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# Electrocatalytic and transport properties of hybrid Nafion® membranes doped with silica and cesium acid salt of phosphotungstic acid in hydrogen fuel cells

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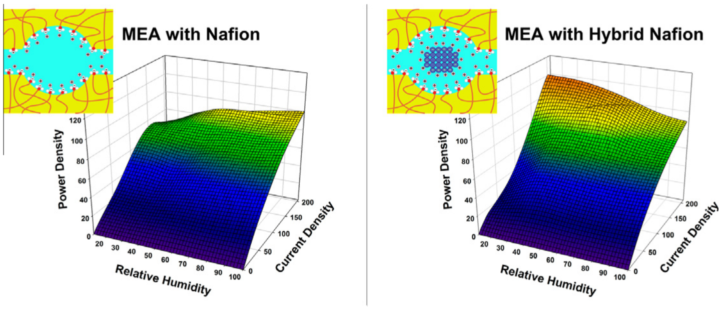
## HIGHLIGHTS

- Nafion 212 based hybrid membrane with high proton conductivity is synthesised.
- Resistance of oxygen reduction reaction at low RH is decreased for hybrid membrane.
- Power density of the FC with the hybrid membrane increases with decreasing RH.
- Power density of FC with the hybrid membrane is higher as compared with Nafion 212.
- The hybrid membrane shows a higher proton conductivity over the entire RH range.

## GRAPHICAL ABSTRACT



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## ABSTRACT

This work is devoted to preparation of a hybrid material based on Nafion® 212 membrane doped with nanoparticles of silica and cesium acid salt of phosphotungstic heteropolyacid. The benefits of this material are concerned with its increased conductivity at low humidity. Conductivity and properties of the membranes were studied as a function of relative humidity under the FC operating regime at room temperature. As compared with the commercial Nafion® 212 membrane, the MEA based on this material shows a lower power density at 100% relative humidity of the supplied gases (hydrogen, air). As the relative humidity decreases, power density of the cell based on hybrid membrane increases and overruns the performance of the commercial Nafion® 212 membrane at 100% RH. Explanation of the observed phenomena is proposed.

## 1. Introduction

Hybrid membranes are widely used in modern technologies. Initially, these membranes were developed for their use in fuel cells (FC) [1–7] but, later, these materials were found to be applicable in gas separation processes, being coined as “mixed matrix membranes” [8–10]. Depending on the types of membranes and

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*Abbreviations:* DC, direct current; DL, double layer; FC, fuel cell; MEA, membrane electrode assembly; RH, relative humidity; TEM, transmission electron microscopy.

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incorporated dopants, the morphology of the final hybrid material, characteristics of the resultant membranes can be appreciably different. For ion-exchange membranes, the use of dopants boosts both conductivity [11–16] and selectivity of the transport processes [13,17,18] but permeability of gases and nonpolar liquids decrease is usually observed [19–23]. In some works, the effect of dopants is reported to provide improved thermal stability and mechanical properties [24–27]. Increased water uptake due to hydrophilicity of dopant particles is considered to be a key reason behind changes in conductivity [28]. A noticeable effect of dopants hydrophilicity on the conductivity of the membranes was highlighted in earlier reports [29–33]. However, this reasoning fails to explain an improved conductivity of membranes due to incorporation of finely dispersed hydrophobic dopants and depressed mobility of an interpore solution [34,35]. To rationalize the above phenomena, we proposed a model, according to which incorporation of dopants into the membrane pores entails their widening and as a consequence widening of the conductivity-limiting channels [36]. However, as the concentration of dopants exceeds 2–3 vol%, dimensions of the dopant particles tend to increase, and proton conductivity decreases [27,33]. Moreover, a special value is attributed to the chemical nature of dopant particles. Due to their effect on water uptake (hydrophilicity or hydrophobicity) and concentration of carriers (acidity of the dopant surface), the resultant characteristics of membranes can be substantially varied [37].

Principal advantage of hybrid membranes is the maintenance of high proton conductivity at low humidity when conductivity of conventional membranes is known to be deteriorated by several orders of magnitude due to dehydration and reduced volume of pores and channels [38]. This tendency is highly undesirable when membranes are used in FC [5]. Conductivity at low humidity can be improved by the incorporation of heteropolyacids into the membranes as individual compounds [11,39] or in their combination with oxides [40,41]. The benefits of this modification are concerned with marked improvement in proton conductivity both at low humidity and elevated temperatures, reduced hydrogen crossover, and improved FC performance at high temperatures and at low humidity. However, high solubility of heteropolyacids results in their ready washout from membranes. From this standpoint, the attractive route includes preparation of the membrane materials based on insoluble salts of heteropolyacids with bulky cations of alkali metals, including cesium, which are deposited on the silica surface. In this case, easy substitution of cations by protons on the surface of the above salts [42] provides their high acidity. In some publications, a positive effect of this modification on the performance of the Nafion® membranes was reported [43–45]. In our opinion, doping of the Nafion® membranes with acidic salts of heteropolyacids can assist the achievement of the optimum FC performance.

In this connection, the principal objective of this work addresses the synthesis and characterization of the conducting properties of hybrid materials based on the Nafion® 212 membrane with a low content of incorporated nanoparticles of silica and cesium salt of phosphotungstic heteropolyacid. Special attention is focused on the characteristics of this material at low humidity and its approbation as novel membrane materials for hydrogen-air FC.

## 2. Materials and methods

### 2.1. Reagents and solutions

In this work, we used Nafion® 212 membranes (Sigma Aldrich), aqueous solution of ion-exchange Nafion® DE-1020 resin, tetraethoxysilane [$Si(OC_2H_5)_4$, >98%, Sigma Aldrich], phosphotungstic heteropolyacid ($H_3PW_{12}O_{40}\cdot H_2O$, extra-pure grade, Merck), cesium carbonate ($Cs_2CO_3$, Aldrich, 99.9%), solutions of hydrochloric acid, hydrogen peroxide, ammonium hydroxide, and ethanol (KhimMed, Russia, extra-pure grade). For synthesis and washing of membranes, deionized water was used (with a resistance of 18.2 MΩ). For MEA fabrication, 25% Pt/C catalyst (Pt deposited onto a Vulcan XC-72 carbon black) was prepared by the reduction of $H_2PtCl_6$ with sodium borohydride. Average size of Pt nanoparticles was equal to 3 nm.

### 2.2. Membrane modification

Prior to the synthesis of hybrid membrane, the Nafion® 212 membrane was pre-conditioned by its successive treatment with 10% solutions of HCl, $H_2O_2$, and deionized water at 80 °C for 3 h. The membrane was *in situ* modified by incorporation of a dopant into the matrix of the prepared film. For the incorporation of hydrated silica particles, the to-be-modified sample was allowed to stay in the aqueous solution of ethanol (volume ratio $C_2H_5OH/H_2O$ was equal to 4) at room temperature under continuous stirring for 30 min. Then, the sample was placed into the alcohol solution of tetraethoxysilane (volume ratio $Si(OC_2H_5)_4/C_2H_5OH$ was equal to 1.5) at room temperature under continuous stirring for 1 h. Then, the membrane was washed with minor amounts of deionized water and immersed into 12% aqueous solution of ammonia. The as-prepared Nafion 212 + $SiO_2$ sample was treated by 10% hydrochloric acid for 3 h at room temperature in order to provide the protonic form and washed with deionized water until pH = 7.

Then, the Nafion 212 + $SiO_2$ membrane was treated with 0.05 M $H_3PW_{12}O_{40}$ solution at room temperature under continuous stirring for 3 h. To remove excessive $H_3PW_{12}O_{40}$ from the surface, the membrane was washed with minor amounts of deionized water and immersed into 0.1 M solution of $Cs_2CO_3$ for 3 h at room temperature under continuous stirring. The as-prepared sample was repeatedly treated with 10% solution of hydrochloric acid for 3 h and washed several times with deionized water until pH = 7. Obtained hybrid membrane was stored in hydrated state in deionized water. Obtained membrane has a whitish tint which retains during storing. Hereinafter, the Nafion + $SiO_2$ + $Cs_xH_{3-x}PW_{12}O_{40}$ sample will be coined as "*hybrid*" *membrane*, and the initial commercial sample – as "*Nafion 212*".

### 2.3. Methods

Microstructure of the hybrid membrane was studied by TEM observations on a JEOL JEM 1011 TEM microscope (100 kV). Prior to TEM measurements, the membranes were ultrasonically dispersed in methanol and supported onto carbon coated Cu grids. To estimate the content of the incorporated dopant and $SiO_2/Cs_xH_{3-x}PW_{12}O_{40}$ ratio, the weighed amount of the sample was conditioned at 200 °C for 30 min for dehydration and annealed at 600 °C for the removal of the host polymer matrix. Nafion 212 membrane was conditioned and annealed in the same conditions in order to determine dopant concentration exactly. Residue of Nafion 212 is less than 0.05 wt%. The burnt residue was dissolved in 25 wt% aqueous NaOH solution. Chemical analysis of the samples was performed using an emission ICP IRIS Advantage spectrophotometer. An accuracy in $SiO_2$ and $Cs_xH_{3-x}PW_{12}O_{40}$ concentration determination is 0.1%.

Investigation of dopant particle dispersion on the surface and in the cross-section of the hybrid membrane was performed with the use of EDX analysis of tungsten. Microstructure of the materials was examined on a Carl Zeiss NVision 40 provided with Oxford Instruments X-MAX energy-dispersive X-ray analyzer operating at an accelerating voltage of 20 kV. In order to get satisfactory