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VANADIUM OXIDE COMPOUNDS PREPARED BY ANODIC DEPOSITION AND ALSO AS GLASSES FOR THE LITHIUM ACCUMULATORS

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Vanadium oxide compounds (VOC's) prepared by means of anodic deposition from aqueous vanadyl sulphate electrolytes and also as glasses have been studied as compared with crystalline V_2O_5 applicable to lithium accumulator. The following VOC's have been investigated: (i) V_2O_5 oxides with GeO_2, TeO_2, P_2O_5, B_2O_3 or Bi_2O_3 as glass forming substance; (ii) electrolytic V_2O_5, Na,V-bronzes (β-$Na_xV_2O_5$); (iii) crystalline c-V_2O_5. The structures of crystalline lattice, absorption IR spectra of the VOC's and its characteristics in the redox reaction with lithium were determined. The open circuit voltage, the primary discharge capacity, and its loss at cycling of VOC's have been analyzed. The electrolytic Na-V-oxides and amorphous V_2O_5-(GeO_2 or TeO_2) demonstrated the best coulomb cycling efficiency in thick VOC's electrodes with acetylene black. The discharge capacity and cycling efficiency of electrolytic crystalline V_2O_5 in thin layer electrodes without carbon addition exceed those typical of thick composite electrodes.

Keywords: electrolytic vanadium oxide; amorphous modification; discharge capacity; lithium accumulator.

Although Li-ion intercalation voltage of V_2O_5 is lower than $LiCoO_2$ or $LiMn_2O_4$, oxide V_2O_5 is still regarded as one of the most popular cathode candidates for Li-ion batteries both in academia and industry due to the following advantages: higher energy and power density than $LiCoO_2$ and $LiFePO_4$; more controlled fabrication method than $LiMO_2$ (M=Ni, Mn, Co. Fe); higher capacity and better cycling stability than $LiMn_2O_4$.

Vanadium oxide compounds (VOC) − V_2O_5, V_6O_{13}, $Li_xV_3O_8$, $Na_xV_2O_5$ in the intercalation electrodes of lithium accumulators have a common property − a tendency toward condensing intercalated lithium ions in some phases while discharged. A phase shift is followed by the parameter change of the elementary cell of VOC lattice. The reorganization of VOC lattice leads to the irreversibility of electrode intercalation reaction and discharge capacity loss during cycling. The irreversibility problem increases at macro level in a porous material. To increase the cycling efficiency of V_2O_5 it is modified, and the various technological methods are approved. Thus, due to the production of aerogels [1], nanofibers [2], V_2O_5-nano-electrodes [3], specific discharge V_2O_5 characteristics have been approached to the theoretical values at a high cycling efficiency. However, the methods modifying an oxide are not always suitable for the industrial production. In scientific publications there is no unity of views in determining the better modification of V_2O_5, since its specific discharge characteristics depend on the detailed features of synthesis and vary substantially.

In connection with the above circumstances a synthesis of vanadium oxide compounds as products of an electrolysis and as a glasses have been investigated as compared with a crystalline V_2O_5 applicable to lithium accumulator.

Experimental

To produce amorphous a-V_2O_5 a simple method was used to cool the melt of the mixture of V_2O_5 with glass forming substance on a steel plate. GeO_2, TeO_2, P_2O_5, B_2O_3 or Bi_2O_3 oxides in 10−15 mol % quantity, as well as the mixture of GeO_2, TeO_2 or P_2O_5 with MoO_3 or WO_3 (2 mol.%) were used as a glass network former. Metal oxides batch was alloyed at 800−1100⁰C (0.5−2.0 h).

The synthesis of electrolytic (e) VOC was carried out from acid vanadyl sulphate electrolytes [4,5]. The deposition was carried out anodically on a stainless steel from a "pure" electrolyte and from the electrolyte with Na^+ addition. After electrolysis the deposition was affected by a high temperature treatment (300−520⁰C).

Crystalline V_2O_5 (L-V_2O_5) with a crystalline size of 760Å was synthesized by a thermal decomposition of ammonium metavanadate under laboratory conditions; the reagent U-V_2O_5 (350 Å) produced by the Ural Plant of Chemical Reagents was also used.

Structure of VOC crystalline lattice

L-V_2O_5 has the structure of crystalline vanadium pentoxide c-V_2O_5 of ortorhombic syngony (PMMN). In L-V_2O_5 X-ray pattern the most intensive reflexes are within the range of diffraction reflection of $2\theta=12-40$ deg, (Fig. 1, difr. 1). The lattice parameters of L-V_2O_5, Å: a=11.4204; b=3.54; c=4.3504 are close to those cited in the publications for c-V_2O_5.
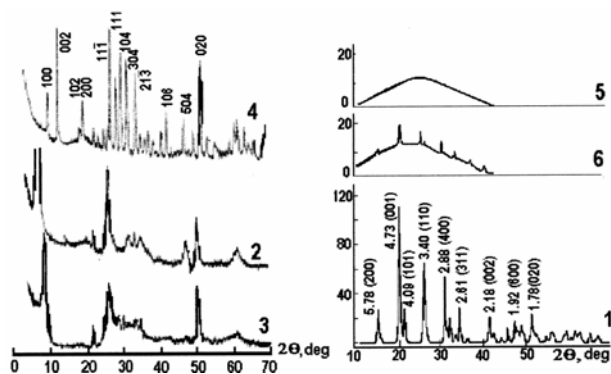

Fig. 1. XRD patterns of: 1. L-V_2O_5; 2. e-VOC (18^{0}C); 3. e-VOC-Na-20 (18^{0}C); 4. b-$Na_xV_2O_5$; 5. a-V_2O_5+TeO_2; 6. a+c-(V_2O_5+B_2O_3)

Chemical composition and structure of the e-VOC depend on the intensity of after electrolysis thermal effect. The e-VOC dried in the air at 18−25^{0}C is a fine-grained formation of a black color, which is composed of V_2O_{5-x}xyH_2O (x=0.4−0.6; y=1.4−1.5) and has the disordered layer structure of orthorombic V_2O_5 and interlayer distance d=11.0−13.6 Å. A crystallite size is 130−160 Å. The difractogram of this oxide is shown in Fig. 1, difr. 2. A high temperature favors a structure ordering − the bands of diffraction reflection become narrower, their intensity increases, and the interlayer distance decreases. At T>300^{0}C the e-VOC composition approaches to V_2O_5 with the following lattice parameters, Å: a=11.51; b=3.559; c=4.371 and d=6.6−6.8.

At electrolysis in Na^+-containing electrolytes the part of Na^+ is included into e-VOC composition with entering in a lattice as evidenced by the reflexes difference of difractograms 2,3 (Fig. 1). The further changes of e-VOC structure occurs due to a thermochemical reaction (T=520^{0}C). The difractogram of this reaction product is shown in Fig. 1, difr. 4. The oxide sodium-vanadium bronze β-$Na_xV_2O_5$ of a monoclinic structure with the homogeneity range of x=0.22−0.40 is the end product of a synthesis.

The composition of V_2O_5 with the glass network formers (mol %): GeO_2 (10), TeO_2 (10), the mixtures of GeO_2 (5) or (TeO_2 (5)+MoO_3 (2) or WO_3 (2) are slightly expressed in terms of X-ray structure. In the X-ray powder diffraction patterns of above compositions the sharp lines are unavailable, there is only a wide halo typical of amorphous state (Fig. 1, difr. 5).

For the borate and bismuthate compositions of V_2O_5 containing not more than 10−15 mol.% of boron or bismuth oxide a complete amorphous state has not been achieved. In the amorphous component of these compositions a microcrystalline phase is crystallized − against a background of the amorphous halo of XRD pattern there are also the lines of V_2O_5 diffraction reflection of a weak intensity (Fig 1, difr. 6). At high temperature $BiVO_4$ (d, Å=3.618, 2.069; 2.035, 1.002) is formed as a result of the chemical interaction between V_2O_5 and Bi_2O_3 oxides. The X-ray diffraction patterns of phosphate glasses are poorly reproducible. With the compositions of V_2O_5 (93)+P_2O_5 (5)+MoO_3 (2) or WO_3 (2) in some experiments homogeneous glasses were produced, in the others in an amorphous component a microcrystalline phase was observed.

According to the thermal analysis data the crystallization of the glasses produced starts at 190−220^{0}C.

The absorption IR spectra of VOC

L-V_2O_5 spectra are in agreement with those published for c-V_2O_5. The maxima of absorption bands within the frequency range of 1100−400 cm^{-1} correspond to the stretch and deformation vibrations of V−O in V_2O_5 (Fig. 2, curve 1).
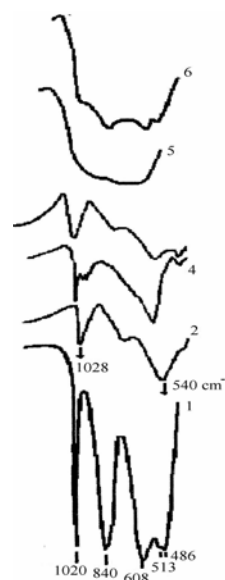

Fig. 2. Absorption IR spectra: 1. L-V_2O_5; 2. e-VOC (18, 300^{0}C); 3. Na-e-VOC (18^{0}C); 4. β-$Na_xV_2O_5$; 5. a-V_2O_5+TeO_2; 6. a+c (V_2O_5 +B_2O_3)

In e-VOC composition the nature of chemical bonds changes depending on the temperature treatment of a deposit. The vibration of e-VOC

(T_{treat}=18, 300⁰C) and Na-e-VOC (T_{treat}=18⁰C) bonds is practically the same within the frequency range of 1100−400 cm^{-1} (Fig. 2, curves 2,3). e-VOC spectrum (T_{treat}=520⁰C) corresponds to the c-V_2O_5 spectrum. The Na-e-VOC (T_{treat}=520⁰C) spectrum is identical with those of thermal β-Na-e-VOC comprising $Na_xV_2O_5$ with x=0.22−0.40 (Fig. 2, curve 4).

In the IR spectra of such amorphous compositions as V_2O_5 (85)+GeO_2 (15) or V_2O_5 (85)+TeO_2 (15) the maxima are smeared and form a wide absorption band within the range of 1000−500 cm^{-1} (Fig. 2, curve 5).

In the spectrum of amorphous V_2O_5, comprising microcrystalline vanadium pentoxide, against a background of a wide absorption band there are also narrow indistinct absorption bands with a maxima position, cm^{-1}: 990 and 1000, 790−840, 620, 540 (Fig. 2, curve 6). These spectra X-ray crystal structure and the spectroscopic data of V_2O_5 modifications show that the structure order increases in a series of a-V_2O_5<e-VOC (T_{treat}=18, 300, 520⁰C)<c-V_2O_5 .

Electrochemical characteristics of VOC

Difference in the lattice structure of elementary cell and the chemical bonds of VOC modifications determinates their different electrochemical behavior. The discharge galvanostatic curves of the investigated VOC modifications in composite electrodes containing acetylene black and binder are different (Fig. 3). On the discharge curves of c-V_2O_5 (Fig. 3, curve 1) there are the horizontal regions of voltage, V: 3.40, 3.20, 2.40−2.35, 2.10−2.05, reflecting a known phase formation during the intercalation of lithium ions in V_2O_5.
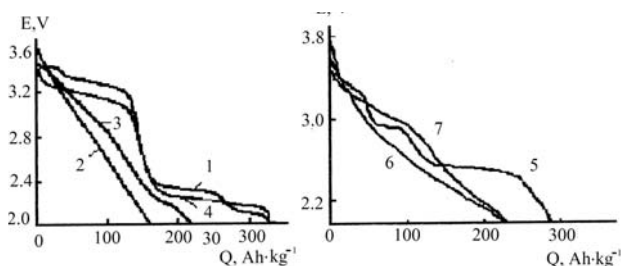

Fig. 3. Discharge curves at 0.1 mA cm^{-2}; electrolyte: PC, DME+1 M $LiClO_4$: 1. c-V_2O_5; 2. e-VOC(18⁰C); 3. e-VOC (300⁰C); 4. e-VOC (520⁰C); 5. $Na_xV_2O_5$; 6. a-V_2O_5+TeO_2; 7. a+c-(V_2O_5 +B_2O_3)

Discharge profiles of e-VOC depends on their thermal treatment. The electrolytic deposits with T_{treat}=18⁰C are discharged with a monotonous variation of voltage (Fig. 3, curve 2). As the thermal effect increases e-VOC discharge curve transforms, assuming the discrete horizontally sloping regions of voltage (Fig. 3, curve 3). At above 450⁰C it is transformed into the analogues of c-V_2O_5 discharge curve for a sodium-free VOC deposit (Fig. 3, curve 4) and into those of $Na_xV_2O_5$ β-bronze − for the

Na-containing VOC (Fig. 3, curve 5).

For a-V_2O_5 compositions a smooth voltage decrease during discharge is typical (Fig. 3, curve 6). The discharge curve of compositions, where an amorphous phase coexists with microcrystalline one, it is intermediate one between the phase obtained for a-V_2O_5 and c-V_2O_5 (Fig, 3, curve 7).

The specific discharge characteristics of VOC modifications are shown in Table 1 for the ten cycles, when the largest discharge capacity drop of VOC takes place followed by stabilization.

Table 1

Electrochemical characteristics of VOC modifications in composite electrodes

VOC	OCV, V	$E_{disch(end)}$, V	$Q_{disch (max)}$, Ah kg^{-1}	
			1st cycle	10th cycle
L-V_2O_5	3.55	2.0	250–320	160–180
U-V_2O_5	3.55	2.0	250–320	160–190
e-VOC (300⁰C)	3.70	2.5	180–185	160–170
e-VOC (5 Na)*	3.65	2.5	230–225	210–215
β-$Na_xV_2O_5$*$_*$	3.60	2.0	250–320	140–145
β-$Na_xV_2O_5$	3.60	2.5	180–185	160–170
a-V_2O_5-TeO_2	3.75	2.0	190–220	165–190
a-V_2O_5-GeO_2	3.75	2.0	190–220	165–190

Note: * − VOC (5Na) and β-$Na_xV_2O_5$ were produced in the presence of Na$^+$ in the deposition electrolyte in quantity of 5 and 20 g l^{-1} respectively followed by a high temperature treatment of the deposit.

Table 2 shows the characteristics of ballast-free VOC electrodes (BFE). Such electrodes present compact e-VOC deposits with a mass of 2−3 mg cm^{-2} on a conducting substrate depending on a thermal effect at discharging up to voltage of $E_{disch(end)}$=2.0 V at 0.1 mAcm^{-2}.

Table 2

Electrochemical characteristics of e-VOC on dependence a thermal effect

e-VOC (T_{treat}, ⁰C)	OCV, V	$Q_{disch (max)}$, Ah kg^{-1}	
		1st cycle	10th cycle
BFE (18)	3.85	205	107
BFE (300)	3.85	320	147
BFE (520)	3.55	320	270

The analysis of obtained results shows that the open circuit voltage (OCV) is in the rage of 3.55−3.85 V. The primary discharge capacity of V_2O_5 in crystalline state is higher than amorphous V_2O_5 has. Its loss at V_2O_5 cycling in the crystalline state depends on the crystalline size and grows in a series of e-VOC <U-V_2O_5<L-V_2O_5. The highest cycling efficiency of the synthesized VOC compositions is achieved for electrolytic modifications in thin layer BFE (520⁰C). Synthesized electrochemically Na-containing VOC (5Na) have become promising

material for lithium accumulators. Capacity decrease of VOC (5Na) is < 10% of initial capacity at cycling in the range of (OCV-2.5) V with demonstration of discharge capacity equals of 210−220 mAh.g⁻¹.

Conclusion

The reversibility of the intercalation reaction of Li^+ ions is the degree function of a VOC structure order. The high reversibility of the intercalation reaction in a glass may be qualitatively explained by the lack of the long-range order in a vanadium oxide sublattice that decreases the probability of its ordering in the presence of Li^+. According to the data for BFE electrodes the discharge capacity and cycling efficiency of e-VOC depends on water content in the interlayer space of e-VOC's structure. Evidently while heated BFE along with decreasing the amount of intercalated water, the vacancies energetically advantageous for intercalated Li^+ are created.

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