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Properties of Polyaniline Doped with Ferrocyanic Acid Estimated by Mössbauer, Positron, and Impedance Spectroscopy

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Abstract—An electrically conducting polyaniline doped with ferrocyanic acid was synthesized by oxidative polymerization of the aniline salt of ferrocyanic acid. The aniline salt of the acid and the obtained polyaniline were studied by nuclear γ-resonance, positron annihilation lifetime, and impedance spectroscopy.

Keywords: polyaniline, positron annihilation lifetime spectroscopy, impedance

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The conducting polymer polyaniline (PANI) captured the intense attention, because it combines a high chemical stability and sufficiently high electrical conductivity. The synthesis and characteristics of PANI have been studied in sufficient detail [1–4]. It should be noted that the physical and chemical characteristics of PANI are to a great extent depend on the procedure and conditions of its synthesis [1, 5–7]. The chemical composition [4–8], morphology [9, 10], doping, and redox state of PANI [11–14] were studied at different synthesis conditions. The electrical conductivity of PANI as a function of its redox state and doping level was also studied [15, 16]. The majority of conducting forms of PANI are polysalts comprising a certain number of protonated benzoid and quinoid groups.

The aim of the present work was to study the number of negatively charged centers in the salt and polymeric matrix of PANI by means of positron annihilation lifetime spectroscopy (PALS) and to follow the changes in the electronic environment of the ferrocyanide ion by means of Mossbauer spectroscopy, as well as to compare the electric conductivity of pelleted PANI samples fabricated at varied pelleting pressures with the data of positron spectroscopy.

Oxidative polymerization was used to obtain two polyaniline samples, one of which was doped with ferrocyanic acid (Scheme 1). The elemental analyses of the obtained samples are listed in Table 1.

The IR spectra of the obtained samples (Fig. 1) contain absorption bands of the N–H (3426 cm^{-1}), C–H (2920–2922 cm^{-1}), C=N (1563 cm^{-1}), and C≡N (1240 cm^{-1}) bonds in the quinoid and benzoid fragments (1482, 1297, 2099 cm^{-1}). The bands of the quinoid fragment in the spectrum of PANI are weaker

Scheme 1.

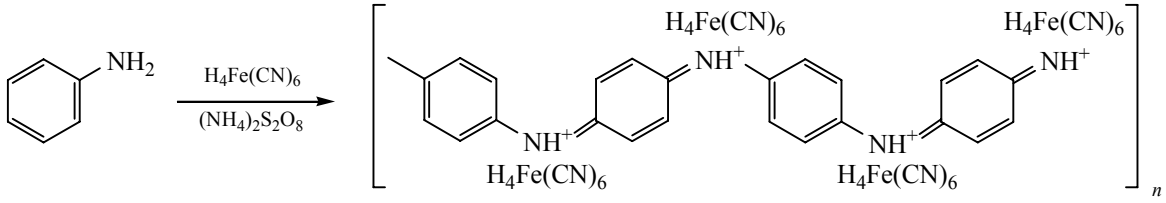

Table 1. Elemental analyses of PANI and PANI doped with ferrocyanic acid

Sample	C, %			Fe, %		
	calculated	found	found by thermal analysis	calculated	found	found by thermal analysis
PANI	65.6	65.8	69.2	–	–	–
PANI·$H_4Fe(CN)_6$	59.7	60.9	–	5.2	5.9	–

compared to the bands of the benzoid fragment (Fig. 1, spectrum *2*), but their intensity increase in the spectrum of PANI doped with ferrocyanic acid (Fig. 1, spectrum *3*).

The Mössbauer spectrum of ferrocyanic acid (Fig. 2a) shows a doublet of nonequivalent hydrogen atoms, implying an unsymmetrical environment of the iron atom [17]. The spectrum of the aniline salt of ferrocyanic acid contains a singlet (Fig. 2c), which suggests the formation of an onium fragment with ferrocyanic acid. The Mössbauer spectrum of the polyaniline salt, like the spectrum of the aniline salt, shows a singlet shifted upfield due to a stronger effect of the nitrogen atom on the electronic state of iron in the ferrocyanide anion, which does not contradict previously obtained data (Table 2) [18].

The X-ray diffraction pattern of PANI prepared from the salt of aniline with ferrocyanic acid contains reflexes belonging to the salt. Their shift appears to be caused by the reaction of the acid with the nitrogen of the polymer chain. Two large broadened bands at 16.5° and 26.7° suggest an amorphous structure of the polymer, which agrees with the data in [19]. However,

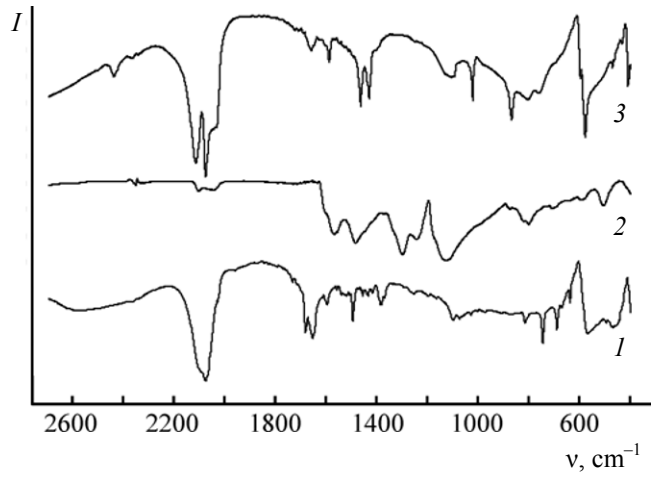

Fig. 1. IR spectra of (*1*) aniline salt of ferrocyanic acid, (*2*) PANI, and (*3*) PANI doped with ferrocyanic acid.

doping PANI with ferrocyanic acid resulted in the appearance of reflexes assignable to a salt. This finding can be considered as evidence in favor of the above suggestion made from the Mössbauer spectroscopy data on the formation of onium fragments on the basis of the acid and the amine nitrogen in the polymer chain. The IR spectrum of PANI doped with ferrocyanic acid (Fig. 1, spectrum *3*) shows in the range 2040–2106 cm^{-1} a two-peak band different from the two-peak band in the spectrum of the parent acid (2020–2040 cm^{-1}), which, too, supports the presence of onium fragments in the polymer chain.

Taking into account the use of PALS in studying the properties of semiconductors [20], we performed a PALS study of the obtained polyanilines and their salts, as well as pelleted PANI samples fabricated at different pressures. Lifetimes (τ) and intensities (*I*) were measured for three components of the spectra (Tables 3 and 4).

The PALS data are indicative of a high electric conductivity (1.1 cm/cm^2) of PANI·[$Fe(CN)_6$], which is associated with a great number of polaron centers in the polymer matrix and is indicated by high intensity (I_2 39.14) and annihilation rate (K_2 249 L/ns). The K_2, I_2, and N_e^+ values for free PANI and the aniline salt with ferrocyanic acid are lower or comparable (Table 3).

As shown by Jean et al. [21], PALS data allow assessing the effect of pressure on the conductivity of polymers. Therefore, we made use of PALS to study pelleted PANI samples fabricated at pressures varied from 1000 to 5000 kg/cm^3 (Tables 5 and 6).

The concentration of defects and their related free volume $V_{f\,(e+,\,Ps)}$ can be found by Eq. (1) [22–25].

$$V_{f(e+,\,Ps)} = \frac{V_{(e+,Ps)}R^2_{(e+,\,Ps)}}{3D}. \qquad (1)$$

Here $V_{(e+,\,Ps)}$ are the relative unit free volumes of positron and positronium traps, respectively, $R^2_{(e+,\,Ps)}$, trap radius, and D (D_{e+}, D_{Ps}), positron and positronium

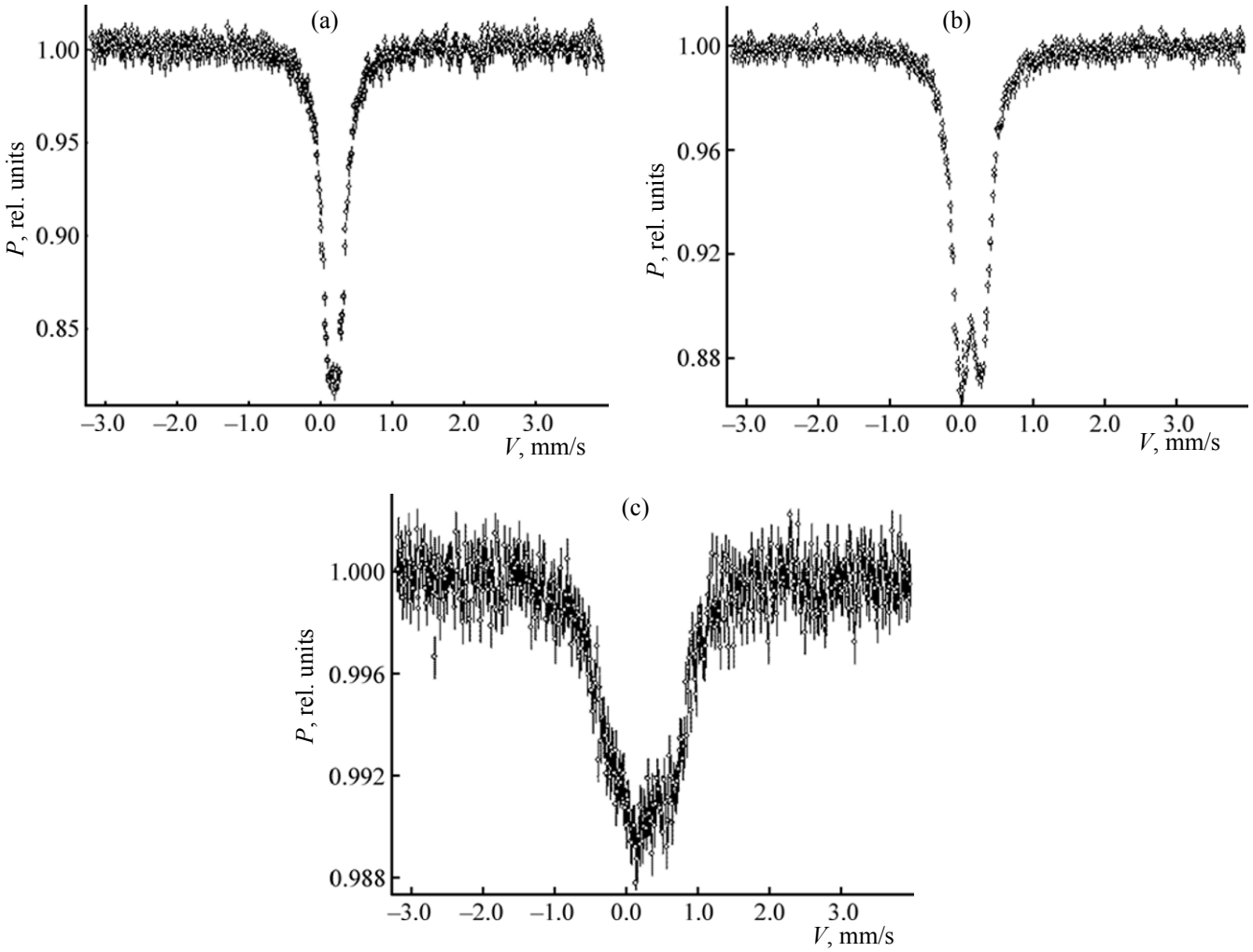

Fig. 2. Mössbauer spectra of (a) ferrocyanic acid, (b) aniline salt of ferrocyanic acid, and (c) PANI doped with ferrocyanic acid.

diffusion coefficients, respectively. The diffusion coefficients were about 0.1 cm^2/s for e^+ and 10^{-4} cm^2/s for positronium.

The specific free volumes ([$Å^3$]) of ordered V_{e+} and disordered $V_{(Ps)}$ sample regions were calculated by Eq. (2).

$$V_{e+} = V_{fe+}/(V_{fPs} + V_{fe+})N_{e+},$$

$$V_{Ps} = V_{fPs}/(V_{fPs} + V_{fe+})N_{Ps}, \quad (2)$$

Here V_{fe+} and V_{fPs} are the relative free volumes and $N_{e+,Ps}$, concentrations of the related traps, $1/cm^3$.

The resistance of pelleted samples was measured by impedance spectroscopy, and the obtained data were compared with the PALS results (Table 7).

Figure 3 shows the dependence of intrinsic disordered volume (voids) on pressure. At the same time, the dependence of specific electrical conductivity on pressure has a maximum at 3000 kg/cm^3 and descends at 5000 kg/cm^3. Apparently, the polymer destruction occurred and as a result the intrinsic specific volumes and the matrix increased and the electrical conductivity decreased.

The electron microscopy of PANI·$[Fe(CN)_6]$ (Fig. 4) revealed aggregated polymer chains as ball-

Table 2. Mössbauer spectroscopy data for ferrocyanic acid and its salts with aniline and polyaniline[a]

Compound	δ, mm/s	ΔE_Q, mm/s
$H_4[Fe(CN)_6]$	0.1266 d	0.3034
$(C_6H_5NH_3)_4[Fe(CN)_6]$	0.1870 s	–
PANI·$[Fe(CN)_6]$	0.2199 s	–

[a] The chemical shifts were measured against sodium nitroprusside.

Table 3. PELS data for PANI and aniline and PANI salts of ferrocyanic acid

Sample	τ_1, ns	τ_2, ns	τ_3, ns	I_1, %	I_2, %	I_3, %	K_2, 1/ns	K_3, 1/ns
PANI·$[Fe(CN)_6]$	0.106	0.326	0.396	58.84	39.14	2.01	249.64	13.94
PANI	0.198	0.276	0.972	78.67	19.15	2.18	27.38	8.78
$(C_6H_5NH_3)_4[Fe(CN)_6]$	0.181	0.290	0.740	70.68	26.95	2.37	55.66	9.87

Table 4. Calculated PELS parameters for PANI and aniline and PANI salts of ferrocyanic acid

Parameter	PANI·$[Fe(CN)_6]$	PANI	$(C_6H_5NH_3)_4[Fe(CN)_6]$
N_{Ps}, *1E 20, 1/cm^3	10.49	7.00	8.39
N_e+, *1E 20, 1/cm^3	136.00	14.50	30.16
Trap R_{Ps}, Å	4.42	4.58	4.46
Trap R_e+, Å	4.36	4.46	4.42
U_{Ps}, *1E 8, 1/s^3	1.3979	0.9667	0.1129
U_e+, *1E 8, 1/s^3	17.8878	1.9519	0.4025
Trap V_{Ps}, [Å^3]	0.379	0.282	0.312
Trap V_e+, [Å^3]	4.723	0.312	1.094

Table 5. Experimental PELS data for PANI·$[Fe(CN)_6]$

Pressure, kg/cm^3	τ_1, ns	τ_2, ns	τ_3, ns	I_1, %	I_2, %	I_3, %	K_2, 1/ns	K_3, 1/ns
1000	0.176	0.339	0.719	77.35	21.00	1.65	57.41	7.07
2000	0.189	0.292	0.849	83.21	14.07	2.72	26.31	11.20
3000	0.212	0.326	0.864	78.40	19.99	1.57	33.27	5.60
5000	0.226	0.285	0.970	74.85	23.67	1.48	21.83	5.02

shaped ordered formations which were destroyed at increased pressures.

EXPERIMENTAL

Aniline (Reakhim) was purified by vacuum distillation before synthesis. $K_4[Fe(CN)_6]\cdot 6H_2O$ (Reakhim) was preliminarily dried at 90°C.

The Mössbauer spectra were measured on a Ms-1104 Em Mössbauer spectrometer. The IR spectra were obtained on a Spectrum 1000 BX-II instrument in KBr pellets. The X-ray phase analysis was performed on a Bruker D8 Advance diffractometer.

The PEL study of the samples was performed using a scintillation lifetime spectrometer assembled by a fast delayed coincidence circuit principle on the basis of an AI-1024 multichannel pulse analyzer with the detector including fast plastic detectors and FEU 87 photomultipliers ($^1T_0 \approx 310$ ps), positron source ^{44}Ti ($A = 0.6 \times 10^6$ Bq). The spectra were measured on a PALS ORTEC spectrometer [26], positron source ^{22}Na (A = 300 kBq); the spectra were recorded using a BPA-

Table 6. Calculated PELS parameters for PANI·$[Fe(CN)_6]$

Pressure, kg/cm^3	N_{Ps}, *1E 20, 1/cm^3	N_e+, *1E 20, 1/cm^3	Trap R_{Ps}, Å	Trap R_e+, Å	U_{Ps}, *1E 8, 1/s^3	U_e+, *1E 8, 1/s^3	Trap V_{Ps}, [Å^3]	Trap V_e+, [Å^3]
1000	5.46	30.98	4.47	4.36	0.7364	4.0759	0.248	1.077
2000	8.58	14.13	4.54	4.42	1.1736	1.8840	0.335	0.511
3000	4.45	17.51	4.73	4.43	0.6005	2.3389	0.167	0.637
5000	4.31	11.40	4.49	4.46	0.5837	1.5354	0.163	0.425

Table 7. Electric conductivity and PELS data for PANI·$[Fe(CN)_6]^+$

Pressure, kg/cm^3	N_{Ps}, *1E 20, 1/cm^3	V_{Ps}, *1E 20, Å	Trap V_e+, [Å^3]	R, Ω/cm	σ, S/cm × 10^{-4}
1000	1.359	342	262	4609	0.778
2000	2.003	461	427	971.3	1.02
3000	0.995	466	452	629.6	2.17
5000	0.850	642	6340	2140	0.771

05 (ASPEKT) multichannel analyzer and acquired on a PC on the basis of a Tektonix DPA-7254 oscillograph. The lifetime spectra were processed using the TaUfit and PALSfit (ver. 2.23) programs. The annihilation parameters were calculated by a trap model using the TRAP program [26].

The electrochemical impedance spectroscopy measurements of the electrical conductivities of pelleted polymers were performed by the two-point method on a SI 1260 impedance/gain-phase analyzer and a 1296A dielectric interface with a 12962A sample holder. Pellets 15 mm in diameter were pressed at a pressure of 1–5 × 10^3 kg/cm^2. The surface morphology was studied by scanning electron microscopy on a Hitachi S-5500 instrument (Japan).

The elemental analysis for carbon was performed on a Shimadzu-AA-6601 F atomic absorption spectrometer; the samples were prepared by acid digestion with a mixture of sulfuric acid and potassium iodate.

Synthesis of ferrocyanic acid. To a cold (0°C) solution of 42 g of potassium hexacyanoferrate(II) in 350 mL of water, 100 mL of conc. HCl and water to

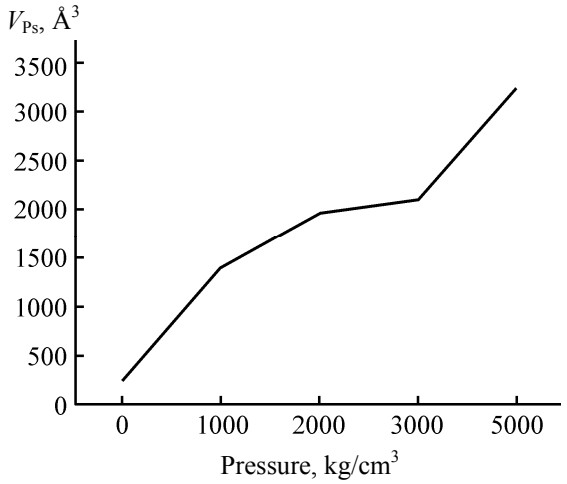

Fig. 3. Dependence of VPs on pelleting pressure for PANI doped with ferrocyanic acid**.**

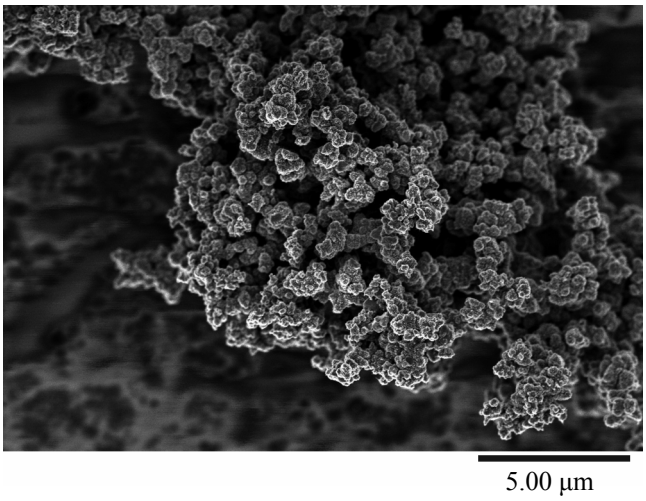

Fig. 4. Scanning electron micrographs of PANI doped with ferrocyanic acid.

dissolve potassium chloride were added. The mixture was cooled to room temperature and, after addition of 50 mL of diethyl ether, left to stand for 2 h. The precipitate of the ether solvate of the acid was filtered off, washed with HCl solution in diethyl ether, and dissolved in 60 mL of ethanol. Potassium chloride was filtered off, 70 mL of diethyl ether was added to the filtrate, and the crystals that formed were filtered off and washed with ether. The solvate was decomposed by heating in a vacuum at 50–60°C. Yield 23.12%.

Synthesis of the aniline salt of ferrocyanic acid. Freshly distilled aniline, 1.8 mL, was added to a solution of 1 g of ferrocyanic acid in 5 mL of water. A white precipitate formed and was filtered off, washed with ethanol (2 × 5 mL), and dried. Yield 81%.

Synthesis of the polyaniline salt of ferrocyanic acid. Freshly distilled aniline, 1.8 mL, was added to a solution of 1 g of the aniline salt of ferrocyanic acid in 5 mL of water. A white precipitate formed and was filtered off, washed with ethanol (2 × 5 mL), and dried. Yield 86%.

Synthesis of polyaniline. A solution of 6.2 g of sodium persulfate in 62 mL of 1.5 M HCl was added in portions over the course of 1 h to a cooled (0°C) mixture of 62 mL of 1.5 M HCl and 5 mL of aniline. The reaction mixture was left to stand at room temperature for 4 h. Polyaniline was filtered off, washed with water (2 × 25 mL), ethanol (2 × 15 mL), and diethyl ether (2 × 8 mL), and dried. Yield 90%.

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