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FORMATION OF THE ORGANIC-INORGANIC PROTON EXCHANGE MEMBRANE

A.O. Maizelis, B.I. Bairachniy, G.G. Tul'skiy. Формування органо-неорганічної протон-обмінної мембрани. Застосування електролізерів низькотемпературного розкладання води з твердою полімерною мембраною є перспективним для одержання водню з використанням відновлювальних джерел енергії. Однак висока вартість мембранних матеріалів перешкоджає масовому впровадженню таких електролізерів. Більшу частину досліджень, направлених на розробку методик формування мембран, альтернативних Nafion®, присвячено органічним матеріалам. **Мета:** Метою роботи є розробка методики формування конкурентоспроможної протон-провідної мембрани на основі полівінілового спирту (ПВС) і неорганічних гідратів. **Матеріали і методи:** Для одержання мембрани у 2...10 %-ий розчин ПВС додавали гідратований оксид олова, перемішували і пошарово наносили на інертну основу, від якої готову мембрану у подальшому відокремлювали. Для покращення її механічних властивостей використовували армуючу сітку. Гідратований оксид олова одержували взаємодією розчинів хлориду олова і гідроксиду амонію. **Результати:** Досліджено умови формування протон-обмінної мембрани на основі полівінілового спирту і гідратованого оксиду олова. Одержано серію мембран зі вмістом гідратованого оксиду олова 30, 50, 70, 80 і 90 %. Показано, що суцільна плівка мембрани товщиною понад 100 мкм може бути отримана, якщо зміст полівінілового, що дорівнює або перевищує 30 %. Показано, що необхідно проводити шшивку ПВС у одержаній плівці. Структура одержаної протон-провідної мембрани являє собою ланцюги ПВС, зшиті альдегідом, між якими розташовані глобули гідратованого оксиду олова. Провідність мембрани забезпечується як рухомістю протонів гідроксильної групи ПВС, так і за рахунок часткової дисоціації гідратованого оксиду на поверхні глобул з утворенням утворень $\text{H}_3\text{O}^+/\text{H}_2\text{O}$ і $\text{OH}^-/\text{H}_2\text{O}$.

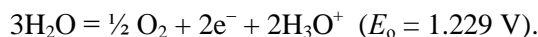
Ключові слова: протон-провідна мембрана, полівініловий спирт, гідратований оксид олова.

A.O. Maizelis, B.I. Bairachniy, G.G. Tul'skiy. Formation of the organic-inorganic proton exchange membrane. The use of electrolyzers for the low-temperature water electrolysis with the solid polymer membrane is perspective for production of hydrogen using renewable energy sources. However, the high cost of membrane materials obstructs the mass commissioning of such electrolyzers. Most of the researches devoted to the technologies of membranes formation, alternative to Nafion®, deal only with organic materials. **Aim:** The aim of this research is to develop the method for formation of the competitive proton exchange membrane based on polyvinyl alcohol (PVA) and inorganic hydrates. **Materials and Methods:** The hydrated oxide of tin was added to the 2...10 % PVA solution, mixed and applied to inert base layer by layer for formation of the membrane. Then the membrane was separated from the base. The reinforcing mesh was used to improve mechanical properties of the membrane. The hydrated tin oxide was prepared by reaction of tin chloride and ammonium hydroxide solutions. **Results:** The conditions of formation of proton-exchange membranes based on polyvinyl alcohol and hydrated oxide of tin were investigated. The series of membranes containing 30, 50, 70, 80 and 90 % of hydrated tin oxide are obtained. It is shown that a solid membrane film with the thickness over 100 μm can be obtained if the content of PVA exceeds 30 %. It is shown that it is necessary to crosslink the chains of PVA in the resulting film. The structure of the obtained proton exchange membrane consists of PVA chains crosslinked by aldehyde, between which the globules of hydrated tin oxide are situated. The membrane conductivity is provided by both proton mobility of hydroxyl group of PVA and $\text{H}_3\text{O}^+/\text{H}_2\text{O}$ and $\text{OH}^-/\text{H}_2\text{O}$ groups that are formed due to the partial dissociation of hydrated oxide on the surface of the globules.

Keywords: proton exchange membrane, polyvinyl alcohol, hydrated tin oxide.

Introduction. Recently, high interest is paid to finding the ways to improve the material for creation of hydrogen electrochemical generators with a solid polymer electrolyte. This generator (electrochemical cell) consists of two electrodes pressed against the proton exchange membrane (PEM), forming a membrane-electrode assembly. The distilled water serves as electrolyte.

The main chemical reaction on the anode is water oxidation that leads to formation of the hydronium ions and oxygen:

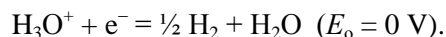


Oxygen is removed through the gas diffusion layer of the electrode. Hydronium ions pass through the proton exchange membrane, which is a solid electrolyte in electrochemical cell.

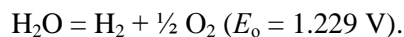
The main chemical reaction on the cathode is the reduction of hydronium that leads to the water release and hydrogen evaluation:

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Thus, the overall reaction is:



Due to the formation of protons, the media in the electrochemical cell (which is fed by deionized water) changes to acidic: the estimated concentration of protons at the standard load is about $1 \text{ mol} \cdot \text{dm}^{-3}$, i.e. pH is 1. This fact complicates both the selection of electrode materials and membranes.

The most expensive components of the cell with a solid electrolyte are proton exchange membrane and catalysts of electrode processes. The most used catalysts are platinum-group metals (platinum, palladium, iridium and ruthenium) in the form of nanoscale particles and their oxides. The most widely used solid electrolyte membrane is Nafion[®]. This membrane is a co-polymer of tetrafluoroethylene and co-monomer with side chains of perfluorinated vinyl ether ending by sulfo-group, so that proton is transferred from one sulfo-group to another one.

Among the requirements for the proton exchange membrane, that are used in water electrolysis, are high proton conductivity, low electron conductivity, low permeability of the gases (hydrogen and oxygen), high chemical stability in the acidic media, providing high speed electrode reactions, mechanical strength in the dry and humid condition, minor water transport across the membrane by diffusion and electroosmosis effects, as well as availability of materials and low production cost.

The high cost of Nafion[®] membranes has led to an active research for more reasonably priced membrane compositions. The similar perfluorinated membrane called MF-4SK was created in USSR. The number of another membranes were developed [2], but they are inferior to Nafion[®] membrane on the number of important characteristics. One of the developments is membrane based on polyvinyl alcohol (PVA) with addition of phenol-2,4-disulfonic acid [3]. PVA can conduct protons through a inherent system of hydrogen bonds. It also has high gas impermeability, which is one of the essential requirements for membranes (solid electrolytes) in electrochemical cells for hydrogen production and fuel cells. Additionally, the low cost of PVA led to the interest in practical application. However, the use of PVA is limited by its solubility in water and its insufficient proton conductivity.

On the other hand, it is known that some of the hydrated metal oxides (inorganic hydrates) of globular structure have proton conductivity. The composition of the globules inside is close to the metal oxide and the surface contains many high-active OH⁻-groups and water molecules, which provide proton conductivity [4]. For example, hydrated oxides of antimony and tin are used in sensors for hydrogen detection as a layer of a proton-conductive electrolyte. However, these precipitates are not mechanically stable hydrates and this prevents their use as membranes.

The aim of this research is to develop the method for formation of the competitive proton exchange membrane based on polyvinyl alcohol (PVA) and inorganic hydrates.

Materials and Methods. The tin chloride, ammonium hydroxide, polyvinyl alcohol and sodium sulfate ("chemically pure" qualification) were used in the work. The photographs were taken by a hardness measuring instrument PMT-3 and digital camera Canon PowerShot A1100IS. The PVA solution with concentration of 2...10 % was prepared by dissolving PVA in the heated to 50...70 °C distilled water during 2 hours and holding at room temperature until solution becomes clear.

The precipitate of hydrated tin oxide was obtained by the reaction between ammonium hydroxide and tin chloride (IV) solutions. The resulting precipitate was washed until the pH of filtrate becomes neutral. To prevent the loss of the hydrated water the prepared precipitate was stored in air at 100 % humidity.

Results and Discussion. The proton exchange membrane was formed by the method described in [5], by "brush" method using layering of PVA solution with addition of certain amount of hydrated tin oxide on an inert substrate. Free water was removed from each layer using heated (40...60 °C) air, preventing its complete drying, since the loss of the hydrated water significantly reduces the conductivity of the obtained membrane.

After applying the half of layers, the reinforcing mesh was stacked, and then the rest of the layers were applied. The use of reinforcing mesh improves the mechanical strength of the membrane.

The degree of swelling in hot water (50 °C) of the obtained membrane with PVA content 50 % was 640 % after 2 hours of exposing. The higher temperatures lead to slow dissolution, due to the solubility of PVA. To increase the heat resistance of membrane the crosslinking of PVA chains on the surface of the membrane was performed by treatment with aldehyde in the solution containing 2...5 wt. % of aldehyde, 20 wt. % of sulfuric acid and 20...25 wt. % of sodium sulphate at 60...70 °C during 25...30 minutes. The sulfuric acid acts as a catalyst, sodium sulfate reduces swelling degree of the membrane.

The series of membranes containing 30, 50, 70, 80 and 90 wt. % of hydrated oxide are marked as M30, M50, M70, M80 and M90, respectively. Samples containing 30...70 % of $\text{SnO}_2 \cdot n\text{H}_2\text{O}$ have a uniform structure for both thicknesses of 100 μm (Fig. 1, *a, b, c*) and 200 μm (Fig. 2, *a, b, c*).

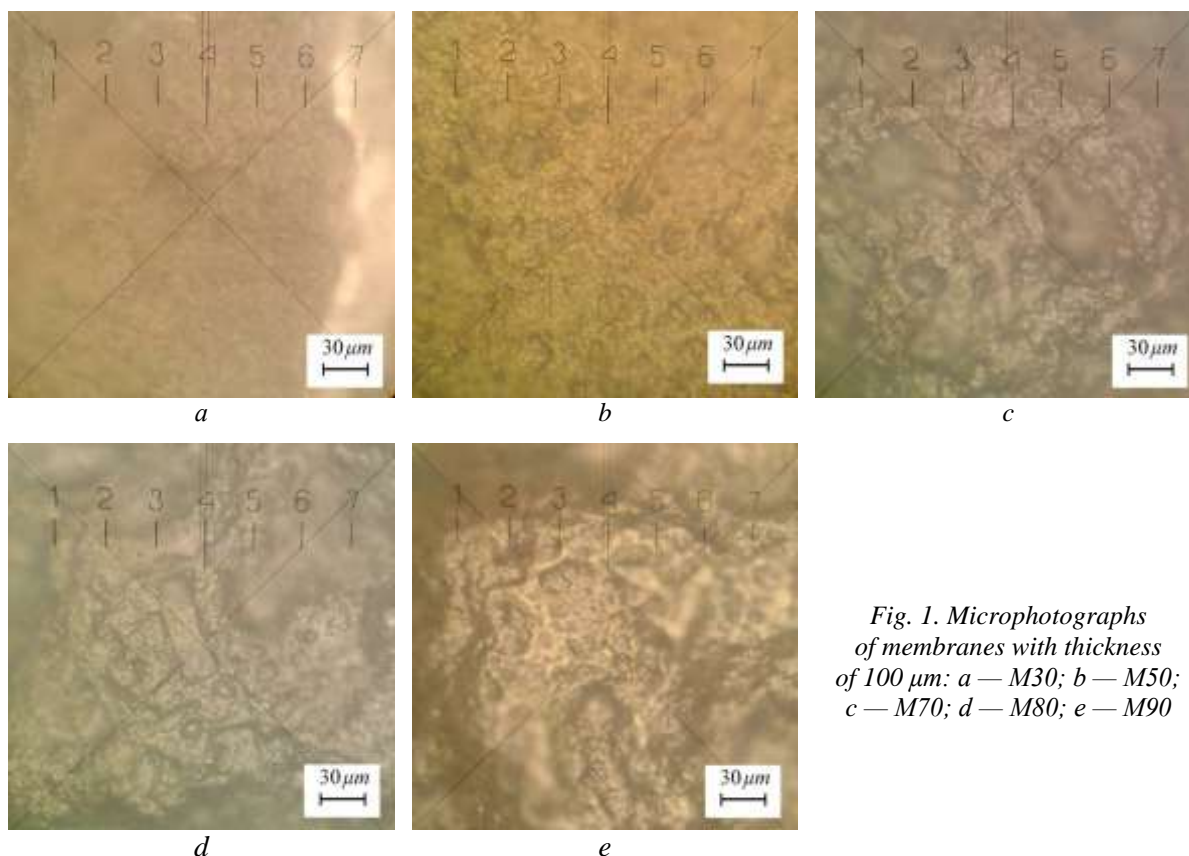
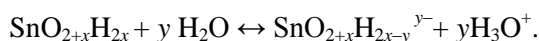


Fig. 1. Microphotographs of membranes with thickness of 100 μm : a – M30; b – M50; c – M70; d – M80; e – M90

With the further increase of $\text{SnO}_2 \cdot n\text{H}_2\text{O}$ content (Fig. 1, *d, e*, Fig. 2, *d, e*) the disadvantage of the PVA binder is critical for the film thickness higher than 100 μm : the cracks in the M80 membrane sample can be seen using microscope with a 400 times magnification, cracks in M90 membrane sample are visible with the naked eye.

The probable structure of proposed proton exchange membrane based on polyvinyl alcohol and addition of hydrated tin oxide is shown in Fig. 3, *a*. The chains of polyvinyl alcohol are crosslinked by aldehyde, which makes the polymer insoluble. There are the globular hydrated tin oxide and water molecules between PVA chains. This leads to the partial dissociation of $\text{SnO}_{2+x}\text{H}_{2x}$ producing hydronium ion:



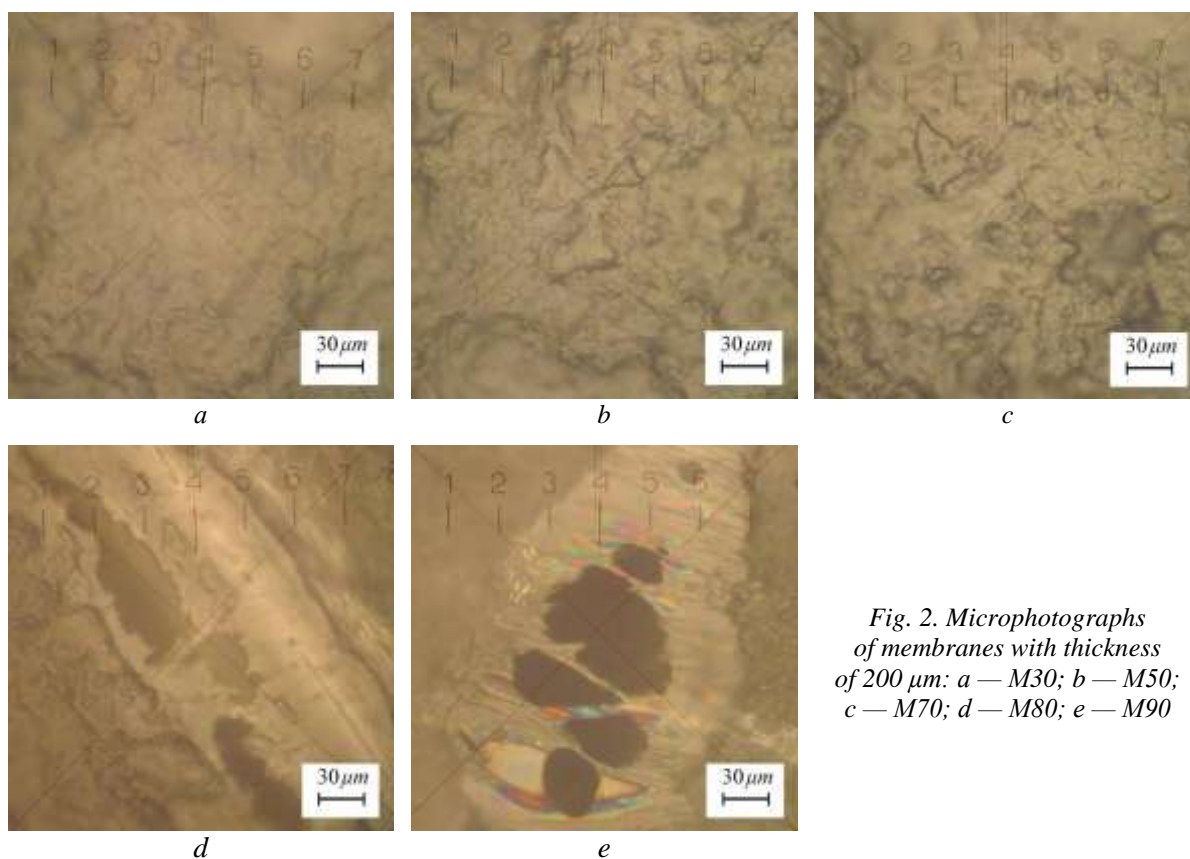


Fig. 2. Microphotographs of membranes with thickness of 200 μm : a – M30; b – M50; c – M70; d – M80; e – M90

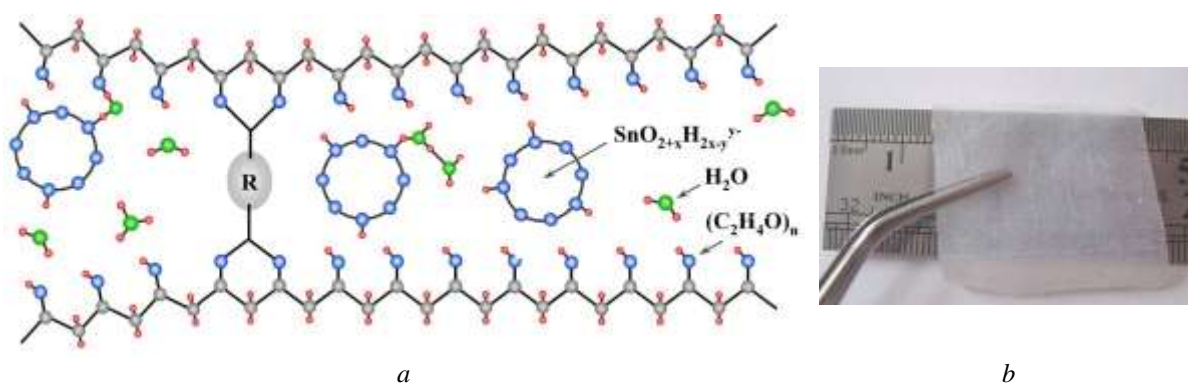


Fig. 3. Proton exchange membrane of polyvinyl alcohol and a hydrated tin oxide: a – the structure, b – exterior membrane M50

Thus $\text{H}_3\text{O}^+/\text{H}_2\text{O}$ and $\text{OH}^-/\text{H}_2\text{O}$ proton-containing groups are formed and the proton transfer process occurs by Grotthuss mechanism, which consists in proton overshoot between the proton exchange groups and their reorientation. Fig. 3, b shows a photograph of M50 membrane sample with 200 μm thickness.

Conclusions. Thus, a method of formation of the proton exchange membrane using reasonable materials, polyvinyl alcohol and hydrated tin oxide obtained from the tin chloride and ammonium hydroxide is proposed.

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