Characterization of Cathodes for Rechargeable Lithium Batteries Based on New Vanadium Oxides and PEO/PPz Polymer Blends

J. L. ACOSTA LUQUE,[1,*] E. MORALES BERGAS,[1] and J. R. JURADO EGEA[2]

[1]Instituto de Ciencia y Tecnología de Polímeros del CSIC, c/ Juán de la Cierva 3, 28006 Madrid, Spain;
[2]Instituto de Cerámica y Vidrio del CSIC, 28500 Arganda del Rey, Madrid, Spain

SYNOPSIS

Three new vanadium oxides were synthesized and characterized using an X-ray. Once incorporated into different polymer systems containing either poly(ethylene oxide) or a poly(ethylene oxide)-polyphosphazene (PPz), together with carbon black (CB) as an electronic crosslinker, kinetic isothermal and nonisothermal crystallization studies were conducted, as well as an electrical characterization study through complex impedance spectroscopy for the purpose of examining, on the one hand, the effects exerted by the different vanadium compounds on the microstructure of the systems into which they are incorporated, and, on the other hand, of determining which of the synthesized vanadium compounds possesses the best conducting properties. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Advanced materials[1] have attracted worldwide attention, due to their wide spectrum of potential applications, ranging from energy storage to telecommunications, including the software, aircraft, and space industries. There is a great need for new materials with peculiar electrical properties, in particular, in those European countries which are dependent on foreign countries for energy supplies.

Rechargeable lithium batteries are one of the applications where the synthesis of new and advanced materials would have a major incidence, both from the point of view of developing new polymeric electrolytes and new active materials for electrodes, able to act as true lithium-intercalation compounds. Among the lithium-intercalation compounds, some of the most widely studied have been vanadium oxides and bronzes,[2] both for their ready availability as well as for their lithium-intercalation properties.[3,4] For the present, it is known that the efficacy of vanadium compounds does not only depend on their valance state or their morphology, but also on the synthesis method. This explains why in this research three new vanadium oxides were synthesized ceramically (actually, they are stoichiometric and nonstoichiometric blends situated between V_2O_5 and V_2O_4) with the aim of incorporating them into different polymeric systems based on poly(ethylene oxide) (PEO) and/or polyphosphazene (PPz) to improve the conductivity of the resulting systems and also to gain insight into the effect exerted by each of them on the microstructure and the morphology of the experimental systems.

EXPERIMENTAL

Poly(ethylene oxide) (PEO) was purchased from Aldrich; poly(octofluoropentoxytrifluoroethoxy phosphazene) (PPz) was supplied by Firestone; carbon black (CB) was supplied by Cabbot under the trade name Isaf (20–25 μm average diameter); V_2O_5(VA) and VO_3NH_4 were supplied by Merck.

The vanadium oxide B (VB) was obtained by means of V_2O_5 reduction under constant $N_2—H_2$ (90–10) flow in an oven heated to 450°C for 2 h. The vanadium oxides C (VC) and D (VD) were obtained through VO_3NH_4 reduction in a hermetically

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[*] To whom correspondence should be addressed.

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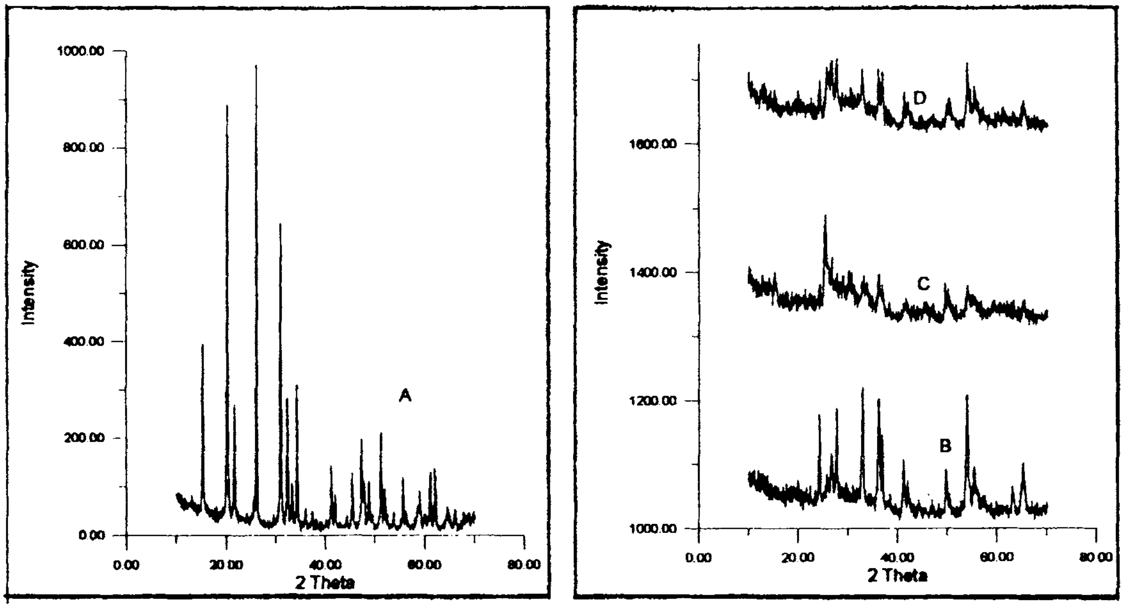

Figure 1 X-ray diffractograms of the different vanadium oxides: (A)VA; (B)VB; (C)VC; (D)VD.

sealed oven under a constant N_2—H_2 (90–10) flow for 1 and 2 h, respectively.

PEO and its mixtures were dissolved in acetonitrile. After the polymers had dissolved, the vanadium powder and the CB were added to the solution under vigorous stirring. To obtain uniform dispersion, the aggregates were destroyed in an ultrasonic bath. Films were then obtained by casting the dispersion over Teflon plates. These were subsequently dried under vacuum conditions at 50°C for 48 h.

DSC thermograms were recorded in a Mettler TA 4000 differential scanning calorimeter operated under nitrogen. The samples were heated to 100°C and held there for 10 min to erase any previous thermal history. Then, they were quenched at various rates (1, 5, and 10°C/min) to −20°C and subsequently reheated to 100°C at a heating rate of 10°C/min. Thermograms in which two or more peaks overlapped were deconvoluted using a peak analysis software package (Peakfit from Jandel Scientific) applying a five-parameter adjusting equation.

Mechanodynamic tests were conducted utilizing a Metravib viscoelasticimeter and applying the forced vibration technique under tensile compression. Cylinder-shaped samples, diameter 6 mm and height 4 mm, were tested in the temperature range of −80–20°C at frequencies of 5, 10, and 20 Hz.

The X-ray diffraction spectra of the samples were obtained with a Siemens D-500 diffractometer emitting a Ni-filtered CuK X-ray beam excited at 40 kV. Complex plane impedance and inductance analyses were conducted in an impedance analyzer (Hewlett-Packard, Model 4192 A) coupled to a computer (Model 9000-216) in the frequency range of 10–10^7 Hz.

RESULTS AND DISCUSSION

Characterization of the Vanadium Oxides

The temperature chosen for the obtention of the different vanadium oxides from V_2O_5 or VO_3NH_4 was 450°C, as at this temperature it is possible to eliminate VO_2 from the resulting blend, an undesirable oxide for our purposes. The time span allowed for the reaction was 120 min maximum, as at higher reaction times VO_2 began to reappear.

The structural analysis of the different vanadium oxides was done via X-ray, the respective graphs being shown in Figure 1. The interpretation of the diffractograms of samples VC and VD determines them as fairly amorphous samples, which, in terms of their diffraction angles, may be classified as a complex blend of the following vanadium oxides: V_6O_{13}, V_2O_5, and V_3O_5. Sample VB, however, could be a new nonstoichiometric vanadium oxide, as it was completely impossible to identify all the diffraction angles when comparing them to known oxide blends.

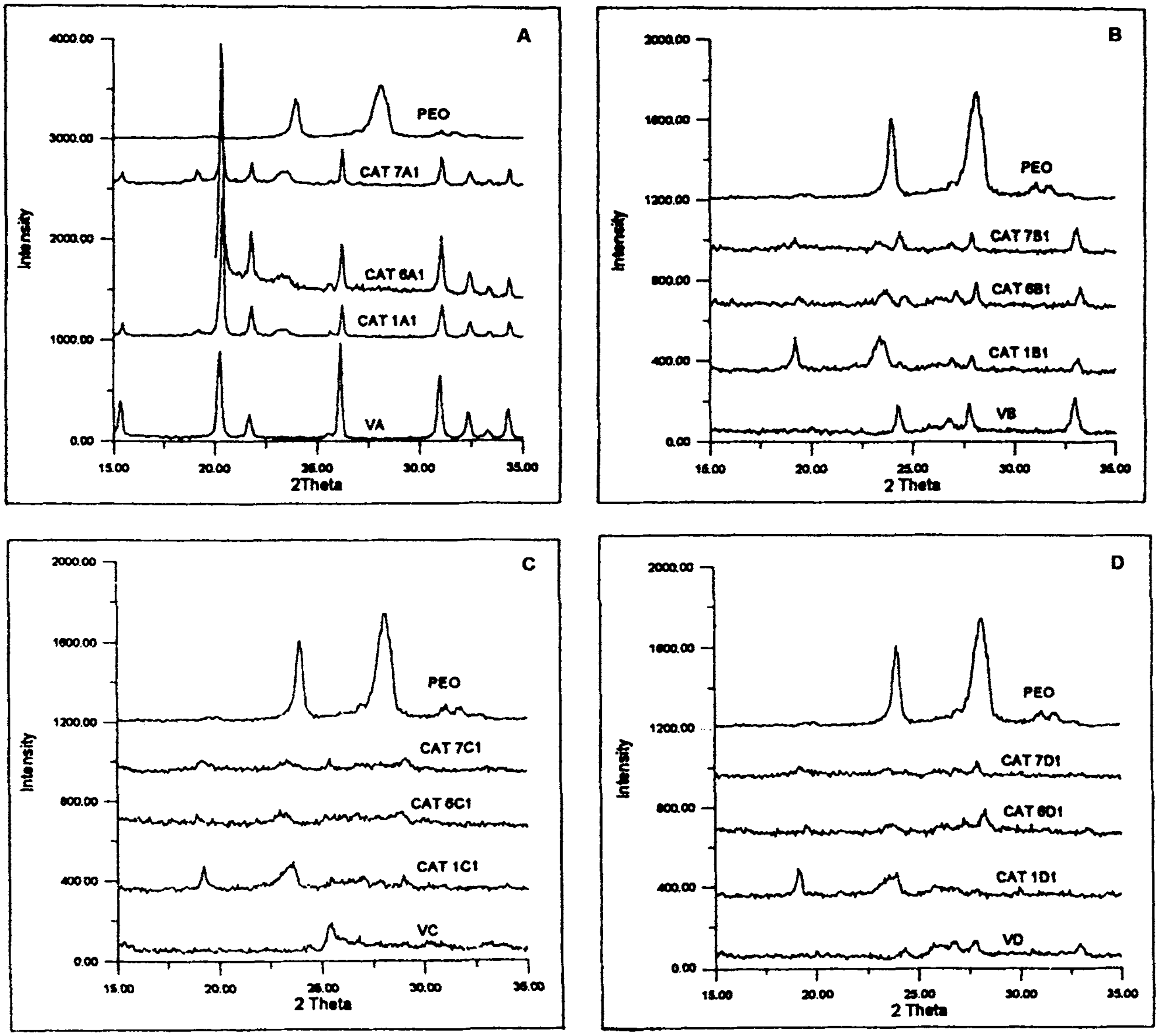

Figure 2 X-ray diffractograms of the different cathodes.

Microstructure of the Polymer Composites

The incorporation of the different vanadium composites obtained into polymeric PEO matrices or into their blends with PPz gave rise to important changes in the host matrix and especially in the crystalline structure of PEO. As can be seen in Figure 2, which compiles the X-ray diffractograms of all the samples of the series, the oxides VA (V_2O_5) and VC disturb or modify the crystalline grid of PEO, when the polymeric matrix only contains PEO (Cat 1A1 and Cat 1C1) or a blend of different PEO/PPz composition (Cat 6A1, Cat 6C1, Cat 7A1, and Cat 7C1). This modification is confirmed by both the disappearance of the diffraction angle of PEO at 28.02 (2θ) and the shift of the diffraction peak at 23.95 (2θ) to lower angles [Fig. 2(A) and (C)].

Nevertheless, the vanadium oxides VB and VD produce a different type of disturbance in the PEO network. While the diffraction peak at 28.07 (2θ) remains practically unaltered by the presence of VB and VD, as well as by the PEO/PPz ratio [Fig. 2(B) and (D)], the PEO diffraction peak at 23.95 (2θ) shifts to lower angles as a consequence of VB or VD interaction with the matrix. The differences in the effect exerted by the different vanadium compounds on the crystalline microstructure of PEO is further evidenced in the relaxation phenomena of the different synthesized composites, as well as in their thermal and kinetic properties, as will be shown below.

Table I Composition, Glass Transition Temperature, and Conductivities of the Samples

	Composition					
Samples	PEO/PPz (Wt %)	Vanadium (Wt %)	CB (Wt %)	$T_{g_{PEO}}$ (°C)	$T_{g_{PPZ}}$ (°C)	σ (s cm^{-1})
PEO	100/0	—	—	−53.6	—	<1.0E-11
PEO/PPZ	80/20	—	—	−55.6	−75.1	<1.0E-11
PEO/PPZ	50/50	—	—	−54.5	−74.8	<1.0E-11
CAT-1A1	100/0	40 (VA)	10	−39.7	—	3.4E-3
CAT-1B1	100/0	40 (VB)	10	−37.1	—	6.6E-3
CAT-1C1	100/0	40 (VC)	10	−46.5	—	1.0E-3
CAT-1D1	100/0	40 (VD)	10	−23.2	—	5.1E-3
CAT-6A1	80/20	40 (VA)	10	−14.0	−72.1	5.1E-3
CAT-6B1	80/20	40 (VB)	10	−23.6	−68.1	5.7E-3
CAT-6C1	80/20	40 (VC)	10	−42.3	−74.4	3.6E-3
CAT-6D1	80/20	40 (VD)	10	−43.8	−72.2	1.4E-2
CAT-7A1	50/50	40 (VA)	10	−45.1	−59.3	2.8E-2
CAT-7B1	50/50	40 (VB)	10	−34.2	−59.3	9.3E-3
CAT-7C1	50/50	40 (VC)	10	−49.3	−66.8	1.5E-2
CAT-7D1	50/50	40 (VD)	10	−30.6	−64.7	5.1E-2

Table II Isothermal Crystallization and Melting Behavior of the Samples

		Crystallization		Melting	
Samples	T_c (°C)	n	$-\log K$ (min^{-1})	T_m (°C)	ΔH (J/g)
PEO	50	2.25	2.21	69.0	103.2
	51	2.19	2.68	69.3	109.0
	52	2.19	2.98	69.7	106.5
PEO/PPz 80/20	54	1.95	2.03	70.0	104.9
	55	2.02	2.50	70.7	106.8
	56	2.19	3.43	71.3	108.2
PEO/PPZ 50/50	53	2.16	2.20	69.5	90.7
	54	2.08	2.45	69.9	86.4
	55	2.30	2.70	70.4	89.3
CAT-1A1	53	2.38	2.08	70.0	94.4
	54	2.43	2.72	70.1	85.1
	55	2.47	3.36	70.5	86.4
CAT-1B1	45	1.94	1.85	57.7	102.5
	46	1.96	2.33	57.9	98.9
	47	1.92	2.83	58.6	90.0
CAT-1C1	44	1.98	1.70	56.4	98.7
	45	2.08	2.05	56.7	90.4
	46	1.94	2.25	56.9	87.6
CAT-1D1	45	2.01	2.26	58.6	88.6
	46	2.13	2.45	58.7	90.3
	47	1.99	2.99	59.0	89.3

Table III Isothermal Crystallization and Melting Behavior of the Samples

		Crystallization				Melting			
		Peak 1		Peak 2		Peak 1		Peak 2	
Samples	T_c (°C)	n	$-\log K$ (min^{-1})	n	$-\log K$ (min^{-1})	T_m (°C)	ΔH (J/g)	T_m (°C)	ΔH (J/g)
CAT-6A1	33	3.31	1.32	3.24	2.10	56.0	103.1	—	—
	34	2.76	1.93	3.36	2.14	56.3	104.6	—	—
	35	3.30	1.97	3.12	2.46	56.6	104.3	—	—
CAT-6B1	42	2.06	1.87	—	—	59.8	91.4	—	—
	43	2.28	3.31	—	—	60.0	80.4	—	—
	44	2.26	3.83	—	—	60.0	85.6	—	—
CAT-6C1	37	1.86	1.54	—	—	54.7	77.9	—	—
	38	1.78	1.76	—	—	55.1	76.7	—	—
	39	1.90	1.99	—	—	56.1	77.1	—	—
CAT-6D1	38	1.63	1.60	—	—	53.8	42.1	70.6	5.1
	39	1.62	1.88	—	—	54.2	39.6	72.0	4.1
	40	1.79	2.53	—	—	54.7	32.9	72.3	3.8
CAT-7A1	40	1.74	1.38	1.52	1.60	56.0	99.4	—	—
	41	1.90	1.65	1.72	1.71	56.4	89.6	—	—
	42	1.82	2.37	1.85	2.17	56.8	83.2	—	—
CAT-7B1	37	1.89	1.57	—	—	54.1	58.4	—	—
	38	1.74	1.81	—	—	54.5	55.7	—	—
	39	1.61	2.08	—	—	54.8	53.8	—	—
CAT-7C1	28	2.06	1.93	—	—	47.7	55.2	70.8	2.5
	29	1.80	2.07	—	—	48.7	54.7	70.0	2.7
	30	1.95	2.68	—	—	48.5	53.1	69.8	2.7
CAT-7D1	29	1.80	1.22	—	—	47.2	47.5	61.1	0.5
	30	1.77	1.57	—	—	47.5	44.4	61.8	0.9
	31	1.86	1.84	—	—	46.7	43.8	62.9	1.2

The glass transition temperature (T_g), which marks the border between elastic and viscoelastic material behaviors, is known to be one of the most sensitive polymer relaxations vis-à-vis any perturbation at the molecular level. The temperature at which this phenomenon appears is influenced by any factor having an impact on chain mobility, such as a different crystalline array or the simple presence of (organic or inorganic) particles whose interaction with the polymer immobilizes the polymeric chains at the interface or plasticizes them. In Table I, the T_g values of all the synthesized systems are listed. The interpretation of the values obtained is based on the following considerations: First and foremost, when the system PEO/PPz is free of any vanadium compound, the glass transitions are independent of blend composition, and, hence, the system is incompatible from a thermodynamic point of view.[5] When these systems are incorporated, the previously synthesized vanadium compounds, the T_g of PEO shifts, as a general rule, toward much higher temperatures, while the shifts undergone by the T_g of PPz are much less significant, which, in both cases, is indicative of a rigidization of the system as a consequence of the presence of the inorganic additives. This rigidization becomes increasingly weaker the greater the PPz portion in the blend.

By the same token, the crystallization kinetics of these systems is sensitive vis-à-vis the changes produced in the polymeric matrix, also as a consequence of the presence of the different vanadium oxides. Studying in depth the kinetics of isothermal and nonisothermal crystallization allowed these effects to be proven.

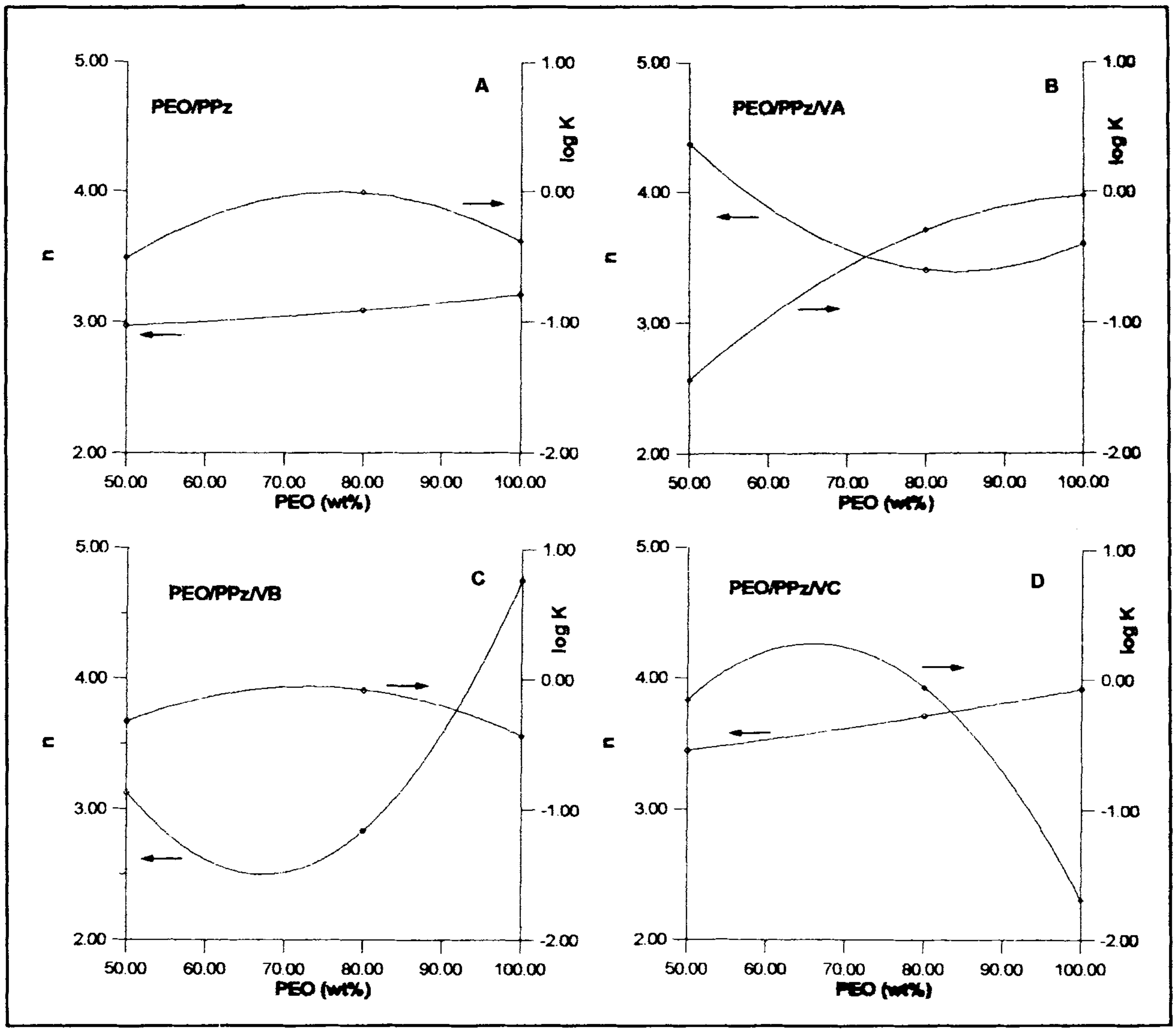

Figure 3 Plot of the isothermal crystallization kinetic data of the samples.

The data referring to isothermal and nonisothermal crystallization of the samples were analyzed applying Avrami's equation.[6]

$$X(t) = 1 - \exp(-Kt^n) \qquad (1)$$

where $X(T)$ is the weight fraction of crystallized materials at time t, K represents the rate constant of the crystallization, and n is the Avrami exponent, which depends on the type of nucleation taking place, as well as on the growth geometry.[7] The values n and K are the slope and the Y-intercept of the respective straight lines obtained when plotting log $\{-\ln[1 - X(T)]\}$ against log t for each crystallization temperature in the case of the isothermal procedure and for each cooling rate in the case of the nonisothermal method.

Tables II and III show the kinetic parameters obtained under isothermal conditions, as well as the melting data when the samples crystallized under the isothermally predetermined conditions are being molten. These data enable us to study the effect produced by the different vanadium compounds used, not only on the growth geometry of PEO, but also on the growth rate of the different crystalline structures which coexist in some of the samples.

In Table II, the kinetic data are compiled for the samples which do not contain polyphosphazene as a second component in the polymeric matrix. Under these conditions, isothermal crystallization gener-

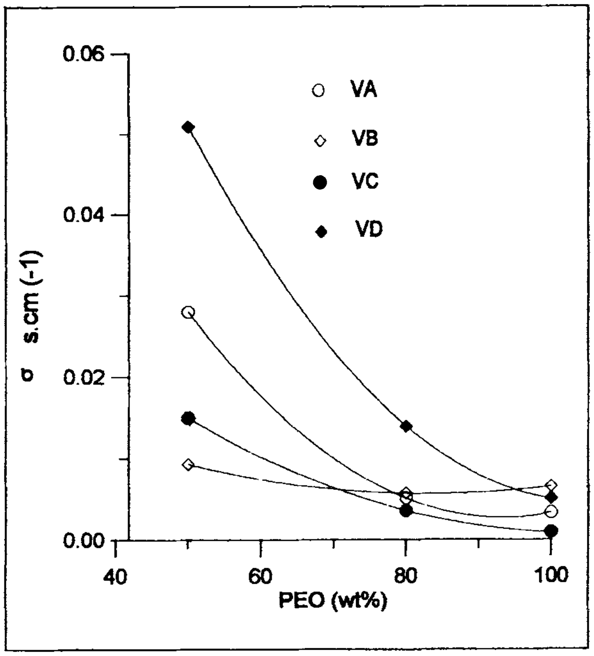

Figure 4 Electronic conductivities of the different cathodes.

ates a single crystalline phase whose growth geometry is essentially bidimensional ($n = 2$), except for the samples containing VA, which present a hybrid growth geometry, i.e., bi- and tridimensional, taking into account the experimental value of n ($n = 2.5$). This latter circumstance causes the melting temperatures of all the isothermally crystallized samples to be 10°C below that of the VA sample. In addition, it should be highlighted that the value of K, i.e., the rate at which the crystalline phase is being formed, is different for each of the vanadium compounds present.

Table III lists the kinetic parameters obtained for the PPz-containing samples. In isothermal crystallization, these samples attain either two crystallization peaks or two melting peaks (the VC and VD samples), one of which (the one with the higher temperature) is almost negligible in respect to the principal one. The main characteristics of the first peak, as to the kinetic parameters, are slightly different from those of the phosphazene-free samples, i.e., the VA samples present a clearly tridimensional growth geometry ($n = 3$) for PPz contents of 20%, whereas the rest of the samples present bidimensional growth geometries, according to the respective n values.

In the light of these findings, it is legitimate to conclude that the melting temperature of PEO, which is present as a component in the different samples, is not governed by any rule or consistent behavior, yet most of the samples present melting temperatures of about 12°C below that of pure PEO, except at the highest PPz content, the samples containing VC or VD, which melt at a temperature approximately 20°C below the reference. The cause of these notable variations of n, K, and T_m in the sample series is to be attributable to the joint and simultaneous interaction of the different vanadium and PPz composites.

The analysis of the kinetic crystallization parameters through nonisothermal measurements yields results which may be interpreted similarly to those obtained isothermally. The only difference found was considerably higher n values than in isothermal crystallization, which can be explained, however, by the nature of the non-isothermal process.[8] In Figure 3, we plotted the kinetic parameters n and K at a crystallization rate of $b = 5°C/min$. The other rates present analogous behaviors. The vanadium-free samples [Fig. 3(A)] possess an n-value of three ($n = 3$), which is practically independent of PPz concentration, until this latter component reaches the value of 4.5, whereas the rate constant diminishes proportionally. In the samples containing VB, n decreases inversely proportionate to PPz content, whereas K remains invariable. Finally, for the VC or VD samples, n is constant and independent of blend composition, whereas K increases with PPz content. This behavior confirms the different effects exerted by the different vanadium compounds obtained, which may act in several ways: (1) In some cases, they may act as nucleating agents in PEO crystallization (those vanadium compounds which, in the same crystallization conditions, have a higher crystallization rate than that of others); (2) they may act as PEO crystallization inhibitors (i.e., contrary to the previous case); and (3) they may have partially compatibilizing effects on the originally inmiscible polymer system, taking into account the drop of the melting points of PEO as a consequence of the presence of the respective compounds.

Electrical Characterization

From an electrical point of view, the samples were subjected to complex impedance spectroscopy at room temperature. All the samples in this series yielded an arc in the impedance or admittance planes, from which their respective conductivities were determined, as shown in Table I. The plot of these values against PEO or PPz content is shown in Figure 4, for which the following aspects should be underlined:

1. Independent of the vanadium compound present, conductivity at room temperature diminishes inversely proportionate to PPz content.
2. The vanadium compound most sensitive against the presence of PPz is VD, whose conductivity decreases by a factor of 10 for PPz concentrations of 50%.
3. The highest conductivities are achieved when PEO constitutes the polymeric matrix, and among the different vanadium compounds, VC presents the best-conducting properties, nearly six times greater than those of VB, which is the compound with the lowest conductivity levels.

These findings support the statement that, similar to the effects exerted by the vanadium compounds on the crystalline microstructure of the PEO/PPz polymer systems, into which they are incorporated, they have a bearing on their electronic conductivity, which fact explains the highly diverging results in the literature. The electrochemical characterization of these systems is under study at present.

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