

## Proton Conductivity of Water in Mesoporous Materials

M. I. Ryzhkin<sup>a</sup>, I. A. Ryzhkin<sup>a, b, \*</sup>, A. M. Kashin<sup>b</sup>, E. A. Galitskaya<sup>a</sup>, and V. V. Sinitsyn<sup>a</sup>

<sup>a</sup> Institute of Solid State Physics, Russian Academy of Science, Chernogolovka, Moscow region, 142432 Russia

<sup>b</sup> Inenergy Company Group, Moscow, 111524 Russia

\*e-mail: ryzhkin@issp.ac.ru

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A model explaining a high proton conductivity of water in mesoporous materials has been proposed. The model is based on the theory of an intermediate phase of water with an ordered oxygen lattice and a destroyed proton lattice and involves various types of interaction of water molecules with an interface. The model is in fact based on an analogy of the interface and a liquid-like surface layer of ice. Possible methods for increasing the proton conductivity, experiments for testing the proposed model, and application of the results to the creation of efficient proton-exchange membranes have been discussed.

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### INTRODUCTION

Water and ice as its solid phase are the most widespread, important, and unusual materials on the Earth. Their physical properties were studied in thousands of works. In the last two decades, attention was focused on the study of confined water, which has properties significantly different from the properties of bulk water and plays a significant role in biology, chemistry, and technology. In particular, in most of the efficient proton-exchange membranes used to create hydrogen fuel cells, proton transport occurs through water filling a porous medium. An increase in the proton conductivity of such membranes, the upper limit of working temperatures, and the time of continuous operation is an important applied problem.

At the same time, a detailed understanding of the nature of a high proton conductivity of water in mesoporous materials is still absent. Indeed, the specific proton conductivity of fairly efficient proton-exchange membranes can be as high as about 10 S/m at a temperature of 298 K [1]. At the same time, upper estimates of the diffusion coefficient and concentration of  $\text{H}_3\text{O}^+$  ions for pure bulk water are  $3.5 \times 10^{-9} \text{ m}^2/\text{s}$  and  $1.1 \times 10^{22} \text{ m}^{-3}$ , respectively. As a result, the conductivity of bulk water is about  $10^{-4} \text{ S/m}$ , which is five orders of magnitude below the conductivities of the best membranes.

Why is the proton conductivity of water confined in channels of mesoporous materials noticeably higher than the conductivity of bulk water? How can the size of channels responsible for a high proton conductivity be estimated? What is the role of impurities in the formation of a high proton conductivity? How can the conductivity be further increased? The aim of this

work is to develop a theoretical model to partially answer these questions.

It is also noteworthy that numerous ab initio molecular dynamics studies of the behavior of confined water have already been reported. These studies give many interesting results but do not provide the complete solution of the problem for the following reasons. First, they do not provide a qualitative understanding of proton transport in confined water. As a result, it is impossible to give practical recommendations for increasing the proton conductivity. Second, the accuracy of numerical results because of the finite dimensions of a cluster and a finite simulation time remains unclear. The latter circumstance is particularly important because the energy spectrum of various configurations of water molecules has numerous local minima, which results in a very slow relaxation. For these reasons, in this work, we try to develop a simple analytical model of proton transport in confined water.

### DESCRIPTION OF THE MODEL

Our model is based on the existence of a liquid-like surface layer of ice [2, 3], which has an anomalously high surface conductivity many orders of magnitude higher than the conductivity of bulk ice [4]. To describe the physical properties of this layer, a model based on an intermediate state of ice with the ordered oxygen lattice and disordered proton lattice was recently proposed [5, 6]. To describe the behavior of water in a mesoporous material, in view of experimental data, we assume that water near pore walls is also in this intermediate state. Violations of the ice rules or point proton defects move over a network of hydrogen

bonds through the Grotthuss mechanism [7], thus ensuring proton transfer such as in ordinary ice [8]. In fact, our approach is a direct analog of the model of the liquid-like surface layer of ice [5]. A more detailed description of all foundations of the model is given below.

In ordinary hexagonal ice at zero absolute temperature, oxygen ions form an ordered wurtzite-type lattice, whereas protons are distributed over hydrogen bonds according to the ice rules: two protons near each oxygen ion and one proton on each hydrogen bond. Such a structure of the proton subsystem is frozen; i.e., neither the relaxation of the proton sublattice nor proton transport is possible [9]. Ice at a nonzero temperature includes  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  ionic defects and  $D$  and  $L$  bond defects violating the ice rules [10]. These defects in the physics of ice serve as classical quasiparticles whose motion is responsible for electric relaxation and proton transport. Their effective charges, mobilities, and equilibrium concentrations can be extracted from various experiments [11].

A pair of ionic defects is formed at the displacement of a proton along bond, and a pair of bond defects is formed at the displacement of a proton from one bond to another. The pair formation energy consists of two terms: the formation energy of defects with opposite charges at the minimum distance and energy of their separation at a large distance (about an average distance between defects). The latter term of the energy decreases with increasing concentration of defects due to the screening of the Coulomb interaction. However, a decrease in the formation energy results in an increase in the concentration. This positive feedback at increasing temperature leads to a sharp stepwise increase in the concentration of defects, i.e., to the melting of the proton sublattice at the held structure of the oxygen lattice [6].

In this case, the oxygen lattice in bulk samples also becomes unstable, the complete melting of ice occurs, and the intermediate state called liquid ice or solid water does not appear. However, the intermediate state with the melted proton sublattice and held oxygen lattice can appear in certain situations, e.g., in the surface layer of ice. In [5], we showed that the combination of outward ordering of protons on the surface and the transition to the aforementioned intermediate phase results in the formation of a fairly wide surface layer with an increased concentration of defects violating the ice rules. This liquid-like layer of ice is responsible for a low coefficient of friction, adhesion of ice, flow of glaciers, freezing of snow, and a high surface proton conductivity. The inner part of the layer, where the concentration of bond defects is below the critical value for the destruction of the oxygen lattice is a Faraday layer, which differs from both ice and water [2]. The concentration of bond defects in the outer part is above the critical value; for this reason, the oxygen lat-

tice is destroyed, and this part is a usual water film or a Thomson layer [3].

## BASIC EQUATIONS

We now describe water filling a cylindrical channel in a hydrophobic material. Taking into account numerous experimental results, we assume that water in a sufficiently narrow channel is much more ordered in oxygen than bulk water. For this reason, the description of proton transport in confined water by the Jaccard model is even more justified than the description in bulk water [12, 13]. Consequently, the Jaccard theory initially developed for ice can be further used to describe proton transport. The interface between water with the hydrophobic material is physically similar to the ice–air interface, and we assume that water molecules at the interface will also be oriented with protons toward the channel walls.

Using the results obtained in [5], we represent the free energy in electronvolts per hydrogen bond as a function of the concentration of bond defects in the form

$$f(n) = \left[ E_{34}^1 + \frac{E_{34}^2}{1 + \kappa b} \right] n + kT[2n \ln(n) + (1 - 2n) \ln(1 - 2n)]. \quad (1)$$

Here,  $E_{34}^1 = 0.05$  eV is the formation energy of a pair of bond defects at the minimum distance  $b = \sqrt{2/3}r_{\text{OO}}$ , where  $r_{\text{OO}}$  is the hydrogen bond length;  $E_{34}^2 = 0.63$  eV is the separation energy of bond defects at a large distance;  $n = N_{34}/2N$  is the relative concentration of bond defects; and  $N_{34}$  and  $N$  are the volume concentrations of bond defects and water molecules, respectively. The inverse screening length is given by the formula

$$\kappa = \sqrt{\frac{16\pi N}{\epsilon_{\infty} kT} q_{34}^2 n}. \quad (2)$$

Here,  $\epsilon_{\infty} \approx 3.2$  is the high-frequency dielectric constant and  $q_{34} = 0.36e$  is the effective charge of bond defects, where  $e$  is the elementary charge. The concentration of ionic defects can be neglected at this stage because it is five or six orders of magnitude lower than the concentration of bond defects [6]. The equilibrium concentration of defects is determined by minimizing Eq. (1), which is schematically shown in Fig. 1. The right minimum corresponds to a metastable state at temperatures below the transition temperature and to a stable state at temperatures above the transition temperature.

The concentration near the interface with pore walls and channels is nonuniform; i.e., it depends on coordinates  $n(\mathbf{r})$ . In this case, instead of Eq. (1), one

should minimize the functional including gradient term:

$$F[n(\mathbf{r})] = N \int_V \left[ \frac{\lambda}{2} (\nabla n)^2 + f(n) \right] dV, \quad (3)$$

where the parameter  $\lambda$  characterizes the capability of the system to keep a uniform concentration distribution [5, 14]. This parameter can be either constant in a model with a short-range interaction or a function of the concentration in more complex models. In the former case considered in this work, this constant is  $\lambda = Er_{00}^2$ , where  $E$  is the energy constant about the formation energy of a pair of bond defects (about 1 eV). The equation obtained by minimizing functional (3) should be supplemented with boundary conditions characterizing the interaction of water molecules with walls:

$$n(\mathbf{r}_S) = n_S. \quad (4)$$

For the free surface of ice,  $n_S = 0.5$ , and this condition is also assumed for the interface between water and the hydrophobic surface. This physically corresponds to the orientation of molecules near the interface by protons to the surface. In this case, the boundary value of the concentration of  $L$  defects will be equal to the above value.

In the next section, we use the derived equations to describe the concentrations of proton defects and to estimate the conductivity of water in narrow cylindrical channels.

## RESULTS

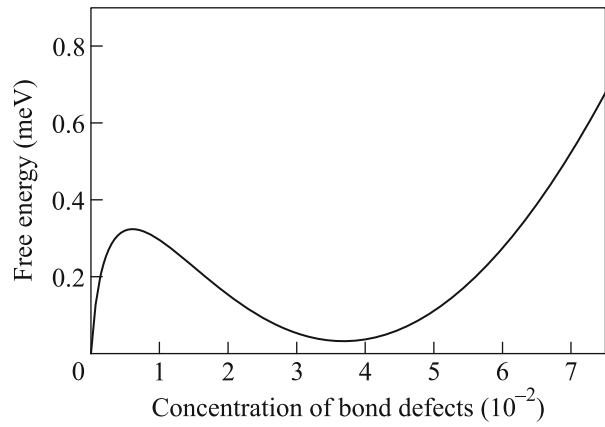
The minimization of the functional for the cylindrical channel geometry (in the case of axial symmetry) gives the problem

$$\frac{d^2 n}{dr^2} + \frac{1}{r} \frac{dn}{dr} = \frac{1}{\lambda} \frac{df}{dn}, \quad n(r=R) = n_S. \quad (5)$$

After the determination of the concentration of bond defects  $n(r)$ , the concentration of ionic defects  $m(r)$  can be calculated with a sufficient accuracy by the formula

$$m(r) = \frac{2}{3} \exp \left[ - \left( E_{12}^1 + \frac{E_{12}^2}{1 + 443\sqrt{n/T}} \right) / 2kT \right], \quad (6)$$

where  $m = N_{12}/N$  and  $N_{12}$  are the relative and volume concentrations of ionic defects, respectively, and  $E_{12}^1 = 0.67$  eV and  $E_{12}^2 = 0.73$  eV are the formation and separation energies of ionic defects, respectively, similar to  $E_{34}^1$  and  $E_{34}^2$  for bond defects, respectively [5]. The physical meaning of Eq. (6) is very simple. It is the usual Arrhenius law, where the formation energy of defects depends on coordinates because of the screening of bond defects. The knowledge of the concentra-



**Fig. 1.** Free energy of the proton subsystem versus the concentration of bond defects at the critical temperature of a first order phase transition. The concentration of defects decreases with increasing distance from the surface: motion on the line from right to left. The largest contribution to the transient layer comes from the region of the right minimum, because the rate of change in the concentration with the distance is proportional to the square root of the free energy.

tion will allow us to find the low- and high-frequency conductivities.

Nonlinear equation (5) with the function  $f(n)$  specified by Eq. (1) can be solved numerically. However, an analytical solution can also be obtained with a sufficient accuracy. To find it, we note that our aims require knowing the behavior of the function  $f(n)$  only near the first minimum in Fig. 1. For this reason, we take this function in the form

$$f(n) = \frac{\alpha}{2} (n - n_{\min})^2. \quad (7)$$

The substitution of Eq. (7) into Eq. (5) gives the zeroth order Bessel equation

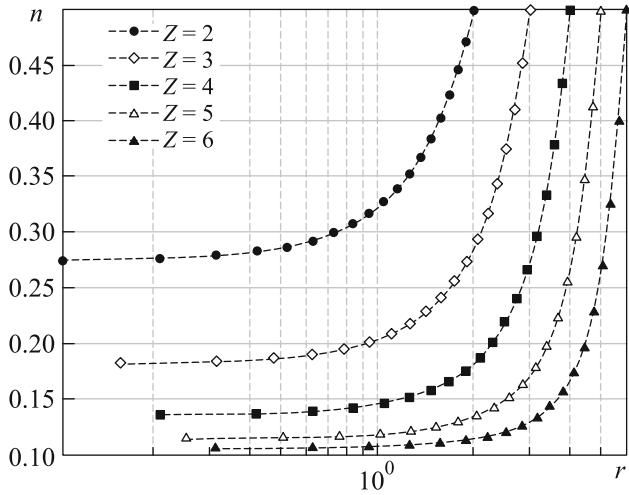
$$r^2 n'' + rn' - \frac{\alpha}{\lambda} r^2 (n - n_{\min}) = 0. \quad (8)$$

Its solution satisfying the boundary condition can be written in the form

$$n(r) = (n_S - n_{\min}) \frac{I_0(r/a)}{I_0(R/a)} + n_{\min}, \quad (9)$$

where  $I_0$  is the zeroth order modified Bessel function and  $a = \sqrt{\lambda/\alpha} \approx r_{00}$ , if  $\alpha \approx E$ . The condition of absence of any singularity at the center of the channel was taken as the second condition for the second-order equation.

Figure 2 shows the dependence of the concentration of bond defects  $n(z)$  on the dimensionless distance from the center of channel  $z = r/a$  for various channel radii  $Z = R/a$ . According to Fig. 2, the concentration of bond defects decreases rapidly with increasing distance from the wall. The effect of the



**Fig. 2.** Concentration of bond defects versus the dimensionless distance from the center of the cylindrical channel with the radii  $Z = 2, 3, 4, 5,$  and  $6$  at room temperature of  $T = 298$  K.

surface on the concentration at the center of the channel is manifested only for a channel radius of about several hydrogen bond lengths, i.e., for a channel diameter of about several nanometers. In this case, the concentration increases not too strongly, and the proton conductivity of water confined in the channel is seemingly about the conductivity of bulk water.

However, this conclusion disregards that the interaction of water molecules with the channel walls assumingly keeps the structure of the oxygen lattice. This means that the mobilities or diffusion coefficients of defects in confined water can be taken from the physics of ice and be extrapolated to the corresponding temperatures. We numerically estimate the low- and high-frequency conductivities of water. Using the mobilities at a temperature of 253 K for ice and activation energies from [11], we obtain the following values for the diffusion coefficients of defects at a temperature of 298 K:

$$\begin{aligned} D_1 &\approx 3.1 \times 10^{-9} \text{ m}^2/\text{s}, & D_2 &\approx 1.06 \times 10^{-9} \text{ m}^2/\text{s}, \\ D_3 &\approx 0 \times 10^{-9} \text{ m}^2/\text{s}, & D_4 &\approx 2.3 \times 10^{-9} \text{ m}^2/\text{s}. \end{aligned} \quad (10)$$

Using these values and formulas for the low- and high-frequency conductivities of ice, we arrive at the formulas [15]

$$\sigma_0 = \frac{4580}{Z^2} \int_0^Z m(z) z dz, \quad \sigma_\infty = \frac{255}{Z^2} \int_0^Z n(z) z dz. \quad (11)$$

Further, from Eqs. (6), (9), and (11), we obtain the following estimates of specific conductivities at channel radii  $Z = 2, 3, 4, 5, 6$ :

$$\sigma_0 = 1.41, 1.29, 1.19, 1.12, 1.0 \text{ (} 10^{-3} \text{ S/m)}, \quad (12)$$

$$\sigma_\infty = 4.83, 4.02, 3.48, 3.10, 2.83 \text{ (} 10^1 \text{ S/m)}. \quad (13)$$

According to these results, the low-frequency conductivity of confined water characterizing the proton transport rate is about an order of magnitude higher than the corresponding conductivity of bulk water. This excess is due to the assumption that the oxygen lattice holds, i.e., that the mobilities of proton defects in ice can be extrapolated to high temperatures in water. The high-frequency conductivity determining electric relaxation times is several times higher in confined water than in bulk water.

The reported results indicate a slight increase in the low-frequency proton conductivity in confined water. However, this increase is insufficient to explain the experimental conductivity of water in porous polymeric membranes. In order to correct this deficiency of the theory, we first note that a comparatively low low-frequency proton conductivity is due to the low concentration of ionic defects calculated by Eq. (6). In fact, we consider bond defects as the main type of defects leading to a phase transition and impose boundary conditions on bond defects by analogy with the free surface of ice. In this case, the concentration of ionic defects is five or six orders of magnitude lower than the concentration of bond defects in the layer immediately adjacent to the wall; i.e., the relative concentration of ionic defects near the wall is about  $10^{-6}$  or even lower.

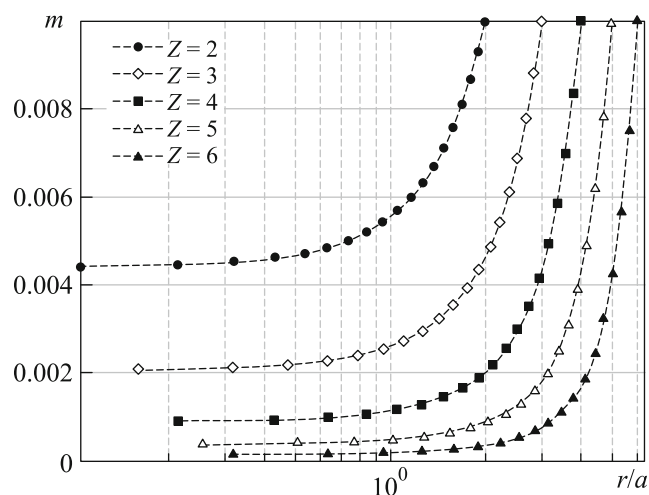
Let the material of the wall contain protons and be able to release them to empty dangling bonds of water as, e.g., in Nafion films. This mathematically means that a boundary condition such as  $m(R) = m_S$  should be imposed on the concentration of ionic defects. The function  $m(r)$  also satisfies an equation similar to Eq. (8), which has a solution similar to Eq. (9) with only one difference: the concentration of ionic defects in the right minimum  $m_{\min}$  will be much lower. An analog of solution (9) can be represented in the form

$$m(r) = (m_S - m_{\min}) \frac{I_0(r/a)}{I_0(R/a)} + m_{\min}, \quad (14)$$

where  $m_S \approx 10^{-2}$  and  $m_{\min} \approx 10^{-6}$ . Figure 3 shows the dependences of  $m(r)$  on the distance from the center of the channel. Using these results, we obtain the following estimates for the average specific low-frequency conductivity:

$$\sigma_0 = 16.0, 12.4, 9.9, 8.2, 7.0 \text{ (} \times 10^0 \text{ S/m)}. \quad (15)$$

These conductivity values are comparable with the conductivity of Nafion films. It is seen that the addition of only one proton on the channel wall side per 100 interface molecules results in a very high proton conductivity and the addition of excess protons can further increase the low-frequency proton conductivity.



**Fig. 3.** Concentration of ionic defects versus the dimensionless distance from the center of the cylindrical channel with the radii  $Z = 2, 3, 4, 5,$  and  $6$  at room temperature of  $T = 298$  K.

### CONCLUSIONS

We emphasize that our model is based on two assumptions. First, it is assumed that the rules of ice are strongly violated in channels with nanometer radii; i.e., the proton sublattice is in fact melted but the oxygen lattice keeps its structure. This circumstance allows the extrapolation of mobilities (or diffusion coefficients) characteristic of ice to room temperature. This assumption is confirmed by numerous experimental results [16–19]. Second, it is assumed that interface molecules interact with channel walls; as a result, molecules are ordered with protons toward walls. This slightly increases the low-frequency proton conductivity, but this increase is insufficient to explain a high proton conductivity of such materials as Nafion. Finally, under the assumption that channel walls can release at least a small number of protons to dangling bonds of water molecules, the highest proton conductivity of currently used proton-exchange membranes can be explained.

In application to Nafion, the last assumption means that protons from lateral acid branches of Nafion are transferred to dangling bonds of water molecules; thus, these acid branches provide proton doping. This interpretation allows the following recommendation for increasing the proton conductivity: the conditions of polymerization and final processing of polymeric proton-exchange membranes should

ensure an increase in the concentration of lateral acid branches of Nafion molecules.

An increase of the average proton conductivity with decreasing channel radius has also been revealed. Therefore, the second recommendation is to ensure polymerization conditions under which narrow channels are formed. An additional effect of narrow channels is that they will better confine water and keep the oxygen lattice at higher temperatures. In this case, a high proton conductivity will be conserved at higher temperatures.

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### REFERENCES

1. M. A. Hickner, H. Ghassemi, Y. S. Kim, B. R. Einsla, and J. E. McGrath, *Chem. Rev.* **104**, 4587 (2004).
2. M. Faraday, *Philos. Mag.* **17**, 162 (1859).
3. J. Thomson, *Proc. R. Soc., Ser. A* **11**, 198 (1861).
4. N. Maeno and H. Nishimura, *J. Glaciol.* **21**, 193 (1978).
5. I. A. Ryzhkin, M. I. Ryzhkin, V. V. Sinitsyn, and A. V. Klyuev, *JETP Lett.* **106**, 760 (2017).
6. M. I. Ryzhkin, A. V. Klyuev, V. V. Sinitsyn, and I. A. Ryzhkin, *JETP Lett.* **104**, 248 (2016).
7. C. J. T. de Grotthuss, *Ann. Chim.* **58**, 54 (1806).
8. C. Jaccard, *Phys. Condens. Mater.* **3**, 99 (1964).
9. J. D. Bernal and R. H. Fowler, *J. Chem. Phys.* **1**, 515 (1933).
10. H. Granicher, *Z. Kristallogr.* **110**, 432 (1958).
11. V. F. Petrenko and R. W. Whitworth, *Physics of Ice* (Oxford Univ. Press, Oxford, 1999).
12. A. V. Klyuev, I. A. Ryzhkin, and M. I. Ryzhkin, *JETP Lett.* **100**, 604 (2014).
13. V. G. Artemov, I. A. Ryzhkin, and V. V. Sinitsyn, *JETP Lett.* **102**, 41 (2015).
14. J. W. Cahn and J. E. Hilliard, *J. Chem. Phys. A* **28**, 258 (1958).
15. V. F. Petrenko and I. A. Ryzhkin, *J. Phys. Chem. A* **115**, 6202 (2011).
16. F. Sedlmeier, J. Janecek, C. Sendner, and L. Bocquet, *Biointerphases* **3**, 23 (2008).
17. J. Kofinger, G. Hummer, and C. Dellago, *Proc. Natl. Acad. Sci. U.S.A.* **105**, 13218 (2008).
18. S. Strazdaite, J. Versluis, E. H. G. Backus, and H. J. Bakker, *J. Chem. Phys.* **140**, 054711 (2014).
19. F. Corsetti, O. Matthews, and E. Artacho, *Sci. Rep.* **6**, 18651 (2016).

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