Positron annihilation study in polyaniline conducting polymer

Z.L. PENG, S.Q. LI, Y.Q. DAI, B. WANG, S.J. WANG, H. LIU* and H.Q. XIE*

Department of Physics, Wuhan University, Wuhan 430072, P.R. of China

** Dept. of Chem., Huazhong Univ. of Sci. & Tech., Wuhan 430072, P.R. of China*

ABSTRACT

The positron lifetime spectra in polyaniline have been measured as a function of protonation level (pH from 7 to -0.8). We observed that (1) the short lifetime τ_1 decreased with the protonation level; (2) the intermediate lifetime was constant ($\tau_2 \sim 360$ ps), whereas its intensity I_2 increased with increasing protonation level which was related to the conductivity of material. These results are discussed in terms of conducting island model.

1. INTRODUCTION

The polyaniline family of polymers have been the focus of recent investigation due to the special characteristics and application [1,2]. Series corresponding variation in physical properties with the protonation level has been reported [3]. In order to understand the nature of physical process which occur in polyaniline due to doping, we performed the positron lifetime measurement as a function of protonation level and discussed its sensitivity to the microstructural changes in the polymer matrix.

2. EXPERIMENT

Polyaniline powder was prepared by chemical synthesis as described by Macdiarmid et al [1]. The powder obtained was extracted with CH_3CN , dried and then equilibrated with constant stirring in 0.1M NH_4OH for 24h giving deprotonated. The polyaniline powder with different protonation states were obtained by treatment of its base form of powder with different acidity aqueous HCl solution and compressed into 1mm thickness pellets under 150kg/cm^2 and its conductivity was measured by four-probe method. Positron lifetime spectra were measured using a fast-fast coincidence system with time resolution of 245ps and each spectrum contained one million counts.

3. RESULT AND DISCUSSION

(1). Conductivity measurement at room temperature

The variation of the conductivity of polyaniline powder at room temperature with the protonation state is shown in fig.1. The emeraldine base form of polyaniline has a conductivity of 10^{-10} S/cm. Through treatment with aqueous HCl of pH varying from 7 to -0.8, protons were added to a fraction of formerly unprotonated nitrogen sites, while Cl^- remain interstitially for charge neutrality. Though the number of electrons on the polymer chain remains constant, the conductivity increased to 3 S/cm. At higher degree of the protonation states ($\text{pH} \leq 1$), the conductivity reaches a maximum value and does not change with the varying pH. Therefore, an insulator to metal transition for samples was observed.

(2). Positron annihilation parameter

Positron spectrum of polyaniline has been best resolved into three component by using PATFIT program [4]. Since the intermediate lifetimes almost remain 360ps, so we fixed τ_2 at 360ps to reduce the statistical error.

As we know, the short lifetime τ_1 and the intermediate lifetime τ_2 are attributed to positron annihilation mainly from the bulk and trapped state, respectively, and the long-lived component ($\tau_3 = 1.93 \pm 0.12 \text{ ns}$, $I_3 = 2.2 \pm 0.3\%$) is due to o-Ps annihilation on the surface of the material which is nearly independent to protonation level. The τ_1 decreases with the protonation level, whereas I_2 first increases with the protonation level and then remains constant for higher doping level ($\text{pH} \leq 1$), as shown in fig.2 and 3. The decrease of the τ_1 with increase of protonation level indicated the increase of the electron density in bulk of material. Comparing fig.1 and fig.3, intermediate intensity I_2 is obviously related to the conductivity of our sample, so we pay the special attention to the variation of the intermediate component with respect to protonation level.

In the base form of polyaniline, the trapping sites might be voids in the amorphous regions and not-totally collapsed chlorine anion vacancies left by deprotonating. In protonated emeraldine, the localized chlorine dopant anions should perturb the intermolecular force in its vicinity and create local lattice distortions in a manner so as to create local negatively charged regions which will trap the positrons [5]. The increase amount of the trapping sites in sample is essentially determined by the concentration of the chlorine dopant anion. According to the model of conducting island [2], in polyaniline, partial protonation leads to phase segregation into metallic (fully protonated) regions and insulating (unprotonated) regions. The amount of metallic regions increases with the protonation level, and the formation of large amount of metallic regions will reduce potential barrier and leads to the increase in conductivity. The increase of I_2 is just an indicator of the metallic regions, so as the equilibrium pH of aqueous HCl solution decreases, the increase of I_2 has the same tendency as the conductivity. The larger the I_2 value, the greater is the conductivity.

Fig.1 The variation of conductivity with protonation level in polyaniline

Fig.2 The positron lifetime τ_1 against protonation level in polyaniline

Fig.3 The positron intensity I_2 against protonation level in polyaniline

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