

NAFION-BASED NANOCOMPOSITES WITH LIGHT FULLERENES AND THEIR FUNCTIONALIZED DERIVATIVES

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Abstract. Nafion – fullerene (C_{60} , C_{70}), Nafion – fulleranol ($C_{60}(OH)_n$ ($n=22-24$), $C_{70}(OH)_{12}$) and Nafion – fullerene tris-malonate ($C_{60}[C(COOH)_{2,3}]$) composite films were prepared by casting from alcohol–water Nafion solutions doped with these additives and then drying. Proton conductivity (σ) of the films was measured at different relative humidity (RH) levels using impedance spectroscopy. It was found that Nafion – fullerene (C_{60} , C_{70}), Nafion – fulleranol ($C_{60}(OH)_n$ ($n=22-24$), $C_{70}(OH)_{12}$) and Nafion – fullerene tris-malonate ($C_{60}[C(COOH)_{2,3}]$) composite films demonstrated increasing proton conductivity compared to pure Nafion (especially at $RH < 60\%$). It may be possible to use them as humidity sensing membranes.

1. INTRODUCTION

In recent years, there has been a growing interest in studying nanoionic materials and their applications in solid state electrochemical devices. In this context, an increasing attention is paid to development of composite polymer membranes for fuel cells and humidity-sensitive elements of humidity sensors [1].

The interest in Nafion-based composite materials is apparently caused by the absence of commercially available ionomers whose performance considerably exceeds that of perfluorinated ionomer membranes that could successfully substitute Nafion in fields like fuel cell technology [2,3]. For this reason, the attention of many researchers is now focused on finding composite materials with characteristics excelling bare Nafion. The main property that is commonly dealt with is proton conductivity at high temperatures and low levels of relative humidity (RH). Specifically, very low proton conductivity under such conditions complicates its precise measurement that is, in turn, an obstacle to using

Nafion as a humidity sensing material. Other characteristics of concern include mechanical properties and some fuel cell technology related features like swelling behavior, methanol permeability etc. In many studies, Nafion membranes doped with oxide or inorganic salt nanoparticles were investigated. The dopants such as titanium oxide in form of particles and nanotubes [4–6], zirconium phosphates [7], silica [8–10], alumina and oxides of hafnium, tantalum, zinc and tungsten and complex materials like ZrO_2-SiO_2 , $ZrO_2-P_2O_5-SiO_2$ [11–13] were in focus of research. Introduction of such hydrophilic dopants usually aims at improving water-retention capacity of ionomer membranes that helps to keep their proton conductivity high up to temperatures of 100–140°C. It is also necessary to mention studies that investigate imbedding of heteropoly-acids having high self-proton-conductance, such as phosphotungstic acid and silicotungstic acid, into Nafion matrix. In order to obtain the most efficient retention of these compounds within a polymer matrix, they were immobilized on the silica gel particles [11]. The composite

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material samples produced with this technique demonstrate increased proton conductivity values.

Generally, methods of creation of new composites that involve grafting of various functional groups on the surface of dopant particles deserve close attention. This approach allows to perform "fine-adjustment" of properties of the additives introduced into composite matrix thus making way for development of materials with desired characteristics. For instance, imbedding of SiO₂ nanoparticles modified with –SO₃H groups into Nafion matrix produces a visible increase of proton conductivity of this ionomer [14].

Attempts of making Nafion-based composites by imbedding of various polymers (polytetrafluoroethylene, phenol-formaldehyde resin etc.) usually aim at enhancing mechanical properties like membrane strength in swollen state or reducing methanol permeability. Some materials were also reported to show improved proton conductivity [11].

A new field of research is development of Nafion composites doped with fullerooids, that is, fullerenes, carbon nanotubes and their derivatives. The composite Nafion membranes containing fullerene (C₆₀) and fullerlenols (C₆₀(OH)_n, n~12) as dopants [15] have shown increased proton conductivity compared to unmodified Nafion, especially at low RH. It is interesting to note that fullerlenols, in contrast to fullerenes, demonstrate a certain degree of self-proton-conductance [16].

Composite films were made from carbon nanotubes (CNTs) and Nafion [17] and tested as the humidity sensing element of a Quartz Crystal Microbalance (QCM). Using of CNT as a dopant was reported to improve sensitivity of the obtained sensors, i.e. to increase the amount of water absorbed by a composite film per unit relative humidity. Another research on the same subject [18] also suggests that Nafion – CNT composite films are an excellent humidity sensing material for QCM sensors. The samples of humidity detectors exhibit short response and recovery time, high sensitivity and linearity of calibration curves.

The objective of this work is a synthesis of Nafion-based composite films using various fullerooids as dopants, evaluation of proton conductivity of the obtained samples at different RH-levels and assessment of the possibility of using these composites as sensitive elements of resistive humidity sensors.

2. EXPERIMENTAL

We used a 15 wt.% solution of Nafion (the equivalent weight of Nafion was 1100) from Ion Power Inc.

and a mixture of water (45 wt.%) and isopropanol (40 wt.%) as a solvent. Fullerenes (C₆₀ and C₇₀) and fullerlenols C₆₀(OH)_{22–24} and C₇₀(OH)₁₂ were acquired from ZAO "ILIP" (St. Petersburg) and used as received.

The other reagents used were reagent grade DBU, α-bromomalonic ester, NaH, 1,2-dimethylbenzene, H₂SO₄, methanol (purchased from Vecton Ltd, St.-Petersburg). The synthesis of the C₆₀-tris-malonic derivative was carried out according to [19,20]. 0.5 mol of C₆₀ fullerene was dissolved in o-xylene, then 10 mol of DBU (1,8-Diazabicyclo[5.4.0]undec-7-ene) and 10 mol of α-bromomalonic ester were added to the solution of fullerene. The obtained mixture was stirred at ambient temperature for 7 days. After that, the solvent was distilled off at 60 °C and the residue was extracted by diethyl ether and separated from the solid phase. Then the diethyl ether was distilled off and the solid phase was dried at 60 °C. The obtained fullerene diethyl malonate (100 mg) was dissolved in toluene (50 ml) under nitrogen in the presence of a twentyfold molar excess of NaH for 3 h at 60 °C. After this procedure the NaH was almost homogeneously suspended in toluene while the diethyl malonate was unaffected. The transformation of the malonate was accompanied by a vigorous gas evolution and the quantitative precipitation of the sodium salt of the fullerene malonic acid took place after the addition of methanol (1 ml). The formation of the acids occurs presumably by hydrogenolysis of the OEt bonds. After centrifugation and removal of the liquid, the precipitate was washed with toluene, 2 mol·dm⁻³ H₂SO₄, then water, and finally dried under vacuum at 60 °C for 12 h. The yield of the reaction was equal to 80%.

A C, H, and N elemental analysis was carried out by the Department of Organic Chemistry of Saint-Petersburg State University on a 185B Carbon Hydrogen Nitrogen Analyzer Hewlett Packard. C₆₉O₆H₆: calculated: 80.71 (C), 0.59 (H), 18.70 (O), found: 80.73(C), 0.54(H), 18.70 (O).

Infrared spectra (4000–400 cm⁻¹) were recorded on a Shimadzu FTIR-8400S instrument in KBr pellets. Experimental IR main reflexes data in $\tilde{\nu}$ (cm⁻¹) were the following: 3470, 1811, 1723, 1715, 1431, 1405, 1410, 1222, 1231, 1057, 820, 833, 730, 580, 528, 522. Obviously the long-wavelength part of spectrum: $\tilde{\nu} = 522\text{--}1715\text{ cm}^{-1}$, corresponds to oscillations of C–C bonds in fullerene C₆₀. At the same time, the short-wavelength part of spectrum: $\tilde{\nu} = 1700\text{--}1725\text{ cm}^{-1}$, corresponds to oscillations of C=O bonds in malonate groups of C₆₀[(=C(COOH))_{2,3}]; $\tilde{\nu} = 3450\text{--}3550\text{ cm}^{-1}$ corresponds to oscillations of rather free O–H groups. The reflex at $\tilde{\nu} = 1811$

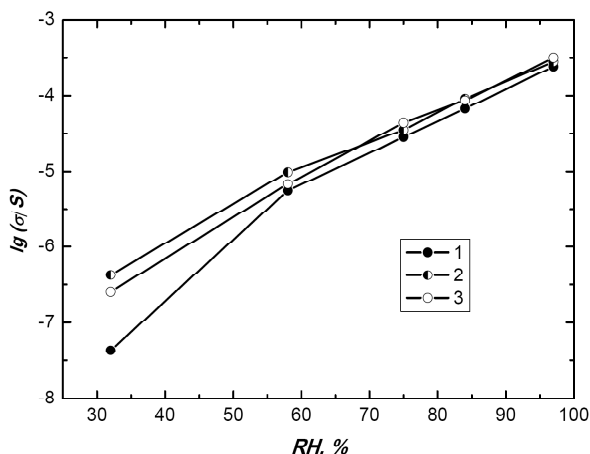


Fig. 1. Dependence of the proton conductivity of the (1) Nafion, (2) Nafion – 0.9% C_{60} and (3) Nafion – 0.2% C_{70} composites on the relative humidity of air at 25 °C.

cm^{-1} can be attributed to oscillations of C–C bonds in external carbon triangles in tris-malonates.

1H and $^{13}C\{^1H\}$ NMR spectra were recorded on Bruker Avance II+ 400 MHz (UltraShield Magnet) and Avance II+ 500 MHz (UltraShield Plus Magnet) spectrometers at ambient temperature in D_2O . Experimental NMR-reflexes in ppm were the following: δ_H (300 MHz, D_2O): 11.7 (wide singlet, H – from carboxyl groups –COOH); δ_C (75.5 MHz, D_2O): 166.57, 166.54, 166.27, 150.04, 148.79, 147.91, 147.85, 147.59, 147.05, 146.86, 146.74, 146.68, 146.47, 146.24, 146.15, 146.12, 145.90, 145.68, 145.53, 145.33, 144.85, 144.54, 144.47, 143.54, 143.28, 143.16, 143.07, 140.40, 140.13, 74.32, 69.16, 62.25.

Electrospray ionization mass spectrum was obtained on a Bruker micrOTOF spectrometer equipped with electrospray ionization (ESI) source (Saint Petersburg). The instrument was operated in the positive ionization mode ($[C_{60}(=C(COOH)_2)_3-H]^+$). The determined value of M/z (M is the ion mass in atomic units, z is the ion charge) was equal to the calculated value of M/z ($z = 1$) in the positive charged form: $M/z = 1026 + 1 = 1027$ a. u.

The samples of Nafion-based composite films were obtained by dropping 20 μl of the casting solution onto a textolite substrate equipped with golden interdigitated electrodes followed by drying at room temperature and formation of film and then drying at 100 °C. Several approaches were employed for preparation of the mixtures used for composite film casting that were primarily imposed by limitations of dopant solubility. The mixtures used for preparation of Nafion – fullerene composite films were obtained by adding specified portions of fullerene to

the Nafion solution – distilled water mixture (ratio 1:6) and thoroughly shaken till solubilization is achieved. The masses of fullerene additions were calculated to have fullerene contents in the dried films equal to 1, 2, 4, and 6 wt.%.

Due to poor solubility of fullerenes C_{60} and C_{70} in water, isopropanol and Nafion solution, the above method can not be used for preparation of Nafion – fullerene composites. For this reason, a saturated solution of fullerene C_{60} in isopropanol was prepared and then mixed with Nafion solution in the ratio of 1:3. The obtained mixtures were used for composite film casting.

The proton conductivity of the composite films was studied by impedance spectroscopy in the frequency range from 1 MHz to 100 Hz. An Autolab PGSTAT302 potentiostat/galvanostat was used for this purpose. The conductivity σ was derived from the equation $\sigma = 1/R$, where R is a resistivity value obtained by analysis of impedance frequency spectra. The relative humidity of air (RH) in the range of 12–97% was set in the measuring cell using saturated solutions of salts ($LiCl$, $MgCl_2$, $NaBr$, $NaCl$, KCl , K_2SO_4). The cell was thermostabilized at 25 °C. Using the experimental data, the functional relationships $lg \sigma - RH$ were plotted for the investigated Nafion composite films (Figs. 1–3).

3. RESULTS AND DISCUSSION

All the composite film samples demonstrated increased proton conductivity values compared to undoped Nafion films, especially at $RH < 60\%$, that is in good agreement with the results obtained in [15], where similar Nafion – fullerene and Nafion –

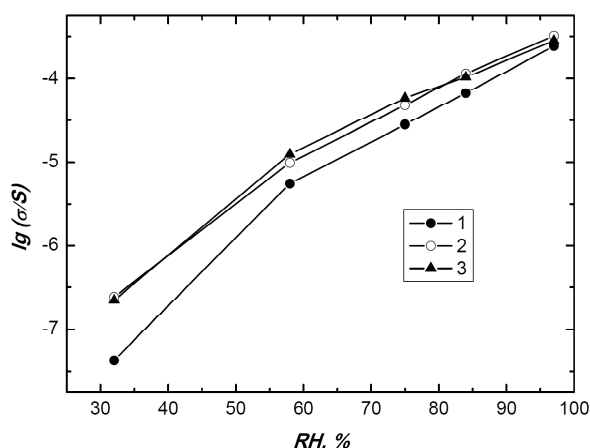


Fig. 2. Dependence of the proton conductivity of the (1) Nafion, (2) Nafion – 1% $C_{60}(OH)_{22-24}$ and (3) Nafion – 1% $C_{70}(OH)_{12}$ composites on the relative humidity of air at 25 °C.

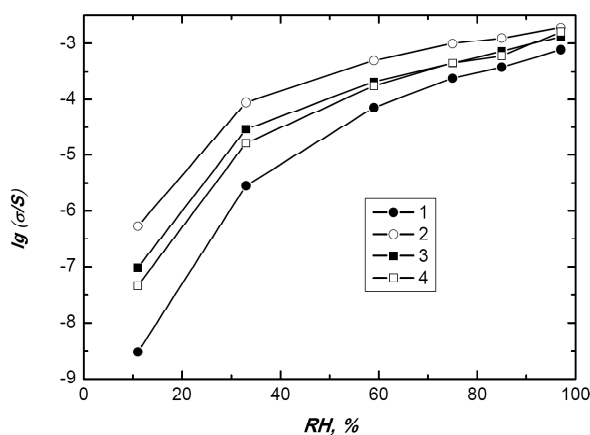


Fig. 3. Dependence of the proton conductivity of the (1) Nafion and (2)–(4) Nafion – $C_{60}[C(COOH)_{2,3}]$ composites (2 – 1.7%, 3 – 2.1%, 4 – 3.4% $C_{60}[C(COOH)_{2,3}]$) on the relative humidity of air at 25 °C.

fullerenol composite membranes were investigated, with the only difference being the composite preparation procedure in [15] that included direct impregnation of Nafion 117 membranes with dopant solutions.

Composites containing fullerenes C_{60} (0.88 wt.%) and C_{70} (0.20 wt.%) demonstrate 10- to 12-fold increase of conductivity compared to that of pure Nafion at $RH=32\%$ (Fig. 1). For Nafion – fullereneol $C_{60}(OH)_{22-24}$ and $C_{70}(OH)_{12}$ composite films containing from 1 to 6 wt.% of dopant, no significant dependence of conductivity on concentration and type of dopant was detected. Fig. 2 shows conductivity change vs. relative humidity of air for Nafion composite films, containing 1 wt.% of fullereneol ($C_{60}(OH)_{22-24}$ and $C_{70}(OH)_{12}$). It should be noted that the shape of these relationships is similar to that of composites containing fullerenes C_{60} and C_{70} , except that the conductivity value at $RH=32\%$ also increases within one order of magnitude. The most significant influence of concentration of dopant on the conductivity of Nafion composite films was observed for $C_{60}[C(COOH)_{2,3}]$ (Fig. 3). The Nafion composite containing 1.7 wt.% of $C_{60}[C(COOH)_{2,3}]$ demonstrates maximum proton conductivity; at $RH=32\%$ it is about 30 times as high as that of pure Nafion.

It should be noted that mechanisms of enhancement of proton conductivity of the obtained composite materials are not always clear. While high proton conductivity of Nafion – fullereneol and C_{60} -tris-malonic derivative composites can be attributed to hydrophilicity of dopants that helps to retain additional water in Nafion matrix necessary for proton migration, the cause of proton conductivity growth in Nafion-fullerene systems containing hydrophobic

dopants (C_{60} and C_{70}) is less easy to understand. Probably, the fullerene molecules and their agglomerates are located in the hydrophobic phase of Nafion matrix creating structure defects or additional paths of proton conduction.

The results of the investigation allow us to conclude that among the prepared composite films, the most promising material for humidity sensing applications is Nafion – C_{60} tris-malonic derivative (1.7 wt.%) composite that shows high proton conductivity at low RH .

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