POROUS CARBON MATERIALS FOR ELEMENTS IN LOW-TEMPERATURE FUEL CELLS

POROWATE MATERIAŁY WĘGLOWE STOSOWANE DO BUDOWY ELEMENTÓW W NISKOTEMPERATUROWYCH OGNIWACH PALIWOWYCH

The porosity, distribution of pores, shape of pores and specific surface area of carbon materials were investigated. The study of sintered graphite and commercial carbon materials used in low-temperature fuel cells (Graphite Grade FU, Toray Teflon Treated) was compared. The study covered measurements of density, microstructural examinations and wettability (contact angle) of carbon materials. The main criterion adopted for choosing a particular material for components of fuel cells is their corrosion resistance under operating conditions of hydrogen fuel cells. In order to determine resistance to corrosion in the environment of operation of fuel cells, potentiokinetic curves were registered for synthetic solution 0.1M H$_2$SO$_4$ + 2 ppmF$^-$ at 80°C.

Keywords: fuel cell, bipolar plates, corrosion resistance, porosity, carbon materials

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) belongs to the low-temperature generator of electricity and heat. Most of fuel cells designed for electricity production make use of hydrogen oxidation on the anode and oxygen reduction on the cathode. Individual cells contain two electrodes separated by the membrane, diffusion layers and bipolar plates. Electrolytic membrane, electrodes and diffusion layers are located between bipolar plates, with channels for equal distribution of fuel and oxidant. Most of the elements in the cell are made of carbon-based materials. The significant part of the PEMFC stack is the bipolar plates, which account for about 80% of total weight [1] and 45% of generator cost [2]. The requirements for a bipolar plate material are good thermal and electric conductivity, chemical stability in anodic and cathodic environmental, lightweight, inexpensive and easily manufactured [3,16]. By many authors, the ideal material for bipolar plates is graphite despite its brittleness and lack of mechanical strength or composites based on graphite [4-6].

Another carbon material was used for diffusion layers in PEMFC. Gas diffusion layers (GDL) support the effective diffusivity of gases through the layer [7, 8]. For the proper functioning of GDL, it is typically coated with non-wetting polymer polytetrafluoroethylene (PTFE) to create hydrophobic surface and pores of appropriate size [9]. The type of pores provide proper transport media in the cell. The influence of porosity on the efficiency components of the fuel cell is dealt by Lee et al. [10]. In this work, they prepared different porous gas diffusion layers by applying. Also, there are information about finding the optimum porosity and distribution of pore size in GDL. A novel composite bipolar plates based graphite were examined by Kuan and al. [11]. The porosity of the composites increased as the graphite size is decreased from 1000-177 µm. The graphite composites with vinyl ester resin show good corrosion resistance and excellent flame retardence.

By IUPAC (International Union Pure and Applied Chemistry) the porous material can be distinguished in the field of micro pores (diameter <0.002 µm), mesopores (diameter 0.002-0.050 µm) and macro pores (diameter >0.050 µm) [12]. Micro pores and mesopores determine the size of the inner surface and have an important role in adsorption processes. Macro pores act as transport routes for access to smaller pores (transport pores). The next important factor, in addition to pore size, is their shape. The pores can take the form of spherical bubbles, narrow slits, rods [13]. They can be open or closed.
It is also important the dimensional distribution of pores in the material. The pores shape is illustrated in Fig. 1a.

Knowledge of the distribution and shape of the pores allows for a variety of application (see Fig. 1b). Following the prospect of the use of materials on elements of fuel cells, information on the structure and size of pores, channels, over two discontinuities, are extremely important. Furthermore, knowledge of the nature of the porous material allows for various possibilities of using materials for diffusion layers, porous membranes, bipolar plates [14].

2. Experimental Part

The graphite powder Graphite FC manufactured by Schunk Kohlenstofftechnik GmbH (Germany) was investigated. The graphite powder was compacted with the load of 200 MPa by axial compression, and then sintered at the temperature of 1250°C for 30 minutes in vacuum. In order to compare the properties of sintered graphite materials used in the construction of a low-temperature fuel cell, commercial Graphite Grade FU 4369, and carbon paper Toray Teflon Treated were tested.

3. Results and Discussion

The samples were subjected to structural testing by means of an Axiovert optical microscope. Hardness tests for the carbon materials were carried out by means of Rockwell method.

The density and hardness of carbon materials were depicted in Table 1.

<table>
<thead>
<tr>
<th>Material</th>
<th>Density [g cm(^{-3})]</th>
<th>Hardness Rockwell</th>
</tr>
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<tbody>
<tr>
<td>Sintered Graphite</td>
<td>1.97</td>
<td>97 HRF</td>
</tr>
<tr>
<td>Graphite Grade FU</td>
<td>1.87</td>
<td>100 HRB</td>
</tr>
<tr>
<td>Toray Teflon Treated</td>
<td>0.67</td>
<td>Not tested</td>
</tr>
</tbody>
</table>

The porosity were carried out using mercury porosimeter PoroMaster 33. Properties of the sinters are presented in Table 2.

<table>
<thead>
<tr>
<th>Material</th>
<th>Porosity [%]</th>
<th>Contact angle [deg]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sintered Graphite</td>
<td>10.73</td>
<td>102 ±0.37</td>
</tr>
<tr>
<td>Graphite Grade FU</td>
<td>0.93</td>
<td>70 ±0.15</td>
</tr>
<tr>
<td>Toray Teflon Treated</td>
<td>63.0</td>
<td>110 ±0.45</td>
</tr>
</tbody>
</table>

Microstructure analysis revealed visible, irregular pores which were unevenly distributed throughout the material (Fig. 2).

![Fig. 1. a) The pore shape diagram; O - open; B - bottle; C - closed; T - transport; b) Characteristic hysteresis loops for pores formed within aggregates [15]](image)

![Fig. 2. Microstructure of the carbon materials, magnitude 500x](image)

![Fig. 3. Hysteresis of mercury intrusion/extrusion in carbon materials](image)
Distribution of pores in examined materials is observed in Fig. 4. The Graphite Grade FU had a monomodal pore size distribution varying in the range of pore size 0.009-0.013 µm and porosity 0.93%. For Toray Teflon Treated and Sintered Graphite the distribution of pores is a heterogeneous form. In the case of a heterogeneous pore volume distribution curve for interpretation of the description of the actual structure of the pores inside the particles is difficult. Most of the larger pores can be, for example, on the surface of the carbon particles or between micro particles while the narrower pores may be within the grain, being an extension of the wider pores. The pores size of Sintered Graphite and Toray Teflon Treated are respectively 0.032-0.046 µm; 0.05-0.787 µm and 0.01-10 µm. The consequence of the high porosity of the material is its high active surface (Fig. 5). Toray Teflon Treated with 63.0% porosity shows the specific surface area about 2.64 cm² g⁻¹.

Surface properties of materials such as porosity, surface roughness, are closely affect of wettability. The analysis of wettability was carried out through evaluation of Θ angle. Sintered Graphite and Toray Teflon Treated belong to a group of hydrophobic materials (Table 2, Fig. 6) (Θ angle above 90°).

Corrosion resistance of materials depend on wettability. The presence of water on the material surface initiates the corrosion processes. Fig. 7 presents potentiokinetic curves recorded for carbon materials in solution of 0.1 mol dm⁻³ H₂SO₄ + 2 ppm F⁻ (PEMFC environmental) at 80°C. It was observed on the basis of the course of potentiokinetic curves that the carbon materials do not show a passive range (after exceeding of corrosion potential, solubilization of the material occurs with the rate increasing with rise in the level of potential).

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Polarization curves were used for determination and evaluation of corrosion parameters: corrosion potential (E_corr) [V], current density (i_corr) [A cm⁻²] (Table 3). The highest corrosion resistance (the low value of current density) is observed for Sintered Graphite and Toray Teflon Treated.

### Table 3

<table>
<thead>
<tr>
<th>Material</th>
<th>E_corr [V]</th>
<th>i_corr [A cm⁻²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sintered Graphite</td>
<td>0.098</td>
<td>1.663 · 10⁻⁴</td>
</tr>
<tr>
<td>Graphite Grade FU</td>
<td>0.092</td>
<td>0.012 · 10⁻¹</td>
</tr>
<tr>
<td>Toray Teflon T.</td>
<td>0.248</td>
<td>1.404 · 10⁻⁴</td>
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4. Conclusion

In Figure 8 summarizes the results of the study. It demonstrated the relationship between the wettability of the material and a corrosion-resistant porous material. The porosity of less than 10% gives a material wettable. The increase in porosity of the material changes the surface properties and provides a hydrophobic material.
Fig. 8. Effect of porosity onto contact angle and corrosion resistance of carbon materials

Effect on the corrosion resistance of the material structure, chemical composition, corrosive environment (a kind of solution, temperature, mixing) were examined. Taking into account the porosity of the material, the general conclusion can be drawn that the value of in excess of 10% ensures high resistance to corrosion in the tested conditions. Positive effect on the corrosion resistance is also a property of repulsion of drops of the solution (hydrophobicity).

REFERENCES