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Alumina membranes as a mask for the structures used in hydrogen energy[☆]

V.A. Moshnikov^{*}, E.N. Muratova, Yu.M. Spivak

Saint Petersburg Electrotechnical University “LETI”, 5th Prof. Popova St., Saint-Petersburg, 197376, Russia

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ABSTRACT

The paper deals with the advantages of porous alumina membranes as templates for technological structures used in hydrogen economy and describes the features of membrane technology as well as characterization methods of their geometrical parameters. In order to determine surface porosity, two methods (such as theoretical calculations and digital image processing) have been used. It has been shown that the results are in good agreement with each other.

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Introduction

Permanent attempts to solve problems related to hydrogen synthesis and the use of hydrogen as alternative fuel in various spheres of production could be the driving force for the development of new approaches, while developing the technology of forming the materials capable to decompose water into hydrogen and oxygen [1]. An active research work in the field of hydrogen economy has resulted in considerable enhancing the potential of membrane technologies. The release of hydrogen and hydrogen purification are considered to be one of the main problems, so selectivity, thermal and chemical stability, as well as permeability and strength have become key parameters for membranes.

Nanoporous materials may be a challenging trend in catalysis [2], and they could be used as micro- and nano-reactors [3], as well as high-selective and highly sensitive sensors [4]. The porous structure may have a property package

(variants of analytical response). The existence of cavities could result in a drastic increase of specific surface area along with a change in heat conductivity and other physical properties of the material [5]. Such properties may allow using porous silicon, for example, as composite proton exchange membranes or fuel-cell (cathode, anode) electrodes as a component of a monolithic fuel cell [1]. Membranes based on nanoporous alumina (por- Al_2O_3) have been used in its turn in this field of science independently as well as in combination with porous silicon [6] as masks (templates) due to the controllable porous structure. The masks may allow forming ordered carbonic gas separation membranes [7], membranes for hydrogen separation containing a porous substrate made of Al_2O_3 with a deposit of palladium [8] etc.

The review of membranes such as Nafion and MF-4SK used in fuel cells today has shown that not all pores may be filled with water in these membranes and make a contribution to protonic conductivity, so the so-called dormant channels

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^{*} Corresponding author.

E-mail address: Sokolovaeknik@yandex.ru (V.A. Moshnikov).

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Nomenclature

a	Coefficient in formula
j	Current density
n	Coefficient in formula
nm	Nanometer
mole %	Mole percent

Greek Letters

μm	Micrometer
τ	Time, min

Acronyms

AFM	Atomic force microscopy
GSR	Galvanostatic regime
MF-4SK	Type of the ion-exchange membrane
SEM	Scanning electron microscopy
PSR	Potentiostatic regime
por- Al_2O_3	Porous anodic alumina
RFBR	Russian Foundation for Basic Research

Superscripts and subscripts

-a	A degree in the formula
membr	Membrane

would be formed. While the membranes based on alumina may represent a solid monolith of vertical homogenous through pores aligned in relative positions [9].

Thus, the purpose of the paper is to investigate properties and parameters of the membranes based on por- Al_2O_3 as well as their applicability for developing hydrogen economy structures.

The method for producing porous alumina

The forming of por- Al_2O_3 has been carried out by electrochemical anodizing at constant current (galvanostatic regime – GSR) or at constant voltage (potentiostatic regime – PSR) in one-compartment cell with provision for system temperature

control. The electrolytes based on water solutions of orthophosphoric (H_3PO_4) and sulphuric (H_2SO_4) acids [10].

The control over anodizing process in the *in situ* regime has been exercised by the analysis of potentiostatic and galvanostatic dependences for Al/electrolyte systems. The quality of the running process (forming of the membrane, the existence of the mordant etc.) could be evaluated by their curves. Fig. 1 illustrates Al/electrolyte system curves for several set of samples (aluminum foil is a source material; 20% H_2SO_4 is electrolyte).

The presented results show that the curves may almost mirror one another. This could indicate the process repeatability. Two areas could be marked out on the plot: I is an area of a porous layer forming (before t_{membr}); II is an area of the membrane forming (after t_{membr}). For the dependences corresponding to weaker anodizing current (Fig. 1b), an area of voltage peak may start later in time (t_{membr}). This could be explained by the fact that the higher current density is, the more active the porous layer growth would be as well as the more rapidly a source substrate would be expended, and etching of the barrier layer would occur. Anodizing time may be decreased almost twice as little with the increase of anodizing current twofold. The porous layers of a given depth could be formed by varying time and current density.

Results and discussion

The methods of scanning electron microscopy (SEM) and atomic force microscopy (AFM) may be used widely while investigating the parameters of por- Al_2O_3 porous structure and other porous materials [11,12]. It is conventional to use the ordering coefficient which is the ratio of number of cells arranged hexagonally relative to each other to the total number of cells over the selected por- Al_2O_3 surface area for the quantitative assessment of the por- Al_2O_3 crystallinity degree. The assessment of the ordering at macrolevel is of importance as this parameter may determine the characters and the sizes of working spaces of functional structures based on por- Al_2O_3 .

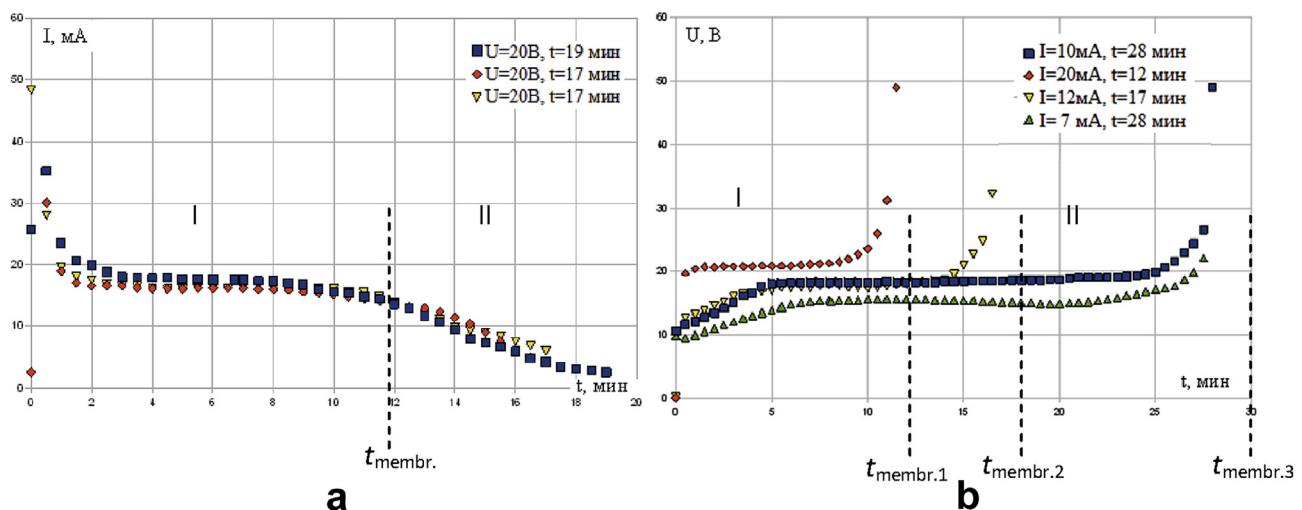


Fig. 1 – Potentiostatic (a) and galvanostatic (b) curves of Al/electrolyte system: I is an area of a porous layer forming (before t_{membr}); II is an area of the membrane forming (after t_{membr}).

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