

Lewis Acid–Base Property of P(VDF-*co*-HFP) Measured by Inverse Gas Chromatography

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ABSTRACT: Poly (vinylidene fluoride-*co*-hexafluoropropylene) P(VDF-*co*-HFP) is an excellent material for polymer electrolytes of lithium ion battery. To enhance the lithium ion transference number, some metal oxides were often embedded into P(VDF-*co*-HFP). The promising mechanism for the increase in lithium ionic conductivity was Lewis acid–base theory. In this experiment, the Lewis acid–base properties of P(VDF-*co*-HFP) were measured by inverse gas chromatography (IGC). The Lewis acid constant K_a of P(VDF-*co*-HFP) is 0.254, and the base constant K_b is 1.199. Compared with other polymers characterized by IGC, P(VDF-*co*-HFP) is the strongest Lewis basic polymers. Except aluminum ion, lithium ion is the strongest

Lewis acidic ion according to their η value of Lewis acids. Therefore, a strong Lewis acid–base interaction will exist between lithium ion and P(VDF-*co*-HFP). This will restrict the transference of lithium ion in P(VDF-*co*-HFP). To enhance the lithium ion transference by blending other metal ions into P(VDF-*co*-HFP), it is suggested that the preferential ions should be Al^{3+} , Mg^{2+} , Na^+ , and Ca^{2+} because these metal ions have relative large η values. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 1642–1646, 2008

Key words: P(VDF-*co*-HFP); inverse gas chromatography; Lewis acid–base; lithium ions

INTRODUCTION

Lithium battery is an important energy source for electric vehicles and portable electronic devices. Generally, gel polymer electrolytes are used as the media for lithium ions transport or the separators between anodes and cathodes in lithium polymer batteries because of polymer electrolytes make the battery highly safe and flexible. The gel polymer electrolytes can be obtained by embedding organic solutions of lithium salt into porous polymer matrices (polymer membranes). Many polymers have been used as the matrices of polymer electrolytes, such as polyethylene oxide, polyacrylonitrile, polymethylmethacrylate, polyvinylchloride, polyvinylidene fluoride, and poly (vinylidene fluoride-*co*-hexafluoropropylene) (P(VDF-*co*-HFP)).¹ Recently, P(VDF-*co*-HFP) has received many special attentions as a promising material for polymer electrolytes because of its excellent properties.^{1–9}

P(VDF-*co*-HFP) is a semicrystalline polymer, which is the copolymer consisting of crystalline vinylidene fluoride (VDF) and amorphous hexafluoropropylene (HFP) units. Generally, P(VDF-*co*-HFP) electrolytes are prepared by solution casting and then reswollen in lithium salt electrolyte solution. The VDF unit makes P(VDF-*co*-HFP) have excellent chemical stabil-

ity and mechanical strength. The amorphous HFP unit can trap more liquid electrolyte. Therefore, P(VDF-*co*-HFP) electrolytes have high ionic conductivities and good mechanical properties.^{2–5} In 1996, P(VDF-*co*-HFP) membranes were used as polymer matrix of polymer electrolytes in the commercialized lithium ion batteries by Telcordia Technologies (formerly Bellcore).^{1,2,6}

To enhance its performances, many researchers sought new methods of preparing P(VDF-*co*-HFP) membranes, such as using supercritical CO_2 induced phase separation technology,⁴ using poly(vinyl pyrrolidone) (PVP) as plasticizer instead of DBP,⁶ changing the solvents or nonsolvents.^{5,7,8} Moreover, some works concentrated on embedding inorganic nanoparticles into P(VDF-*co*-HFP) membranes. When metal oxides were included in P(VDF-*co*-HFP) membranes, the properties such as ionic conductivity, lithium ions transference number, and activation energy for ions transport will be improved. The nanoparticles included TiO_2 , ZnO , MgO , Al_2O_3 , SiO_2 , $\text{AlO}[\text{OH}]_n$, etc.^{2,3,9} Some researchers thought that the inclusion of inorganic nanoparticles in P(VDF-*co*-HFP) led to a better lithium ionic transport properties by the suppression of Li^+ -F interactions.³ A promising mechanism for the increase in ionic conductivity was that metal oxides acted as solid plasticizer hindering the reorganization of polymer chains and could interact with polar groups of polymer by Lewis acid–base interaction.^{2,3,9}

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TABLE I
Characteristics of Probe Solvents^{10,13}

Probes	a (Å ²)	r_1^d (mJ/m ²)	$a(r_1^d)^{0.5}$ (Å ² (mJ/m ²) ^{0.5})	AN* (kJ/mol)	DN (kJ/mol)
<i>n</i> -C ₆	51.5	18.4	221	–	–
<i>n</i> -C ₇	57.0	20.3	257	–	–
<i>n</i> -C ₈	63.0	21.3	291	–	–
<i>n</i> -C ₉	69.0	22.6	329	–	–
CHCl ₃	44.0	25.9	224	22.7	0.0
Acet	42.5	16.5	173	10.5	71.4
EtAc	48.0	19.6	212	6.3	71.1
THF	45.0	22.5	213	2.1	84.4

a , molecular area of probe; r_1^d , surface free energy of probe; AN* and DN, Gutmann's modified acceptor number and donor number of probe.

n-C₆, *n*-hexane; *n*-C₇, *n*-heptane; *n*-C₈, *n*-octane; *n*-C₉, *n*-nonane; CHCl₃, trichloromethane; Acet, acetone; EtAc, ethylacetate; THF, tetrahydrofuran.

Nowadays, using Lewis acid–base concept for describing special interaction is increasingly accepted.^{10–12} The usual techniques for measuring Lewis acid–base parameters are isoelectric point, indicator dye adsorption, X-ray photoelectron, calorimetry, and inverse gas chromatography (IGC). For polymer materials, IGC technique is more often used than other methods.^{10–12} To our knowledge, the Lewis acid–base property of P(VDF-co-HFP) are not measured until now. In this study, IGC was used to characterize quantitatively the Lewis acid–base properties of P(VDF-co-HFP). The Lewis acid constant K_a and base constant K_b were decided.

INVERSE GAS CHROMATOGRAPHY

Inverse gas chromatography (IGC) is an inversion of conventional gas chromatography. The main difference between GC and IGC is that the interested species is the polymer material acting as the stationary phase in IGC column. Probes (organic solvents) with

known properties are injected in the column and the retention times of these probes are measured at infinite dilution. The interactions between the probes and the polymer material are calculated from the retention times, and then the Lewis acid–base properties of the polymer are determined by the following procedures.

The adsorption free energy of probes by polymer stationary phase is obtained from the net retention volume by the following equation:¹⁰

$$-\Delta G_a = RT \ln(V_n) \quad (1)$$

where ΔG_a is the adsorption free energy, R is the gas constant, T is the temperature of column, V_n is the net retention volume. V_n is calculated according to eq. (2):

$$V_n = (t_r - t_0)FCJ \quad (2)$$

where t_r is the retention time of probe, t_0 is the retention time of noninteracting probe, F is the flow rate of carrier gas, which is measured by a bubble flow meter. C is a correction factor for the vapor pressure

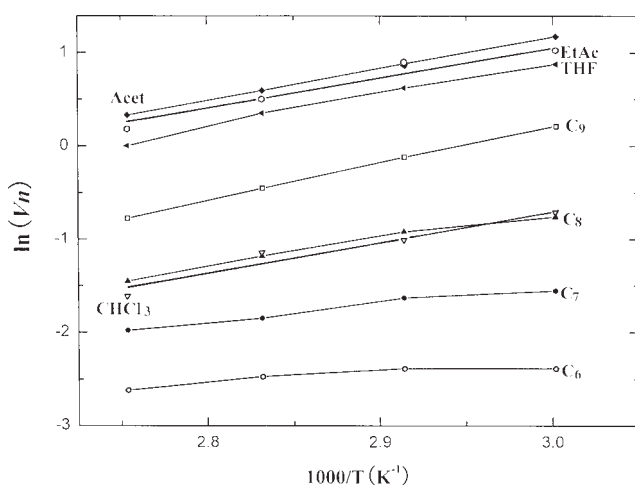


Figure 1 Plot of $\ln(V_n)$ versus $1000/T$ for the probes.

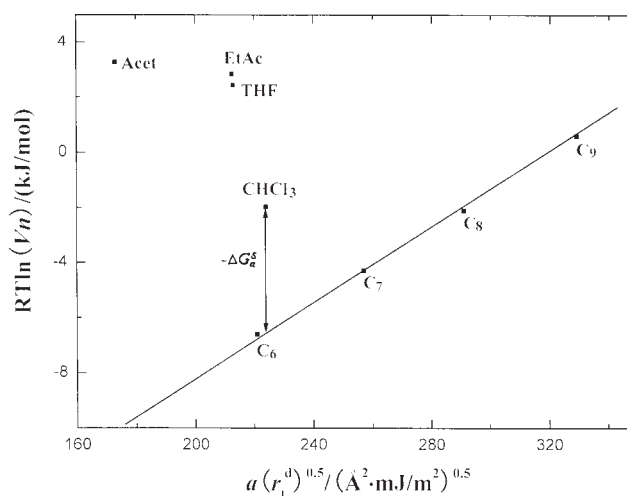


Figure 2 Adsorption free energy versus $a(r_1^d)^{0.5}$ for the probes at 333.2K.

TABLE II
Adsorption Free Energy by Lewis Acid–Base Interaction of Polar Probes ΔG_a^s (kJ/mol)

Temperature (K)	CHCl ₃	Acet	EtAc	THF
333.2	-4.5038	-13.1227	-10.0756	-9.6318
343.2	-3.7534	-12.2057	-9.8890	-9.0634
353.2	-3.8008	-11.7132	-9.2722	-8.7965
363.2	-2.6247	-11.3310	-8.6843	-8.2993

of water at the temperature of using the bubble flow meter. The expression is:

$$C = 1 - P_{\text{H}_2\text{O}}/P_0 \quad (3)$$

where $P_{\text{H}_2\text{O}}$ is the saturated vapor pressure of water at ambient temperature, P_0 is the atmospheric pressure. J is a compression correction term determined as follows:

$$J = \frac{3}{2} \frac{(P_i/P_0)^2 - 1}{(P_i/P_0)^3 - 1} \quad (4)$$

where P_i is the inlet pressure of carrier gas. When polar solvents are injected into the column, the adsorption free energy by Lewis acid–base interaction ΔG_a^s , is calculated by the following expression:¹²

$$\Delta G_a = \Delta G_a^d + \Delta G_a^s \quad (5)$$

where ΔG_a^d is the adsorption free energy of dispersive interaction, which is determined with a series of n -alkanes. ΔG_a^s results from the distance between the $RT \ln(V_n)$ value of polar solvent and the straight n -alkane line. The reference parameter of n -alkanes line is $a(\tau_1^d)^{0.5}$, where a is molecular area of probe solvent, and τ_1^d is surface free energy of probe solvent. The adsorption enthalpy of Lewis acid–base interaction ΔH_a^s , is calculated according to the following expression:¹⁰

$$\Delta G_a^s = \Delta H_a^s - T\Delta S_a^s \quad (6)$$

where ΔS_a^s is the adsorption entropy of Lewis acid–base interaction. ΔH_a^s results from the slope of the plot of $\Delta G_a^s/T$ versus $1/T$. The Lewis acid constant K_a , and Lewis base constant K_b are calculated according to the following expression:¹⁰

$$-\Delta H_a^s = K_a \times \text{DN} + K_b \times \text{AN}^* \quad (7)$$

where DN and AN* are the Gutmann's Donor and modified Acceptor number of polar solvents, respectively. When plotting $-\Delta H_a^s/\text{AN}^*$ versus DN/AN^* , the slope gives K_a , and the intercept gives K_b .

TABLE III
Enthalpy of Lewis Acid–Base Interaction ΔH_a^s (kJ/mol)

Probes	CHCl ₃	Acet	EtAc	THF
ΔH_a^s	-22.972	-32.737	-25.996	-23.836

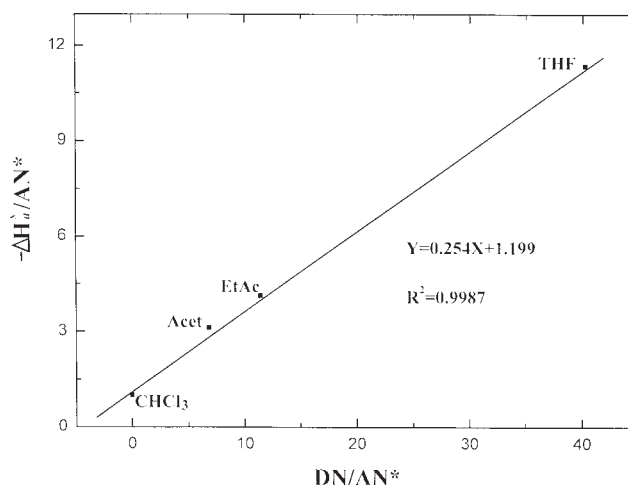


Figure 3 Determination of K_a and K_b for the Lewis acid–base constants of P(VDF-co-HFP).

EXPERIMENTAL

Materials

P(VDF-co-HFP) was purchased from Solvay Solexis, Belgium. For the IGC analysis, the n -alkanes probes were n -pentane (C₅), n -hexane (C₆), n -heptane (C₇), n -octane (C₈), and n -nonane (C₉). The polar probes were trichloromethane (CHCl₃), acetone (Acet), ethylacetate (EtAc), and tetrahydrofuran (THF). They were analytical grade solvents and purchased from Tianjin Kermel Chemical Reagents Development Centre, China. C₅ was adopted as the noninteracting probe instead of methane that was generally used as noninteracting probe in most IGC experiments, because the retention times of C₅ were the shortest in this experiment. The characteristics of probe solvents are listed in Table I.

IGC Instrument

The instrument was a GC-900A gas chromatograph equipped with a flame ionization detector (FID),

TABLE IV
Lewis Acid Number K_a and Base Number K_b of Some Polymers

Polymers	K_b	K_a	Reference
P(VDF-co-HFP)	1.199	0.254	this work
PBT	0.96	0.49	14
PC	0.48	0.09	14
PMMA	0.354	0.076	15
PANI	0.255	0.071	16
PVC	0.218	0.149	15
POT	0.091	0.08	16

PBT, poly (butylene terephthalate); PC, polycarbonate; PMMA, poly (methyl methacrylate); PANI, polyaniline; PVC, poly vinylchloride; POT, poly (3-octyl thiophene).

TABLE V
Hardness Values (η) of Lewis Acids (eV) for Some Metal Ions¹²

Li ⁺	Na ⁺	Cu ⁺	Ag ⁺	Au ⁺	Cd ²⁺	Mg ²⁺	Ca ²⁺	Ti ²⁺	Mn ²⁺	Fe ²⁺	Ni ⁺	Cu ²⁺	Zn ²⁺	Pb ²⁺	Al ³⁺	Fe ³⁺	Hg ⁺
35.1	21.1	6.3	6.9	5.7	10.3	32.5	19.7	7.0	9.3	7.3	8.5	8.3	10.8	8.5	45.8	13.1	7.7

which was purchased from Shanghai TianPu Analytical Instrument, China. Nitrogen was used as the carrier gas. The flow rate was 6.2 mL/min measured from the end of the column with a soap bubble flow meter. The injector and FID were heated to 130°C. The probe solvents were injected manually, using a 1.0 μ L Hamilton syringe. The injection volumes were 0.1 μ L.

The column was a stainless steel tube (0.76 m length, 2.56 mm i.d.). It was washed with Acet prior to use. P(VDF-co-HFP) stationary phase was prepared by vaporizing solvent method. First, P(VDF-co-HFP) was dissolved in Acet. Then, some inert support chromosorb (80–100 mesh) was added into the polymer solution. The solution was heated at 40°C to vaporize the solvent. 0.26 g P(VDF-co-HFP) was packed in the column. The column was conditioned at 100°C and fast carrier gas flow rate for 4 h prior to use. The IGC experiments were performed at 60, 70, 80, and 90°C.

RESULTS AND DISCUSSION

Figure 1 shows the plot of $\ln(V_n)$ versus the inverse of the column temperature for *n*-alkanes and polar probes. The linear relationships of the plots are well. From the values of net retention volumes of the probes, the Lewis acid–base properties of P(VDF-co-HFP) are determined. Figure 2 shows the calculation for the adsorption free energy by Lewis acid–base interaction ΔG_a^s of polar probes at 60°C. Table II lists the data of ΔG_a^s at all temperatures.

According to eq. (6), the enthalpies of Lewis acid–base interaction ΔH_a^s for every polar probe are calculated from the adsorption free energy of Lewis acid–base interaction listed in Table II. The results are listed in Table III.

Then, the Lewis acid–base constants are calculated according to eq. (7). Figure 3 shows the plot of $-\Delta H_a^s/AN^*$ versus DN/AN^* for the polar probes. The linear correlation for the four polar probes is fine. The Lewis acid constant K_a is 0.254, and the base constant K_b is 1.199.

Table IV lists the Lewis acid–base numbers of some polymers measured by IGC in recent years. The data in Table IV show that these polymers are all Lewis basic materials. The basic value of P(VDF-co-HFP) is the largest in these polymers. It is even larger than PC and PBT, which contain strong Lewis basic site of ester groups. Therefore, P(VDF-co-HFP) will form

stronger Lewis interaction with a Lewis acidic matter than other polymers.

Table V lists the Lewis acidic property of some metal ions, which is characterized by η , the resistance of the chemical potential to a change in the number of electrons.¹² Lithium ion has the strongest Lewis acid in these metal ions except aluminum ion. Therefore, lithium ion has a strong interaction with P(VDF-co-HFP) through Lewis acid–base sites. This will restrict the transference of lithium ion in P(VDF-co-HFP). When other metal ions particles are blended in P(VDF-co-HFP), they must interact with the Lewis basic site of P(VDF-co-HFP), and reduce the restriction of P(VDF-co-HFP) to lithium ion. To enhance the lithium ion transference, the preferentially chosen metal ions should be Al³⁺, Mg²⁺, Na⁺, and Ca²⁺ according to their η values listed in Table V, because these ions possess high η values.

CONCLUSIONS

In this experiment, the Lewis acid–base properties of P(VDF-co-HFP) were measured by IGC. The Lewis acid constant K_a is 0.254, and the base constant K_b is 1.199. Compared with other polymers characterized by IGC, P(VDF-co-HFP) is the strongest Lewis base polymer. According to the η values of Lewis acids listed in Table V, lithium ion is the strongest Lewis acidic ion except aluminum ion. Therefore, a strong Lewis acid–base interaction will exist between lithium ion and P(VDF-co-HFP). This will restrict the transference of lithium ion in P(VDF-co-HFP).

To enhance the lithium ion transference by blending other metal ions into P(VDF-co-HFP), it is suggested that the preferential ions should be Al³⁺, Mg²⁺, Na⁺, and Ca²⁺ because these metal ions have higher η values, compared with other ions listed in Table V.

References

- Cao, J. H.; Zhu, B.K.; Xu, Y.Y. *J Membr Sci* 2006, 281, 446.
- Wu, C. G.; Lu, M. I.; Tsai, C. C.; Chuang, H. J. *J Power Sources* 2006, 159, 295.
- Kim, K. M.; Park, N. G.; Ryu, K. S.; Chang, S. H. *Electrochim Acta* 2006, 51, 5636.
- Cao, J. H.; Zhu, B. K.; Ji, G. L.; Xu, Y. Y. *J Membr Sci* 2005, 266, 102.
- Stephan, A. M.; Renganathan, N. G.; Gopukumar, S. *Teeters, D. Mater Chem Phys* 2004, 85, 6.

6. Wang, Z. L.; Tang, Z. Y. *Mater Chem Phys* 2003, 82, 16.
7. Stephan, A. M.; Teeters, D. *Electrochim Acta* 2003, 48, 2143.
8. Pu, W. H.; He, X. M.; Wang, L.; Jiang, C. Y.; Wan, C. R. *J Membr Sci* 2006, 272, 11.
9. Stephan, A. M.; Nahm, K. S.; Kulandainathan, M. A.; Ravi, G.; Wilson, J. *Eur Polym J* 2006, 42, 1728.
10. Santos, J. M. R. C. A.; Guthrie, J. T. *Mater Sci Eng R* 2005, 50, 79.
11. Sun, C. H.; Berg, J. C. *Adv Colloid Interface Sci* 2003, 105, 151.
12. Mukhopadhyay, P.; Schreiber, H. P. *Colloids Surf A* 1995, 100, 47.
13. Santos, J. M. R. C. A.; Guthrie, J. T. *J Chromatogr A* 2005, 1070, 147.
14. Santos, J. M. R. C. A.; Fagelman, K.; Guthrie, J. T. *J Chromatogr A* 2002, 969, 119.
15. Abel, M. L.; Chehimi, M. M.; Fricker, F.; Delamar, M.; Brown, A. M.; Watts, J. F. *J Chromatogr A* 2002, 969, 273.
16. Chehimi, M. M.; Abel, M. L.; Perruchot, C.; Delamar, M.; Lascelles, S. F.; Armes, S. P. *Synth Met* 1999, 104, 51.