Surface Modification of Nafion Membrane Electrolyte by Ion Beam Assisted Deposition of Platinum and Rare Earth Metals from Vacuum Arc Discharge Plasma

Модифицирование поверхности мембранного электролита Nafion ионно-ассистируемым осаждением платины и редкоземельных металлов из плазмы вакуумного дугового разряда

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Nafion membrane, which is a fluorocarbon polymer contained functional sulfogroups, has proton conductivity in the wet state and is used as an electrolyte for low-temperature hydrogen and direct methanol and ethanol oxidation fuel cells (DMFC, DEFC) – perspective chemical sources of electric current. Catalysts are needed for effective operation of fuel cells.

The main functional component of a fuel cell with a polymer membrane electrolyte is the membrane electrode assembly (MEA) consisting of an ion-conducting membrane, catalytic layers and diffusion layers from porous materials in contact with it, through which the fuel and oxidizer are supplied, the current is collected, and the products of the electrochemical reaction are removed (Fig. 1).

We have developed a method for the formation of catalytically active layers on the surface of carriers by introducing active metals during their ion beam assisted deposition (IBAD) from a vacuum arc discharge plasma. The deposition of the metal and the mixing of the deposited layer with substrate by accelerated ions of the same metal were performed with use of the experimental setup from neutral fraction of metal vapor and ionized fraction of plasma, respectively, of a vacuum arc discharge of the pulsed arc ion source.

In particular, by IBAD of platinum and one of the rare earth metals active surface were formed on the diffusion layers from special carbon AVCarb® Carbon Fiber Paper P50 and Toray Carbon Fiber Paper TGP-H-060 T catalyst carriers in order to obtain electrocatalysts for DMFC and DEFC [1].

The aim of this work is to study the composition of similar catalytic layers prepared on Nafion™ N115 membrane by IBAD of platinum as basic catalytic metal and one of rare earth metals (Gd, Dy, Ho) as an activating additive.

Experimental

Formation of catalytic layers:

Ion beam assisted deposition (IBAD) of platinum or platinum and one of rare earth metals (Gd, Dy, Ho) is implemented out in experimental setup of neutral fraction of metal vapor and ionized plasma of pulsed electric arc. The ions of the deposited metal have an effect of ions assisting to the process.

Ion accelerating voltage 5 kV; vacuum 10^{-2} Pa; RT.

Support samples – Nafion™ N115 membrane; *d* = 127 μm, 50 × 50 mm.

Methods for investigation of the layers composition and microstructure:

SEM + EDX (JSM-5610LV microscope, EDX JED-2201 spectrometer (JEOL); 20 keV);
(LEO1455VP microscope, AZtec Energy Advanced X-Max80 (Oxford Instruments) spectrometer; 20 keV);

WDX-XRF (LiF (200) crystal; PANalytical Axios spectrometer, Netherlands);

RBS (^{4}He; E_0 = 1.5 MeV; Θ = 170°; AN-2500 accelerating complex (High Voltage Engineering Europe))

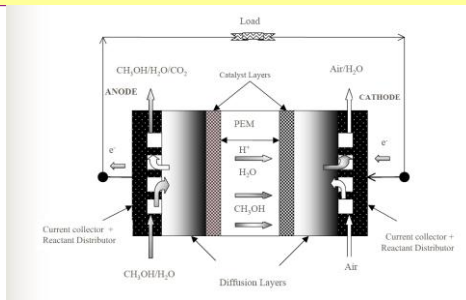

Fig 1. Operating principle of direct methanol fuel cell (DMFC) with polymer membrane electrolyte

Source: S. Basu FUEL CELL SYSTEMS http://web.iitd.ac.in/~sbasu/FC-Descrip.pdf

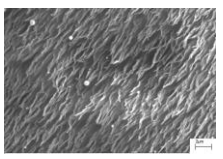

Fig. 2. SEM image of the Nafion™ N115 membrane with layer formed by the IBAD of platinum [2]

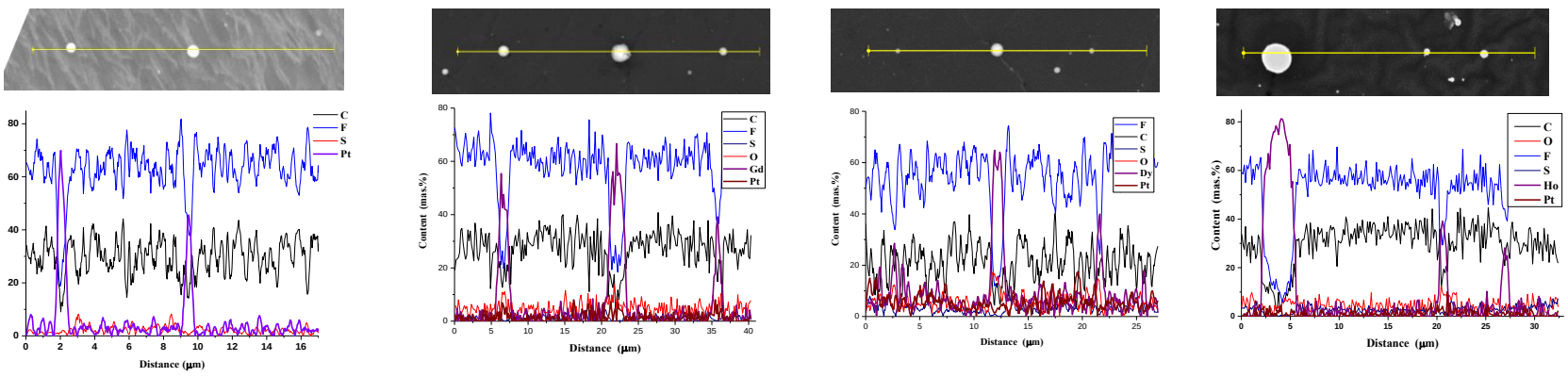

Fig. 3. SEM images and distributions of atoms of elements across the scanning line (according EDX) over the surface of the Nafion™ N115 membrane with investigated layers

Composition of the studied layer includes atoms of the deposited metals and atoms of components of the membrane itself: carbon, fluorine and sulfur, also oxygen as an impurity (Fig. 3–5).

The deposited metals are distributed over the entire surface of the samples with a concentration of several percent. Against the background of the regular structure of the studied surface, there are inclusions of deposited metals about a micrometer in size due to the deposition of metal droplets from the arc discharge of an ion source (Fig. 2, 3).

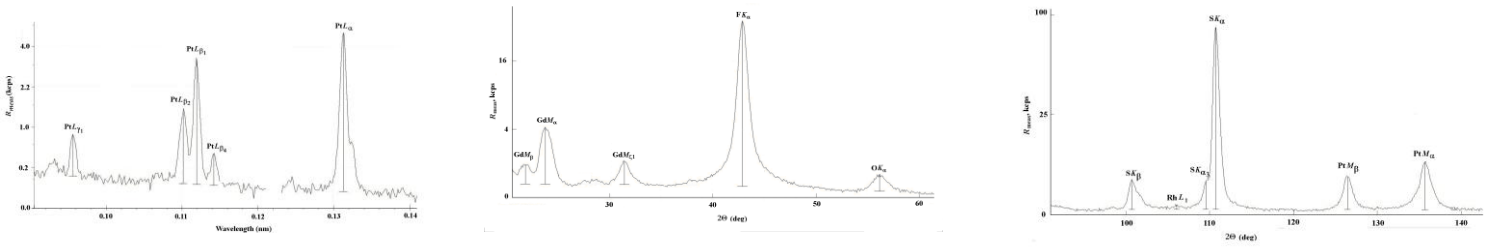

Fig 4. Fragments of the WD-XRF spectra of elements in the composition of the layer formed by IBAD of platinum and gadolinium on Nafion™ N115 membrane.

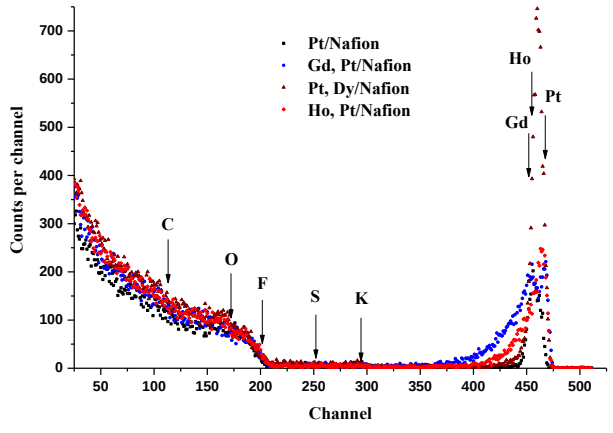

Fig. 5. RBS spectra of ^{4}He ions from surface of Nafion membrane with layers formed by IBAD of platinum and rare earth metals

Conclusions

Modification of the surface of the polymer membrane Nafion™ N115, which is used as an electrolyte for fuel cells, was performed by ion beam assisted deposition (IBAD) of platinum as basic catalytic metal and one of rare earth metal (Gd, Dy, Ho) as an activating additive from a neutral vapor fraction and plasma of a vacuum arc discharge of a pulsed electric arc ion source, respectively. The choice of deposited metals is determined by the peculiarities of the mechanism of catalytic electrochemical oxidation of methanol and ethanol.

In the process of IBAD of metals in the proposed mode multicomponent catalytic layers are formed due to radiation mixing of the atoms of the deposited metal with the atoms of the Nafion substrate by accelerated ions.

The thickness of the prepared layers is ~30 nm; content of each of deposited metal atoms in the layers – ~(0.5–1) × 10^{16} cm^{-2}. In the maximum of distribution located near the surface, the concentration of each of the deposited metals is about several atomic percent (RBS data).

[1] J. Surf. Investig. X-ray, Synchrotron and Neutron Techniq. 13 (2019) 1314.

[2] IEEE Book Series: 7th International Congress "Energy Fluxes and Radiation Effects" (EFRE-2020) 756.