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

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ABSTRACT

Using computational approaches we predict the microstructure of high-performance alkaline polymer, quaternary ammonium polysulfone hydroxide (QAPS-OH) 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. 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.

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 $\sim 10^{-2}$ 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, ~0.05 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

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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 to study the dynamic properties of the QAPS-OH membrane. At each temperature we first performed a 10 ps NPT dynamics continued with a 100 ps NVT dynamics.

Diffusion coefficients were calculated based on the mean square displacement (MSD) (see Supplementary material)

$$\mathrm{MSD}\ (m) = \left\langle |r(t)-r|^2 \right\rangle = 1/n \sum_{i-1}^{n} |r(m+i)-r(i)|^2$$

where r is the position of the particle, t is the time, k is the total number of snapshots ($k=m+n>0$), m is the maximum number of points allowed for the MSD calculation ($m=k/2$ in our calculations), n is the number of data points used for averaging, and i is the step counter.

The self-diffusion constant is obtained using the Einstein relation

$$D = \frac{1}{6Nt} \langle |r(t)-r|^2 \rangle$$

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

$$D(T) = D_o \exp(-E_a/kT)$$

where E_a is the activation enthalpy.

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

$$\sigma = \frac{DczF}{RT}$$

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 ~6 to 12 Å (see Fig. 2), which are similar to distances between side chains in Nafion [8]. Predicted distances between N atom

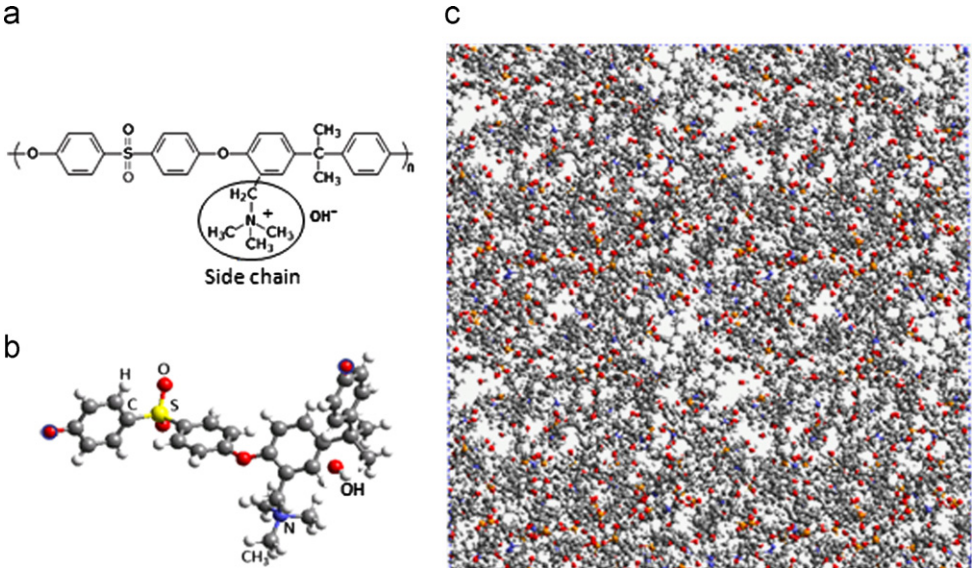

Fig. 1. The QAPS-OH chemical formula (a), structure unit (b) and dry microstructure, $2 \times 2 \times 1$ unit cells (c) obtained from our MD simulations.