ХІМІЧНІ НАУКИ

Demydova Kh.V.
Post-Graduate Student;
Yevchuk I.Yu.
Candidate of Chemical Sciences;
Demchyna O.I.
Candidate of Chemical Sciences,
Department of Physico-chemistry of Fossil Fuels L.M. Lytvynenko Institute of Physico-organic Chemistry and Coal Chemistry NAS of Ukraine
Kopylets V.I.
Candidate of Chemical Sciences,
H.V. Karpenko Physico-Mechanical Institute NAS of Ukraine
Koval Z.M.
Candidate of Chemical Sciences;
Romaniuk H.V.
Candidate of Chemical Sciences,
Lviv Polytechnic National University

COMPUTER MODEL OF PROTON TRANSFER IN PROTON CONDUCTING POLYMER MEMBRANE

Proton conducting membrane is a key element of fuel cell. Fuel cells are gaining more and more popularity due to their efficiency and environmental performance (hydrogen or methanol usually serves as a fuel for fuel cells). In addition, fuel cells are compact and relatively cheap, which makes their use in transport, in energy and in household appliances. A large number of publications related to the synthesis and study of proton conductive properties of different materials indicates the growing interest in this area of research over the last couple of years.

Proton conducting membrane for fuel cell must meet a number of requirements. The main function of membrane in fuel cell is proton transfer from cathode to anode. Proton conducting membrane must be heat-resistant, strong, and it must also separate fuel and oxidant.

Leading position among the materials for making membranes is occupied by polymer materials. In particular, Nafion membrane is the mostly used in fuel cell applications and the only commercial available. This is a perfluorosulfonated membrane with hydrophobic backbone and short side chains containing hydrophilic sulfogroups.

Nafion membranes exhibit high proton conductivity ($\sim10^{-2}$Sm/cm), good thermal and mechanical properties. However, they are expensive, have methanol permeability. Additionally, at high temperature and low humidity, their proton conductivity significantly reduce. Therefore, the attempts to develop the alternative materials for manufacturing membranes for fuel cells are actual.

Various ionic polycondensation materials based on poly(benzimidazoles), poly(vinyl alcohol), poly(ether ether ketones), poly(arylphosphazenes) *etc.* are tested as proton conducting materials.

Synthesis of composite organic-inorganic materials is a new promising approach to creating proton conducting membranes for fuel cells.

It should be noted that up-to-date the theoretical study of proton conducting membranes was conducted mainly for conventional Nafion membranes. In the earliest works the authors used approaches with a large number of empirical parameters, so these methods, though allowed to draw some conclusions about the structure of the investigated membrane, did not allow to model the structure of proton conducting membrane with sufficient reliability.

Afterwards researchers began to use atomistic modeling methods for theoretical investigation of membrane structure. With the help of these methods phase distribution of polar polymer fragments in polymer matrix was determined. Mechanism of diffusion of water and hydroxonium ions in polymer matrix was studied. The role of sulfocontaining side chains of fluoropolymers in formation of proton channels was established as well.

Recently, successfully developed a method of mesoscopic dynamics, based on the density functional method, is successfully developed [1]. It allows to study the structure and behavior of membrane systems at large spatial and temporal scales.

The most accurate information on the properties of different molecular groups and mechanisms of proton transfer is provided by quantum-mechanical calculations.

The search for alternative materials for proton conducting membranes cuases the need for theoretical study of their structure and properties by methods of computer modeling.

The aim of this work is the theoretical research of synthesized sulfocontaining membranes.

We have synthesized polymer sulfocontaining membrane by photoinitiated polymerization of composition: 3-sulfopropylacrylate potassium salt, acrylamide and acrylonitrile. Curing of thin films of composition takes place in the presence of photoinitiator 2,2-dimethoxy-2-fenylacetofenone (IRGACURE) under UV irradiation with intensity of 14 W / m^2. The resulting films were washed from unreacted monomers in distilled water some times.

The presence of sulfocontaining groups in synthesized polymer provides a proton conducting properties of the material. It was confirmed by the method of impedance spectroscopy.

There have been synthesized organic-inorganic membrane by similar way – photoinitiated polymerization of polymer composition in the presence of sol-gel system based on tetraethoxysilane. Sol-gel system TEOS : C_2H_5OH : H_3PO_4 : H_2O was introduced into polymer composition and during curing of this composition sol-gel transformation occurs simultaneously with the process of the poplymer4 chain formation. Thus a joint organic-inorganic composite structure in formed,where organic and inorganic components are combined at nanoscale. The features of such joint network determine the properties of the composite.

In the theoretical study of the properties of polymer and hybrid organic-inorganic membranes synthesized by the method of photoinitiated polymerization of monomers containing sulfogroups (for the last ones in the presence of sol-gel system TEOS : C_2H_5OH : H_3PO_4 : H_2O) modeling and calculation of their proton conductivity are important.

Investigation of transport properties of polymer membranes includes the analysis of molecular interactions and topology of ion channels formed in polymer matrix.

It is known that the properties of polymers with ionic groups strongly depend on their morphology, which in turn depends on the chemical structure of polymer.

There are two mechanisms of proton transport in polymer membranes [1]. According to the Grotthuss mechanism, proton transfer takes place in the aquatic environment along the center of the channel through continuous proton exchange between water molecules and hydroxonium molecules.

Another mechanism suggests that protons are transmitted both through the diffusion transport of hydroxonium ions H_3O^+ and through the exchange of protons between neighboring sulfogroups located along the channel walls.

The value of proton conductivity depends largely on the water content in the membrane, which is determined by the number of water molecules corresponding to one sulfogroup. According to the modern ideas the ability of proton conducting material to bind water is related with the complex coordination of water molecules by active groups ($–SO_3H$, $–PO_3H_2$ *etc*.).

However, the reasons of the formation of the joint channels in polymers are not yet fully understood. Thus, the proton conductivity of Nafion membranes increases significantly already at small amounts of water when the volume fraction of hydrated ionic groups is relatively low and they would exist in the form of isolated clusters [1].

In this paper, a model of bulk polymer on the basis of sulfopropylacrylate, fragments (6 monomers) of which form a closed loop of sulfogroups, directed inside each cycle, is constructed. All cyclic polymers are cross-linked by single transversal bonds (the number of such connections was 5).

Founded structure resembled a tube and modeled polymer pore. At each sulfogroup six water molecules were coordinated with an average length of hydrogen bonds O ... H equal to 1.95Å.

Proposed system is the ultimate model in which one can see the lowest activation energy of proton separation from sulfogroup (~ 0.12 eV) following by its subsequent coordination by two molecules of water. In the form of H_3O^+ cation proton passes through three planes of polymer cycles with activation energy of about 0.08 eV, which is commensurate with the energy of thermal motion of water molecules at 258 K.

Using the method of molecular dynamics the estimation of the values of coefficient of proton diffusion at the temperature of 25˚C for this model was made, which was equal to $7.2 \cdot 10^{-6}$ cm^2 / s.

In contrast to the results obtained previously (e.g., in the publication [2], where the authors have used the precise method of functional density and have constructed too simplified model of proton transfer for another polymer materials) we propose the model, where a complex system was constructed, that allows to obtain satisfactory results of calculation of proton transfer parameters in polymer matrix based on the semiempirical quantum-chemical method PM6 and the method of molecular dynamics.

Henceforth this model will be improved in order to take into account the inorganic components which are present in the composite organic-inorganic membranes on the basis of polymers and alkoxycompounds using sol-gel method.

References:

1. Komarov P.V., Veselov I.N., Khalatur P.G. Nanoscale morphology in ionomer membranes on the basis of sulfonated aromatic poly (ether ether ketones): mesoscopic modeling // Vysokomolekuliarnyje soyedinieniya. – 2010. – 52(2). – P. 279-297.

2. Kreuer K.-D., Paddison S.J., Spohr E., Schuster M. The modeling of molecular structure and ion transport in sulfonic acid based ionomer membranes // Journal of New Materials for Electrochemical Systems. – 2001. – 4 (4). – P. 197-208.

Карнаухова Ю.О.
студентка,
Одеський національний університет імені І.І. Мечникова
Луцюк А.Ф.
інженер І категорії,
Фізико-хімічний інститут імені О.В. Богатського
Національної академії наук України

СИНТЕЗ ПОХІДНИХ N,N’-ДИКАРБОКСИМЕТИЛДІАЗА-18-КРАУН-6 З ПОТЕНЦІЙНОЮ ПРОТИВІРУСНОЮ АКТИВНІСТЮ

Краун-етери та їх похідні мають широкий спектр біологічної активності. Вони проявляють анальгетичну, антимікробну, ноотропну, протисудомну дію, виявляють протипухлинну та антивірусну активність [1, 2]. Біологічна активність краун-етерів обумовлена їх здатністю змінювати іонну проникність клітинних мембран і внаслідок цього полегшувати транспорт біологічно активних сполук через гістогематичні бар'єри. Особливий інтерес у цьому плані становлять діазакраун-етери, які, з одного боку, можуть забезпечити ефект концентрування антивірусних сполук, а з іншого – підвищити ефективність їх транспорту та біодоступність.

У зв’язку з цим, нами синтезовано N,N’-дикарбоксиметилдіаза-18-краун-6 і досліджено взаємодію з естерами ε-амінокапронової та *п*-амінометилбензойної кислот (бензиловим і *трет*-бутиловим) з метою створення на їх основі потенційних противірусних препаратів з вільною карбоксильною функцією.