Information Technology in Development of Solid Polymer Electrolyte Fuel Cells

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Abstract. The proton-conducting hybrid organic-inorganic composites based on tetraethoxysilane and sulfonated styrene (St) and allyl glycidyl ether (AGE) copolymers, which are characterized by high exchange capacity and specific conductivity, are formed by sol-gel synthesis. The results of a quantum-chemical calculation of the geometry of the structure of an organic-inorganic composite (for a model consisting of 78 atoms) allow us to associate an increase in the proton conductivity of hybrid membranes, compared with the initial copolymer, with the generation of crystallization water and free sulfuric acid during the formation of the composite.

1. Introduction
A hydrogen-air fuel cell with a proton-conducting polymer membrane (PPM) is a system where hydrogen gas is oxidized at the anode, giving off two electrons to the gas diffusion layer (GDL) and two protons in the proton-conducting polymer membrane. Protons that pass through the membrane by the electrochemical potential combine with oxygen at the cathode, forming a water molecule. A catalyst applied to the membrane on both sides is in contact with a porous fibrous electronically-conducting material (GDL), where gaseous reagents are supplied to the membrane, electrochemical reaction products (water) are removed and current collection takes place. The construction composed of the PPM, catalyst and GDL is called the Membrane Electrode Assembly (MEA). Worldwide development is in progress to improve the structure of MEA elements. The efforts of the authors of this work are aimed at studying both the structure and properties of sulfonate hybrid organic-inorganic PPMs characterized by significant heat resistance, mechanical strength, proton conductivity, and low cost as well. Hybrid organic-inorganic materials assume particular importance as part of the membrane-electrode unit of fuel cells (FC) due to the modification of their conductive, mechanical and chemical properties by changing the type of components included in their structure. Such membranes are superior to traditional membranes such as Nafion in a number of indicators, e.g., mechanical strength and the ability to control the hydrophilic component. Earlier we have obtained and investigated the hybrid membranes based on tetraethoxysilane (TEOS) and sulfonated copolymer of styrene and allyl glycidyl ether using physical and chemical methods [1]. It was established that the process of the copolymer sulfonation proceeds both through the aromatic ring of St and the epoxy groups of AGE. As a result, units of styrene sulfonic acid (SSA), 1-(allyloxy)propane-1, and 2-disulfonic acid (ADA) are formed in the copolymer. It was also shown [2] that the specific
conductivity of membranes formed out of hybrid composite exceeds more than an order of magnitude the conductivity of membranes based on sulfonated copolymers without additional proton-conducting groups in them. Such facts have already been pointed out by some researchers [3], however, the appropriate explanation wasn’t given. The aim of this work is to identify the structural features of the PPM and to discuss the mechanism of their proton conductivity using numerical methods.

2. Formulation of the problem

In the synthesis of hybrid ion-exchange materials, organic and inorganic (for example, silicon-containing) compounds are successfully used. TEOS, whose hydrolytic polycondensation forms polysilsesquioxanes due to the cleavage of ethoxy groups, can be used to add a silicon fragment into the hybrid membranes composition. In the case of excess water, the process goes on until silicon dioxide is formed. At this, the surface of silicon dioxide is hydrated and contains hydroxyl groups. Various crystalline modifications of silicon dioxide (which are stable under close to standard conditions) are inorganic hetero-chain polymers based on a siloxane linkage (–O–Si–O–). They are thermodynamically and chemically stable and are characterized by a highly symmetrical structure. The structural element of polymers is a silicon-oxygen tetrahedron, there is a silicon atom in the center of the regular tetrahedron, and oxygen atoms at the vertices. Each oxygen atom in a polymer is bonded to two silicon atoms. The average Si–O bond length, which varies for different modifications of silicon dioxide, is 1.62 Å, and the average distance between oxygen atoms is 2.65 Å (along the edge of the tetrahedron).

The macromolecules of the sulfonated copolymer St and AGE contain a hydrophobic hydrocarbon skeleton, where the number of carbon atoms in the macromolecular chain is from 12 to 232, a phenyl radical with the hydrogen atom replaced by a sulphonic-acid group, and an oxirane ring to which a sulfate group is attached by ether bond. As a result, low-polar copolymer macromolecules get polar groups with negative induction and mesomeric effects. Sulfo and sulfate groups give the copolymer proton conductivity in water medium. When a composite is formed on the basis of organosilicon precursor (TEOS) and sulfonated organic copolymer (SSt–ADA), the molecules of organic and inorganic polymers are combined together (Figure 1). We consider all possible variants of the aggregation between polymers, using systemic approaches of information technology.

![Figure 1. The structure of the composite based on the copolymer SSt–ADA and polysilsesquioxane: where x = 2-72; y = 3-43; z = 1.](image)

**Variant I.** The highly symmetric fragment of silicon dioxide containing surface hydroxyl groups can be the composite nuclear. The composite is formed due to intermolecular hydrogen bonds between the surface hydroxyl groups of silicon dioxide and the sulfo and sulfate groups of the copolymer. Such structure, which is a supramolecular associate, seems likely in relation to symmetry and interaction energy.

**Variant II.** The formation of composite nuclear takes place due to Van der Waals forces with copolymer molecules by binding the hydrocarbon skeleton of macromolecules. Under this option of bonding, sulfo and sulfate groups will be faced out the nucleus and are capable of binding silicon dioxide macromolecules through intermolecular hydrogen bondings. However, the stability of such composite, confined in the nucleus by weak intermolecular forces of physical nature, will be less than that of a silicon dioxid aggregate with fixed sulfonated copolymer macromolecules.
**Variant III.** The formation of the composite nuclear with sulfonated copolymer can take place due to the formation of intermolecular hydrogen bonds between sulfo and sulfate groups of macromolecules. In this way, the low-polar hydrocarbon part of the copolymer will contact silicon dioxide due to Van der Waals forces. The second and third variants of aggregation of the composite components won’t ensure its stability, because Van der Waals forces, that keep macromolecules of the components together or in the composite nuclear, are weak intermolecular forces of physical nature. The polar groups in the organic and inorganic parts of the composite provide an electrostatic interaction between them, but it becomes weak as temperature increases. Formed only due to the Van der Waals interaction PPM won’t be stable at operating temperatures of the fuel cells.

**Variant IV.** Due to configuration effects of the organic fragment molecules the part of sulfo or sulfate groups are used to form the composite nuclear. Free groups can attach silicon dioxide fragments by hydrogen bonds. From the point of view of the entropy factor, such model is more likely than the models in the second and third variants of aggregation of organic and inorganic polymer fragments.

**Variant V.** Due to the sulfate groups of the ADA and the hydroxyl groups of the silicon dioxide fragment, the formation of the covalent C–O–Si link with the simultaneous abstraction of the sulfuric acid molecule is possible between the organic and inorganic macromolecules of the composite. The emergence of covalent bonding in the composite was confirmed by IR spectroscopy [1].

For quantitative evaluation and optimization of five considered above variants for the formation of the organic-inorganic composite, numerical methods of quantum mechanics in chemistry are used. After test calculations were made, the electron density theory method, considering the Van der Waals interaction, was chosen as the optimal quantum chemical method [4, 5]. Optimization of structures geometry was carried out by BP method of density functional (Becke and Perdew), taking into account the density of zero vibrations with the basic set def2-SVP and taking into account the zero-point oscillation energy [6]. The approximate method of integration in Coulomb and exchange interactions RIJK was used to accelerate the process of optimization. Taking into account the inhomogeneity of the electron density distribution, the BP method, or BP86 method, relates to generalized gradient methods (GGA). It is used to calculate the electronic structure and optimize the geometry of polyatomic systems, which are significantly different from uniform electron gas systems [7]. The BP86 method in combination with the def2-SVP basic set as well use of the acceleration option by approximating Coulomb core-electron integrals (RIJ), improves productivity (compared to B3LYP), while maintaining the accuracy of calculations [8].

At the first stage of the composite calculation, the energy of structures was optimized for two different starting geometries. Starting geometries varied in different relative positions of the polymer organic molecule and the silicon dioxide fragment, which contacted each other due to nonspecific and specific intermolecular interactions. The structure of the covalently bonded sulfonated organic copolymer and the fragment of silicon dioxide are modeled in view of experimental detection of C–O–Si covalent link in the composite. In the program package Orca, the internal energy, enthalpy, free energy in standard thermodynamic conditions (T = 295 K, P = 1 atm) were calculated by the density functional method [6] and the geometry of composite nanosystems was optimized based on a silicon-oxygen block and a sulfonated organic macromolecule (SS–ADA and polysilsesquioxane). The structure comprised of 78 atoms was used in modeling, as shown in Figure 2.

**3. The discussion of the results**

As calculated, the preceding structure in the self-organization of copolymer molecules with a silicon dioxide polymer in a composite is the Van der Waals complex with a tetrahedral (dendritic) fragment of silicon dioxide, which is located far from the sulfo and sulfate groups of the organic fragment of the composite, shown in Figure 3. Inorganic and organic fragments are independent molecules coordinated among themselves due to non-specific intermolecular forces. Three intramolecular hydrogen bonds promote to the optimization of the geometric structure in each independent
components of the complex. Given complex further entered more dynamically and thermodynamically stable forms containing a fragment of silicon dioxide in a ring configuration (Figure 4-9).

\[
\text{CH}_3\text{-O-OSO}_3\text{H} \cdot \left[\text{Si}_4\text{O}_3\text{(OH)}_{10}\right]
\]

**Figure 2.** Model structure of organic-inorganic composite.

General crystal chemical analysis of the five above-considered variants for the formation of the organic-inorganic composite lets substantiate three ways of self-organization of a sulfonated copolymer and silicon dioxide: 1) the molecules of the organic and inorganic polymers form a complex due to Van der Waals forces (Van der Waals complex); 2) molecules of organic and inorganic polymers form a supramolecule due to external hydrogen bonds between silicon dioxide and a sulfonated copolymer; 3) molecules of organic and inorganic polymers form a molecule through the C–O–Si covalent link with additional intermolecular hydrogen bonds. Numerical quantum chemical calculation of these three ways of structural optimization will show the preference of the composite self-organization according to one of three directions. The analysis of the results of the computer experiment is presented below.

**Figure 3.** Van der Waals complex model of the SSt–ADA composite with a tetrahedral silicon dioxide fragment.

In Figures 3-9, the dark gray spheres are carbon atoms, light gray spheres are hydrogen atoms, red spheres are oxygen atoms, yellow spheres are sulfur atoms, dark green spheres are silicon atoms.

The model of the silicon dioxide fragment in the ring configuration is stable both dynamically and thermodynamically. As its precursor (intermediate) in a process of hybrid membranes synthesis, the dendritic configuration is thermodynamically stable, while remaining dynamically unstable, that is reflected through negative vibrational frequencies at the central node of dendrite (Figure 4, 5, Table 1). The transition from dendritic configuration to ring one is accompanied by the release of a water molecule into the given nitrogen dioxide group. In this case, the water molecule remains bound to the ring configuration of the inorganic polymer by two intermolecular hydrogen bonds (the so-called crystallization water). The molecular formula of the model didn’t change in this replacement. Therefore, models structures can be intercompared by electronic energy. The ring configuration of silicon dioxide provides the dynamic stability of the composite macromolecules formed with its participation. If the water molecule “evaporates”, then the structure will become less stable.
Figure 4. Changing in the silsesquioxane fragment in the structure of the composite model. 

Figure 5. The structure of the silsesquioxane fragment after optimization.

Table 1. Comparison of energy of states parameters in dendritic and ring silicon dioxide models.

| Structure                  | Electronic Energy (E), Eh | Free Energy (G), Eh | Difference E/G, kJ/mol | Number of Hydrogen Bonds |
|----------------------------|----------------------------|---------------------|------------------------|--------------------------|
| Si₄O₃(OH)₁₀, line          | -2141.7104                 | -2141.6018          | 34.3/26.5              | 3                        |
| Si₄O₄(OH)₈*H₂O, cycle      | -2141.7235                 | -2141.6119          | 0/0                    | 4                        |

In table 2 results of calculating the formation of four models of the organic-inorganic composite with a ring configuration of silicon dioxide fragment are presented. The first structure in table 2 and figure 6 is a supramolecular associate in which the interaction between the fragments of the SSt–ADA copolymer and silicon dioxide takes place due to the hydrogen atoms of the hydroxyl groups and oxygen atoms of the inorganic polymer, as well as two sulfate and one sulfo groups of the organic part of the composite. Between these groups there are intermolecular hydrogen bonds in the number of 10 pieces per supramolecule under examination. Oxygen of the ether link is not involved in the process of self-organization of the supramolecule. Inorganic and organic polymers are independent nanomolecules coordinated with each other due to intermolecular bonds. The optimization of the geometric structure of each of the independent composite particles is promoted by intramolecular hydrogen bonds in nanomolecules of silicon dioxide and a sulfonated copolymer. The model shown in Figure 6 corresponds to the maximum resistance of the composite supramolecule, which is in the ground energy state.

Table 2. Comparison of energy of states parameters in composite models.

| Model number | Electronic Energy, Eh | Free Energy, Eh | Electronic Energy, in units of state 4, Eh | Free Energy, in units of state 4, Eh | Electronic Energy, in units of state 4, kJ/mol | Free Energy, in units of state 4, kJ/mol | Number of Hydrogen Bonds (n) |
|--------------|-----------------------|-----------------|---------------------------------------------|-------------------------------------|-----------------------------------------------|----------------------------------------|----------------------------|
| 1            | -4784.2896            | -4783.8304      | 0.0181                                      | 0.0128                              | 47.70                                         | 33.55                                  | 10                        |
| 2            | -4784.2592            | -4783.8042      | 0.0485                                      | 0.0390                              | 127.37                                        | 102.21                                 | 6                         |
| 3            | -4784.2687            | -4783.8105      | 0.0391                                      | 0.0327                              | 102.48                                        | 85.70                                  | 9                         |
| 4            | -4784.3078            | -4783.8432      | 0                                           | 0                                   | 0                                             | 0                                      | 10                        |

The second model of the composite supramolecule (Figure 7) is in an excited energy state. Electronic energy of the second modal is 80 kJ/mol higher than electronic energy of the first modal. The ether oxygen atom and one (outermost) sulfate group of the organic fragment of the composite
participate in the formation of intermolecular bonds, the sulfo group of the benzene ring is distance away and does not form bonds while the formation of the composite. On the part of the silicon dioxide fragment, hydroxyl groups are involved. The total number of hydrogen bonds in the structure of the second model is 6. Both in the first and second structures, intramolecular hydrogen bonds are present in the silicon dioxide and organic fragments. The structures of models 1 and 2 contain one molecule of crystallization water, which was formed due to optimization of the structure of the silsesquioxane block (Si$_x$O$_y$(OH)$_z$).

The third model of the composite structure is a covalently bound molecule of a fragment in a sulfonated organic copolymer and a fragment of silicon dioxide. Similar structures are formed as a result of heat treatment of composite material. The formation of covalent link confirms the presence of a signal in the IR spectrum (1170-1100 cm$^{-1}$) corresponding to the Si–O–C bond. The third model structure (Figure 8) was obtained by replacing the extreme sulfate group of ADA formed while copolymers sulfonation on the oxirane ring, with a silicon dioxide fragment. The configuration of the composite molecule is in the excited state. Through to the Si–O–C covalent link, the resulting particle is an independent molecule with intramolecular hydrogen bonds, which are formed between the sulfo group of the benzene ring, the rest of sulfate group of the SS$_x$–ADA copolymer. The separated sulfuric acid molecule and the water molecule constituting the solvent phase are involved in the formation of intermolecular bonds with the composite molecule. The total number of hydrogen bonds per structure of the third model is 9.

**Figure 6.** Spatial structure of composite, model 1.  **Figure 7.** Spatial structure of composite, model 2.

**Figure 8.** Spatial structure of composite, model 3.  **Figure 9.** Spatial structure of composite, model 4.
The fourth model of the composite structure (Figure 9) is a molecule in which the crosslinking of the organic and inorganic fragments occurred with the participation of the second carbon atom ADA. Hydrogen atoms of the hydroxyl groups and oxygen atoms of the silicon dioxide part, the rest of sulfate group and the sulfo group of the benzene ring of the organic part in the macromolecule are involved in formation of intramolecular bonds. Solvent molecules (H$_2$O, H$_2$SO$_4$) are bound by intermolecular bonds to the composite macromolecule. In this case, the water molecule gives three hydrogen bonds with different components of the composite in model 4. The total number of hydrogen bonds per model is 10.

4. Conclusion
Crystallization water formed at the stage of ring formation is present in all structures of the composite and stabilizes them through different channels. A water molecule binds oxygen of the ring part of the composite with hydrogen bonds by one hydrogen atom, and also ether oxygen or sulfate oxygen of the organic part of the composite by another hydrogen atom. In the fourth model, the water molecule forms three bonds, the third bond through the oxygen of water bonds crystallization sulfuric acid. The appearance of crystallization water and sulfuric acid in the structure of the composite molecules explains the observed increase in the proton conductivity of PPM.

Additional energy obtained in transition from the Van der Waals complex with a dendritic silicon dioxide fragment through the Van der Waals complex with the ring structure of the inorganic fragment into the structures of supramolecules and covalently bound molecules can be explained by increasing in the number of hydrogen bonds and an energy gain due to covalent C–O–Si bonds, which compensates for the departure of one acid molecule. A special role in stabilizing the configuration of the composite is given to crystallization water accompanying the quartz fragment with a ring configuration in models 1–4.

The structural features of the PPMs containing silicon dioxide, found by a numerical method, explain the increase in their proton conductivity in comparison with the SST–ADC copolymer.

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