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POLYMERIC COMPOSITES BASED ON VANADIUM OXIDES AS CATHODES FOR RECHARGEABLE LITHIUM BATTERIES—I. MICROSTRUCTURAL AND ELECTRICAL CHARACTERIZATION

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Abstract—A new vanadium oxide has been obtained from a V_2O_5 thermochemical treatment. This material was incorporated into polymeric systems formed by mixtures of poly (ethylene oxide) (PEO), a polyphosphazene (PPz) and carbon black (CB) with the aim of analyzing the possibilities, from an electrical view point, of using this new oxide as a cathode constituent in rechargeable lithium batteries. In this paper the effect produced by this new vanadium oxide in the crystalline microstructure of PEO and its mixtures with PPz was studied and compared with the effect produced by the original V_2O_5 by means of the analysis of crystallization kinetics under non-isothermal conditions of the different samples. In addition, the samples have been electrically characterised by impedance analysis, all samples having good conductivity properties.

INTRODUCTION

The recent development of portable systems and mainly, the great interest to develop a profitable and practical electric vehicle, has directed the studies in the field of electrochemical generators towards the development of rechargeable batteries of lightweight and high energy density. At present, an increasing number of advanced batteries are appearing. They consist of an anode (Li, Na, Mg, etc.), a polymeric electrolyte constituted by a polymer solvated by a metallic salt and composite cathodes made from transition metal oxides incorporated into a polymeric matrix susceptible to forming lithium salts such as polyethers.

Vanadium oxides have been extensively studied as cathode materials for both secondary and primary batteries given the ability with which they accept the insertion of lithium. Within the extensive range of vanadium oxides those most often employed are V_2O_5 and V_6O_{13} [1]. The characteristics of V_2O_5 as a cathode component can be summarized as follows: a slow discharging process [2], generally poor reversibility (although in some systems complete reversibility has been observed) [3], low electronic conductivity [4] and a noted solubility in certain organic solvents [5]. In addition, certain structural failings have been observed as the result of the lithium insertion, which are not recommended in electrochemical cells since they distort the orthorhombic cell unit [6], thus breaking the V—O bond forming irreversible Li—O, etc. All of these inconveniences have limited the use of V_2O_5 as a constituent element in cathodes.

More reversible cathodes were obtained from V_2O_5 and P_2O_5 glasses [7], due to the higher stability of V—O bonds. V_6O_{13} presents a higher charge density, greater reversibility [8, 9] and practical insolubility in organic solvents when compared to V_2O_5 [10]. Despite this, little effort has been spent in developing other vanadium oxides that would present better characteristics than those previously mentioned. Thus, one of our objectives has been the synthesis and characterization of new stoichiometric and non-stoichiometric vanadium oxides located between V_2O_5 and V_2O_4 in order to obtain cathodes with a greater number of life-cycles, better reversibility and higher energy density.

In this paper, we study the effect that two vanadium oxides, V_2O_5 and a new vanadium oxide, obtained from V_2O_5 thermochemical treatment have on the microstructure and electrical properties of poly(ethylene oxide) (PEO), and its blends with polyphosphazene (PPz) systems used in this study as supports to the vanadium oxides in the cathodes.

EXPERIMENTAL

Materials

Poly(ethylene oxide) (PEO) was supplied by Aldrich-Chemie. Poly(octofluoropentoxytrifluoroethoxy phosphazene) (PPz) was supplied by Firestone. Carbon black was Isaf N-200 (CB) (20–25 nm average diameter) supplied by Cabot. V_2O_5 (V_A) was supplied by Merck. Vanadium B (V_B) was obtained by the reduction of V_2O_5 under a constant flow of N_2—H_2 (90/10) in a oven at 450°C for 2 hr.

Sample preparation

Poly(ethylene oxide) and its mixtures with PPz were dissolved in acetonitrile. After the polymers had dissolved, the vanadium powder and the carbon black were added, under vigorous stirring to the solution. To obtain a uniform dispersion, aggregates were destroyed in an ultrasonic bath. Films were then obtained by casting the dispersion over Teflon plates. These were subsequently dried under vacuum at 50°C for 48 hr.

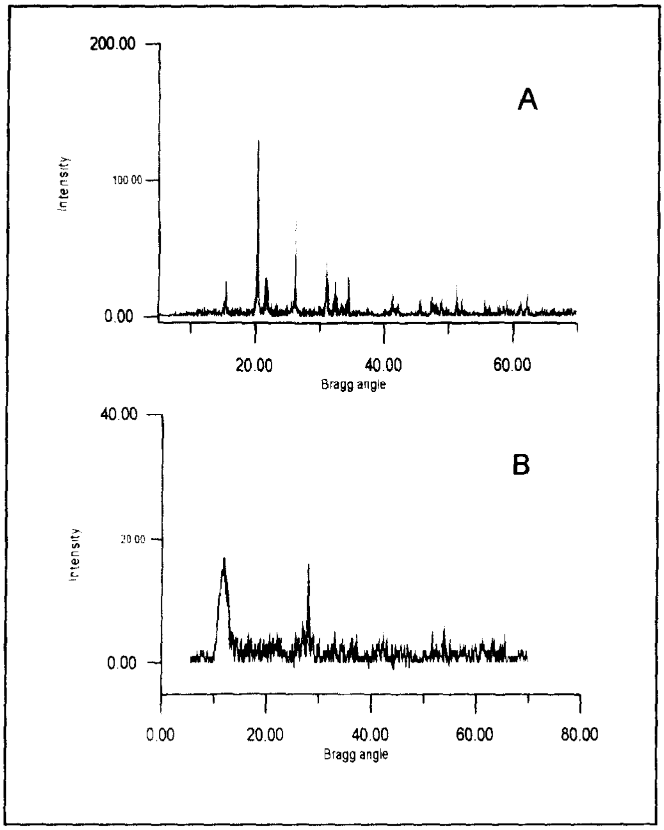

Fig. 1. X-ray of V_A y V_B oxides.

Thermograms were recorded in a Mettler TA4000 differential scanning calorimeter operated under nitrogen. Samples were heated to 100°C and held there for 10 min to erase any previous thermal history. After that, they were cooled down at one of three cooling rates (1, 5 and 10 deg/min) to −20°C, then reheated to 100°C at a heating rate of 10 deg/min. Thermograms in which two or more peaks overlapped were deconvolutionated using a peak analysis software package (Peakfit from Jandel Scientific) using a five parameter adjusting equation.

X-ray diffraction spectra of the samples were obtained using a Siemens' D-500 diffractometer with an Ni-filtered CuK X-ray beam excited at 40 kV.

Impedance and inductance complex-plane analyses were conducted in a 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

A new vanadium oxide (or mixture of oxides) was obtained by the reduction of V_2O_5 under a constant flow of N_2—H_2 (90/10) in a closed oven at 450°C for 2 hr. Figure 1 shows the X-ray spectra of V_2O_5 (V_A) and the chemically synthesised vanadium B (V_B). It can be seen that this oxide is quite amorphous. Several peaks, some of which are very broad, stand out and cannot be associated with any known oxide or mixture of oxides. This suggests we have come across the presence of a new vanadium oxide whose characteristics we are working on.

Both the original V_2O_5 (V_A) and the oxide obtained by the method mentioned above (V_B) were incorporated into PEO, PPz and their mixtures. The resultant materials whose function is to act as cathodes in rechargeable lithium batteries were studied from an electrical and microstructural point of view, the results of which are presented below.

Crystalline microstructure

The effect caused by V_A and V_B in the crystalline microstructure of PEO in the different samples was analyzed using the non-isothermal crystallization kinetics and melting behaviour of the samples. Sample composition and kinetic parameters obtained are presented in Tables 1 and 2.

When comparing the kinetic results obtained for the various polymeric cathodes which contain both vanadium oxides, a marked difference in melting behaviour can be observed. In fact, during dynamic crystallization of systems containing V_A it can be observed that, independently of the crystallization rate employed, only one peak is recorded in the melting, whose temperature decreases as the concentration of PPz in the blend increases (Fig. 2). This fact can be attributed to a certain compatibility in an otherwise incompatible system (PEO/PPz) as a result of specific interactions produced by the presence of V_A.

However, in samples containing V_B the crystallization and melting thermograms show two peaks (Fig. 3). Main peak melting temperature decreases slowly as the concentration of PPz in the mixture is increased. However, the melting temperature of the

Table 1. Parameters extracted from non-isothermal crystallization analysis of polymer cathodes containing vanadium A

	Composition			Non-isothermal kinetic data			Melting behaviour	
					Peak		Peak	
Sample	PEO/PPz wt.%	CB wt.%	V_A wt.%	β °C/min	n	log K (min^{-1})	T_m °C	ΔH J/g
CAT-0	100/0	—	—	1	3.53	−2.23	69.2	135.6
				5	3.20	−0.38	68.7	132.9
				10	3.00	0.36	68.7	132.3
CAT-1A1	100/0	10	45	1	4.23	−2.27	69.0	112.0
				5	3.60	0.03	68.6	107.1
				10	3.34	0.58	68.1	106.7
CAT-6A1	80/20	10	45	1	3.55	−2.65	57.7	138.3
				5	3.41	−0.28	56.8	135.0
				10	3.00	0.47	56.3	133.9
CAT-7A1	50/50	10	45	1	4.93	−4.73	63.7	200.9
				5	4.37	−1.44	62.3	196.4
				10	3.98	−0.11	62.3	190.7

second peak (of little relevance from an enthalpy viewpoint) remains, independent of the concentration of PPz. These observations can be related to the fact that V_B induces the formation of two different crystalline entities each one with different characteristics as demonstrated below in the analysis of the non-isothermal kinetic data obtained for all samples.

The data referring to non-isothermal crystallization of the samples were analyzed applying Avrami's equation [11]

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

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's exponent, which depends on the type of nucleation taking place as well as the growth geometry. The values n and K are the slope and the ordinate at the origin of the respective straight lines obtained when plotting $\log[-\ln(1 - X(T))]$ against $\log t$ for each cooling rate. Experimental values obtained for all samples studied are compiled in Tables 1 and 2.

The plots of n and $\log K$ as a function of the PPz concentration for all samples crystallized at 5°C/min are shown in Figs 4 and 5. The remaining data obtained at other crystallization rates can be found in Tables 1 and 2.

Based on data from Table 1 which refers to the non-isothermal crystallization of cathodes which contain V_A it can be stated that independently of the concentration of PPz the Avrami exponent (n) remains practically constant (approx. 4). However, the crystallization rate is strongly affected by the presence of PPz, $\log K$ being continuously decreasing as the amount of PPz in the blend increases. This fact indicates that V_A acts as a compatibilizer for the PEO/PPz system.

The kinetic behaviour of samples containing vanadium B is totally different. Two crystallization peaks appear, each one with its own kinetic characteristics (Table 2) thus indicating that V_B addition to the polymer blend induces the formation of two different crystalline entities each with its own geometry. Leaving aside peak 2 due to its relative unimportance from an enthalpy viewpoint, the value obtained for n indicates the existence of a crystalline phase with a geometry radically different to that of V_A cathodes (in V_B cathodes $n \sim 3$ compared to $n \sim 4$ in V_A cathodes). An exception to this however is the system containing only PEO where a high value of $n = 4.76$ is reached. Therefore the crystallization rate constant $\log K$ is practically independent of PPz concentration in the mixture thus differing from V_A cathodes indicating that V_B does not make increase the compatibility of the PEO/PPz system.

The high values obtained for the Avrami exponent (n) based on non-isothermal crystallization can be explained by inherent conditions in this type of crystallization [12].

Electrical characterization

The cathodes whose composition appear in Table 3 were obtained in film form according to the method described in the experimental section. They were analyzed, from an electrical viewpoint, by complex impedance spectroscopy at room temperature. The

Table 2. Parameters extracted from non-isothermal crystallization analysis of cathodes containing vanadium B

	Composition			Non-isothermal kinetic data					Melting behaviour			
					Peak 1		Peak 2		Peak 1		Peak 2	
Sample	PEO/PPz wt.%	CB wt.%	V_B wt.%	β °C/min	n	$\log K$ (min^{-1})	n	$\log K$ (min^{-1})	T_m °C	ΔH J/g	T_m °C	ΔH J/g
CAT-1B1	100/0	10	45	1	5.14	−3.47	4.66	−3.01	57.0	146.0	65.9	1.5
				5	4.76	−0.44	4.66	−1.22	56.5	141.0	65.8	2.3
				10	4.20	0.61	4.42	−0.36	53.0	130.6	66.4	12.9
CAT-6B1	80/20	10	45	1	3.17	−1.97	—	—	5.42	99.4	66.7	1.9
				5	2.84	−0.08	2.08	0.28	53.2	85.1	66.2	10.7
				10	2.55	0.40	1.96	0.61	53.1	84.9	66.3	10.9
CAT-7B1	50/50	10	45	1	3.20	−2.07	—	—	53.5	64.4	—	—
				5	3.17	−0.33	2.56	0.15	52.9	61.7	64.6	3.2
				10	2.73	0.31	2.53	0.27	49.4	95.7	65.9	12.2

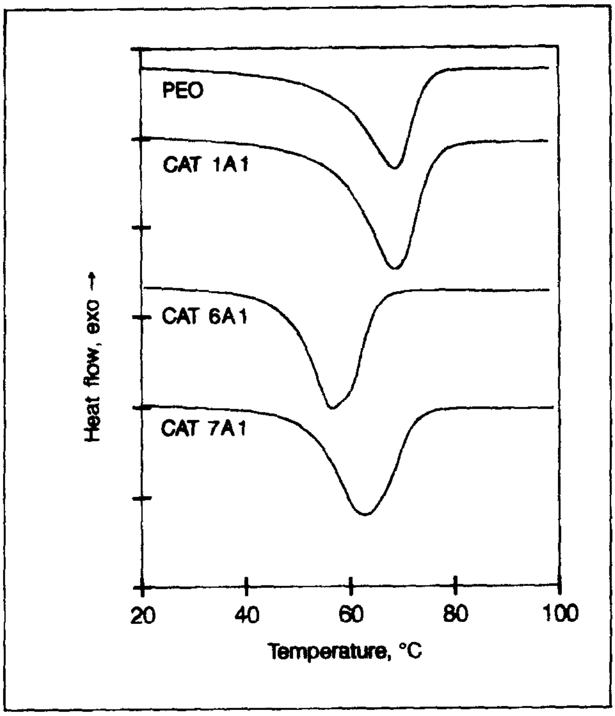

Fig. 2. DSC melting thermograms of PEO composites containing V_A crystallized from the melt at 5 deg/min.

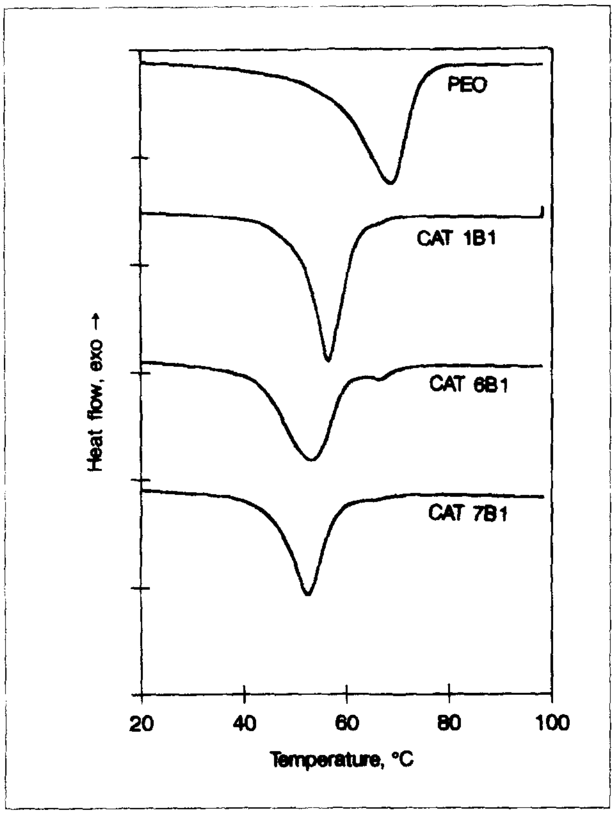

Fig. 3. DSC melting thermograms of PEO composites containing V_B crystallized from the melt at 5 deg/min.

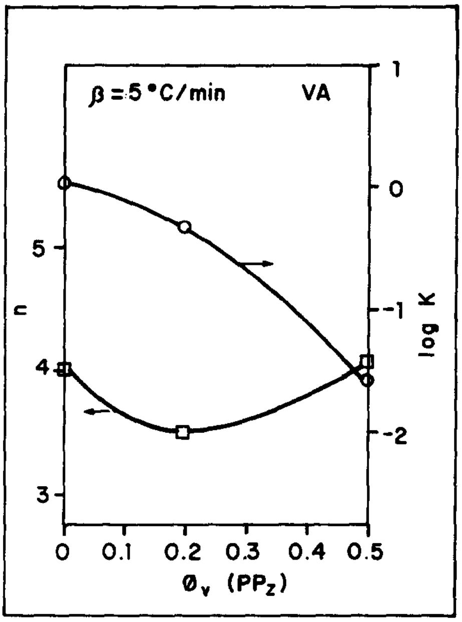

Fig. 4. Avrami's equation parameters of PEO composites containing V_A crystallized from the melt at 5 deg/min vs PPz content.

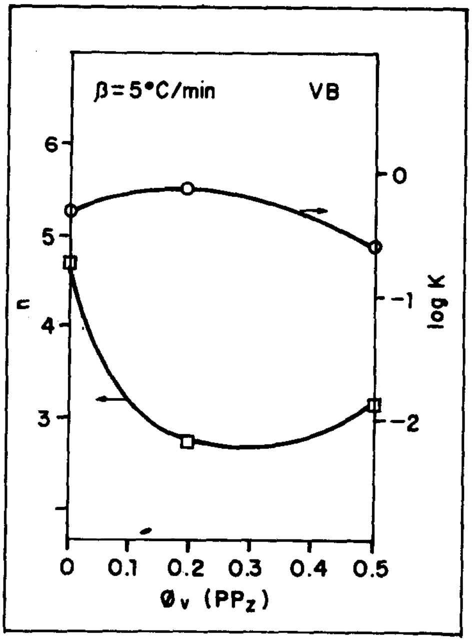

Fig. 5. Avrami's equation parameters of PEO composites containing V_B crystallized from the melt at 5 deg/min vs PPz content.

arcs obtained for all samples are shown in Fig. 6, where appear the plots of the impedance (Z) or the admittance (Y) in complex co-ordinates, that is:

$$Z = Z' - jZ'' \tag{2}$$

$$Y = 1/Z = Y' + jY'' \tag{3}$$

It can be observed (with the exception of the cathode Cat 6B1 whose arc appears on the admittances plane) that the arcs appear on the impedances plane and demonstrate conductivities of around $10^{-3}\,\mathrm{S\cdot cm^{-1}}$. This represents a relatively high electronic conductivity, result of the additive effect of the vanadium oxides of V_A or V_B together with the carbon black. In addition, through the arc analysis using an appropriate deconvolution programme (computer assisted electrochemical a.c.-immitance data analysis) it can be seen that in all cases which appear in the impedances plane, the arc obtained is in reality the sum of two electrical conducting phases which correspond to the active species included in each one of the cathodes that is: V_A or V_B and the carbon black. Analysing the arcs together, that is, based on the sum, gives the electrical characteristics listed in Table 3. Interpretation of this data indicates that all the materials obtained except the Cat 6B1, have an equivalent circuit consisting of a parallel resistance with a constant phase element (CPE) in the impedance plane; the main characteristics of this CPE element can be defined through the parameters: Y_0 (adjustable parameter containing the diffusion coefficient) and **p** (it has been suggested [13] that this corresponds to the reciprocal of the characteristic fractal dimension of the CPE element) whose values for each sample are listed in Table 3.

The only exception found in the studied cathodes is the Cat 6B1 which, as previously mentioned, gives an arc in the admittances plane. This cathode demonstrates a conductivity approx. 100 times greater than the other cathodes and some inductive characteristics analogous to those of metals. This cathode displays a series circuit of a resistance and an inductance in the admittances plane. Considering the composition of the polymeric systems which support both the vanadium and the carbon black it seems that low concentrations of PPz favour the percolation of the active elements explaining the high conductivity level detected. Large concentrations of PPz (for example Cat 7B1) cause a return to the previous situation, that is, to a medium conductivity level. The opposite

Table 3. Electric characteristics of the samples

	Composition					CPE		
Samples	(PEO/PPZ) wt.(%)	CB wt.(%)	V_A wt.(%)	V_B wt.(%)	σ $\mathrm{S\cdot cm^{-1}}$	Y_0 moh	p	L Henri
CAT 1A1	45(100/0)	10	45		9.4×10^{-3}	2.8×10^{-8}	0.92	
CAT 1B1	45(100/0)	10		45	8.3×10^{-3}	2.0×10^{-9}	1.00	
CAT 6A1	45(80/20)	10	45		1.6×10^{-3}	2.2×10^{-8}	0.99	
CAT 6B1	45(80/20)	10		45	6.1×10^{-1}			3.8×10^{-7}
CAT 7A1	45(50/50)	10	45		7.2×10^{-3}	3.7×10^{-9}	1.00	
CAT 7B1	45(50/50)	10		45	2.9×10^{-3}	5.1×10^{-8}	0.84	

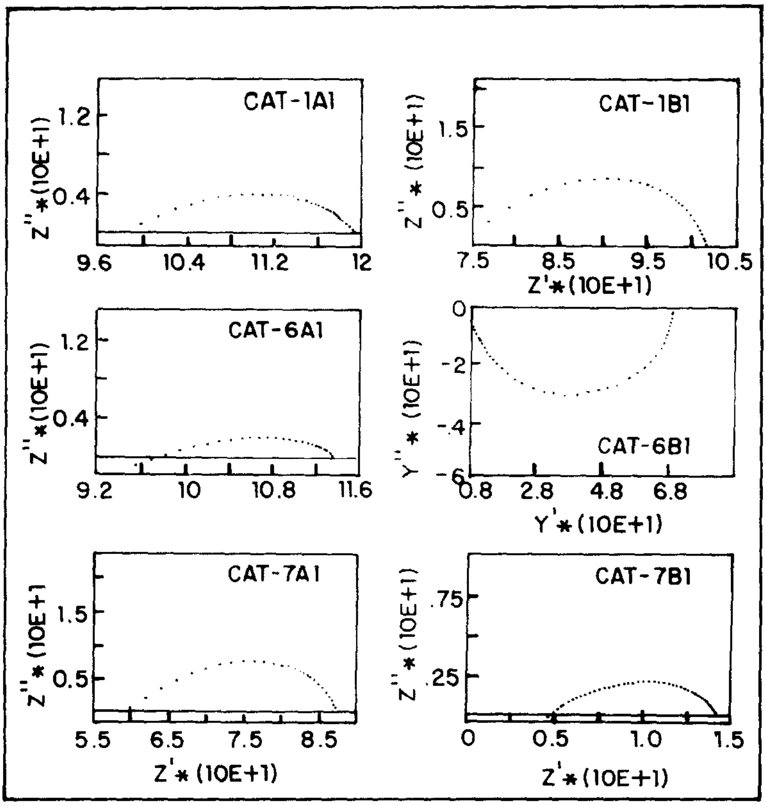

Fig. 6. Complex impedance spectroscopy diagrams of the different samples. I.

phenomenon, although to a lesser extent, is produced with cathodes which contain V_A (Table 3).

Based on the results obtained it can be concluded from an electrical viewpoint that conductivity depends not only on the type of vanadium used but also on the composition of the polymeric system to which the active electrical components join. In addition, the additive effects of the employed vanadium, carbon black and the polymeric systems produce materials of high electronic conductivity of which the cathode Cat 6B1 is outstanding.

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