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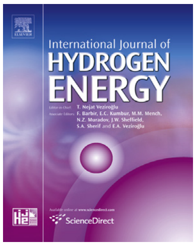

Building block candidates for the design of proton exchange membranes: Maleimide and its homologues

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ABSTRACT

Density functional theory (DFT) calculations are applied to the study of proton transport in maleimide and its homologues, succinimide and phthalimide. The calculations reproduce correctly their structural characteristics and reveal the hydrogen bonding and proton hopping properties. Specifically, the calculations show that the potential barrier for proton transfer between two maleimide molecules is about 30.60 kcal mol^{-1} mediated by one or two water molecules with correction of solvation effect by water, and will decrease to about 13.22 kcal mol^{-1} if ethylphosphonic acid molecule is used as mediator with correction of solvation effect by phosphoric acid. In addition, the calculations also show that succinimide and phthalimide possess similar characteristics compared to maleimide. Finally, it is concluded that maleimide and its homologues are building block candidates for the design of high-temperature proton exchange membranes.

Introduction

High-temperature proton exchange membrane fuel cells (HT-PEMFCs) have been paid more and more attention as energy conversion devices because of higher energy conversion efficiency, noiseless operation and low pollution emission, especially the humidity-independent performances, enhanced electrocatalytic activity, and improved tolerance to impurities in fed-gas [1]. Nevertheless, the large scale commercialization of HT-PEMFCs depends heavily on the high-temperature performances of the proton exchange membranes (PEMs) [2]. Though perfluorosulfonic acid polymers (PFSA) have achieved great progress in proton conductivity, chemical and electrochemical stability, the application of PFSA in PEMFCs is limited to temperatures that liquid water exists. At high temperature, the liquid water which hydrates the PFSA evaporates and the proton conductivity of PFSA degrades. Therefore, the development of novel proton conducting materials possessing high proton conductivity at high temperature and dehydrated or even anhydrous states is of the utmost importance.

Researches on PEMs are being conducted through experimental and theoretical efforts toward better performance at high temperature [3]. For example, the proton conductivity and mechanical property can be improved by doping with inorganic compounds as water adsorption or retention

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materials [4,5], or by addition of organophosphates and azoles or amides to substitute water as hydration solvent [6–8]. Studies have shown that membranes functionalized by phosphonic acid groups possess much better proton conductivity under dehydrated or even anhydrous states attributing to the self-dissociation and amphoteric character of the phosphonic acid group [9]. The complex H-bonding network between phosphonic acid groups tethered to the polymer backbones result in the ability to conduct proton transport via the Grotthuss mechanism at high-temperature and low-humidity conditions [10,11]. During past years, great efforts have been devoted to the synthesis of phosphonic acid functionalized polystyrene, poly(ether sulfone), polyimides and so on [12–15].

Maleimide (MI) is also an interesting amphoteric molecule, with a dissociation constant $pK_a = 5.57$ evaluated from conductivity measurement (provided as Fig. S1 in the supporting information). Actually, the H-bonding donor and acceptor of a MI molecule is similar to those of triazole molecules, both 1,2,3-triazole and 1,2,4-triazole, which are widely accepted as building blocks in the design of proton conducting materials at high temperature under a water deficient environment [16,17]. As being shown in triazole, the tautomerization is an important characteristic for the proton transfer in hydrophilic compounds, which promotes long-range network structures for facile proton transfer [18]. MI also shows abundant tautomerization pathways, especially with the mediation of other hydrophilic compounds, like organophosphates [15]. In this aspect, Kalia et al. studied both the gas phase and water-assisted tautomerization of MI based on density functional theory [19], and Li et al. studied the proton transport in solid state MI using ab initio molecular dynamics simulations [20]. Based on these considerations, we propose that MI and its homologues, such as succinimide (SI) and phthalimide (PI), are building block candidates for the design of high-temperature proton conducting materials.

Density functional theory (DFT) calculations are widely applied to the study of proton transport in the field of proton exchange membrane. For example, Kreuer et al. applied DFT calculations to the study of sulfonic acid, phosphonic acid, and imidazole functionalized heptane in terms of bond rotational barrier of the functional groups and intermolecular H-bonding, and concluded that the imidazole is most labile when tethered to an alkyl chain and the energy penalty for proton transfer is greatest for imidazole and least for phosphonic acid [21]. Yue et al. studied the proton transfer pathways between ethylphosphonic acid (EPA) and 1,2,3-triazole using DFT calculations and concluded that the existence of EPA will greatly reduce the tautomerization activation energy of triazole [22]. Zhou et al. developed a phosphotungstic acid functionalized and mesoporous silica-based high conductivity PEM, and revealed that the proton transfer involves both inter- and intra-molecular proton transfer pathways and evaluated the activation energy based on DFT calculations [23]. Inter- and intra-molecular H-bonding and proton transport in a series of acid–base complexes including different acid groups and nitrogenous heterocyclic rings were also studied by DFT calculations [24,25].

In this work, DFT calculations will be applied to the characterization of proton transport in MI and its homologues, SI and PI, in terms of transition states and proton hopping. First, we will describe the DFT method in next section. And then, we will optimize the density functional and basis set in Section Density functionals and basis sets optimization, and will compare the intermolecular H-bonding energies in Section H-bonding energies of MI and its homologues. Third, we will study the transition states and energy barriers of proton transport mediated by water or EPA molecules as ethylene phosphonic acid is the most occurred repeat unit in PEMs. In addition, we also measured the overall conductivity of composites of MI and methyl phosphonic acid (MPA, the simplest organic phosphonic acid) at various compositions using electrochemical impedance spectroscopy (EIS). Finally, we will summarize the important results and propose that the MI and its homologues are building block candidates for the design of proton conducting polymers.

Methods

Calculation method

The generalized gradient approximation (GGA) functionals and hybrid functionals are widely accepted in quantum chemistry because these functionals can provide reasonably accurate predictions for geometries and thermodynamics of small covalent molecules [26–28]. However, the dispersion and H-bonding interactions are insufficiently represented by these functionals. In order to evaluate adequately the dispersion and H-bonding interactions, more accurate functionals, such as the meta-GGA functionals (the M06 family), dispersion corrected functionals (the B97-D), and long-range corrected functionals (the CAM-B3LYP), are developed [29–31]. Among the many physical and chemical processes, the proton transport is such a typical process which is greatly related to the weak intermolecular interactions, especially the H-bonding interaction. In order to evaluate their applicability to the proton transport in MI and its homologues, three functionals, including the hybrid B3LYP functional, the meta-GGA M06-2X functional and the counterpoise-corrected ωB97X-D functional, are compared in terms of intermolecular H-bonding interaction based on the MP2 reference. For these three functionals, the B3LYP is widely accepted for the calculation of organic molecules and considered being able to provide chemistry accuracy. The M06-2X and ωB97X-D functionals contain empirical dispersion corrections, especially suitable for the modelling of structures and energies of H-bonding interaction [30]. In addition, suitable basis set is selected from five basis sets including 6-311G(d), 6-311+G(d), 6-311+G(d,p), 6-311+G(2d,p), and 6-311++G(2d,2p). Based on the optimized functional and basis set, proton transport in molecular systems composed of MI, SI, PI, water, and EPA is studied in terms of geometric optimizations, frequency calculations, and transition state locations. Besides, the basis set superposition error (BSSE) are evaluated using counterpoise correction for energetics related to both intermolecular H-bonding and activation of proton transfer. The solvent effect is evaluated based on polarizable continuum model (PCM) using, respectively, water and phosphoric acid as solvents. The static dielectric constant of phosphoric acid is assumed to be 18.90

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