Gaz Diffusion Layers from functional carbon materials for fuel cells used in energy installations

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Abstract. Gas Diffusion Layers (GDL) for fuel cells are two-dimensional carbon materials designed to obtain a smaller thickness, greater bending stiffness, lower residual deformation and lower compressibility compared to analogs. To produce it, functional carbon materials were used: activated carbon of own production, from vegetable raw materials, acetylene black and single-walled Tuball nanotubes. Dependence on the amount of binder is shown, as are the properties of electrodes made by calendering. The resistance of the rolled electrodes is much lower than that of the sputtered electrodes. There are proposed 4 variants of electrodes, which can be used in fuel cells and are used in power energy installations.

1 Introduction

The use of electricity as the most convenient, effective and widely used in various sectors of the economy and in the life of the energy carrier, in contrast to other intermediate energy carriers, whose energy is stored in chemical or other forms, requires at every moment a strict equality of the electric power supplied to the consumer and consumed by it. At present, research in the field of new materials and technologies for sources and accumulators of electrical energy is being carried out quite intensively all over the world. This is due to the hopes for solving a number of problems of energy, ecology, transport and some industries through the use of cheap and safe sources and accumulators of electrical energy with a long service life. The role of the development of new materials, technologies for the formation of active layers and electrodes, electrolytes and other components is crucial in achieving the targets for prices, service life, specific characteristics of energy sources.

At present, fuel cells (FCs) and batteries are widely used for power generation in transport, utilities, portable electronic devices and other applications. The most common types of fuel cells are phosphoric acid, with polymeric proton-exchange membranes, alkaline, methanol, direct conversion, regressive, zinc-air, solid oxide, etc.

One of the necessary components of the FC is a structural element in the form of sheet material with a high porosity, a good gas permeation, involved in electrochemical reactions, having a high electrical conductivity. According to the existing terminology, such an element is called a gas diffusion layer (GDL).

GDL is an important component of FC and perform the following functions: deliver gases and liquid reagents (fuel and oxidant) to the desired electrodes and distribute the reagents in a necessary and controlled

manner; provide mechanical support for membranes and electrocatalytic catalyst beds; lead and withdraw electrons to / from the electrodes; help to remove heat; ensure the transfer of loads of the seals of the fuel cell assembly; participate in the interfacing of the internal parts of the FC battery.

It is not surprising that the world's leading manufacturers of fuel cell systems pay close attention to both the technical and operational characteristics of GDS, and their cost. The most important components for the fuel cell battery market are bipolar plates and membrane-electrode blocks (OIE). The OIE is a structure consisting of a catalyst-coated membrane between two layers of HDPE, which are sintered by hot pressing. GDL and catalytic inks are the most expensive subcomponents of the OIE in the FC battery. To create cheaper and more affordable GDL from functional carbon materials, our work is directed.

The proposed GDL has a two-layer construction in which a conductive microporous layer is applied over a macroporous carbon substrate. The sublayer of the basic material consists of hydrophobized macroporous activated carbon and acetylene black. Microporous sublayer is thinner and in turn consists of microporous activated carbon with nanocarbon additives (nanotubes, soot, etc.).

The porous structure and properties of the functional carbon material from which it is made play a decisive role in the efficiency of the electrode (GDL with the catalyst on its surface) functioning. To obtain the maximum specific electrochemical characteristics of MEAs, a certain type of carbon material is selected for each GDL sublayer, so for the main layer – macroporous carbon, with wider pores, and for the upper, active layer – microporous coal with a developed surface. The most suitable material is activated carbon

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(AU). It has a relatively low cost, is widely available, stable in many environments, has high conductivity [1].

The main surface area of the porous coal is in the micropores. However, it is necessary to select the optimal porous structure of coal, achieving the maximum specific electrochemical characteristics of the MEAs and the minimum internal resistance.

In addition to the effect of pore size distribution on activated carbons, an important factor is the porous structure of the layer itself, namely its formation method.

In our case, we offer a method of cold calendaring (rolling), in comparison with conventional spraying. The internal resistance of electrodes formed by the sputtering method is higher than when using electrodes made by calendaring. Most likely, this is due to the peculiarities of the formation of the electrode structure for various methods of their manufacture. Sputtered electrodes have a more friable structure [2]. Their density is lower than that of electrodes made by calendaring. Consequently, the contact of the coal particles with each other and, mainly, with the conductive substrate in the case of sputtered electrodes is much worse than in the case of the rolled up electrodes. Nevertheless, thin sprayed electrodes show the best performance even at high currents.

The method of calendaring electrodes is more technologically advanced than the method of sputtering. It allows to manufacture electrodes in a wide range of thicknesses. The resistance of the rolled electrodes is much lower than that of the sputtered electrodes.

2 Technique of the experiment

For the production of GDL, functional carbon materials were used: activated carbon of own production, from vegetable raw materials and single-walled nanotubes Tuball. When mixing a mixture of coal and fluoroplastic, as well as in the manufacture of electrodes, the temperature of the mixture was always above 19°C. This is important in terms of fibrillation of fluoroplastic particles. Fluoroplast F-4 has two phase transitions: at 19°C and 30°C [3, 4]. At a temperature below 19°C, the formation of fibers (ie, "unwinding" of PTFE particles) does not practically occur. At temperatures above 19°C and 30°C, fluororesin is increasingly fibrillated. When kneading a creamy mixture of coal and a fluoroplastic slurry, it manifests itself in the adherence of the whole mixture to one lump (kneading at low temperatures does not lead to the formation of a lump). However, such a mixture does not yet have strength (like plasticine). This is due to the low percentage of "unwound" PTFE particles. During calendaring, the number of unwound PTFE particles sharply increases and the electrode, in addition to becoming the desired shape, also acquires the necessary strength. However, bringing the electrode to the ready state has a number of subtleties. Even a small feature during calendaring can affect the final characteristics of the electrode.

3 Results and discussion

With an increase in the proportion of the binder, the density of the GDL increases, which, firstly, is due to the replacement of porous carbon by a continuous fluoroplastic, and, secondly, to the denser packing of coal particles in the electrode (Fig. 1). For the rolled GDL, their hydrophobicity strongly increases with increasing the proportion of PTFE in the electrode. With a large proportion of the binder, hydrophobic formations from fluoroplastic filaments cover a substantial portion of the coal particles, blocking the access of the electrolyte to the micropores.

Thus, the choice of the amount of binder based on the aqueous suspension of PTFE, in the first place, can be determined by the requirements for manufacturability of the manufacture and strength of the electrodes and has little effect on the electrochemical characteristics of the electrodes.

Fig. 1 Dependence of the internal resistance of the fuel cell on the content of fluoroplastic in the rolled GDL 1-thickness GDL 200 mkm, 2- electrode thickness 100 mkm.

Depending on the amount of binder, the properties of the electrodes vary, such as strength, specific and contact resistance, hydrophobicity and capacity. From the point of view of further introduction of these technologies into mass production of HDS, calendaring technology is more preferable, since it is easier to implement. With its help, it is possible to produce electrodes of large thickness, which have low resistance and sufficiently high specific electrochemical characteristics. Sputtering technology can find application in the formation of a catalytic layer on an already prepared GDL.

The gas diffusion layer is a porous layer that ensures effective diffusion of the reagents to the catalytic layer. In addition, the GDL must have good electrical conductivity, since it is a conductor through which electrons are transferred to and from the catalytic layer. Usually GDL is made of a porous carbon material with a thickness of 100 ... 300 mkm. GDL also participates in water management, allowing some water to reach the membrane and moisten it.

One of the important components of the electrode is the insignificant (less than 1%) addition of carbon nanotubes increasing the strength and electrical conductivity of the GDS. Figure 2 shows a micrograph of the layer with the addition of Tuball nanotubes from OCSiAL, which shows the highly developed active surface of the GDL.

Fig. 2 SEM microphotographs for GDL electrodes with conductive additive – Tuball single-walled carbon nanotubes.

Gas diffusion layers for fuel cells are two-dimensional carbon materials designed to obtain a smaller thickness, greater bending stiffness, lower residual deformation and lower compressibility compared to analogs. Table 1 lists 4 types of GDL developed: GDL1A, GDL1B, GDL2A, GDL2B, with the corresponding characteristics.

Table 1. Properties of GDL.

Characteristic	Units	GDL1A	GDL1B	GDL2A	GDL2B
Thickness	mkm	190	235	190	235
Volume weight	g/m ²	54	100	40	86
Porosity	%	84	76	88	80
Breathability	cm ³ /(cm ² ·s)	60	0,6	210	1,0
Electrical resistance (perpendicular to the surface)	mOm·cm ²	< 10	< 12	< 10	< 12

4 Conclusion

The GDL is proposed as a two-layer construction in which a conducting microporous layer is deposited over a macroporous carbon substrate. To produce it, functional carbon materials were used: activated carbon of own production, from vegetable raw materials, acetylene black and single-walled Tuball nanotubes.

The results of the research showed that the internal resistance of electrodes formed by the sputtering method is higher than when using electrodes made by the method of cold calendering (rolling). The method of calendering

electrodes is more technologically advanced than the method of sputtering. It allows to manufacture electrodes in a wide range of thicknesses. The dependence on the amount of binder is shown, how the properties of the electrodes change, such as strength, specific and contact resistance, hydrophobicity and capacity.

Thus, four variants of electrodes have been developed, which can be used in fuel cells used in power energy installations.

References

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