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Kinetics of the reduction of doped manganese dioxides by hydrazine

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The rate of reduction of different doped and undoped manganese dioxide samples by hydrazine solution was followed by estimating the nitrogen liberated. The rate of this reaction may be used to estimate the depolarizing activity of the various manganese dioxides. Compared to the undoped sample, a higher rate of N_2-evolution was observed in the case of samples doped with ions of valency higher than 4, whereas a lower rate was found for samples doped with ions of valency $\leqslant 4$. On the other hand, the oxidation of a Cr(III)-solution by the different doped and undoped samples exhibited the reverse trend to the oxidation of the hydrazine solution, suggesting that the mechanism of the two oxidation reactions are different.

1. Introduction

The rate of reduction of MnO_2, used as a depolarizer in Leclanché cells, by hydrazine solution may give an idea about the reduction in the dry cell, since the chemical and electrochemical reductions of MnO_2 are similar [1, 2]. The rate of hydrazine reduction can be generally correlated with the depolarizing activity of various dioxides in the dry cell, although there are some exceptions. Uchijima *et al.* [3] used aqueous hydrazine for the reduction of the surface excess oxygen of nickel oxide catalysts and suggested that oxides such as manganese dioxide react with hydrazine similarly. Drotschmann [4] summarized the different factors affecting the rate of the reduction of MnO_2 by hydrazine.

The rate of oxidation of Cr(III) ions by different forms of manganese dioxide and by the lower manganese oxides was reported by Basak and Malati [5], but the exact mechanism of this oxidation reaction is not known.

2. Experimental

The preparation of the doped and the undoped manganese dioxide samples were reported elsewhere [6, 7]. The solids were characterized by chemical analysis and by X-ray diffraction and by their surface areas, determined by nitrogen adsorption and calculated by Sing's α_s-method [8].

2.1. *Reduction of manganese dioxides using hydrazine*

The apparatus used for following hydrazine reduction, Fig. 1, consisted of a 50 cm^3 flask A connected to a 50 cm^3 flask B, that could be turned through 180° around Quickfit joints to allow the hydrazine solution in B to flow into the reaction flask A. The volume of nitrogen liberated from the reaction was measured by a micro-burette C filled with water and attached to a side tube in A via a polyethylene tube.

1.0 g of the sample was added to 15 cm^3 of standard 1 M ammonia solution in A. After stirring at a constant rate for 5 min at 25° C, 12 cm^3 of 5% AR hydrazine hydrate solution were introduced into B. B was turned to allow the hydrazine solution to flow into A. The volume of nitrogen was measured in C at intervals over a period of about three hours.

2.2. *Reduction of manganese dioxides using Cr(III)*

27 cm^3 of 0.1 M chrome alum solution, in a 50 cm^3 double-wall beaker, was thermostated to ± 0.5° C for 30 min at 90° C by circulating water from an

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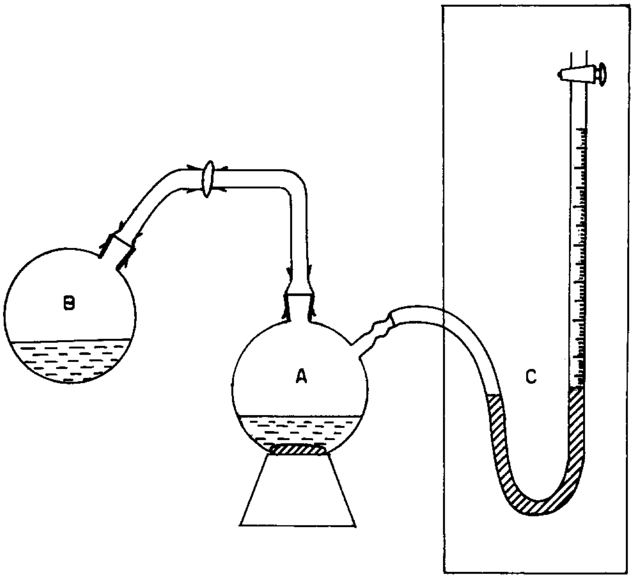

Fig. 1. Sketch of the apparatus used in the reduction of doped and undoped MnO_2 samples using hydrazine.

Ultra thermostat. The solution was stirred at a constant rate under a nitrogen atmosphere. 1.0 g of a solid sample was then added, and the pH adjusted to 3. After 60 min the reaction was quenched by cooling. After centrifuging and filtering through a G4 sintered glass, the filtrate was potentiometrically titrated using a bright platinum electrode against a standardized 0.025 M iron(II) sulphate solution freshly prepared by dilution. The concentration of $Cr_2O_7^{2-}$ formed in the solution was determined and the percentage oxidation of Cr(III) was calculated. The experiments were repeated using 0.5 g of a sample under identical conditions.

3. Results and discussion

The kinetic results, expressed as volume of nitrogen per m^2 of surface, are plotted against time in Figs. 2 and 3. The effect of changing the concentration of vanadium in the doped samples on the rate of nitrogen liberation is shown in Fig. 4. Duplicate determinations showed that the reproducibility was within ± 5%.

Figs. 2–4 show that, compared to the undoped sample, samples doped with cations of valency > 4 [Mo(VI) and V(V)] showed a higher rate of nitrogen liberation in the hydrazine reaction, whereas samples doped with cations of valency $\leqslant 4$ [Li^+, Cr(III) and Th(IV)] exhibited a lower rate of nitrogen evolution. The rate of nitrogen liberation of the 0.1% doped samples decreased in the series:

$$\mathrm{Mo(VI)} > \mathrm{V(V)} > \text{undoped} > \mathrm{Th(IV)} \simeq \mathrm{Cr(III)} > \mathrm{Li^+}$$

Fig. 4 demonstrates that the rate of nitrogen evolution increased on increasing the vanadium concentration in the doped sample.

The results obtained for the percentage oxidation of Cr(III)-solution by the different doped and undoped samples are collected in Table 1. Also given are the values of the degree of oxidation, $1 + x$, for the different samples. Compared to the undoped sample, the values of $(1 + x)$ are generally lower for the samples which oxidized Cr(III) to a greater extent than the undoped sample. The samples having a lower $(1 + x)$ presumably contain more Mn(III) oxide. The observation that these samples oxidize Cr(III) to a greater extent may be ascribed to Mn^{3+} ions which are known to oxidize Cr(III) [9].

The results in Table 1 indicate that increasing the concentration of vanadium in the doped sample led to a decrease in the percentage oxidation of Cr(III). Except for the Th(IV)-doping, which did not seem to affect the percentage oxidation of Cr(III) ions, it can be seen that the oxidation of Cr(III) by the different doped-MnO_2 samples showed an opposite trend to the hydrazine oxidation by the same samples.* This suggests that the mechanism of the two oxidation reactions

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* The Cr(III)-oxidation results represent one kinetic point and are subject to a higher experimental error than the results of the hydrazine reaction which represent complete kinetic runs.

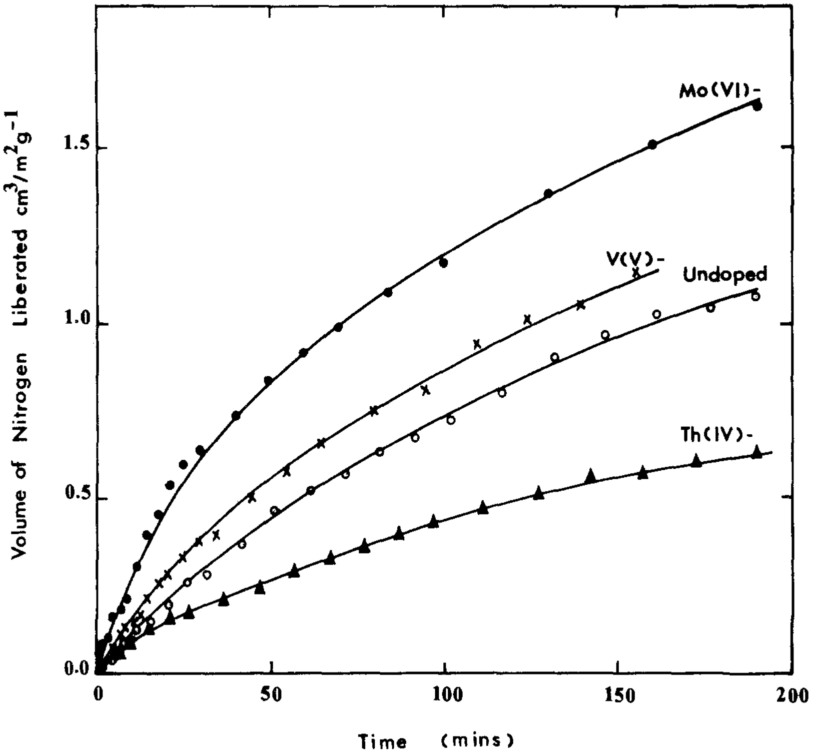

Fig. 2. Kinetic curves of the liberation of nitrogen measured from the hydrazine oxidation by doped and undoped MnO_2 samples (each dopant at 0.1 at%).

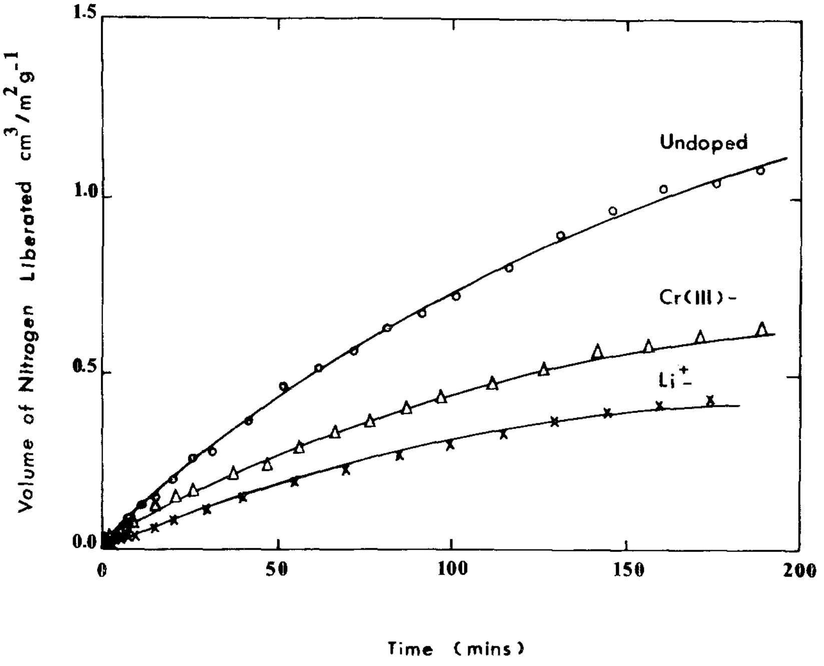

Fig. 3. Kinetic curves of the liberation of nitrogen measured from the hydrazine oxidation by doped and undoped MnO_2 samples (each dopant at 0.1 at%).

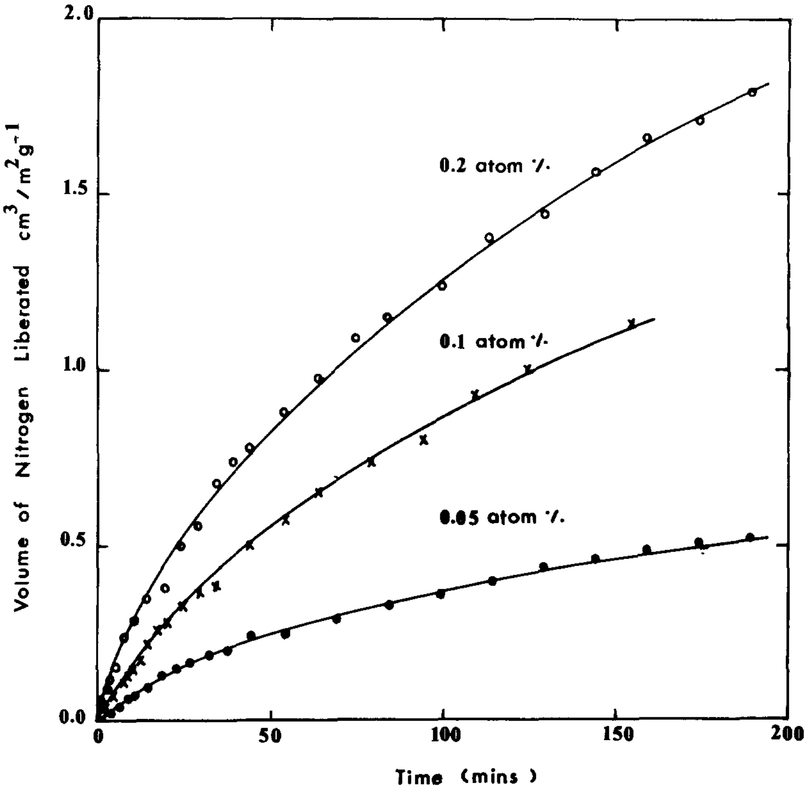

Fig. 4. Kinetic curves of the liberation of nitrogen measured from the hydrazine oxidation by vanadium-doped MnO_2 samples.

are different. In general, it is expected that the reactivity of the dioxide samples towards hydrazine depends on the mobility of protons in the samples.

The higher reactivity of the Mo(VI)-doped sample in the hydrazine reaction, is in agreement with the work of Gardner and Våland [10, 11] who ascribed the effect to the more diffuse structure of the Mo(VI)-doped MnO_2. If it is assumed that the doping Li^+ ions occupy interstitial sites in the MnO_2 lattice, the solubility of Li_2O in MnO_2 may be represented by:

$$Li_2O \longrightarrow 2\,Li^+ + 2e^- + \tfrac{1}{2}O_2.$$

The formation of this oxygen, which may be restricted to the surface [3], could explain the lower rate of nitrogen evolution by the Li^+-doped sample compared to the undoped-MnO_2.

Table 1. % Cr(III)-oxidation by the different doped and undoped MnO_2 samples

Dopant	*Dopant concentration* (at%)	*% Cr(III) ($\frac{1}{2}$g/27 cm³) oxidation* (h^{-1})	*% Cr(III) (1 g/27 cm³) oxidation* (h^{-1})	*MnO_{1+x}*
–	–	3.7	4.1	1.893
Li^+	0.1	5.7	5.9	1.875
Cr(III)	0.1	4.9	5.5	1.890
Th(IV)	0.1	3.8	3.7	1.889
V(V)	0.05	3.9	3.9	1.895
V(V)	0.1	3.3	3.7	1.918
V(V)	0.2	2.9	3.5	1.915
Mo(VI)	0.1	2.3	3.1	1.972

In the present investigation, the results were expressed in terms of the volume of nitrogen evolved per m^2 so that the effect of the surface area does not have to be considered. Drotschmann [4] has reported a higher rate of N_2 evolution by a sample of MnO_2 of a lower surface area than another sample, which gave a lower rate of N_2 evolution. The higher electrochemical reactivity of ϵ-MnO_2 compared to γ-MnO_2 [12] suggests that the state of the surface is more important than the surface area in determining the rate of electrochemical reduction. It is likely that the state of the surface also determines the rate of chemical reduction by hydrazine.

The differential thermo-electric voltage of the undoped and three doped-MnO_2 samples, measured by Preisler's method [13], are shown in Table 2. Table 2 shows that the doped samples had a more negative thermo-electric voltage compared to the undoped sample, the negative sign indicating n-type semiconductivity for the four samples.

However, the valency of the dopant ion did not seem to have a marked effect on the magnitude of the thermo-electric voltage. Accordingly, the results of hydrazine reactivity of the doped samples cannot be interpreted in terms of the semiconductivity and defect structure of MnO_2. Brenet's assumption [14] that manganese dioxides activated by doping with cations of valency higher than 4 would be p-semiconductors, has not been substantiated by the data in Table 2 and by other published results [13, 15].

Table 2. Thermo-electric voltage of some doped and undoped-MnO_2 samples. All dopants were at a level of 0.1 at%.

Sample	*Thermo-electric voltage* ($\mu V K^{-1}$)
Undoped	− 236 (254)
Cr(III)-doped	− 296 (295)
V(V)-doped	− 288
Mo(VI)-doped	− 300

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