



ELSEVIER

Available online at [www.sciencedirect.com](http://www.sciencedirect.com)

ScienceDirect

journal homepage: [www.elsevier.com/locate/he](http://www.elsevier.com/locate/he)

# Hybrid materials based on perfluorosulfonic acid membrane and functionalized carbon nanotubes: Synthesis, investigation and transport properties

I.A. Prikhno, E. Yu Safronova, A.B. Yaroslavtsev\*

N.S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Leninskii Prosp., 31, 119991 Moscow, Russia

## ARTICLE INFO

### Article history:

Received 31 January 2016

Received in revised form

8 April 2016

Accepted 15 April 2016

Available online 11 May 2016

### Keywords:

Proton-conducting membrane

Nafion

Hybrid membrane

Carbon nanotubes

Sulfonated carbon nanotubes

Functionalization

## ABSTRACT

The paper presents the results obtained in a study of the effect of modification of perfluorosulfonic acid MF-4SC membranes (Russian analog of Nafion) with carbon nanotubes, in particular, surface-sulfonated ones. Membrane modification by small amounts of carbon nanotubes results in increased proton conductivity at both high and low relative humidity. The incorporation of carbon nanotubes with sulfonated surface results in additional conductivity increase. The proton conductivity of the MF-4SC + 1 wt % CNT-SO<sub>3</sub>H membrane was  $\sigma = 5.4 \cdot 10^{-3}$  S/cm at a relative humidity of 30% and 25 °C. Modification also increases the interdiffusion coefficient of cations and decreases the diffusion permeability. The incorporation of carbon nanotubes was shown to enhance the MF-4SC membrane elastic stiffness. The experimental results were considered to suggest that carbon nanotubes influence on the formation of the membrane pore and channel system.

© 2016 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

## Introduction

Perfluorosulfonic acid cation exchange membranes like Nafion, including the analogous Russian MF-4SC membrane (manufactured by the LTD Plastpolymer, St.Petersburg), attract a lot of attention of the scientific community [1,2]. This is due to the broad scope of application of these membranes for water treatment, electrochemical synthesis, and development of environmentally friendly power sources, i.e., low-temperature fuel cells (FC) [1,3]. However, efficient use of Nafion type membranes in FC is hampered by a number of factors such as high fuel and/or oxidant permeability, low

conductivity at low humidity, change in the mechanical properties, and considerable volume changes upon hydration and dehydration [4,5]. Among the approaches used to improve the properties of such membranes, noteworthy is the design of hybrid materials containing inorganic nanoparticles [3,6]. Most often, hydrated oxides and compounds containing easily dissociative protons are used as dopants [7–14]. When they are inserted into the membrane matrix, the conductivity increases because of the presence of additional protons and retention of water at elevated temperature and low relative humidity. Hydrophobic compounds, in particular, carbon nanotubes (CNTs) can also serve as dopants. Most often, they are added to Nafion type membranes to improve the

\* Corresponding author. Tel.: +7 4959522487; fax: +7 4959541279.

E-mail address: [yaroslav@igic.ras.ru](mailto:yaroslav@igic.ras.ru) (A.B. Yaroslavtsev).

<http://dx.doi.org/10.1016/j.ijhydene.2016.04.100>

0360-3199/© 2016 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

mechanical properties and decrease the difference between the sizes of the swollen and dehydrated membrane [15–18]. The advantages noted for CNT-containing hybrid membranes include enhanced mechanical strength and Young's modulus and substantially decreased methanol permeability. However, the proton conductivity often decreases upon modification with CNTs, while at higher CNT content, the electronic conductivity increases, which results in the loss of the FC power. In order to improve the proton conductivity of these composites, CNTs to be used as dopants should have proton-donor groups, in particular, carboxyl [19] or sulfo groups [20], on the surface. The increase in the concentration of charge carriers in the membrane matrix provides higher proton conductivity and better FC performance. Furthermore, in the case of membrane modification with hydrophobic CNTs, the CNTs are likely to be located in the hydrophobic matrix, whereas the CNT whose surface bears groups resembling the membrane functional groups are expected to locate, at least partly, in the hydrophilic region. The mechanical and transport properties and the selectivity of the materials are substantially different depending on the location of the dopant in the hybrid membrane matrix.

Thus, this article deals with the study of transport and mechanical properties of hybrid membranes based on MF-4SC modified by both sulfonated and non-sulfonated CNTs.

## Experimental

### Materials and reagents used

The materials and reagents include multilayer CNTs Taunit S12 (manufactured by the LLC NanoTekhTsentr, Tambov, Russia, 20–40 nm outside diameter, 5–10 nm inside diameter, and up to 10  $\mu\text{m}$  length; prepared by catalytic pyrolysis-CVD of hydrocarbons on an Ni/Mg catalyst); a dimethylformamide (DMF) solution of perfluorosulfonated MF-4SC polymer in the lithium form (LTD Plastpolymer, Russia, 8 wt %, equivalent weight  $\text{EW} = 1100$ , exchange capacity  $\text{EC} = 1 \text{ meq/g}$ ); nitric acid (Chimmed,  $\text{HNO}_3 > 70\%$ ), sulfuric acid (Sigma Tech,  $\text{H}_2\text{SO}_4 > 93.5\%$ ), hydrochloric acid (Chimmed, 35–38% HCl), para-toluenesulfonic acid (Acros, 97.5%  $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{H} \cdot \text{H}_2\text{O}$ ), D-glucose (hydrated form, Merck, Ph Eur), and deionized water (resistance 18.2 M $\Omega$ ).

### Purification and treatment of carbon nanotubes

The CNTs were purified from remains of the catalyst used in the synthesis according to manufacturer's procedures: CNTs were suspended in 30% (by weight)  $\text{HNO}_3$  in 1:8 weight ratio and the suspension was kept for 1 h at 90 °C with continuous stirring. After that, the CNTs were washed with a large amount of water to neutral pH and dried in air for 24 h at 90 °C. The sample thus formed was designated by CNT.

The CNT sulfonation was carried out under hydrothermal conditions in the presence of para-toluenesulfonic acid and D-glucose (0.2 g of CNT, 0.25 g of para-toluenesulfonic acid, 0.25 g of D-glucose, and 20 ml of water) at 180 °C for 24 h according to a procedure reported previously [21]. Then the mixture was centrifuged and washed many times with deionized water to

neutral pH and, after that, it was additionally washed with ethanol and dried for 12 h at 110 °C. The sample thus obtained was designated by CNT-SO<sub>3</sub>H.

### Preparation of hybrid membranes

A weighed portion of CNT or CNT-SO<sub>3</sub>H was mixed with a DMF solution of MF-4SC and dispersed by sonication using a Bandelin Sonorex device (35 kHz frequency) for 2 h. The resulting uniform suspension was poured onto a glass Petri dish and the solvent was removed by drying under the following conditions: 1 h at each of 80, 90, 100, and 120 °C and then 4 h at 80 °C. The unmodified MF-4SC membrane was prepared under similar conditions and the polymer solution was also sonicated. After drying, the films were carefully removed from the Petri dish and hot-pressed for 3 min under a pressure of 5 MPa and a temperature of 110 °C to improve the mechanical properties. The samples thus obtained were designated by MF-4SC, MF-4SC-CNT-x, and MF-4SC-CNT-SO<sub>3</sub>H-x, where  $x = 0.5, 1, 1.5, \text{ and } 3 \text{ wt.}\%$ .

To bring the membranes to standard conditions and to remove the monomer traces, the membranes were conditioned by the following procedure: a) keeping in a 5% HCl solution at room temperature for 1.5 h; b) keeping in a deionized water at a room temperature for 1.5 h, repeated twice.

### Methods

The microstructure and the chemical composition of CNT samples were analyzed using a Carl Zeiss NVision 40 scanning electron microscope (accelerating voltage of 1 kV) with an energy-dispersive X-ray (EDX) analysis attachment. The acquisition time of the EDX analysis was 40 s and each sample was investigated at least in 5 spots. The particle size was determined by transmission electron microscopy (TEM) on a JEOL JEM-2100 equipment (accelerating voltage of 200 kV). Prior to the experiment the hybrid membrane samples were dispersed by sonication in methanol. The IR spectra were measured on a Nicolett IR 1200 instrument (Thermo, Intertech Corporation Inc).

The thermal analysis of samples was carried out using a Netzsch-TG 209 F1 thermobalance. The experiment was conducted in platinum crucibles under argon in the temperature range from 25 to 600 °C (for powder analysis) and from 25 to 150 °C (for membrane analysis). The heating rate was 10 K/min. The composition of the evolved gases was determined on a QMS 403C Netzsch Aeolos mass spectrometer. The water uptake of the membrane was determined from the weight difference before heat treatment and after treatment at 150 °C. For standardization and increase accuracy, all samples were balanced at the relative humidity  $\text{RH} = 95\%$ . The accuracy of water uptake determination was about 2%.

The ion exchange capacity (IEC, meq/g) was determined in the following way. Prior to the experiment, the sample was maintained at 150 °C to determine the IEC of dry cation exchanger. A 0.05–0.3 g portion of the material was kept in 45 ml of a 0.1 M solution of NaCl ( $V_{\text{NaCl}}$ , L) for 24 h with continuous stirring. Then the salt solution was titrated with 0.01 M NaOH. The IEC was calculated from the formula

Download English Version:

<https://daneshyari.com/en/article/1270437>

Download Persian Version:

<https://daneshyari.com/article/1270437>

[Daneshyari.com](https://daneshyari.com)