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Preparation and characterization of doped manganese dioxides

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Doped manganese dioxide samples, containing cations of different valency, were prepared. The doped and undoped samples contained small amounts of physically held and chemically bound water. The X-ray diffraction patterns of the doped samples were very similar to the pattern of the undoped sample and they all belong to the β-modification mixed with ϵ-MnO_2 and α-Mn_2O_3. The specific surface area of the samples measured by nitrogen adsorption and calculated by the α_s-method was in the range 2–5 $m^2 g^{-1}$, indicating a lower porosity and a lower reactivity compared to the γ-forms. From measurements of pore radii the pores were classified as lying in the mesopore/macropore range (8–35 nm). A decrease in the mean pore radius was observed for the doped samples except for that doped with Li^+ ions.

1. Introduction

The reactivity of manganese dioxide generally depends on its structure and increases with an increase in its hydration and with an increase in its surface area [1]. The structure and solid state properties of manganese dioxides affect their action as depolarizers in dry batteries.

2. Experimental

Doped manganese dioxide samples were prepared by dissolving Specpure manganese in AR concentrated nitric acid [2]. The Li^+, Cr(III) and Th(IV) dopants were added in the form of the Specpure nitrates, whereas V(V) and Mo(VI) were added in the form of AR NH_4VO_3 and AR MoO_3. For comparison, an undoped sample was similarly prepared. The nitrate solution in a silica boat was pyrolysed in an electric tube furnace at 450° C in a nitrogen atmosphere for 3 h. After cooling under a nitrogen atmosphere, the samples were ground to pass through a BSS 200 mesh sieve and finally heated at 110° C to constant weight.

3. Characterization of the samples

The water content of the samples was determined at 110° C and 450° C by heating in air to constant weight. The degree of oxidation, $1 + x$ was estimated by a modified Gattow's method [3, 4], in which a weight of a sample was treated with acidified KI and the liberated I_2 was titrated against standard $Na_2S_2O_3$ solution and then a known quantity of EDTA was added and the excess was back titrated against standard Zn^{2+} salt solution.

The X-ray powder diffraction patterns of the samples were recorded using unfiltered Fe Kα-radiation. The adsorption isotherms of the samples were determined by the low-temperature nitrogen adsorption method using a conventional volumetric apparatus [5]. About 0.5 g of the solid was outgassed in the apparatus for 3 h at 220° C, then at room temperature for 20 h under vacuum ($\leqslant 10^{-5}$ mm mercury). The specific surface area of the samples was calculated by the α_s-method [6].

3. Results and discussion

The water content and the degree of oxidation of manganese dioxide samples are generally used for their characterization [7–9]. The results of heating the doped and undoped MnO_2 samples at 110° C and 450° C are cited in Table 1. The loss in weight at 110° C is ascribed to the loss of physically held water but the loss in weight at 450° C may not be entirely due to loss of combined water, since it has been shown that some oxygen is lost at tempera-

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Table 1. Loss in weight by heating and the degree of oxidation, 1 + x, of the doped and undoped MnO_2 samples. The accuracy in determining x was ± 0.006

Dopant	*Dopant concentration* (at%)	*% H_2O (at 110° C)*	*% loss in weight (at 450° C)*	*1 + x in MnO_{1+x}*	*% MnO_{1+x}*
–	–	0.06	0.39	1.893	97.6
Li^+	0.1	0.16	0.32	1.875	96.8
Cr(III)	0.1	0.21	0.37	1.890	98.1
Th(IV)	0.1	0.03	0.28	1.889	97.5
V(V)	0.05	0.08	0.30	1.895	97.9
V(V)	0.1	0.06	0.38	1.918	98.8
V(V)	0.2	0.03	0.33	1.915	98.8
Mo(VI)	0.1	0.06	0.46	1.972	99.0

tures higher than 300° C [10]. Oxygen may be also adsorbed above this temperature [11]. Therefore, the overall weight change at 450° C is complex and difficult to relate to the amount of combined water.

It can be seen from Table 1 that all the samples contained small amounts of physically held and chemically bound water which is expected for the β- or ϵ-MnO_2 forms. The latter form consists of a hexagonal close packing of O^{2-} ions with Mn^{4+} distributed statistically over 50% of the octahedral interstices [12].

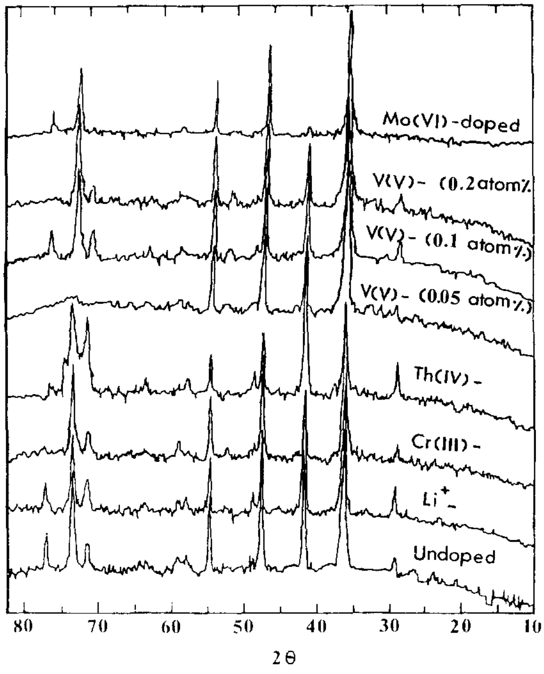

Fig. 1. X-ray diffraction patterns for doped and undoped MnO_2 samples (each dopant at 0.1 at% except vanadium).

From the X-ray diffraction patterns depicted in Fig. 1, it can be seen that the patterns of the doped samples were very similar to that of the undoped sample except for minor differences. The presence of the pyrolusite structure (β-MnO_2) in all the prepared samples is clearly identified by the prominent diffraction lines at (0.309 nm, 36.5), (0.240 nm, 47.6), (0.162 nm, 73.4), (0.211 nm, 54.7) and (0.155 nm, 77.3), were the values of 2θ follow the d-spacings.

On the other hand, the presence of the prominent diffraction line at (0.235 nm, 48.7) characteristic of ϵ-MnO_2, in all the samples except the V(V)- (0.05 and 0.2 at%) and Mo(VI)-doped samples, indicates the presence of small amounts of ϵ-MnO_2 mixed with the β-modification. The higher intensity of the lines observed in all the samples at 0.240, 0.211 and 0.162 nm compared to that of β-MnO_2 also suggest the presence of some ϵ-MnO_2. The prominent diffraction line at (0.271 nm, 41.9) together with the lines at (0.166 nm, 71.4), (0.383 nm, 29.3) and (0.235 nm, 48.7) and the two combined lines at (0.200 nm, 57.9) and (0.184 nm, 63.5) suggest the presence of α-Mn_2O_3* together with the β- and ϵ-MnO_2 modifications.

In conclusion, the X-ray diffractograms indicate that the samples belonged to the β-modification with small amounts of ϵ-MnO_2 and α-Mn_2O_3 (see Table 2). The present X-ray results are in agreement with the results of Pons and Brenet [13] for the products of the thermal decomposition of

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* Generally, the X-ray diffraction patterns of the samples which have a lower value of $(1 + x)$ exhibit the d-spacings characteristic of α-Mn_2O_3 more prominently than the other samples.

Table 2. The prominent diffraction lines of β-MnO_2, ϵ-MnO_2 *and* α-Mn_2O_3

β-MnO_2*			ϵ-MnO_2†			α-Mn_2O_3*		
d (nm)	2*θ*	*I*	*d* (nm)	2*θ*	*I*	*d* (nm)	2*θ*	*I*
–	–	–	0.382	29.4	82	0.382	29.4	10
–	–	–	0.365	30.8	77	–	–	–
0.314	36.0	100	–	–	–	–	–	–
–	–	–	–	–	–	0.271	41.9	100
0.241	47.4	50	0.240	47.6	82	–	–	–
–	–	–	0.235	48.7	100	0.234	48.9	10
0.213	54.1	25	0.210	54.9	95	–	–	–
0.198	58.6	15	–	–	–	0.200	57.9	20
–	–	–	–	–	–	0.184	63.5	30
0.163	72.9	50	0.163	72.9	50	0.166	71.4	90
0.156	76.8	25	–	–	–	–	–	–
–	–	–	–	–	–	0.145	83.8	20
0.143	85.3	15	–	–	–	0.142	86.0	60
0.140	87.6	15	–	–	–	0.139	88.4	20
0.131	95.4	20	–	–	–	–	–	–

* [20]
† [21]

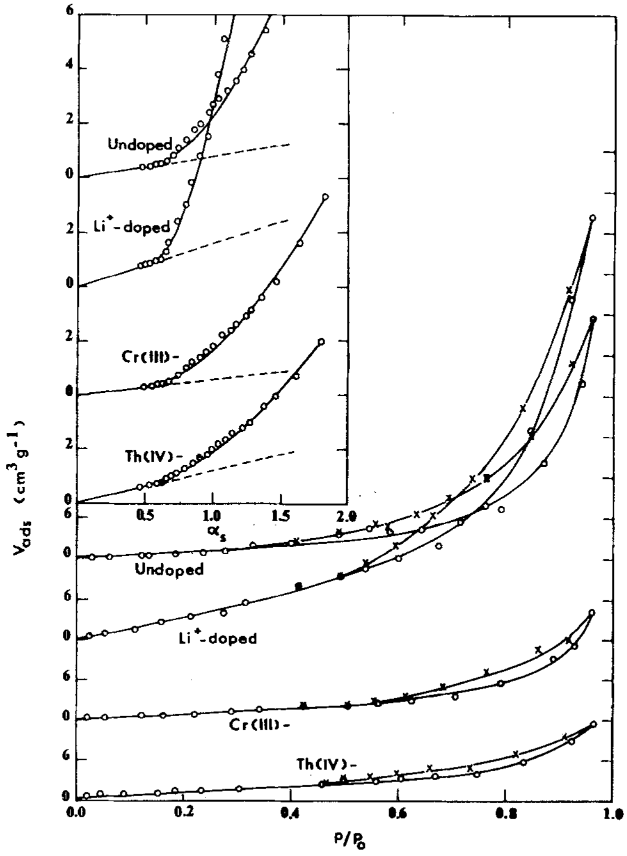

Fig. 2. Adsorption (○)–desportion (×) isotherms of nitrogen on lithium-, chromium- and thorium-doped MnO_2 samples together with the undoped sample, and their α_S-plots (each dopant at 0.1 at%).

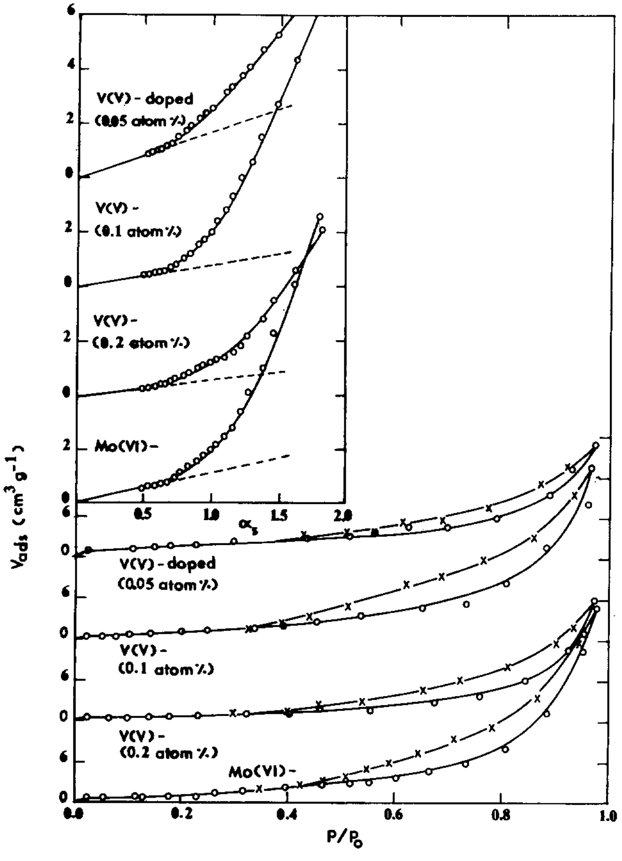

Fig. 3. Adsorption (o)–desorption (X) isotherms of nitrogen on vanadium- and molybdenum-doped MnO_2 samples and their α_s-plots (molybdenum dopant at 0.1 at%).

manganese(II) nitrate under an atmosphere of nitrogen and water vapour.

The nitrogen adsorption isotherms (at − 196° C) are depicted in Figs. 2 and 3 for the different samples. Adsorption of nitrogen was found to be reversible and the vapour was completely desorbed by pumping off at room temperature for 20 h. The adsorption isotherms in Figs. 2 and 3 generally exhibit a behaviour intermediate between types II and III with pronounced hysteresis loops, closing at relative pressures between 0.4 and 0.5 according to the dopant present. Generally, the adsorption isotherms were characterized by ill-defined knees indicating a relatively low heat of adsorption.

The difficulty in the exact calculation of the monolayer capacity from the type III isotherms renders the BET method unsuitable for estimating the area. However, in this case the surface area can be estimated by the α_s-method [6]. Typical α_s-plots for all the prepared samples also appear in Figs. 2 and 3. The plots show upward deviations indicative of the presence of mesopores.

The specific surface areas, S_s, calculated by the α_s-method were obtained from the slope of the initial linear parts of the α_s-plots using the following relation:

$$S_s = N_f \frac{V}{\alpha_s} \qquad (1)$$

where V is the volume of gas adsorbed in cm^3, and N_f is the normalizing factor, obtained from the standard isotherm on a non-porous reference material of known BET surface area. The normalizing factor for nitrogen was determined by Sing *et al.* [14–16], using non-porous silica as a reference material, for which Equation 1 becomes

$$S_s = 2.89 \frac{V}{\alpha_s} \qquad (2)$$

The specific surface area of the doped and undoped samples, calculated from the α_s-method, was in the range of 2–5 m^2 g^{-1}. From the results collected in Table 3, it seems that changing the valency or the concentration of the dopant did not appreciably change the surface area.

Table 3. Texture characteristics of doped and undoped MnO_2 samples

Dopant	*Dopant concentration* (at%)	*Surface area* (m^2g^{-1})	*Total pore volume* $\times 10^3$ (cm^3 liq. g^{-1})	*Mean pore radius* (nm)
–	–	2.3	44	38.2
Li^+	0.1	4.6	89	38.7
Cr(III)	0.1	1.7	22	26.2
Th(IV)	0.1	3.5	16	9.2
V(V)	0.05	4.9	22	8.9
V(V)	0.1	2.3	31	26.9
V(V)	0.2	1.7	20	23.3
Mo(VI)	0.1	3.2	32	20.1

The small areas measured indicate a lower porosity compared to that of the γ-forms [17] and hence the reactivity of the prepared samples are not as high as the γ-samples. However, the nitrogen adsorption surface area may not reflect the activity of a manganese dioxide sample [18]. It is worth mentioning that an increase in the amount of V(V) resulted in a decrease in the surface area (see Table 3).

The total pore volume was determined for the samples by measuring the volume of nitrogen adsorbed near the saturated vapour pressure ($p/p_0 = 0.95$) and the values are also given in Table 3. In general, doping manganese dioxide caused a decrease in the total adsorption space (total pore volume), except for the Li^+-doped sample which showed an abnormal uptake of nitrogen at saturation which may be due to condensation.

The mean pore radius of the doped and undoped samples was calculated [19] and the results are also included in Table 3. The mean pore radii of all the samples were nearly in the mesopore range (8–35 nm), a trend also indicated by the upward deviation of the α_s-plots (Figs. 2 and 3). Except for the Li^+-doped sample, a decrease in the mean pore radius was observed for the doped samples especially the Th(IV)-doped and V(V)-doped (0.05 at%) samples.

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