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Effect of ultrasonic treatment of Nafion® solution on the performance of fuel cells

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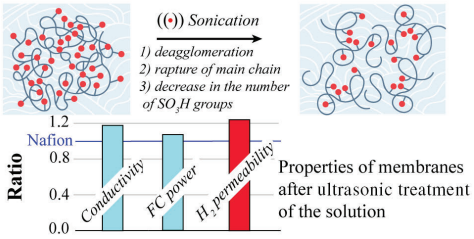
The effect of preliminary high-power ultrasonic treatment of Nafion® alcohol solutions on the properties of membranes and characteristics of membrane-electrode assemblies of membrane-based fuel cells has been explored. The changes in the microstructure of Nafion® membranes upon ultrasonic treatment of their solutions lead to an increase in their proton conductivity, gas permeability and the membrane-based fuel cells power by almost 10%.



Keywords: proton exchange membrane fuel cell, perfluorinated sulfonic acid membrane, functional polymer, ultrasonication, fuel cell performance, proton conductivity, Nafion®.

Perfluorinated sulfonic acid membranes based on polymers with long (Nafion®) and short (Aquivion®) side chains, as well as hybrid materials based on them, are the most widely used electrolytes for low-temperature fuel cells (FCs).[1–4] Casting of thin films from a polymer solution or dispersion makes it possible to reduce the resistance of membrane-electrode assembles (MEAs) in FCs.[5] Moreover, this method is most technologically suitable for incorporation of various additives that optimize the properties of membranes.[6] The main efforts in this area are aimed at obtaining stable materials with high conductivity and reduced gas permeability in comparison with unmodified membranes.[1,7] It is known that Nafion® membranes have a 'memory effect' and their properties change depending on the method of film preparation, as well as the physical and/or chemical treatment of them.[8,9] Ultrasonic (US) treatment of a polymer solution before casting a film is often used to disperse dopant nanoparticles uniformly. It has been shown[10–12] that US treatment of Nafion® solutions results in a significant decrease in their viscosity both due to deagglomeration and a decrease in the length of macromolecules. In addition, some side chains can be broken with loss of functional sulfo groups. Such changes can affect the morphology of perfluorinated sulfonic acid polymers in solution, similarly to the effect of concentration and solvent nature.[13,14] In particular, the degree of agglomeration of macromolecules in solution and membrane pore size change depending on the solvent nature.[15] In turn, the microstructure of membranes determines their sorption and transport properties.[16–18] US treatment of Nafion® solutions makes it possible to increase the proton conductivity of membranes, even at low humidity.[10] However, the effect of these changes on the characteristics of MEAs in FCs has not been studied to date, although US treatment is very often used in fabrication of membranes for FCs.

This work is the first to study the effect of US treatment of Nafion® solutions on the characteristics of MEAs in hydrogen–oxygen fuel cells based on membranes obtained from these solutions. Membranes were obtained by casting from Nafion® solutions without US treatment (Nafion sample) and after 60 min of US treatment (Nafion US60 sample). The sample preparation and pretreatment procedures are described elsewhere[10] and in Online Supplementary Materials.

The results of testing MEAs based on the membranes under investigation are shown in Figure 1. The MEAs with a Nafion US60 membrane are characterized by higher current–voltage and power characteristics as compared to MEAs with Nafion. The maximum power density values for the MEAs with Nafion and Nafion US60 are 520 and 558 mW cm^{-2}, respectively. At the same time, the operating voltage U at a current density of 0.5 A cm^{-2} changes insignificantly (from 702 to 708 mV).

To explain the changes in the FC parameters, let us consider the specific features of morphology and the changes in Nafion membranes that arise upon US treatment of the polymer solution. The properties of perfluorinated sulfonic acid membranes are determined by their microstructure.[19] Due to the difference in the nature of the polymer's main and side

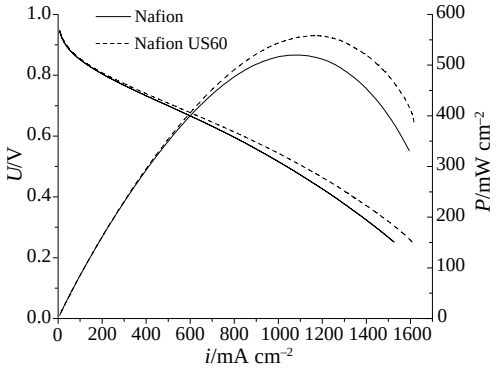


Figure 1 Voltammetric curves and plots of power density *vs.* current density for MEAs in H_2–O_2 FCs.

chains, the hydrophilic SO_3H groups are organized into clusters. Hydration of the latter produces a system of pores and channels through which ionic transfer occurs in the membrane.[20] The morphology and properties of Nafion membranes strongly depend on their prehistory, and when casting is done, they depend on the film preparation conditions (the nature of the solvent, the rate and temperature of its removal) and the state of the polymer in the solution.[13,14,21,22]

US treatment of a Nafion® solution results in irreversible decrease in the viscosity η of the alcohol solution from 15.1 to 6.7 mPa s after 60 min caused by deagglomeration of macromolecules and decrease in their length due to cleavage of C–C bonds in the main chain. Moreover, a fraction of side chains is separated and some functional sulfo groups are lost. This, in turn, leads to a decrease in the ion exchange capacity (IEC) of membranes following US treatment of solutions from 0.95 meq g^{-1} for Nafion to 0.86 meq g^{-1} for Nafion US60. It is the high liability of SO_3H groups to hydration that ensures a high water uptake in perfluorinated sulfonic acid membranes. Therefore, along with a decrease in the IEC after US treatment of a solution, the water uptake decreases from 9.6% in a Nafion membrane to 8.9% in a Nafion US60 membrane [at 25 °C, relative humidity (RH) = 95%].

Despite the decrease in the water uptake, US treatment of a polymer solution enhances the proton conductivity (Figure 2) of the membranes and decreases the activation energy from 10.5 ± 0.7 kJ mol^{-1} in Nafion membrane to 7.5 ± 0.5 kJ mol^{-1} in Nafion US60 membrane in the temperature range of 25–75 °C. The conductivity value at 65 °C and RH = 95% is 34 mS cm^{-1} for a Nafion membrane and 40 mS cm^{-1} for Nafion US60 membrane.

US treatment of Nafion® solutions increases the mobility of Nafion® units and side chains and thus affords membranes with improved interconnectivity of the pores and channels system. Therefore, despite the partial loss of sulfo groups, which determine the concentration of charge carriers, and the water uptake decrease, which should lead to carrier mobility decrease, the proton conductivity of Nafion US60 membrane is higher than that of Nafion membrane. At the same time, the improvement of the pore interconnectivity leads to an increase in the transfer rate of non-polar molecules. The hydrogen permeability through membranes obtained from solution after US treatment increases by 25% compared to the initial membrane [from $(1.58 \pm 0.02) \times 10^{-7}$ cm^2 s^{-1} for Nafion to $(1.96 \pm 0.04) \times 10^{-7}$ cm^2 s^{-1} for Nafion US60 at RH = 100%, 30 °C]. It should be noted that this situation is typical of membranes. Enhancement of conductivity is usually accompanied by a decrease in selectivity, which is reflected by an increase in the membrane's gas permeability.[18] However, despite the increase in the gas permeability, preliminary US treatment of Nafion solution makes it possible to slightly raise the power density of MEA with Nafion US60 membrane as compared to MEA with Nafion membrane due to the optimization of the pores and channels system and the increase in proton conductivity.

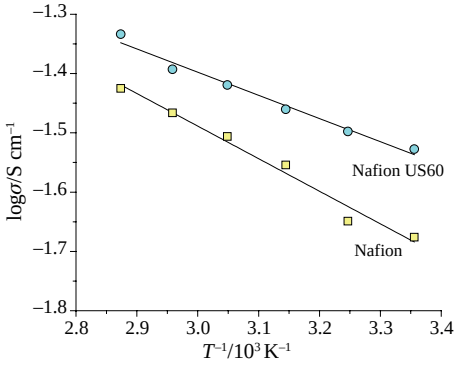


Figure 2 Temperature dependence of proton conductivity of the membranes at RH = 95%.

Thus, it was shown that preliminary US treatment of alcohol Nafion solution followed by casting of membranes results in the formation of a structure with more branched and interconnected system of pores and channels than in membranes obtained from the initial solution. The improvement of the microstructure of membranes results in their proton conductivity enhancement by 20% with simultaneous increase in their gas permeability. Despite the fact that these parameters differently affect the performance of FCs, the maximum power density of MEAs in FCs increases from 520 mW cm^{-2} (membrane obtained from an untreated solution) to 558 mW cm^{-2} (membrane obtained from a solution after US treatment).

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2022.03.023.

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