

Characterization of DNA/Poly(ethylene imine) Electrolyte Membranes

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Abstract: Cast DNA/polyethyleneimine (PEI) blend membranes containing different amounts of DNA were prepared using acid-base interaction and characterized with the aim of understanding the polymer electrolyte membrane properties. Two different molecular weights of PEI were used to provide the mechanical strength, while DNA, a polyelectrolyte, was used for the proton transport channel. Proton conductivity was observed for the DNA/PEI membrane and reached approximately 3.0×10^{-3} S/cm for a DNA loading of 16 wt% at 80 °C. The proton transport phenomena of the DNA/PEI complexes were investigated in terms of the complexation energy using the density functional theory method. In the case of DNA/PEI, a cisoid-type complex was more favorable for both the formation of the complex and the dissociation of hydrogen from the phosphate. Since the main requirement for proton transport in the polymer matrix is to dissociate the hydrogen from its ionic sites, this suggests the significant role played by the basicity of the matrix.

Keywords: DNA, acid-base polymer blend, polymer electrolyte membranes, ab initio, fuel cells.

Introduction

Although the polymer electrolyte membrane fuel cell (PEMFC) is one of the promising candidates for high-energy-density power sources, there is a substantial need for a polymer electrolyte membrane (PEM) which operates at high temperature in order to improve the fuel cell performance and to solve the catalyst's poisoning.¹ Hence, the development of a PEM having high proton conductivity, which operates at a high temperature and under low humidity conditions, is the crucial requirement for the PEMFC technology.^{2,3}

Nafion, a perfluorinated sulfonic acid, is typically used as the PEM in fuel cells because of its high proton conductivity when hydrated, as well as its chemical and mechanical stability. Nafion exhibits a nano-phase-separated morphology when hydrated at low temperature, i.e., it has a two-phase system, containing water dispersed as a second phase in a principally amorphous polymeric fluorocarbon primary phase. The water solvates the polymeric acid groups and promotes proton mobility via both structural diffusion (i.e., Grotthus-type "hopping" of the proton through the hydrogen-bonded network of water molecules) and vehicular motion (i.e., coupled proton-water transport of hydronium

ions).⁴ In proton transport mechanisms through the hydrated Nafion membrane, the presence of water is critical in the formation of hydrated protons (for example, H_3O_2^+ or H_9O_4^+ , etc.) and for mobility of the protons.⁵ In our previous study, the proton transport depended on the morphology of the ionic channels and the connectivity between them, formed by the clustering of the ionic sites,⁶ when the PEM is operated under hydrated conditions. This hydrating requirement of conventional PEMs, including Nafion, results in a problematic operating temperature limited to the boiling point of water.

The design and synthesis of new membranes possessing improved performance characteristics, will require a fundamental, molecular-based understanding of the mechanisms of proton transport in non-hydrated systems. The understanding of the mechanism at a molecular level should help to design a new PEM.

Extensive molecular-level modeling⁷⁻¹² of the acidic functional groups, polymer fragments, proton diffusion, and dielectric saturation in membrane pores for several different PEMs indicate that the proton conduction mechanisms in hydrated PEMs may be understood from a consideration of dissociation of the proton from the acidic site, subsequent transfer of the proton to the medium, and finally diffusion of the proton through the polymer matrix.

For the case of a PEM at high temperature, the dominant

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factor for the proton transport will be the hopping diffusion rather than the vehicular motion at low (or no) water content. The improvement of the proton transport will be solved by the introduction of an ionic channel having an ability for protons to facilitate the transport.

In order to facilitate the proton transport (which moves by hopping diffusion) in low water content, reduction of the diffusion path for the proton will be a solution. This will be conducted by the serial structure of ionic sites along with the channel and the distance between the ionic sites should be optimized for the proton transport after it dissociates from the conjugate base. From that point of view, we chose DNA as a proton conducting material having an ionic channel for the proton transport, since DNA is a rigid, rod-like polymer comprising heteroatomic rings with ionic sites, and it showed the high proton transport.^{13,14} Therefore, the addition of ionic DNA having a regular spacing of ionic sites inside the polymer membranes would facilitate the proton transport channel, since the neighboring ionic sites on the surface of DNA would facilitate proton transport if the proton was dissociated inside the polymer matrix.

In this research, DNA was incorporated into poly(ethylene imine) (PEI) having basic character in order to disperse DNA inside the polymer matrix on a molecular scale by the acid-base interaction. The high density of negatively charged phosphate groups of the double helix provides the ability of DNA to form rather stable complexes with the synthetic basic polymer. The role of PEI is to give mechanical strength to the DNA/basic blend membrane as well as the medium for the proton diffusion after it is dissociated by the matrix. The choice of the material is only based on the functional model to study this research, since DNA, or PEI may not be suitable under the harsh conditions found in fuel cell operations.

The transport of protons through the PEMs connects the equilibrium conformational structure of a membrane and its general composition to molecular processes, including proton dissociation, transfer, diffusion, and distribution. *Ab initio* electronic structure calculations of polymeric fragments and quantum molecular dynamics studies on model PEM systems have provided a basis for understanding the molecular ingredients in the conduction process.

Experimental

Materials. Double-stranded deoxyribonucleic acid (DNA), as the sodium salt from salmon testes, was purchased from Sigma. PEI of different molecular weights (water free, $M_w = 25,000$) and 50 wt% solution in water ($M_w = 750,000$) were purchased from Aldrich and used as received.

Preparation of Membranes. DNA was dissolved in water with pretreatment processing using ion exchange resins in order to substitute Na^+ into the H^+ form. DNA/PEI membranes were prepared as follows. The appropriate

amount of DNA (wt% of DNA: 5, 9, 12, 16) was added to the 10 wt% of PEI/water solution at room temperature. The homogeneous DNA/PEI mixed solution was cast onto the Teflon plate and the membranes were prepared at 60 °C in an oven. The membrane containing higher than 20 wt% of DNA showed heterogeneity, although it was homogeneous in the solution state. The membranes were then dried under vacuum before the measurement.

Characterization of Membranes. The proton conductivity of the membrane was assessed using a four-point probe method, which employed a home-made cell.⁶ Complex impedance measurements were carried out in the frequency range 1 Hz to 8 MHz using an impedance analyzer (IM6; Zahner). During the impedance measurement, the temperature (80 °C) was constantly maintained using a home-made temperature controlling chamber, while purging with N_2 in order to reduce the possible humidity. The impedance spectra of the membranes can be used to generate Nyquist plots,^{15,16} from which the proton conductivity can be calculated.¹⁷

Fourier transform infrared (FT-IR) spectra of the membranes were measured on a DuraSamplIR2 SENIR FT-IR spectrometer. The IR spectrum was measured with a resolution of 4 cm^{-1} .

The thermal stability of the membranes was determined by thermogravimetric analysis (TGA) (TGA 2950 Thermogravimetric Analyzer, Dupont Instruments). All tests were conducted under an N_2 purge over the temperature range 50–500 °C at a scan rate of 10 °C/min.

The cross-sectional morphology of the membranes was studied using a scanning electron microscope (Hitachi S-4700, Japan).

Wide-angle X-ray diffraction (WAXS) measurements were performed using a conventional diffractometer that employed Ni-filtered $\text{Cu-K}\alpha$ radiation. The dried sample membranes were mounted on an aluminum sample holder, and the scanning angle was varied from 5° to 55° at a scanning rate of 5°/min. All the spectra were measured at ambient temperature.

Computational Method. The electronic energies and structures of the stationary species of interest were calculated in the gas phase by full optimization without any geometrical constraint using the density functional theory method with Gaussian 03; Becke's three-parameter hybrid functional¹⁸ with the 6-31+G(d) basis set¹⁷ was used for nonmetallic elements and the effective core potential of the LANL2DZ basis^{19,21} set was used for silver cations. In these calculations, we used d-orbitals (6d-Cartesian function) in order to obtain more accurate results. The nature of all stationary point species was verified by calculating the vibrational frequencies.^{22,23} The charge densities were obtained using natural population analysis. It is unlikely that solvent effects would cause major changes in the geometries of the complex and the application of standard dielectric models to the

systems is problematic, so a theoretical study of the relevant solvent effects is beyond the scope of this paper.

Results and Discussion

DNA/PEI blend membranes exhibit good flexibility and excellent mechanical strength for handling, but the DNA films prepared by casting aqueous solutions of pure DNA are quite brittle.

Figure 1 illustrates the FT-IR spectra of DNA and DNA/PEI membranes with different amounts of DNA, prepared with a molecular weight for PEI of 750,000, which is similar to that of the membrane prepared with PEI having a low molecular weight of 25,000. The main absorption bands of DNA are at 1063 cm^{-1} , corresponding to the symmetric stretching vibration of the phosphate groups, and 1222 cm^{-1} , the asymmetric stretching vibration of the phosphate group.²⁴ It is obvious that the relative intensity of these characteristic peaks increased with increasing DNA content in PEI. With the addition of PEI, the PO_2 asymmetric stretch at 1222 cm^{-1} is increased in intensity and slightly shifted to lower frequencies; the PO_2 symmetric stretch at 1063 cm^{-1} is markedly increased in intensity; and the band at 1042 cm^{-1} , representing either the phosphodiester or the C--O stretch of the DNA backbone, is increased in intensity and slightly shifted to higher frequency.

The microstructures of the DNA/PEI blend membranes were examined using scanning electron microscopy (SEM). For the case of the DNA/PEI membranes, all the samples showed homogeneity and there is no molecular weight dependence of PEI. The interaction between the phosphoric acid of DNA with the N of PEI would help for the miscibility of DNA and PEI.

The WAXS investigation was used to provide information

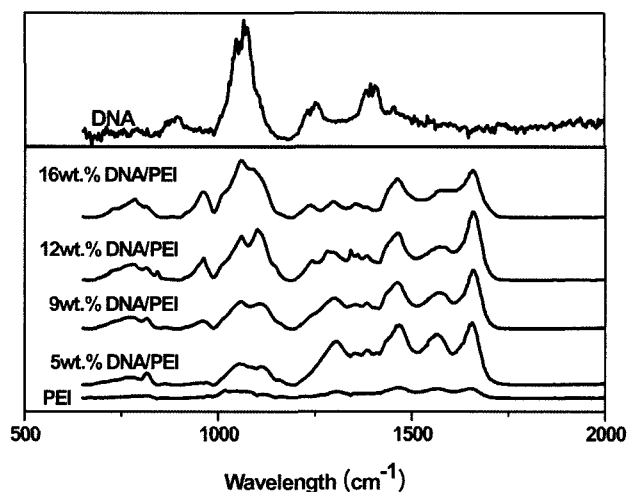


Figure 1. FT-IR spectra of DNA, PEI, and DNA/PEI blend membranes having different amounts of DNA.

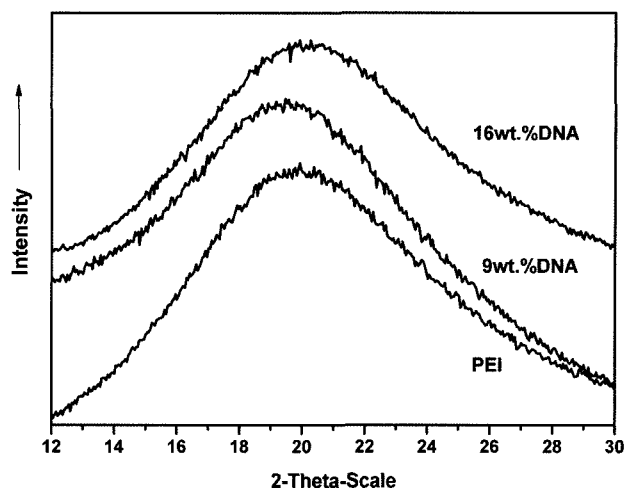


Figure 2. WAXS curves for DNA/PEI blend membranes.

about the morphological properties, the structural changes of the PEI-based blend membranes of the amount of DNA, and the results are shown in Figure 2. Figure displays the WAXS patterns of pristine PEI and DNA/PEI membranes. The molecular weight of PEI was 75,000. The characteristic diffraction peaks of PEI ($2\theta = 19.4^\circ$)²⁵ are obvious. The WAXS pattern of pristine PEI was relatively broad due to the existence of branched sites as well as the lack of crystallinity of the polymer.

Thermal analysis was used to determine the degradation temperature of the membranes as well as the interaction between the acid and base polymers. Figure 3 shows the TGA results of PEI, DNA, and 16 wt% of DNA/PEI membranes. TGA curves show a constant weight loss between room temperature, attributed to desorption of physically absorbed water, and the decomposition of the material. The

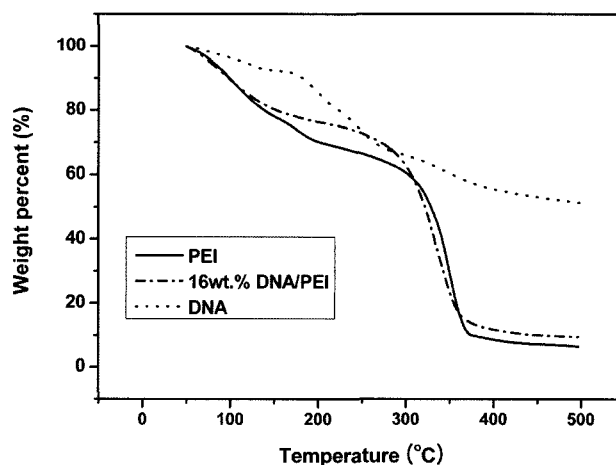


Figure 3. Thermogravimetric analysis of PEI, DNA and 16 wt% of DNA/PEI membranes.

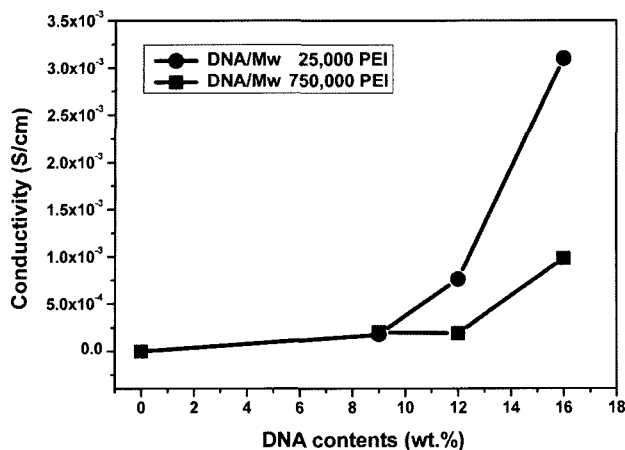


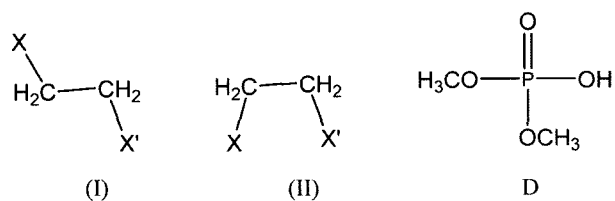
Figure 4. Proton conductivity of DNA/PEI membranes.

rate of weight loss decreased between 200 and 300 °C, and started to decompose significantly above 300 °C. The thermal stability of pristine PEI was lower than that of DNA; therefore it is not easy to see the effect of the thermal stability increment due to the hydrogen interaction between PEI and DNA.

While DNA is itself a polyelectrolyte which has the potential to transfer protons, the microstructure of the membrane must be closely related to the membrane properties. The proton conductivities of DNA/PEI blend membranes for different amounts of DNA measured at 80 °C, during purging N₂, are shown in Figure 4. This is the highest temperature measurable for DNA/PEI membranes, since the DNA/PEI membranes are destroyed above it. The proton conductivity of DNA/PEI was found to increase in accordance with an increase in the amount of DNA. The amount of increment is higher for the membrane prepared with low molecular weight PEI.

Models for DNA, PEI, for the theoretical calculations are shown in Scheme I. *N,N*-Dimethylethylenediamine (2EI) was selected as model for linear PEI. Two different possible stable conformers of 2EI are shown in Scheme I. For example of 2EI, the two nitrogen atoms in this unit can be of the transoid (I) or cisoid (II) type, with respect to the intervening C-C single bond.

The Gibbs free energy difference ($\delta\Delta G$ at 298.15 K) between two conformers was only 0.37 kcal/mol at the b3lyp/6-31+g(d) level. It is reasonable to expect, therefore,



Scheme I. X or X': NHCH₃ or N(CH₃)₂.

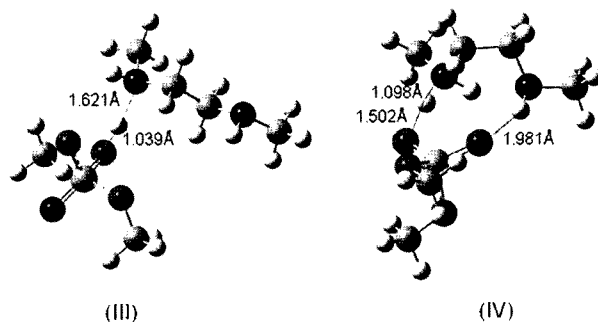


Figure 5. Optimized structures of the complexes (III) and (IV) formed between (I) and (II) of 2EI and D, respectively.

that the two conformers for 2EI will be randomly distributed in a real system for PEI.

As one of the goals of the present work is to understand the molecular connectivity, phosphate groups of D (as a simplified model for DNA) were explicitly added to each of the structures (I) and (II) in Scheme I and full optimizations were performed. The b3lyp/6-31+g(d) minimum energy structures of the 'dry' complexes are displayed in Figure 5. The calculated complexation Gibbs free energy for the formation of the complexes is summarized in Table I. All structures show that the hydrogen bonding through the basic atom of the matrix polymer and the acidic proton of the phosphate group.

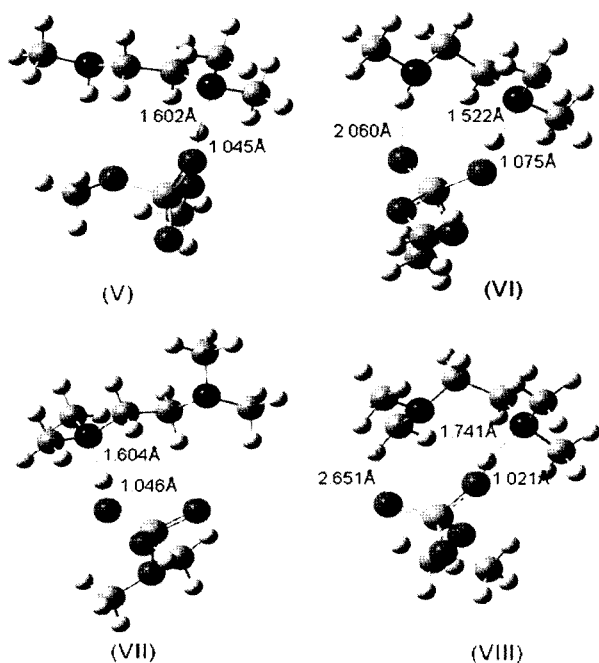
For the case of 2EI, i.e. X = X' = NHCH₃, the Gibbs free energy change for the formation of complex (IV) from D and (II) of 2EI was much more stable (by 7.02 kcal/mol) than that of the complex (III) from D and (I) of 2EI in the gas phase, and the optimized structures are shown in Figure 5. The complex (III) is a monodentate ligand type, whereas the complex (IV) is structurally a bidentate ligand type, i.e. between the hydrogen of D and the basic nitrogen atoms in the matrix as well as the interaction of oxygen (P = O of D) and hydrogen atom of the other unit of 2EI. Therefore the bidentate ligand type complex (IV) could be more stable than (III), due to the high number of stable hydrogen interactions.

Of course, the possibility that one phosphoric acid binds to two nitrogen atoms of two different PEI chains cannot be excluded, since the mole ratio of the ethylene imine unit is 40 times higher than that of DNA even for the 16 wt% of DNA in PEI matrix by simple calculation. However, it could be expected that the effects on complexation energy as well as stereochemistry are very similar to complex (IV).

The PEI we used for the preparation of the DNA/PEI membrane was branched; therefore two models were calculated for the branched PEI for the stable complex with D. The calculated complexation Gibbs free energy for the formation of the complexes is summarized in Table I and the structures are shown in Figure 6. The calculated Gibbs free energy change for the formation of the complex was more

Table I. Calculated Complexation Gibbs Free Energies (ΔG_c in kcal/mol) and the Distance Between the Hydrogen Atom and the Ionic Site in the Gas Phase at 298 K

X	X'	Transoid Form Complex			Cisoid Form Complex				
		ID	ΔG_c Gas Phase kcal/mol	$d(N\cdots H)$ Å	$d(PO\cdots H)$ Å	ID	ΔG_c Gas Phase kcal/mol	$d(N\cdots H)$ Å	$d(PO\cdots H)$ Å
NHCH ₃	NHCH ₃	(III)	-12.89	1.621	1.039	(IV)	-19.91	1.098	1.502
D/2EI	NHCH ₃	(V)	-13.57	1.602	1.045	(VI)	-15.02	1.522	1.075
	N(CH ₃) ₂	(VII)	-14.79	1.604	1.046	(VIII)	-12.52	1.741	1.021

**Figure 6.** Optimized structures of the complexes (V), (VI), (VII), and (VIII) formed between (I) and (II) of 2EI [X = NHCH₃, X' = N(CH₃)₂] or 2EI [X = X' = N(CH₃)₂] and D, respectively.

stable with the addition of a methyl group when the complexes were formed with a transoid type of matrix (see complexes V and VII). On the other hand, the complexation energy formed from the cisoid (II) type branched EI with D decreased with the addition of the methyl group due to the steric hindrance of the neighboring methyl group (see complexes VI and VIII).

In order for proton conduction inside the membrane, the main requirement for proton transport in a dry or low humidity condition is that the proton has to be dissociated from its counter anion. The structural data show that the oxygen-hydrogen bond distance of the acidic proton involved in the hydrogen bond with the matrix has lengthened over that in the isolated oligomeric fragments, i.e. 0.972 Å. The bond length (d_{N-H}) of complex (III) is 1.621 Å and the bond length (d_{PO-H}) increased from 0.972 to 1.039 Å. On the other hand, for the case of model complex (IV), the

bond length (d_{N-H}) is 1.098 Å and the bond length (d_{PO-H}) significantly increased to 1.50 Å. The dissociation of the phosphoric acid hydrogen from its anionic site is more significant and it is almost attached to the nitrogen atom of 2EI for the complex (IV). It is because that the nitrogen attracts the acidic hydrogen more strongly due to the stabilization of another hydrogen bond between the hydrogen of N and the oxygen of the P = O of D.

Theoretically, DNA/PEI form a stable complex in the gas phase, and the dissociation of phosphoric acid occurred and the proton conductivity was observed experimentally. This theoretical result would explain the high proton conductivity measured for the DNA/PEI membrane at low humidity condition (shown in Figure 4). The higher proton conductivity of low molecular weight DNA/PEI can be explained by the high flexibility to form the complex for the short-chain than the long-chain PEI. Since we believe that some water exists and it affects the proton conductivity of the membrane we measured at 80 °C and the low molecular weight PEI would be more likely to be affected by the humidity.

Conclusions

The characteristics of DNA/PEI polymer blend membranes were investigated both theoretically and experimentally in order to understand and design polymer electrolyte membranes at either no or a low humidity condition.

Homogeneous DNA/PEI membranes exhibit high proton conductivity at 80 °C and it depends on the molecular weight of PEI. DNA formed a stable complex with PEI in the gas phase and the calculated complexation Gibbs free energy for the formation of the cisoid form was higher than transoid form obtained using the density functional theory method. The structural data show that the oxygen-hydrogen bond distance of the acidic proton involved in the hydrogen bond with the matrix has lengthened over that in the isolated oligomeric fragments, implying that the requirement for proton transport in a polymer matrix is to dissociate the hydrogen from the ionic sites.

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