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SHORT COMMUNICATION

Model of confined water self-diffusion and its application to proton-exchange membranes

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Abstract

A model of self-diffusion in confined water is proposed. It is based on the idea that confined water forms structures similar to hexagonal ice and its transport characteristics can be described in the framework of a quasiparticle approach. It is assumed that the quasiparticles responsible for self-diffusion are D- and L-bond defects, which in the case of confined water are interstitial H_2O molecules and vacancies in an ice-like lattice. The process of D-defect migration is described as the diffusion of an ideal gas through a porous medium. The analytical expression for the self-diffusion coefficient of confined water depending on the water content quantitatively well describes the experimental data for Nafion-type of proton-exchange membranes.

Keywords Confined water · Self-diffusion · Jaccard theory · Proton-exchange membranes

Introduction

The physical properties of pure bulk water are widely studied experimentally and presented with references on a well-known website [1]. The physical properties of confined water, i.e., the water constrained on a nanometer scale at least in one direction, are much less understood. However, the available experimental data clearly indicate that many physical properties of confined water are radically different from those of bulk water. These are the possibility of significant supercooling of confined water to its glass transition temperature [2, 3], anomalous diffusion [4–8], pronounced quantum effects [8–11], and some others. Recently, it has been found that the static dielectric permittivity of confined water with a characteristic size of ~ 1–2 nm is only $\varepsilon \approx 2$ while $\varepsilon \approx 80$ for bulk water [12]. At that the dielectric permittivity ε rises with the size of confined water and reaches typical values for bulk water for a sample thickness of around 100 nm, which is apparently a scale for anomalous behavior [12].

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Computer simulations and experimental studies show that the structure of confined water is more ordered compared to bulk water and consists of distorted hexagonal rings (hexamers) [13–16], i.e., it is similar to the structure of ordinary hexagonal ice (Fig. 1a). This allows using the Jaccard theory initially developed to describing ice transport characteristics [17, 18] and recently transformed into the liquid state of confined water [19, 20]. According to the Jaccard theory, the transport processes in the hexagonal-like molecular structure of a condensed H_2O state are due to the formation and migration of two types of defects: ionic defects (H_3O^+, OH^-) and bond defects (L-, D-). Both types of defects determine the proton conductivity, and the partial conductivity of ionic defects in hexagonal ice is significantly lower than that of bond defects. This results in the decisive contribution of ionic defects to static dc conductivity and that of bond defects to high-frequency conductivity [17–21]. However, at high pressures of around 20–30 GPa, for static proton conductivity in ice, bond defects become decisive [22]. In this paper, we proposed the model of self-diffusion in confined water based on the connection of the bond defects with vacancies and interstitials and applied the model to polymer proton-exchange membranes.

Model statements

As it was shown in [23–26] the self-diffusion of H_2O molecules in ice-like structure is determined by the

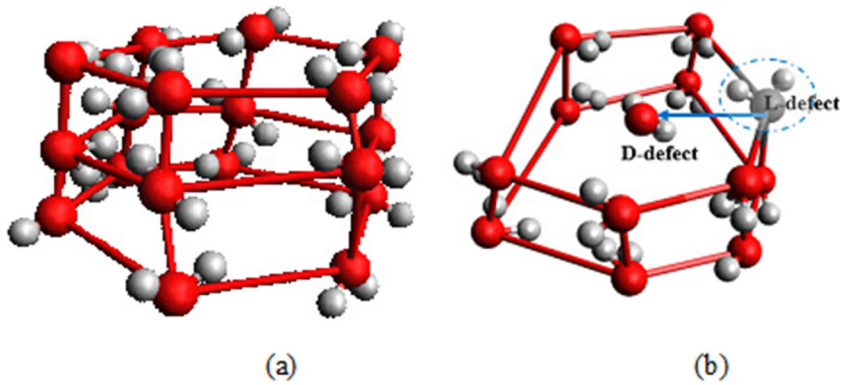

Fig. 1 **a**, **b** Schematic representation of the hexamers of the confined water cluster (**a**) and the formation of L- and D-bond defects in the cluster (**b**)

migration of L- and D-defects, which can be associated with the vacancy and interstitial defects. The formation of L- and D-defects is qualitatively shown in Fig. 1b, and their migration processes are illustrated in Fig. 2 a, b.

The bounded energy of an interstitial D-defect is around 0.2 eV whereas for vacancy (L-defect), this energy is approximately two times higher (~ 0.38 eV) [23]. These energies can be associated with the migration energy of the mentioned defects, and they are close to the activation energies of water self-diffusion coefficient (D_{self}) at high and low temperatures, respectively, measured by NMR-spectroscopy in various materials with confined water [24, 27–33]. For example, for proton-exchange membranes, there is a kink (crossover) in $\ln(D_{self})$ vs. 1/T dependencies at T_c of ~ 240–260 K with an activation energy of ~ 0.18–0.24 eV above and of ~0.33–0.42 eV below the crossover point T_c [24, 27, 28]. The similar $D_{self}(T)$ dependencies are observed for confined water in zeolites [29], gels [29], carbon nanotubes [30], porous silicon [31], sulfonated polynaphthoyleneimides [32], and a metal-organic nanotubes [33], and generalized $D_{self}(T)$ behavior is schematically presented in Fig. 3.

Thus, the temperature dependencies of self-diffusion coefficients for confined water demonstrate general character independently of the chemical composition of the surrounding matrix and the fragmentation degree of the hydrogen-bond network which is governed by water content. So, it can be proposed that at high temperatures, the self-diffusion is mainly determined by the migration of interstitial D-defects, while with a decrease below the crossover point, L-type vacancies start to play a predominant role (Fig. 3).

Now we summarize the main statements for our model:

(1) The self-diffusion of H_2O molecules and proton conductivity in materials with confined water can be described using the Jaccard model that is based on the violations of ice rules [17, 18] and the formation of ionic defects (H_3O^+ and OH^-) and bond defects (L- and D-). These defects are considered as quasiparticles responsible for transport characteristics in confined water.
(2) L- and D-bond defects (or orientation defects) are responsible for the self-diffusion of water molecules. These defects are a kind of quasiparticles that can be considered as an ideal gas by analogy with quasiparticles (electrons and holes) in semiconductors.
(3) We suppose that D-defect migration on the cages (Fig. 2a) is similar to the diffusion of an ideal gas through porous media.

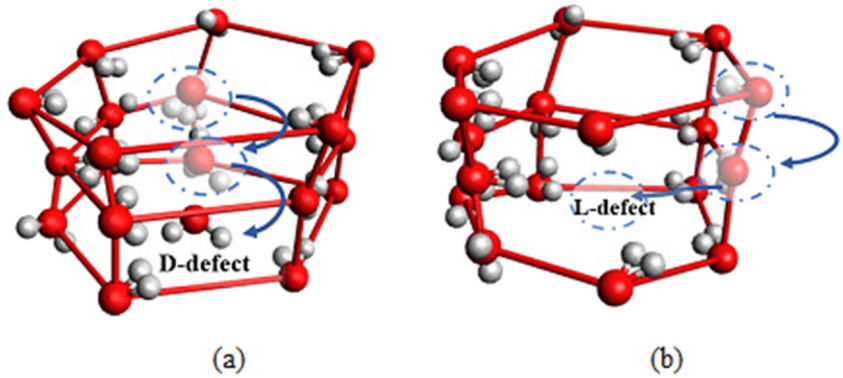

Fig. 2 **a**, **b** Illustrations of D- (**a**) and L- (**b**) bond defect migrations in the approximation of "the frozen surrounding molecule states"

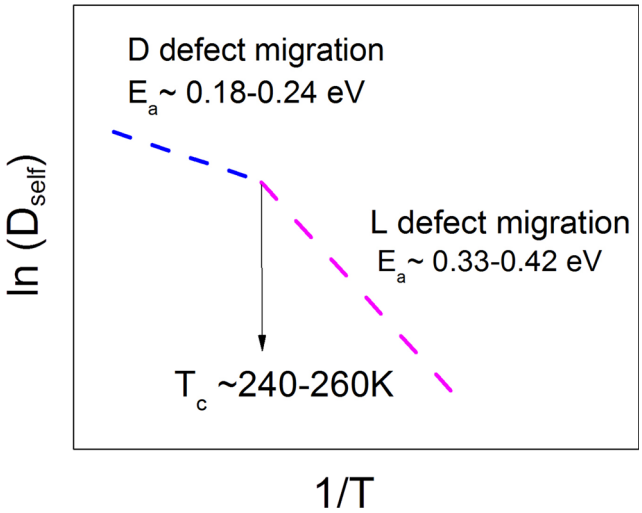

Fig. 3 Typical temperature dependence of self-diffusion coefficient D_{self} in confined water

Model application to proton-exchange membranes

It has been shown experimentally and theoretically [34–36] that the diffusion of a gas through a porous medium can be described as:

$$D = F\exp\left(-G/V_f\right) \tag{1}$$

where F and G are the parameters depending on the size and shape of a diffusing molecule, and V_f is the free volume for a polymer–gas system. In the frame of our model, the free volume V_f corresponds to the pore volume of all hexamers, i.e., it is proportional to the mass or the total number of water molecules N_{H2O} of confined water and thus:

$$D = D_{0m}\exp\left(-m_0/m\right) = D_{0N}\exp\left(-N_0/N_{H_2O}\right) \tag{2}$$

where m and N_{H_2O} are the mass and the number of molecules of confined water in some matrix, and D_{0m}, m_0, D_{0N}, N_0 are the fitting parameters. In particular, polymer proton-exchange membranes where the mass or amount of adsorbed water molecules is determined as the number of H_2O molecules per SO_3H group ($\lambda = N_{H2O}/N_{SO3H}$) the expression for the self-diffusion coefficient D_{self} vs. water content λ can be presented as:

$$D_{self}\ (\lambda) = D(\mathrm{T})\exp(-\lambda_0/\lambda\ ) \tag{3}$$

where λ_0 is the fitting parameter, the physical meaning of which will be discussed below, and D(T) is the diffusion coefficient of water in a given material at a fixed temperature and excess water, i.e., when $\lambda >> \lambda_0$.

It should be noted that application of free volume conception for diffusion description in Nafion was previously proposed in [37–40]. However, the free volume parameter was interpreted in these articles as a free volume fraction of polymer in the water-swollen material which has completely another physical meaning in comparison to our approach.

The applicability of our model is tested on the experimental data on water self-diffusion in Nafion 117 at temperatures of 303 K and 321 K [41] which were fitted with Eq. (3) (Fig. 4). As can be seen, the dependencies of $\ln(D_{self})$ vs. $1/\lambda$ for both temperatures are linear in accordance with Eq. (3). The values of the parameter λ_0 are the same for both temperatures ($\lambda_0 \approx 12$). This value correlates with the number of H_2O molecules for their typical space location ~ 3–4 nm [28, 42, 43] in Nafion. Accepting for water molecule diameter of 0.28 nm [44], the number of molecules packed in this location length is around 11–14.

At the same time, it is obvious that the percolation paths for the diffusion of water molecules in the central part of the channel surely appear. Therefore, the parameter λ_0 can be considered as the boundary value of percolation along the hydrogen-bond network for a given geometry of the transport channel.

The parameter D(T) in Eq. (3) corresponds to the value of the self-diffusion coefficient of water in Nafion 117 at a fixed temperature and $\lambda >> \lambda_0$, i.e., this is a limiting value of self-diffusion coefficient for completely filled channels for given polymeric matrix. The process of H_2O self-diffusion in Nafion is isotropic and three-dimensional [28]. However, the molecule moves in the polymeric matrix along entangled tortuous trajectories that reduce the value of self-diffusion coefficient by the tortuosity factor β in comparison with self-diffusion coefficient of bulk water and thus:

$$D(T) = \frac{D_{H2O}(T)}{\beta} \tag{4}$$

where D_{H2O}(T) is the self-diffusion coefficient of bulk water at the fixed temperature T, and β is the tortuosity factor.

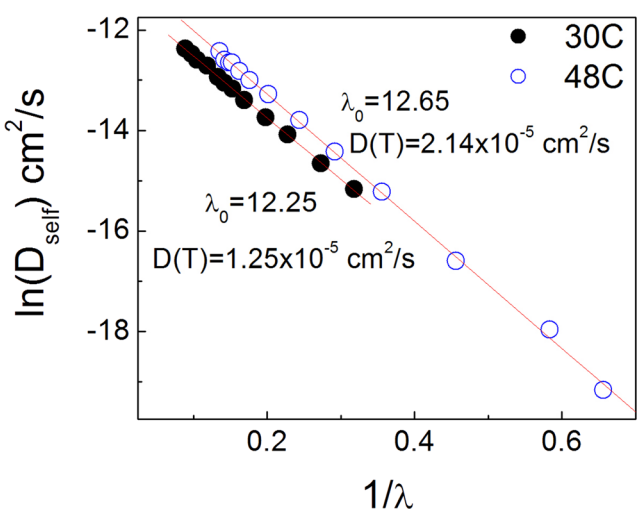

Fig. 4 Fit of experimental data [41] using Eq. (3). The fitting parameters are presented close to the corresponding line

The coefficient β for Nafion 117 was determined experimentally as $\beta \approx 2$ at high water content $\lambda > 6$ [45], which is close to the excess water condition. The values of water self-diffusion coefficients obtained by fitting the experimental data $D_{self}(\lambda)$ using Eq. (3) and taking into account the tortuosity factor with Eq. (4) are equal to $D_{H2O}(T) = 2.5 \times 10^{-5}$ cm^2/s at T = 303 K (30 °C) and $D_{H2O}(T) = 4.28 \times 10^{-5}$ cm^2/s at T = 321 K (48 °C), while the experimental data of $D_{H2O}(T)$ for bulk water are 2.4×10^{-5} cm^2/s at T = 303 K (30 °C) and 3.7×10^{-5} cm^2/s at T = 321 K (48 °C) [46]. It can be seen that there is a good correspondence between these values, i.e., expression (3) describes correctly the self-diffusion coefficient vs. water content.

Conclusion

A model of possible self-diffusion micromechanism in materials with confined water is proposed. It is based on the idea that confined water forms structures similar to hexagonal ice and its transport characteristics can be described in the framework of a quasiparticle approach. The analytical expression for the self-diffusion coefficient of confined water depending on the water content is found and it describes quantitatively well the experimental data for Nafion-type of proton-exchange membranes. The physical meaning of the model parameters is discussed. The parameters can be considered as guidance for the experiment interpretations.

It should be noted that Eq. (3) seems to be possessed universality to various matrixes containing confined water and can be also applied to the analysis of dc conductivity as a function of water content. However, it is a separate study beyond the scope of the short communication.

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Declarations

Conflict of interest The authors declare no competing interests.

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