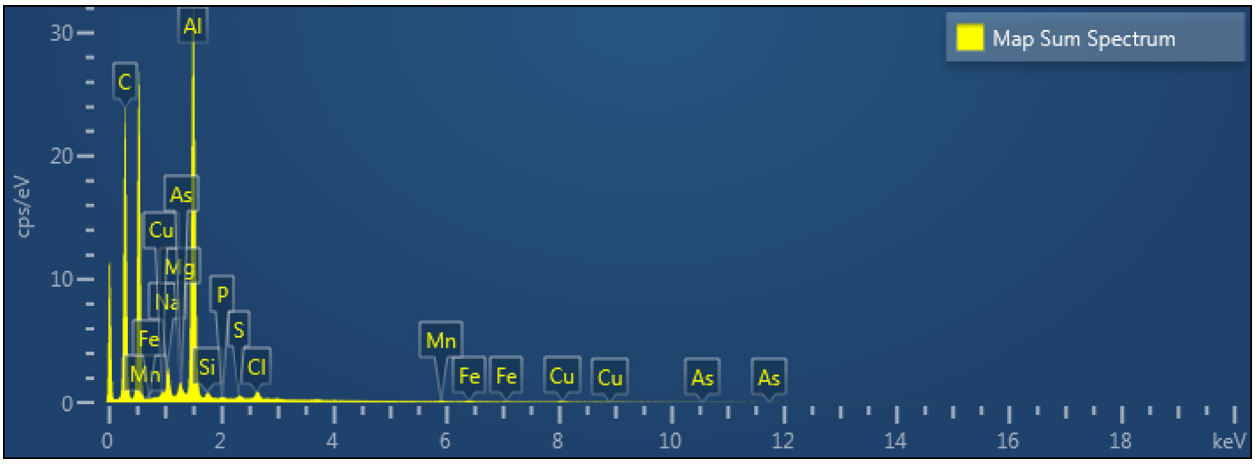


Fig. 5 – EDS analysis results.

Fig. 5, as a result of the EDS analysis, it has been determined that Na and Cl elements precipitate locally in the structure and the regular distribution of other alloying elements. In addition, the removal of NaCl particles from the structure must be done quickly. Otherwise, it was determined that the struts of the foam cells showed signs of corrosion. EDS results show Al_2O_3 in the structure. This is because aluminum foams oxidize very quickly in the open atmosphere. In addition, the reason for the presence of sulfur element in the data received is that it is transmitted from the liquid gasket used as the sealing element to the structure. Pd/Zn catalyst was coated on metal foams by electroplating method.

Vickers hardness measurements were carried out for open-cell aluminum foam samples by applying the penetrating tip with a 136° apex angle to the sample. Hardness measurements were carried out under a load of 1.961 N for 10 s. Hardness measurements are given in Table 5 by taking the average of 6 different traces for each sample.

Fuel cell test results

Fuel cells are electrochemical devices that convert chemical energy in fuel into high efficiency without any energy conversion process. In classical cycle technologies, efficiency decreases, crowded machinery is required, and causes environmental pollution. In fuel cell technology; Uninterruptible electrical energy is generated as long as the fuel is supplied. The main advantages of fuel cells are pure water vapor and heat release as waste, silent operation, better efficiency compared to gasoline and diesel engines, no moving parts in energy production, and remote operation possibility. While a range of energy efficiency is 30–50% in diesel, oil, and steam-gas turbines, it is 50–70% in a fuel cell. The efficiency of the fuel cell is high as well as the energy density. A fuel cell power station with a 2 MW capacity can be installed on an area of less than 20 m^2. In this case, electricity does not need to be produced far from the cities where consumers are located. Thus, there is no need for thousands of kilometers of transmission lines and transformers between power plants and users. In addition, electrical losses in transmission lines are prevented. In the operation of fuel cells, the fuel molecule sent to the anode electrode passes through the channels on the anode, the electron is separated from this molecule and the molecule becomes an ion structure. Since the selectively permeable electrolyte only permits the passage of the ionized fuel, the electrons pass through the external circuit, so the ions reach the cathode through the electrolyte. As a result of the reaction of ion, electron, and oxidant in the medium, they form a waste product according to the type of fuel and oxidant. This product is water for hydrogen/oxygen fuel cells. Electron movement on the external circuit allows direct current to be generated in the system. The reaction also yields heat energy. There is also the use of catalysts to increase the reaction rate in fuel cells. The component consisting of anode, cathode, and electrolyte in a fuel cell is called Membrane Electrode Unit (MEU). The electrical voltage obtained from a MEU varies according to the type of fuel and oxidant.

The most common classification of fuel cells is based on the type of electrolyte used in the cell. The theoretical open circuit voltage for H_2/O_2 batteries is 1.23 V, while for $NaBH_4/O_2$ fuel cells it is 1.64 V. To increase the voltage, each MEA is connected in series and the desired voltage level is reached. This system is called Fuel Cell Stack. To obtain a higher current, it is necessary to increase the number of molecules reacting. This is achieved by increasing the anode, cathode, and electrolyte surfaces. The storage of hydrogen, which is used as fuel in fuel cells, is an important factor in the spread of this technology. Alkaline sodium borohydride solution which is easily stored and transported in liquid form is used in DBFC. The theoretical OCV for DBFC is 1.64 V for oxygen combustion. DBFC has a high energy density (9.3 kW h kg^{-1}). Electrolyte membranes are of great importance in the commercialization of DBFCs. Both anion exchange membranes (AEM) and cation exchange membranes (CEM) can be used in this fuel cell. Anode catalyst studies on DBFCs have been discussed in a wide range of the literature and the effect of many catalysts on borohydride

Table 5 – Vickers hardness values.

Sample	Measurements						Average
A-1	92.2	87	81.6	80	75.5	82.3	83.1
A-2	84.2	81.8	83.2	77.4	81.3	82.1	81.67

oxidation and cell performance has been investigated. The main features required from DBFC electrocatalysts are that; should be highly selective against borohydride oxidation, but as active as possible for borohydride hydrolysis. In this context, it has given the best results as the gold anode electrocatalyst among the electrocatalysts studied so far, however, the gold particles should be nanoscale.

Time-dependent current graphics and energy densities for each metallic foam were shown in Fig. 6. Fig. 6a shows the performance of the A-1 sample produced under laboratory conditions when using a catalyst support layer with 89% porosity. A-1 sample showed a performance value of 0.47 mAh/mg $NaBH_4$ within 1 h of operation. Fig. 6b shows the performance of commercial aluminum foam as a catalyst support layer at 80% porosity. While the commercial aluminum foam provided 30 min of operation in the fuel cell test cell, the foams produced in the laboratory provided operation throughout (1 h of) the test period. The reason for the increase in the energy density value as the thickness of the foams used increases is that it has more surface area where the reaction can occur. It has been demonstrated that aluminum foams can be used with innovative designs in $NaBH_4$ fuel cells. In fuel cell technology, it has been revealed that aluminum foams with different fuels and catalyst types have the potential to reduce

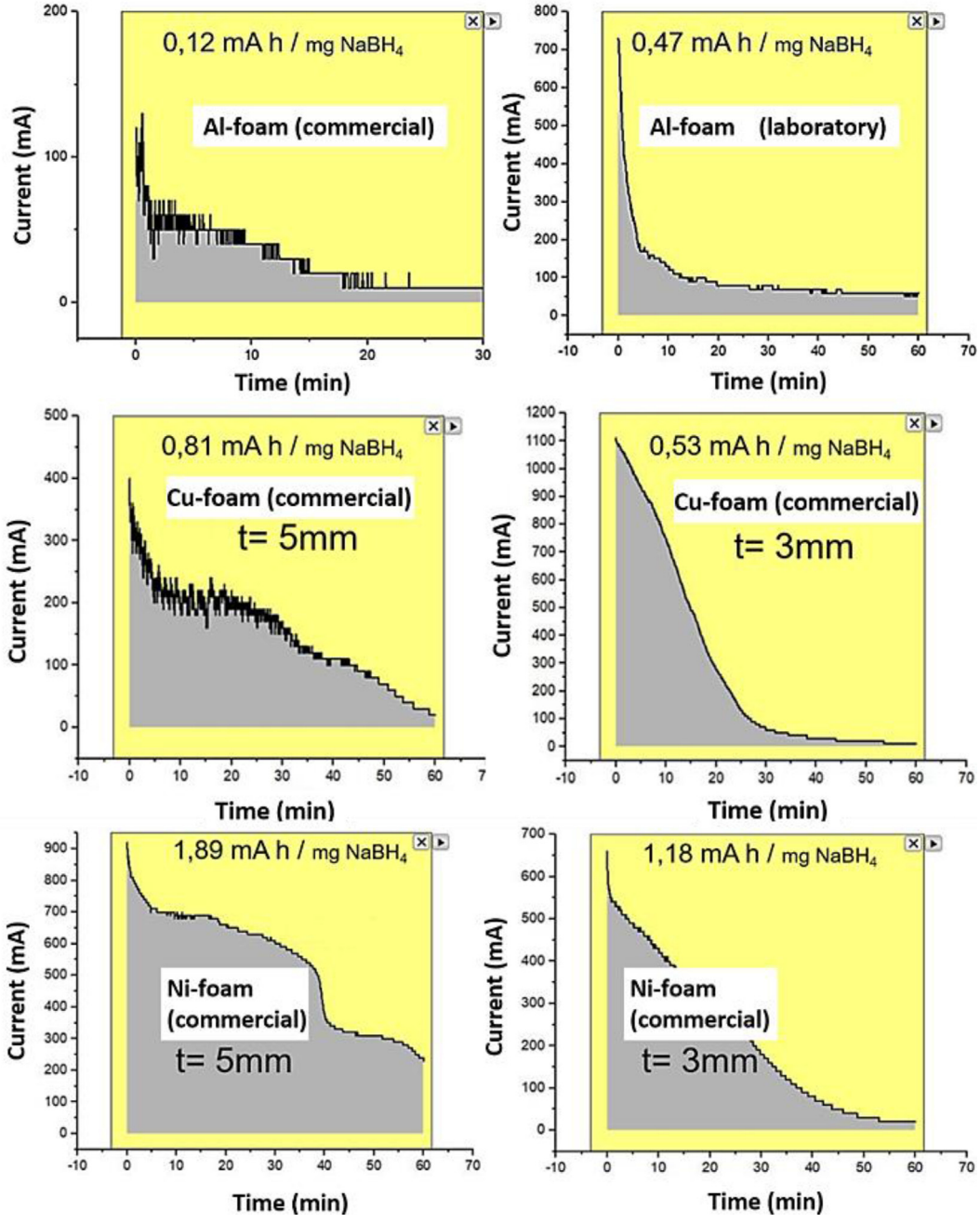


Fig. 6 – Fuel cell test performance of commercial and laboratory-produced metal foams.

fuel cell costs. The results revealed that aluminum foams have the advantage of obtaining high current in a short working period as a consumed cartridge.

Within the scope of this study, a three-dimensional catalyst coating was obtained because the catalysts were coated on metal foams by the electroplating method. Unlike conventional catalyst coating methods, in electroplating the catalyst is not deposited only at the membrane-diffusion layer interface; diffuses throughout the diffusion layer thickness. For this reason, more effective use is achieved by preventing the catalysts from stacking on top of each other. However, this may vary with the thickness and porosity of the metal foam. For this reason, the power densities given in Fig. 6 differ.

Corrosion measurement was not performed on the Al-foam used at the end of the tests. However, no deformation was observed in the visual examination. In Fig. 6A and B, it is observed that the first peaks occur as a result of the reaction in the first moment, but then the reaction continues regularly.

When the porosity and PPI values given in Table 4 are compared with the performances given in Fig. 6, it is seen that the performance of copper and aluminum foams increases as the porosity and PPI value decrease. It is thought that the surface area of the foams depends on the porosity and PPI value and the performance increases despite a decrease in these values and that the Al foam and alkali solution do not contribute to the energy density of the reaction.

Conclusions

Comparing the performance of commercial foams and aluminum foams produced under laboratory conditions in fuel cells. The use of aluminum foams in $NaBH_4$ fuel cells is restricted due to the reaction in the system. The energy densities of commercial aluminum foam, the aluminum foam produced under laboratory conditions, commercial copper foam, and commercial nickel foam were obtained with $NaBH_4$ values of 0.12, 0.47, 0.81, and 1.89 mAh/mg, respectively.

In this respect, an innovative fuel design opportunity has emerged. Aluminum foams can play a role as a consumable fuel that provides high current density due to their porous structure in short-term energy needs such as rocket systems.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgment

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