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The Preparation of V_2O_5 by Ozone Oxidation of $VOSO_4$ Solution for Cathode Active Material of Lithium Secondary Battery

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By oxidizing an aqueous solution of $VOSO_4$ by using ozone, yellowish black, powder-like deposit was obtained, the composition of which coincided with V_2O_5. This deposit had the intermediate structure between crystalline and amorphous V_2O_5 and gave a high capacity of 175 Ah/kg as a cathode active material in a Li secondary battery.

High energy density cathode active materials for rechargeable lithium batteries are earnestly being developed. Vanadium pentoxide(V_2O_5) seems to be one of the most promising materials among the candidates. By using crystalline V_2O_5(c-V_2O_5)$^{1)}$ and amorphous V_2O_5-P_2O_5(a-V_2O_5-P_2O_5),$^{2)}$ a coin type lithium secondary battery was developed and commercialized. In this paper, we present a new preparation method of V_2O_5, i.e., ozone oxidation method. The obtained material(O_3-V_2O_5) showed a more revised discharge profile than c-V_2O_5 and gave a high capacity of 175 Ah/kg, whose characteristics were almost the same as those of electrolytically prepared V_2O_5(e-V_2O_5) from $VOSO_4$ solution.$^{3)}$ The O_3- and e-V_2O_5 have the intermediate structure between c-V_2O_5 and a-V_2O_5-P_2O_5. However, the ozone oxidation method is more efficient than the electrochemical method and is thought to be more useful. To compare the characteristics of O_3-V_2O_5 with other types of V_2O_5, e-$V_2O_5$$^{4)}$ and a-V_2O_5-P_2O_5,$^{3)}$ which has a nominal composition of 95 mol% V_2O_5, are prepared according to a previous paper. The c-V_2O_5 is a reagent grade commercialized product(Wakojunyaku Co.). The preparation of V_2O_5 by the ozone oxidation method is as follows. By bubbling ozone gas prepared using ozonizer(Nihon Ozone Co. 0-1-2) at the rate of 1.5 g/h into acidic 0.2 mol/dm^3 $VOSO_4$ solution(250 ml) at various pHs and temperatures, a yellowish-black precipitate was obtained. The vanadium content in the yellowish-black precipitate obtained at pH 1.9 was analyzed using an atomic absorption method and was found to coincide with the theoretical value for V_2O_5. By increasing the pH value, the production rate of the precipitate increased(Fig. 1). If the oxidation reaction proceeds as in the following reaction,

$$2VO^{2+} + O_3 + 2H_2O = V_2O_5 + O_2 + 4H^+$$

this tendency can be qualitatively explained. Production rate depends on the reaction temperature(Fig. 2) and suddenly increased at about 40 °C. In order to confirm the oxidation state of precipitate, an XPS analysis was carried out using a Shimadzu ASIX-1000 on the sample obtained at pH 2.5 and 80 °C and on other types of V_2O_5s(Table 1). All binding energy calibrations were made against Ag $3d_{5/2}$ at 368.0 eV. The surface charging was corrected by measuring the shift of the adventitious carbon(1s) line at 285.0 eV. Argon ions of 2 kV energy were used for ion bombardment of sample surfaces. These binding energies are nearly equal to each other except for a-V_2O_5-P_2O_5.

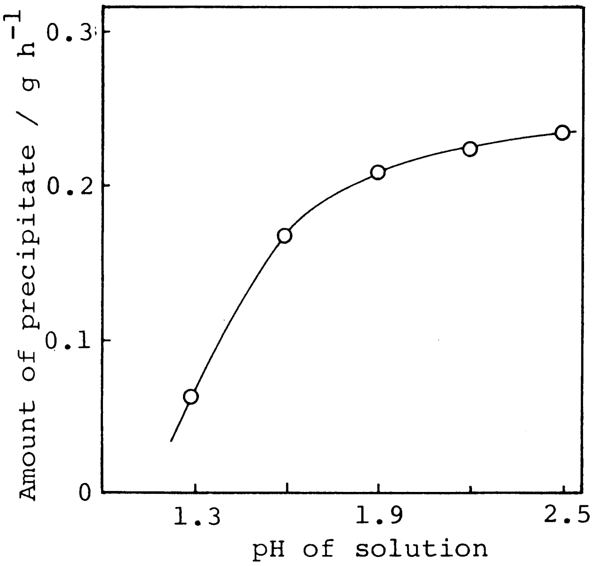

Fig. 1. Relationship between production rate and pH of the solution.

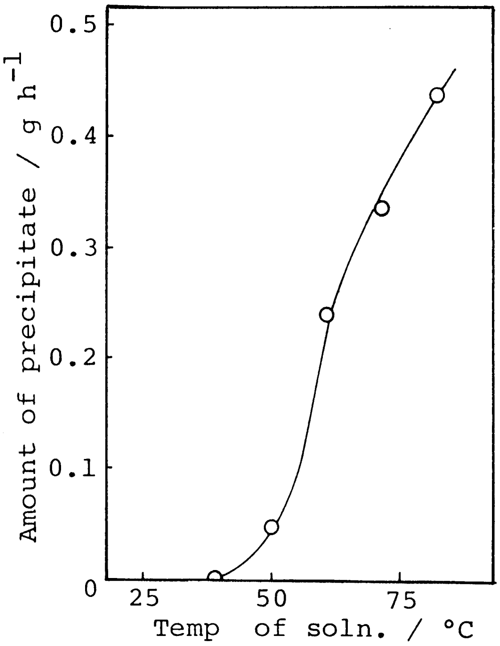

Fig. 2. Relationship between production rate by ozone oxidation and temperature of the solution.

Figure 3 shows the x-ray diffraction patterns of various types of V_2O_5, where A is a diffractogram of a-V_2O_5-P_2O_5 showing only a diffused, broad halo characteristic of an amorphous state. Diffractogram C is that of the ozone oxidation product and is almost the same as that of e-V_2O_5(B). Both diffractograms show small diffraction peaks at 25.7° which seems to correspond to the 110 diffraction peak and halos. By heating the ozone oxidation product at 400 °C, x-ray diffractogram D is obtained, which is similar to that of c-V_2O_5(E). Thus, the ozone oxidation product(C) is considered to be V_2O_5 (O_3-V_2O_5). The structure of O_3- and e-V_2O_5 is intermediate between a- and c-V_2O_5 and seems to be more like an amorphous material rather than a crys-

Table 1. Binding Energy of Various Types of V_2O_5

	Binding Energy / eV			
	O 1s	V 3p	V $2p_{3/2}$	V $2p_{1/2}$
O_3-V_2O_5[a)]	531.8	41.2	517.0	523.8
e-V_2O_5	531.4	41.4	517.0	523.4
a-V_2O_5-P_2O_5	528.4	39.0	514.6	521.4
c-V_2O_5	532.0	42.8	518.0	524.8

a) Obtained in pH 2.5 solution at 80 °C.

talline one. The IR spectra of the five different V_2O_5s are shown in Fig. 4. The spectrum of c-V_2O_5 coincides with that reported by Sanchez and Livage.[5)] The spectrum of O_3-V_2O_5 heated at 400 °C (D) shows a similar spectrum to c-V_2O_5(E). The O_3-(C) and e-V_2O_5(B) had rather broadened absorption bands compared to those of c-V_2O_5(E) showing that the system changed to a random structure with a wide distribution of the V-O bond length and angles like a-V_2O_5-P_2O_5(A).[6)]

Figure 5 shows the charge-discharge curves of the various types of V_2O_5 for the second cycle obtained at a constant current of 0.5 mA/cm^2 from 3.5 V to 2.0 V in a 1M $LiClO_4$ propylene carbonate(PC) solution. Cathode mixtures were fabricated by mixing V_2O_5 powder, graphite powder(Wakojunyaku

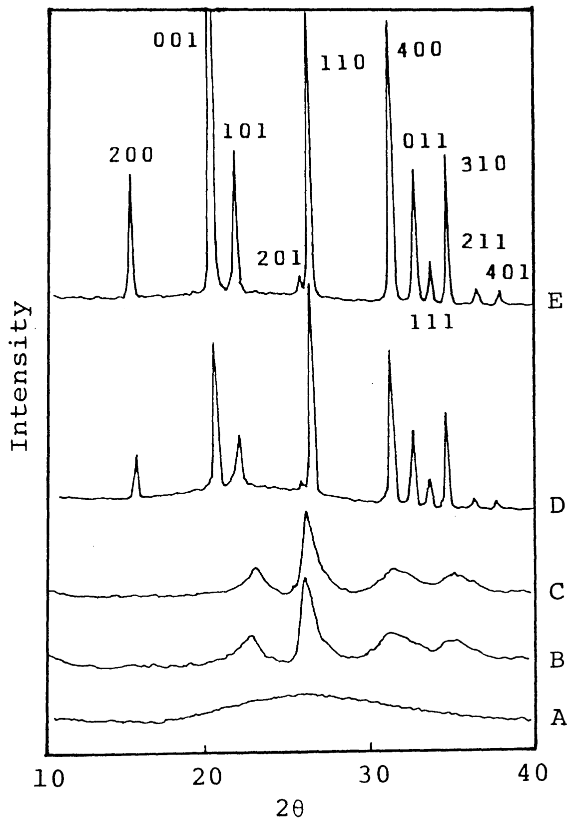

Fig. 3. X-ray diffraction patterns of (A)a-V_2O_5-P_2O_5, (B)e-V_2O_5, (C)O_3-V_2O_5, (D)O_3-V_2O_5 heated at 400°C, and (E)c-V_2O_5.

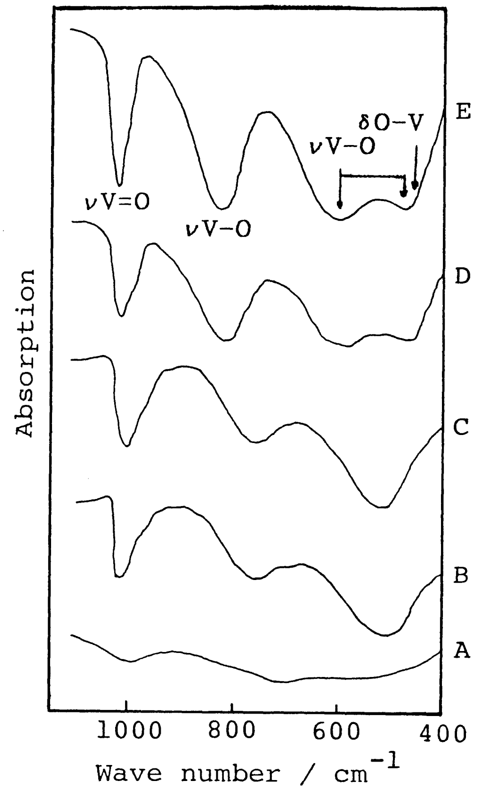

Fig. 4. IR-spectra of (A)a-V_2O_5-P_2O_5, (B)e-V_2O_5, (C)O_3-V_2O_5, (D)O_3-V_2O_5 heated at 400°C, and (E)c-V_2O_5.

Co.) and teflonized acetylene black powder(TAB-2, IBA Sample No.2) and pressing the mixture onto a nickel mesh collector at a pressure of 3 tons/cm^2 to make a 3 cm^2 tablet. C-V_2O_5(D) showed two small steps at about 3.3 V and 2.3 V and one definite step at about 3 V, whereas a-V_2O_5-P_2O_5(A) showed a smooth discharge curve. On the other hand, O_3-(C) and e-V_2O_5(B) showed almost the same shape and intermediate behavior between a-V_2O_5-P_2O_5(A) and c-V_2O_5(D), i.e., two loose steps appeared at about 2.8 V and 2.3 V. The shape of the discharge profile is closely related with the structure of V_2O_5, which provides a site for lithium intercalation. The x-ray and IR data suggested that the crystal structure of O_3- and e-V_2O_5 is not so clear when compared to that of c-V_2O_5. The site of lithium intercalation is estimated to be not fixed so rigidly compared to c-V_2O_5, which reflects the profile showing loose steps. The cyclability of O_3- and e-V_2O_5 was very good. The discharge capacity from the second cycle was about 175 Ah/kg, a little larger than a V_2O_5-P_2O_5 and was almost constant, whereas the capacity of c-V_2O_5 decreased with cycling.

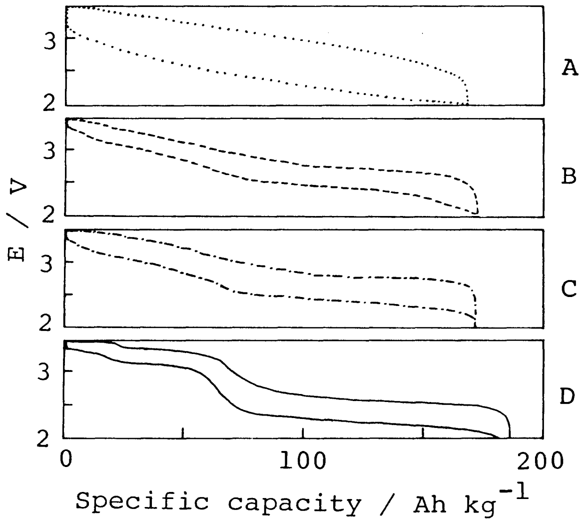

Fig. 5. Charge-discharge profiles of (A)a-V_2O_5-P_2O_5, (B)e-V_2O_5, (C) O_3-V_2O_5, and (D)c-V_2O_5 obtained at 0.5 mA / cm^2.

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