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Influence of Chemical Nature of Aerosilogel Surface on Proton Conductivity of the Nafion-containing Composites

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Abstract—Aerosilogel modified with hydroxylaluminum (=Al–OH) groups has been synthesized via the molecular layering procedure, and aerosilogel modified with aminopropylsilyl groups [$\equiv Si(CH_2)_3NH_2$] has been prepared via chemisorption of (3-aminopropyl)triethoxysilane. The modified aerosilogel have been further used to prepare composite Nafion-containing electrolytes Nafion. Electrical conductivity of the produced materials has been studied by impedance spectroscopy. Chemical modification of the gel surface strongly affects proton conductivity of Nafion-containing composites.

Keywords: Nafion, aerosilogel, molecular layering, proton conductivity

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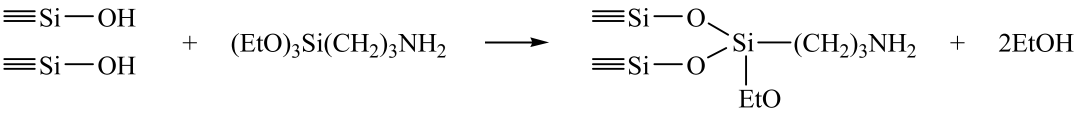
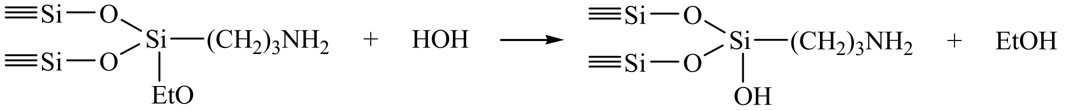
Preparation of novel composite materials based on solid polymer electrolytes and study of their proton conductivity have aroused growing interest of researchers over the past few years. This interest is primarily associated with the potential applications of such materials in various electrochemical devices: fuel cells, humidity sensors, etc. [1–3]. It is expected that the porous morphology and chemical nature of inorganic matrices considerably affect transport properties of the composite solid electrolytes. In the previous paper [4] we reported on preparation of composite solid electrolytes based on Nafion (perfluorinated polymer containing covalently bound sulfonate groups) and silica matrices with varied porosity modified by aromatic sulfonate groups [$\equiv Si(CH_2)_2C_6H_4SO_3H$]. The highest proton conductivity was found in the case of composites containing aerosilogel matrices.

The present work aimed to study the influence of the chemical nature of the aerosilogel surface on the proton conductivity of its composites with Nafion. In particular, we modified the silica surface with basic (3-aminopropyl)silyl groups [$\equiv Si(CH_2)_3NH_2$] and strongly acidic hydroxylaluminum groups (=Al–OH).

Aminopropylsilylation was performed by treatment of the exhaustively hydroxylated aerosilogel surface with (3-minopropyl)triethoxysilane [Eq. (1)] followed by hydrolysis of the alkoxy groups [Eq. (2)] [5].


(1)


(2)

Hydroxylalumination was performed via molecular layering [6, 7]: $AlCl_3$ chemisorption [Eq. (3)] and subsequent hydrolysis of the Al–Cl bonds [Eq. (4)].

Reactions (3) and (4) were performed in a fixed-bed flow reactor at 200–240°C. Nitrogen was used as the carrier gas. Contents of amino groups and

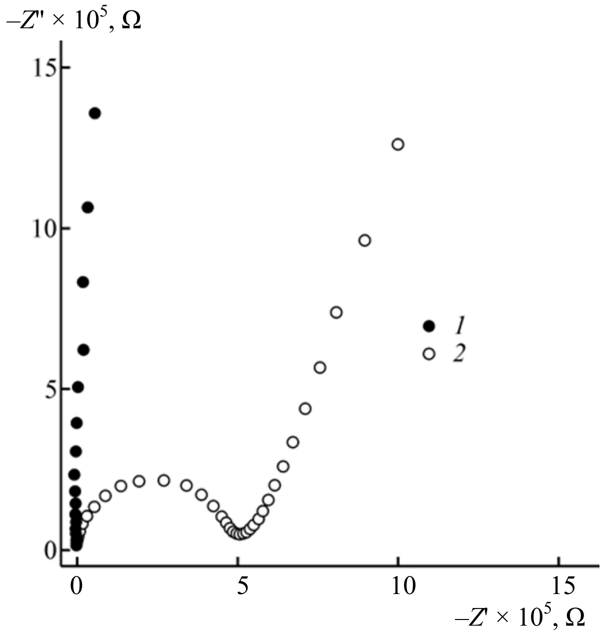


Fig. 1. Impedance plots of (*1*) aerosilogel and (*2*) Nafion Nafion–aerosilogel composite. RH = 33%, $T = 25°C$.

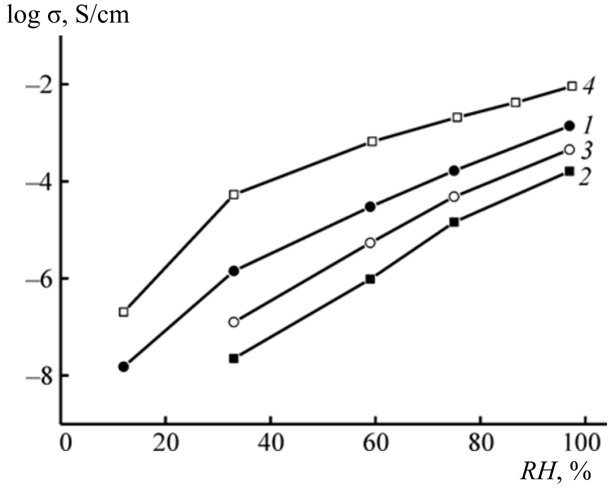
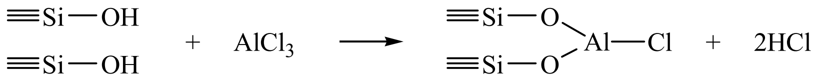
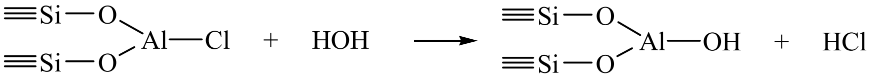


Fig. 2. Proton conductivity of Nafion composites with (*1*) unmodified aerosilogel, (*2*) [=Al–OH]-modified aerosilogel, (*3*) [$\equiv Si(CH_2)_3NH_2$]-modified aerosilogel, and (*4*) [$\equiv Si(CH_2)_2C_6H_4SO_3H$]-modified aerosilogel [4] as function of relative air humidity; $T = 25°C$.



$$2\,\equiv\text{Si–OH} + \text{AlCl}_3 \longrightarrow (\equiv\text{Si–O})_2\text{Al–Cl} + 2\text{HCl} \quad (3)$$



$$(\equiv\text{Si–O})_2\text{Al–Cl} + \text{HOH} \longrightarrow (\equiv\text{Si–O})_2\text{Al–OH} + \text{HCl} \quad (4)$$

aluminum in the samples were of 0.25±0.02 and 0.30±0.02 mmol/g, respectively.

The resulting chemically modified silica matrices, as well as pristine aerosilogel with exhaustively hydroxylated surface were used to produce solid electrolyte composites containing Nafion, the latter was applied via adsorption from its aqueous isopropanol solution. Composition of the so prepared materials is presented in the table.

The influence of environment relative humidity RH and the matrix nature on proton conductivity of the composite materials was studied by impedance spectroscopy. Figure 1 shows impedance plots of the aerosilogel matrix and of its composite with Nafion at relative air humidity of 33% at 25°C. As seen from the plots, the silica gel matrix with exhaustively hydroxylated surface revealed high specific resistance (10^{10}–10^{12} Ω cm); therefore, the electrical conductivity of the resulting composite materials was due to electrolytic properties of Nafion and interactions of its sulfonate groups with functional groups at the silica gel surface.

Figure 2 presents the composites proton conductivity as function of relative air humidity. The highest proton conductivity was observed in the case of the Nafion–fumed silica gel composite containing aromatic sulfonate groups, described in detail

Contents of Nafion in the composite materials

Silica matrix	Nafion contents, mg/g SiO_2
Unmodified aerosilogel	330
Aerosilogel with $\equiv Si(CH_2)_3NH_2$ groups	255
Aerosilogel with =Al–OH groups	30

elsewhere [4]. Conductivity of Nafion composites with hydroxylaluminum- and aminopropylsilyl-modified aerosilogel was lower than that of the composite with the exhaustively hydroxylated aerosilogel.

The enhanced ionic conductivity of composite solid electrolytes is generally ascribed to increased concentration of defects at the dopant–electrolyte interface, resulting from adsorption of mobile ions at the dopant [8, 9]. Therefore, affinity of the solid matrix surface to protons of polymer electrolyte functional groups is of doubtless importance. Bearing this in mind, we could explain the higher proton conductivity of Nafion composite with the silica gel containing amino groups as compared to that of the composite without amino groups. As shown in [10], proton conductivity of perfluorinated sulfonic acid membranes was significantly increased upon doping with small amount of polyaniline. That was considered as confirmation of the vacancy mechanism of proton transport in such membranes. We suggested that the same mechanism was operative in case of the aminopropylsilyl-modified aerosilogel–Nafion composite. The electrical conductivity of the composite of the silica gel with strongly acidic Al–OH groups was lower due to the lack of basic centers at the silica surface.

The lowered conductivity in the case of AlOH-modified silica composite was likely due to the low Nafion content (see table). The unmodified aerosilogel composite revealed higher electrical conductivity as compared to that of the composites bearing surface hydroxylaluminum and aminopropylsilyl groups. In this regard, note that the unmodified silica gel surface was fully hydroxylated, and each silicon atom bore a hydroxyl group (the concentration of the hydroxyl groups was of 8 μmol/m^2 [11]). Chemical modification via reactions 1–4 decreased the Si–OH groups concentration, thus hydrophobizing the gel surface and preventing hydrogen bonds formation between the silica surface and Nafion sulfonate groups. Obviously, that had a dramatic influence on the Nafion composites proton conductivity. The highest proton conductivity was observed in the case of the composite with the sulfonate-modified silica gel. That could result from two factors: first, the acidic groups at the silica gel surface directly contributed to proton conductivity; second, the hydrophobic part of the modifying group could somewhat alter the structure of Nafion conducting channels. Indeed, acidic and hydrophobic dopants often substantially increase proton conductivity of the Nafion composites [1].

To conclude, we demonstrated the dependence of proton conductivity of Nafion-containing composites on the chemical nature of the silica matrix surface.

EXPERIMENTAL

The following reagents were used to prepare composite solid electrolytes: (3-aminopropyl)triethoxysilane (98%, Fluka), $AlCl_3$ ("chemical pure" grade, Vekton), 15% solution of Nafion 1100 in 45 : 40 (w/w) water–isopropanol mixture (Ion Power).

The aerosilogel matrix with the specific surface area of 70 m^2/g and average pore radius of 40 nm was prepared following the procedure adopted from [12]. In order to improve porosity and mechanical properties of the material, hydrothermal treatment of silica was performed at 900°C. As a result, macroporous silica gel showing enhanced capacity with respect to Nafion was prepared. The porous structure of the silica gel was studied by mercury porosimetry using the PA 3M1 device. The specific surface area of the silica gel was measured following the BET procedure with the Micromeritics ASAP 2020 MP analyzer. Nafion content in the samples was determined by titration and gravimetric analysis. Amount of free amino groups was determined via adsorption of Acid Bright Orange Zh [13]. Aluminum was determined with atomic absorption using the MGA-915 instrument.

Proton conductivity of the composites was measured with impedance spectroscopy using the Autolab PGSTAT302 potentiostat/galvanostat over frequency range of 100 Hz to 1 MHz. Relative air humidity of 12–97% in the measurement cell was maintained with the saturated salt solutions. Degussa silver paste was used as electrodes material. Resistance of the samples was determined by extrapolation of the impedance spectrum to the active impedance axis as implemented in Equivalent Circuit software [14]. The electrical conductivity was calculated as follows:

$$\sigma = l/(SR),$$

where R, resistance; l, sample thickness; and S, sample cross-section.

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