Computational modeling of structure and OH-anion diffusion in quaternary ammonium polysulfone hydroxide – Polymer electrolyte for application in electrochemical devices

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Using computational approaches we predict the microstructure of high-performance alkaline polymer, quaternary ammonium polysulfone hydroxide (QAPS-OH) membranes, dry and with \( \sim 14\ \text{wt}\% \) water uptake. The microstructure can be described as a hydrophobic polymer backbone penetrated by a network of three-dimensional interlinked hydrophilic channels of different diameters. Mobile OH-anions are distributed inside the channels. OH diffusion coefficients and corresponding activation energy were calculated from our molecular dynamics simulations of the QAPS-OH membrane at different temperatures. The predicted values are consistent with available experimental data. Possible mechanisms of the OH-anion diffusion have been discussed.

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1. Introduction

Despite the significant progress made in reducing cost of Polymer Electrolyte Membrane Fuel Cells (PEMFCs) due to improving their performance and decreasing Pt loading, it is becoming clear that to reach further progress in commercialization of the fuel cell technology, the focus should be moved to other types of fuel cells which do not require expensive Pt as catalysts. Alkaline fuel cells (AFCs) are more efficient than the acid-based PEMFCs and can operate with cheaper non-precious metal catalysts such as Ni. However, the current AFC technology uses the corrosive liquid electrolyte (e.g. KOH) which raises issues related to safety, reliability and durability of AFC systems. Electrolyte is a critical component of fuel cell systems. Synthesis of polymer alkaline membranes that have high hydroxide-ion conductivity might eliminate this serious disadvantage of AFCs. During last two-three years, new high-performance alkaline polymers, such as quaternary ammonium polysulfone hydroxide (QAPS-OH) and tris(2,4,6-trimethoxyphenyl)polysulfone-methylene quaternaryphosphonium hydroxide (TPQP-OH), have successfully been designed and synthesized [1–5].

QAPS-OH is thermally stable up to 120 °C and can be dissolved in certain solvents. This allows preparation of Membrane-Electrode Assemblies (MEAs) of required thickness and size. The hydroxide-ion conductivity of QAPS-OH is \( \sim 10^{-2}\ \text{S/cm} \) at room temperature and meets the basic requirement for fuel cell applications [1–3].

TPQP-OH can also be successfully used as a soluble hydroxide-conducting ionomer. It turns out that TPQP-OH polymer with a degree of chloromethylation of 152% has excellent hydroxide-ion conductivity, \( \sim 0.05\ \text{S/cm} \) at room temperature, and stability. A fuel cell based on the TPQP-OH electrolyte shows the highest power density (258 mW cm\(^{-2}\)) and lowest cell resistance (0.210 Ω cm\(^{2}\)) reported and has the potential to achieve cell performances of state-of-the-art Nafion-based PEMFCs [4,5].

Despite the great promise, the polymer AFC technology has several technical issues which need to be solved before this technology would be utilized for applications. One of them is identifying polymer backbones and side chains that could form chemically and mechanically stable polymer membranes with high ionic conductivity suitable for employment in fuel cells. However, this process is hindered by lack of information about the structure and structural characteristics that provide the desirable properties. Using computational techniques is an efficient way to advance this issue.

In our paper, we focus on modeling of the structure and hydroxide-ion diffusion of QAPS-OH membranes at different temperatures and water contents.

2. Simulation details

The initial QAPS-OH structure was constructed using the Amorphous Builder of Cerius2 [6]. It uses Monte Carlo techniques...
to build an amorphous structure with a three-dimensional periodic cell. We followed this Monte Carlo build with an extensive series of annealing simulations in which the volume and temperature are varied systematically to achieve a fully equilibrated system at the target temperature and pressure. The QAPS-OH predicted structure was not biased by imposing any particular geometry, density or packing. To build the structure, we used 3 chains with a degree of polymerization of 16. The total number of atoms in the system is 3414 including 48 OH-anions. To describe inter- and intra-molecular interactions, and water, we applied the DREIDING [7] and F3C [9] force fields which were successfully used before to study a Nafion system [8]. The standard geometric combination rules of Dreiding were employed in mixing these force fields.

The initial QAPS-OH structure was relaxed by applying the following annealing procedure. First, the structure was gradually expanded by 50% of its initial volume over a period of 50 ps, while the temperature was simultaneously increased from 300 to 600 K. Next NVT molecular dynamics (MD) simulations were performed at 600 K with the expanded volume for 50 ps. Then the structure was compressed back to the initial volume over 50 ps, while cooling the temperature down to the target temperature, 300 K. This procedure was alternated with a conventional annealing that included heating from 300 to 600 K and cooling back to 300 K with a temperature step 50 K and 10 ps of NPT dynamics at each temperature. We repeated this operation until the structure showed no significant changes (this requires to repeat the cycle 5 times). The calculated density of such a way prepared structure was 0.89 g/cm$^3$. Then we added 200 water molecules, which approximately correspond to 14 wt% water uptake, into the channels and larger voids and equilibrated this structure by repeating the procedure described above. Our approach of temperature-pressure MD annealing allows us to obtain an equilibrated distribution of water in an equilibrated polymer system. The two final structures (dry and with the 14 wt% water uptake) were used for MD simulations at 300, 360, 400, and 450 K

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$$D = \frac{1}{6N}\left\langle \left| r(t) - r(0) \right|^2 \right\rangle$$

where $N$ is the number of atoms. We fitted the temperature dependence of the diffusion coefficient to

$$D(T) = D_0 \exp\left(\frac{-E_a}{kT}\right)$$

where $E_a$ is the activation enthalpy.

Conductivity can be calculated from diffusion coefficient using the Nernst–Einstein equation

$$\sigma = \frac{DcF}{kT}$$

where $D$ is the diffusion coefficient, $c$ the charge carrier concentration, $z$ the carrier charge, $F$ the Faraday constant, $R$ the gas constant, and $T$ is the temperature.

### 3. Results and discussion

#### 3.1. Microstructure of dry QAPS-OH membrane

Fig. 1 shows the QAPS-OH chemical formula (a) and structure unit (b), which were used for our MD simulations to build and optimized the dry microstructure of the QAPS-OH for our MD simulations to build and optimized the dry microstructure of the QAPS-OH membrane (c). This microstructure can be described as a hydrophobic polymer backbone penetrated by a network of three-dimensional interlinked hydrophilic channels of different diameters. The presence of channels containing mobile charge carriers is an important characteristic feature of solid state ionic conductors [10]. According to our results, N(CH$_3$)$_3$ functional groups are mostly located along walls of the channels. The predicted distances between the nearest N atoms, which can be considered as side chain distances, vary from $\sim$6 to 12 Å (see Fig. 2), which are similar to distances between side chains in Nafion [8]. Predicted distances between N atom

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Fig. 1. The QAPS-OH chemical formula (a), structure unit (b) and dry microstructure, $2 \times 2 \times 1$ unit cells (c) obtained from our MD simulations.
and the nearest OH group is \( \sim 5 \) Å with a coordination number of \( \sim 1 \). This indicates that each \( \text{N(CH}_3\text{)}_3 \) functional group is coordinated with one OH-ion. Mobile OH ions are distributed inside the channels. The distance between the nearest OH groups is \( \sim 3 \) Å with a coordination number of \( \sim 0.5 \). This geometry is favorable for the OH diffusion, because it suggests a presence of vacant positions close to the OH groups to which they can jump.

In addition to the channels in the QAPS-OH microstructure, there exist cavities that also contain hydroxide ions. However, mobility of these ions is limited to local diffusion that does not contribute to the long-range diffusion. However in hydrated membranes, some of these cavities may unite and form new channels due to following water uptake and swelling. A void analysis, which was performed according to the procedure reported in Ref. [11], estimates the void volume as being equal to \( \sim 20\% \) of the total volume of the dry membrane.

3.2. Microstructure of QAPS-OH membrane with 14 wt% water uptake

To build the hydrated microstructure of QAPS-OH, we used the method described in Section 2 and carried out a 100 ps MD simulation on this structure at 300 K. Fig. 3 shows the corresponding microstructure (4056 including 200 H\( _2 \text{O} \) and 48 OH-anions) and water distribution in a QAPS-OH membrane with the 14 wt% water uptake. Radial distribution functions (RDF) can be seen in Fig. 4. The QAPS-OH microstructure keeps the features earlier observed for the dry membrane, i.e. it can be described as a hydrophobic polymer backbone penetrated by a network of three-dimensional interlinked hydrophilic channels. \( \text{N(CH}_3\text{)}_3 \) functional groups occupy positions on walls of the channels. The distances between the nearest N atoms remain varying from \( \sim 6 \) to 12 Å, which are similar to distances between side chains in the dry QAPS-OH membrane and Nafion [12]. The mobile OH ions are mostly distributed inside the channels and the OH–OH distances, as well as N–OH, close to those in the dry membrane. However, the coordination number corresponding to the distance between the nearest OH groups (\( \sim 3 \) Å) is significantly lower, \( \sim 0.1 \), in the hydrated membrane compared to that of the dry membrane (\( \sim 0.5 \)). The lower hydroxide ion CN in the hydrated membrane is most probably due to adding water molecules which results in swelling of the microstructure.
and formation of the water shapes around hydroxide ions. The OH–H₂O and H₂O–H₂O intermolecular distances (between oxygen atoms of corresponding molecules) are close to each other and equal to \( \sim 2.9 \, \text{Å} \), which is in good agreement with other computational works (see, for example, [13]). From Fig. 4e, which shows RDF and CN of water, it is clear that the QAPS-OH membrane with the 14 wt% water uptake is far enough from to be considered as fully hydrated. It should be noted that the calculated ion-exchange capacity (IEC) of our QAPS-OH membrane is \( \sim 1.9 \) which allows significantly higher water uptake for the fully hydrated membrane than 14 wt%.

According to [3], the 14 wt% water uptake of the QAPS-OH membrane corresponds to the ion-exchange capacity (IEC) of 

\[
\text{Table 1} \quad \text{Diffusion coefficients (cm²/s) of dry and hydrated (14 wt% water uptake) QAPS-OH membranes.}
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<table>
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<tr>
<th>Membrane</th>
<th>Temperature (K)</th>
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<tbody>
<tr>
<td></td>
<td>300</td>
</tr>
<tr>
<td>QAPS-OH, dry</td>
<td>( \times 10^{-5} )</td>
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<tr>
<td>QAPS-OH, 14 wt% H₂O</td>
<td>( \times 10^{-4} )</td>
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\(~1.04\) and swelling degree (SD) of about 5%. From our MD simulation of the dry and 14 wt% water uptake QAPS-OH membranes, SD can be estimated, using the corresponding microstructure
volumes. We found that SD is equal 7% which is close to the experimental value of 5%.

In general, the QAPS-OH microstructure looks similar to that of Nafion in which hydrophilic clusters connected by channels are embedded into a hydrophobic matrix [14,15].

3.3. OH-diffusion in QAPS-OH membrane

In order to estimate the hydroxide-ion diffusion and its activation energy, we modeled the OH-transport in the dry and hydrated QAPS-OH membranes at different temperatures (300, 360, 400, and 450 K). The calculated diffusion coefficients and corresponding activation energies are listed in Table 1 and their temperature dependences are shown in Fig. 5. We find our computational results are consistent with experiment. The calculated conductivity that corresponds to the diffusion coefficient at $T=300$ K is $\sim 0.7 \cdot 10^{-2}$ S/cm (the experimental value is about $10^{-2}$ S/cm for the membranes with a very low water-uptake degree) and activation energy is exactly the same as in experiment, $E_a=0.14$ eV [3].

In the hydrated membrane with the 14 wt% water uptake, the OH diffusion coefficient increased by $\sim 1$ order of magnitude and reached the value of $D=0.16 \cdot 10^{-4}$ cm$^2$/s at room temperature, which is similar to the value of en masse diffusion in Nafion, $0.17 \cdot 10^{-4}$ cm$^2$/s [16] calculated using the Stokes–Einstein equation, and predicted activation energy is $E_a=0.10$ eV. This is consistent with experimental results observed [1–3].

It is well-known that water has ability to transport charge species, such as $H^+$ and $OH^-$. To present, the OH-anion structural diffusion is much less studied than the proton diffusion. There is no experimental technique that can provide necessary data for the firm conclusion about the detailed mechanism of the diffusion.
hydroxide-ion diffusion. According to neutron scattering experiments [17,18], the hydroxide-ion can accept between 3 and 4 hydrogen bonds and donate one in aqueous environment. 2D infrared (IR) and pump-probe (PP) spectroscopies confirm this result and indicate formation of a Zundel-like configuration, wherein a proton is delocalized between a water molecule and hydroxide ion [19]. The authors of the latter publication [19] came to conclusion that the motion of the proton is coupled to the surrounding solvent environment through dielectric fluctuations that originate in hydrogen bond rearrangements.

Ab initio MD generally suggests two possible scenarios: (1) the hydroxide ion accepts three hydrogen bonds and is able to donate one [20], and (2) the hydroxide ion is overcoordinated and the OH-transport is driven by first solvation shell reorganizations [21–23].

Here we consider two mechanisms for the OH-diffusion which are related to the above-mentioned mechanisms. Fig. 6a shows a configuration where the hydroxide ion accepts three hydrogen bonds from water molecules and donates one. In process of thermal fluctuations, the proton can move from one of the water molecules towards the hydroxide ion to form, first, a Zundel-like ion (Fig. 6b), and then move further to transform the hydroxide ion to the water molecule (Fig. 6c). This mechanism is similar to the Grothuss mechanism for the proton transport in water [24]. Thus, if only this mechanism is realized, we might expect that the corresponding OH-diffusion coefficient should be close to the proton diffusion coefficient in water. However, it is well-known that the OH-diffusion in water is almost twice slower than the proton diffusion [25,26], which makes the mechanism to be inconsistent with experiment.

In the second mechanism, the hydroxide ion is overcoordinated accepting four hydrogen bonds from water molecules and donating one (Fig. 6d). The latter hydrogen bond is most probably longer and weaker, than the first four. A possible scenario is that the proton moves from one of the water molecules towards the hydroxide ion to form a Zundel-like ion. Simultaneously, the adjacent accepted hydrogen bond elongates, while the donated one becomes shorter and stronger (Fig. 6e). The proton continues moving towards the hydroxide ion and transforms it to the water molecule, breaking one of the accepting hydrogen bond (Fig. 6f). This configuration is identical to the configuration shown in Fig. 6c. At this point, next steps of the OH-diffusion might be similar to those described for the first Grothuss-type mechanism, or another water molecule comes closer to the hydroxide ion and then two situations are possible: (1) this water molecule forms a hydrogen bond with the hydroxide ion (the fourth accepted hydrogen bond) and the donated hydrogen bond will elongate, but not break (Fig. 6g) and (2) the donated hydrogen bond breaks and reorients to form a new donated weak hydrogen bond with the coming water molecule (Fig. 6h). The broken hydrogen bond will transform to the accepted one with the same water molecule or with a new one. The rate-determining step for this mechanism is breaking of a hydrogen bond. The newly formed configuration is again overcoordinated with four accepted and one donated hydrogen bonds of water molecules. This mechanism is consistent with the neutron scattering data [17,18], indicating that a hydroxide ion can accept between 3 and 4 hydrogen bonds and donate one in aqueous environment, and theoretical results [22,26,27] which provide evidence that OH favors four accepted hydrogen bonds and is able to donate a fifth one.

The OH-diffusion in a dry QAPS-OH membrane is a proper OH-anion diffusion similar to that of other ions such as Li⁺, Na⁺ or Cl⁻. In hydrated membranes, the OH-diffusion probably combines both the en masse, also called the vehicle [28], (OH-anion diffusion of an aggregated [OH⁻-(H₂O)₅] species) and Grothuss-type proton diffusion mechanisms. The hydroxide ion water coordination number might be different for low- and fully hydrated membranes and increases with increasing the water contents in a membrane.

It should be noted that conventional non-reactive force fields such as Dreiding, can be used for studying en masse OH-anion diffusion, while modeling of the Grothuss-type proton diffusion needs application of a reactive force field, such as ReaxFF [29]. This will allow the relative contributions of these two mechanisms to be estimated.

4. Concluding remarks

Using MD simulations, we predicted the microstructure and OH-diffusion in high-performance alkaline polymer, quaternary ammonium polysulfone hydroxide membranes, dry and with ~14 wt% water uptake. The microstructure can be described as a hydrophobic polymer backbone penetrated by a network of three-dimensional interlinked hydrophilic channels of different diameters. N(CH₃)₃ functional groups are mostly located along walls of the channels. The mobile OH-anions are distributed inside the channels. In consistent with experiment, the calculated hydroxide-ion diffusion coefficient is by ~1 order of magnitude higher for the hydrated membrane with the 14 wt% water uptake compared to that of the dry membrane. It should be noted that the relatively small system used in our MD simulations may have channels that would be closed in larger systems, and therefore the “density” of the channels and OH-diffusion would be lower in such systems. Also, for more accurate estimation of diffusion parameters, longer simulation times are typically required. MD simulations on much larger (~6 times) systems and for significantly longer time (several nanoseconds) are now in progress. Our preliminary results of such simulations show that the geometric characteristics (RDF) of the microstructure remain similar to those described here. However, OH-diffusion coefficients are about one order of magnitude lower than reported in this paper.

We discussed possible mechanisms of the OH-anion diffusion in a QAPS membrane. In the hydrated membranes, the OH-diffusion probably combines both the en masse (vehicle) and Grothuss-type proton diffusion mechanisms. Development of the ReaxFF reactive force field will allow us to perform reactive MD simulations to estimate the relative contributions of these two mechanisms to the total hydroxide-ion diffusion in QAPS membranes.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.memsci.2012.12.010.

References


