New Ionic Conducting Polymer Composite Films Based on Partially Phosphorylated Poly(vinyl alcohol) and Poly(acrylic acid)

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(Received October 6, 1999; CL-990855)

Ionic conductivity of a composite film consisting of partially phosphorylated poly(vinyl alcohol) (P-PVA) and poly(acrylic acid) (PAA) is increased about three orders of magnitude over that of P-PVA film.

Ionic conducting polymers have been of considerable interest because of their potential application as a polymer solid electrolyte. The polymer solid electrolytes have attracted great scientific interest during the last two decades due to their many advantages such as high energy density, electrochemical stability and easy handling.[1,2] Many researches have been investigated using several host polymers such as polyphosphazene,[3,4] poly(itaconate) with side chain grafted PEO[2], and poly(vinylidene fluoride),[5] poly(acrylonitrile),[6-8] poly(methyl methacrylate),[9] poly(vinyl pyrrolidone),[10] and poly(ethyleneglycol diacrylate)[11] plasticized with ethylene carbonate, propylene carbonate, or a mixture of ethylene carbonate and propylene carbonate. The polymers have the mechanical stability and these polymer solid electrolytes containing cations as lithium and alkylammonium ions provide a relatively high ion conductivities.

Recently, we have reported the proton conduction in crosslinking partially phosphorylated poly(vinyl alcohol) (P-PVA) hydrogel films and demonstrated that the hydrogel films are relatively excellent polymer gel electrolyte.[12] Quite recently, the cation conduction in the P-PVA film has been investigated.[13] Here, we describe the preparation of composite films consisting of P-PVA with dipotassium salt and poly(acrylic acid) (PAA) and the effects of PAA on the ionic conductivity.

Partially phosphorylated poly(vinyl alcohol) with dipotassium salt (P-PVA) was prepared and characterized according to the literature.[12,13] The degree of phosphorylation for the P-PVA, which was determined by pH titration and molybdenum blue method, was 0.163 (Figure 1). Polymer sample solutions were prepared as follows. P-PVA was dissolved in distilled water and PAA was added under the conditions of various molar ratios of carboxylic acid residue in PAA to hydroxyl group in P-PVA ([-CO$_2$H]/[-OH]) ≈ 0, 1.0, 2.2, 4.4, 6.5 and 8.7. The standard devices were prepared by casting of the polymer sample solutions on ITO electrode. Sample films were sandwiched between two ITO electrodes, and then slowly dried on P_2O_5.

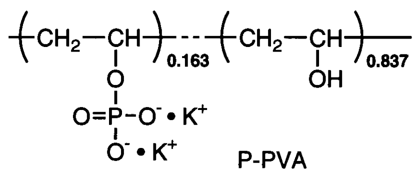


Figure 1. Chemical structure of P-PVA

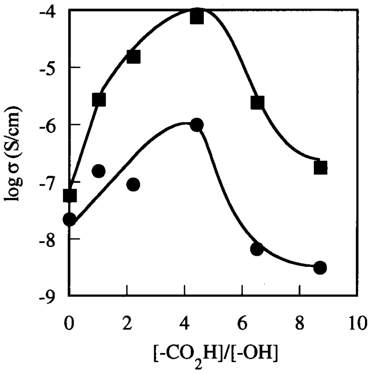


Figure 2. Effects of PAA on ionic conductivity of P-PVA/PAA composite film at 293.15 K (●) and 333.15 K (■).

Figure 2 shows the effect of PAA on the ionic conductivity of P-PVA/PAA composite films at 293.15 K and 333.15 K. For both temperatures, the ionic conductivities increased with addition of PAA and then decreased, through the maximum value at [CO$_2$H]/[-OH] ≈ 4. In particular, the ionic conductivities at [CO$_2$H]/[-OH] ≈ 4 were increased about 1.5 and 3 orders of magnitude over those of P-PVA film at 293.15 K and 333.15 K, respectively. Moreover, the temperature dependence of the ionic conductivity of P-PVA/PAA composite films showed upward curves for all systems as shown in Figure 3, clearly indicating that the ionic conduction is Williams-Landel-Ferry (WLF) type.[14] Activation energy for the ionic conduction

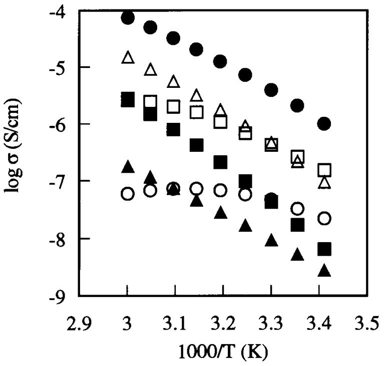


Figure 3. Temperature dependence of ionic conductivities of the polymer composite films with various [CO2H]/[OH]: 0 (○); 1.0 (□); 2.2 (△); 4.4 (●); 6.5 (■); 8.7 (▲).

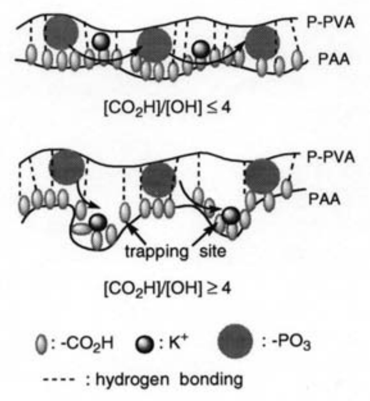
Table 1. Experimental data of P-PVA/PAA composite films.

	Ratio[a]	log σ (S/cm)[b]		Ea [c]	Tg[d]
		293.15 (K)	333.15 (K)	(eV)	(K)
P-PVA	0	-7.64	-7.22	1.22	
Film-1	1.0	-6.79	-5.55	0.90	278
Film-2	2.2	-7.03	-4.8	0.19	278
Film-3	4.4	-5.99	-4.11	0.17	279
Film-4	6.5	-8.16	-5.6	0.21	280
Film-5	8.7	-8.49	-6.73	0.23	281

[a] $[\text{-CO}_2\text{H}]/[\text{-OH}]$. [b] Ionic conductivity. [c] Activation energy. [d] Glass transition temperature.

of these polymer composite films, which is determined by WLF plot and then Vogel-Tamman-Fulcher plot,[15] is summarized in Table 1. The activation energy decreases with increasing PAA concentration up to $[\text{CO}_2\text{H}]/[\text{-OH}] \approx 4$ and is almost constant (slightly increases) at $[\text{CO}_2\text{H}]/[\text{-OH}] > 4$. Although the activation energy is low at $[\text{CO}_2\text{H}]/[\text{-OH}] > 4$, the ionic conductivity decreases. The glass transition temperature was barely changed by addition of PAA. Furthermore, FTIR measurements of the polymer composite films shows the absorption bands around 1560 cm^{-1}, 1400 cm^{-1}, and 920 cm^{-1}, arising from carbonyl group of carboxylate ion. The fact strongly suggests that the ionic conduction is mediated by carboxylic acid residues on the PAA. Based on these results, we propose the mechanism of ionic conduction in the polymer composite films as illustrated in Scheme 1.

Scheme 1.



In the present systems, the ionic conduction takes place through hopping of cations between phosphorylate residues. It is well-known that poly(acrylic acid) and poly(vinyl alcohol) form a polymer complex through hydrogen bonding.[16] Therefore, P-PVA and PAA in the polymer composite film form a polymer complex[17] and many carboxylic acid residues are placed around phosphorylate residues and between phosphorylate residues. Probably, the carboxylic acid residues form an ionic conducting road and accelerate the potassium cation transporting, consequently leading to an increase in the ionic conductivity and decrease in the activation energy. On the other hand, the ionic conducting road would also be formed in the polymer composite films at $[\text{CO}_2\text{H}]/[\text{-OH}] \geq 4$, being supported by the fact that the activation energy for the ionic conduction is low. However, an excess of carboxylic acid residues aggregates through hydrogen bonding and forms a trapping site in which traps potassium cations and inhibits the ion conduction. Therefore, the ionic conductivity is very low in spite of the low activation energy.

In summary, we reveal that the ionic conductivity of the polymer composite film consisting of P-PVA and PAA significantly enhances compared with the single polymer film. In particular, the ionic conductivity of P-PVA/PAA composite film at 333.15 K is increased about three orders of magnitude over that of the P-PVA film. The detailed study is now under progress in our laboratory.

This work was supported by Grant-in-Aid for COE Research (10CE2003) by the Ministry of Education, Science, Sports and Culture of Japan.

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17 The formation of the polymer complex between P-PVA and PAA was confirmed by viscosity measurement in these dilute solutions.