Gas diffusion layers based on graphene flakes doped with nitrogen

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Abstract. Studies of the effect of nitrogen-containing graphene on the structure of the water-repellent agent and the activity of gas diffusion cathodes for air-metal fuel cells have been carried out. The nitrogen-containing graphene is synthesized by plasma method using a DC plasma torch. It was found that the volume of the synthesis of the structure of a plasma jet of graphene has the form of crumpled flakes up to 700 nm in size. The water-repellent agent in the gas diffusion layer based on graphene forms a network that structures the graphene flakes. For comparison of the electrochemical characteristics of gas diffusion electrodes, a gas diffusion layer was made based on activated carbon with a particle size of 700 nm to 10 μm. The method of scanning electron microscopy illustrates the effect of particle size and their packaging on the characteristics of the electrodes. With a decrease in particle size and lower density of fit to each other, the potential of the cathode based on nitrogen-containing graphene in the region of high current densities increases.

1. Introduction
Gas Diffusion Layers (GDL) are key components in various types of fuel cells, including Proton Exchange Membrane (PEM), Direct Methanol (DMFC) and Phosphoric Acid (PAFC) stacks as well as in other electrochemical devices such as electrolyzers. Gas diffusion layers (GDLs) should allow the flow of reactant gases H₂, air/oxygen and product gases to pass through it, help remove by-produced water outside of the catalyst layer and prevent flooding, and keep some water on surface for conductivity through the membrane. From studies [1, 2] it is known that the activity and stability of GDL are determined by their composition, method of manufacture and surface structure. Therefore, there are various methods to optimize the GDLs performance. For example, GDLs are pre-coated with polytetrafluoroethylene (PTFE), which changes the properties of the GDL material from hydrophilic to hydrophobic. According to the literature, the use of nanostructured carbon provides for the creation of a porous structure with optimal hydrophilic-hydrophobic properties, which improves the performance characteristics of gas diffusion electrodes [3, 4]. A feature of graphene is that it is a thin layer of pure carbon, therefore its properties can vary greatly under the influence of contact with various substances. On the other hand, the presence of impurities and defects also has a significant effect on the characteristics of graphene. The substitution of carbon atoms by nitrogen ones influences the atomic charge distribution on the graphene scaffold and creates “active sites” thus significantly increasing the electrochemical activity of nitrogen-doped graphene, known as N-graphene [5, 6]. In this study, plasma-assisted N-graphene was used to fabricate graphene-containing gas diffusion layers to investigate its effect on fuel cell performance.
2. Methods
The optimal composition of air hydrophobized cathodes consisting of two layers was experimentally established: active, containing 90% of the catalyst and 10% of fluoroplastic and gas diffusion, barrier layer consisting of acetylene black (65%) and fluoroplast (35%). The active layer faces the electrolyte and is responsible for the catalysis of the reduction of air oxygen. The gas diffusion layer prevents the penetration of the electrolyte on the side of the electrode facing the air, and ensures the diffusion of the oxidizing agent – oxygen from the air – to the active layer.

This paper presents studies of active layers with catalysts, on the basis of nitrogen containing graphene and, for comparison, with a catalyst based on activated carbon of the UAF brand.

To synthesize nitrogen-doped graphene, we used a plasma jet reactor. A detailed description of the experimental setup is given in [7]. The experiment included the simultaneous introduction of a propane-butane mixture (carbon precursor) with plasma-forming gas (nitrogen) into 42 kW DC plasma torch, wherein heating and decompositions occurred in the plasma jet and in the region of the arc discharge, followed by condensation of the synthesis product on the surface of the коллектора. The rate of carbon precursor, plasma gas flow and the power of the plasma torch varied independently of each other.

To study the products of synthesis, electron microscopy and X-ray photoelectron spectroscopy were used. To visualize the morphology of the gas diffusion layers produced by us, we used a Nova NanoSem 650 scanning electron microscope using the standard technique.

XPS measurements were carried out in an ultrahigh vacuum chamber (∼5×10⁻¹⁰ mbar) equipped with an X-ray source (Mg Kα, 12.5 kV, 250 W) and a hemispherical energy analyzer Phoibos 150 SPECS Germany). The samples were glued in an even continuous thin layer on carbon tape. The adhesive tape was glued to the molybdenum substrate for the samples. The spectrometer was calibrated using Au 3d5 / 2 peaks, whose energy corresponded to 368.27 eV. The survey spectra and spectra of individual peaks were recorded at a constant transmittance energy of the analyzer of 100 and 20 eV, respectively. The relative concentrations of the elements were determined on the basis of the areas under the photoelectronic peaks, which were recalculated in concentration using the software Casa XPS, which takes into account the coefficients of elemental sensitivity and the geometry of the survey.

For the fabrication of gas diffusion electrodes, we used the technology to form the network structure of the polymer [8]. After drying the suspension of the hydrophobic polymer with the filler, the resulting solid phase was repeatedly rolled in one direction. In the process of rolling, a mesh is formed in the material, which has a larger specific surface than the initial agglomerated structure.

The activity of the air cathodes was characterized by a non-current potential and polarization (a change in potential with increasing current density). The setup diagram for the study of electrodes is presented in figure 1.

**Figure 1.** Measurement scheme: 1 – potentiostat, 2 – electrochemical cell, 3 – thermostat, 4 – air cathode, 5 – Ag / AgCl reference electrode, 6 – thermometer, 7 – counter electrode.

A two-layer electrode with a working surface of 7 cm² (4) was installed in an electrochemical three-electrode cell (2). The cell was filled with an alkaline electrolyte and heated using a liquid thermostat (3). When the temperature controlled by the thermometer (6) reached 60 °C in the cell, the electrochemical characteristics of the electrode were measured in the reaction of cathode reduction of
oxygen in air. For this, the Solatron-1285 (1) potentiostat was used, which is controlled by a PC and the CorrWare software package and CView. The cathode potential was determined relative to the reference electrode with silver chloride (Ag / AgCl) (5). The current of this direction and power was maintained by a potentiostat. In galvano-dynamic mode of operation, the potentiostat changed the value of the current flowing between the cathode and the counter-electrode (7). The rate of change of current was 0.08 mA / s. With increasing current, the potential of the cathode shifted towards negative values. When reaching the potential of the cathode below –0.6 V, the process was terminated.

3. Results and discussions

Figure 2 presents the typical morphology of graphene materials. With the decomposition of hydrocarbons in the volume of nitrogen plasma at 350 Torr, the synthesis products are dome-shaped flakes (figure 2(a)). This morphology is explained by the presence of nitrogen atoms on the surface.

It is known that nitrogen atoms are able to penetrate into the graphene lattice in many different ways, characterized by different configuration of interatomic bonds [5]. Three different types of nitrogen impurities are most often observed in graphene and carbon nanotubes: substituting (or graphite-like) N, pyridine N and pyrrole N. Each of these configurations leads to different changes in the electronic properties of graphene. In the spectra of N 1s (figure 2(b)), several states are distinguished. The peaks located at 398.2, 399.5, 400.8 and 402.2 eV are attributed to pyridinic, amino, graphitic and N-O species, respectively.

![Figure 2. SEM image of N–graphene flakes synthesized in nitrogen plasma at 350 Torr (a). The precursor is propane-butane. Fitting the N 1s spectrum of the sample of N–graphene flakes (b).](image1)

![Figure 3. SEM images of top-view of the structure of the active layer of N–graphene flakes (a). SEM images of top-view of activated carbon based active layer structures (b).](image2)

Figure 3(a), (b) shows the image of the structure of the surface layer of the cathode based on N-graphene. The figure 3(a) shows the presence of well-distributed graphene layers in the GDL, on the surface of which a fluoroplast mesh is formed. These layers loosely adjoin each other and thus form irregular thin gaps, which causes an increase in the surface roughness. At the same time, the
aggregates of activated carbon, although connected by filaments of fluoroplast, form rather large gaps (figure 3(b)). In general, electron microscopic examination showed a difference in the microstructure of the catalyst layer of activated carbon and N-graphene. This difference causes the different nature of the polarization curves.

![Figure 4](image_url)

**Figure 4.** Polarization curves (I–V curves) of the PEMFC with NG and with AC.

The polarization curves of cathodes with N-graphene in comparison with cathodes based on UAF activated carbon are presented in figure 4. Up to a current density of 100 mA/cm², the polarization curves overlap each other, which indicate their identical activity. With a further increase in the current density, the polarization of the UAF-based cathode increases due to diffusion difficulties. On graphene, the potential is greater in the region of high current densities. The graphene particles are smaller and it can be assumed that oxygen will penetrate into such a structure faster due to better diffusion.

Thus, the experiments carried out indicate the promising use of graphene doped with nitrogen in fuel cells both as a catalyst carrier with an increased area, and to improve the parameters of the gas diffusion layer.

### 4. Conclusion

In conclusion, it should be noted that the plasma-chemical process was applied to the synthesis of crumpled nitrogen-doped graphene in order to achieve improved characteristics of gas diffusion cathodes. Synthesis in the plasma jet volume plays an important role in the formation of graphene morphology, due to which its aggregation does not occur in the gas diffusion layer. Our electrochemical characteristics showed that a decrease in particle size and an increase in surface roughness due to irregular thin gaps in the layer leads to an increase in gas permeability (oxygen diffusion), which increases the potential in the high current region. The N-graphene cathode fabrication method developed here is simple and compatible with scaling.

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