Study to enhance the electrochemical activity of manganese dioxide by doping technique

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Abstract

A study has been performed to upgrade natural manganese dioxide (NMD) by intentionally inserting traces of impurities, i.e., by 'doping'. Doping is performed directly on NMD at its softening temperature of 450°C using Mo-based oxide as 'dopant'. The samples of NMD (i.e., base sample) and doped NMD are characterized by various techniques such as chemical analysis, X-ray diffraction (XRD) analysis, density, resistivity measurements and activity index measurements. Critical evaluation of the doped samples is carried out by studying the discharge behaviour in Leclanché electrolyte at different constant-current (continuous) regimes of 1, 5 and 10 mA. Distinct improvement in the discharge characteristics is observed with doped MnO_2 samples. It is conclude that the doping method can be used to develop and upgrade NMD for its application as a cathode material, in dry batteries. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Natural manganese dioxide (NMD) is used worldwide as a cathode active material in dry batteries. It is however, inferior in quality compared with its counterparts such as chemically prepared, chemical manganese dioxide (CMD) and activated manganese dioxide (AMD), and electrolytically prepared, electrolytic manganese dioxide (EMD). Due to its cost effectiveness, the NMD is consumed in large quantities in combination with other varieties of MnO_2 (as mentioned above) for the manufacture of dry batteries as per requirements of different categories of products.

Several workers have studied the doping of MnO_2 as a means to upgrade its performance. This has involved in situ doping using $Mn(NO_3)_2$ and an appropriate amount of dopant, at its thermal decomposition temperature [1–6]. By contrast, no studies of the direct doping of NMD have been reported.

This work reports a feasibility study of the direct doping of NMD at its softening temperature in the presence of a known quantity of molybdenum as dopant. The latter is in the form of molybdenum oxide (MoO_3), as reported by

Valand et al. [6]. A second objective is to synthesize doped NMD in a cost-effective way.

2. Experimental

2.1. Base sample and dopant

For the present study, NMD from Bhandara Mines, Nagpur, was taken as the base sample. It was pulverized to the required particle size at source. High purity, molybdenum trioxide (MoO_3) was used as the dopant. The dopant and base sample were not subjected to any treatment.

2.2. Selection of doping temperature

The electrochemical behaviour of MnO_2 is largely dependent on the crystal structure and the physico-chemical features such as chemical composition, density, and conductivity. As the temperature plays a vital role in changing the above parameters [7], the selection of a suitable temperature is of very great importance. The doping temperature was selected from a series of experiments carried out with NMD. The selected temperature was 450°C.

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2.3. Sample preparation

Doped NMD was prepared as follows; 50 g NMD and 0.075 g MoO_3 (i.e., 0.1 wt.% of base material) were thoroughly mixed in an agate mortar and then subjected to heat treatment up to the softening temperature of NMD, i.e., 450°C for 48 h in a muffle furnace. The resultant dioxide was treated with 7.5 M NH_3 and stirred well for about 30 min to remove the unreacted molybdenum as ammonium molybdate. The oxides were then washed with plenty of water dried at 110°C, and stored in a desiccator. The dopant percentage was estimated by means of atomic absorption spectrometry (AAS).

2.4. Characterization of base and doped MnO_2

All samples were characterized in terms of chemical and physico-chemical parameters such as MnO_2 content (purity) [8], Mn content [9], moisture content [8], structural/combined water (chemisorbed) [10], density (as tap density) [11], resistivity [12], and activity index [13,14].

Trace impurities were estimated by AAS. The chemical and physico-chemical characterization of base and heated samples of NMD and Mo-doped NMD are presented in Table 1.

X-ray powder diffraction (XRD) measurements were carried out using nickel filtered Cu Kα radiation ($\lambda = 1.54$ Å) over a range from 5 to 90° (scanning speed at 2θ/min). The principal phase observed in all the samples was β-MnO_2. The XRD data and comparison of the patterns are shown in Table 2 and Fig. 1, respectively.

2.5. Cell assembly and electrode preparation

The three-electrode electrochemical cell system configuration used in the present study was similar to the one used by Fernandes et al. [15] with a slight modification as shown in Fig. 2. The experimental cell consisted of a zinc strip ($45 \times 4 \times 2.5$ mm) counter electrode, a saturated calomel electrode (SCE) reference electrode, and the cathode mix as the working electrode. The working electrode consists of 0.1 g of the MnO_2 dispersed in 1.0 g of acetylene black wetted with 0.5 cm^3 of Leclanché electrolyte (5 M NH_4Cl + 2 M $ZnCl_2$). The cathodic ingredients were thoroughly mixed and pressed in a cell (cylindrical plastic container 50 mm in height and 30 mm in diameter with a spiral platinum wire at the bottom for electrical contact) at a pressure of 100 kg cm^{-2}. A circular, perforated, Teflon disc was placed over the compressed mix which was sandwiched between separator papers for proper ionic transfer and to avoid diffusion of cathodic mix into the electrolyte media. The cell was
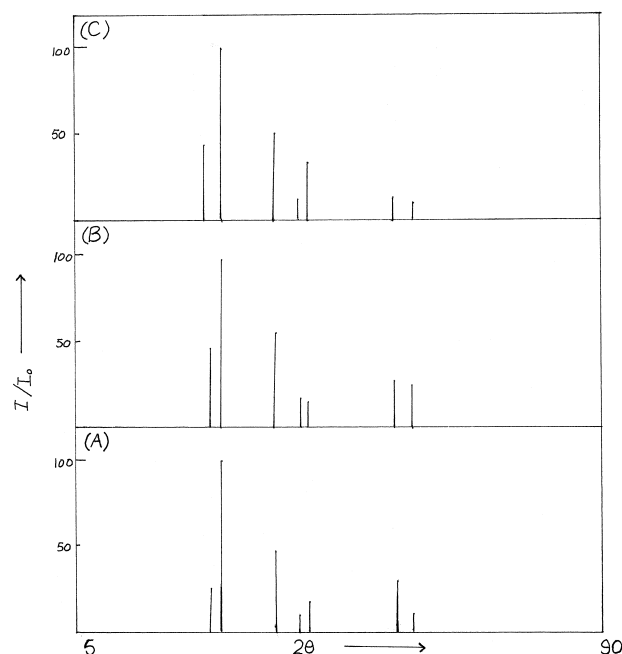
Table 2
X-ray powder diffraction data

NMD		Annealed NMD (at 450°C)		Mo doped NMD	
d Å	Intensity	d Å	Intensity	d Å	Intensity
3.339	26	3.35	45	3.347	44
3.119	100	3.125	99	3.123	100
2.405	48	2.411	55	2.411	52
2.200	11	2.206	17	2.208	12
2.110	16	2.116	14	2.113	34
1.625	29	1.626	15	1.624	13
1.555	11	1.559	15	1.558	9

Table 1
Data from chemical and physico-chemical analysis

Parameter	Sample		
	NMD	Annealed NMD (at 450°C)	Mo doped NMD
MnO_2 wt.% (Purity)	69.65	75.19	74.35
Mn (wt.%)	54.05	53.99	55.38
x in MnO_{1+x}	0.81	0.88	0.85
Moisture	0.37	0.36	0.39
Combined water (wt.%)	0.52	0.040	0.090
pH	5.29	5.85	5.67
Impurites			
Iron (Fe)	5.443	4.422	3.610
Copper (Cu)	0.003	0.002	0.002
Nickel (Ni)	0.008	0.003	0.003
Lead (Pb)	0.004	0.007	0.007
Dopant as Mo (wt.%)	–	–	0.0022
Tap density (g/cm^3)	1.990	2.001	2.105
Resistivity (Ω cm)	1534.52	917.77	641.62
Activity index	16.5	14.8	14.4

Fig. 1. XRD patterns of MnO_2 samples: (A) base sample (NMD); (B) annealed NMD at 450°C; (C) Mo-doped NMD at 450°C.

1 : Spiral Platinum wire
2 : Cathode mix(WE)
3 : Perforated Teflon disc
4 : Separator paper
5 : Cylindrical plastic container
6 : Electrolyte
7 : Counter electrode (Zinc strip)
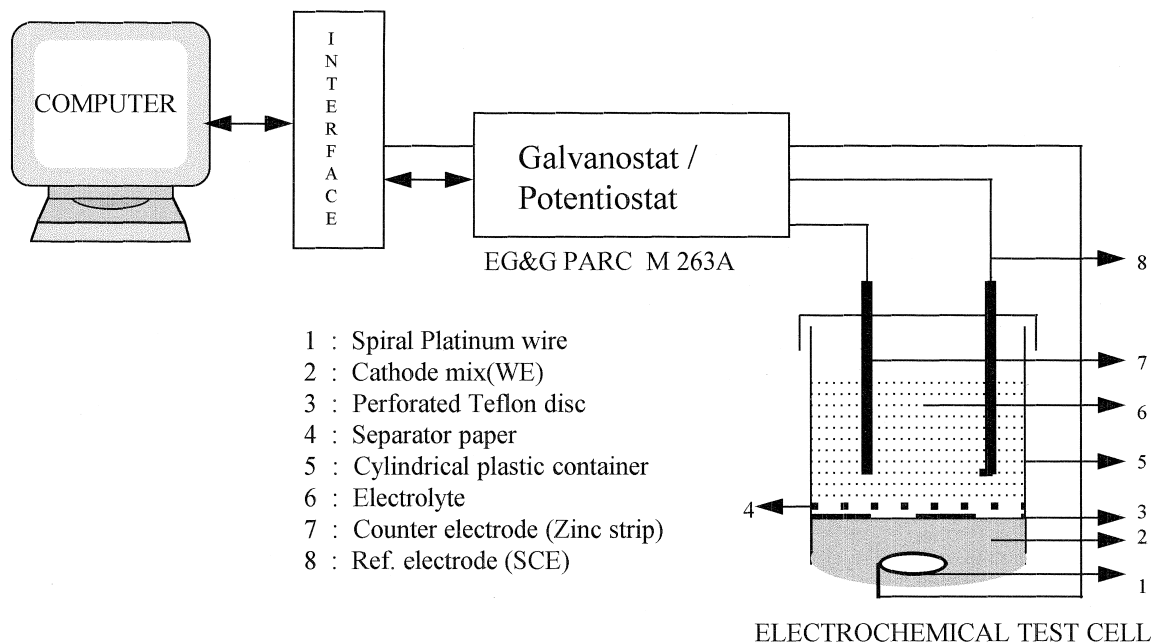8 : Ref. electrode (SCE)

ELECTROCHEMICAL TEST CELL

Fig. 2. Schematic diagram of test cell connected with computer controlled galvanostat/potentiostat for discharge of MnO_2 samples in Leclanché electrolyte (5 M NH_4Cl + 2 M $ZnCl_2$) at constant current. Temperature = 25°C.

activated by taking 15 cm^3 of Leclanché electrolyte. The electrodes were allowed to stabilize at their open-circuit potential before discharge at different constant currents (continuous) of 1, 5 and 10 mA at 25°C. Discharge curves were recorded by means of a computer controlled potentiostat/galvanostat (model 263 A EG&G PARC) to a cut-off voltage of 0.00 V vs. SCE (approximately 1.00 V vs. Zn). A comparison of the discharge plots of different samples is
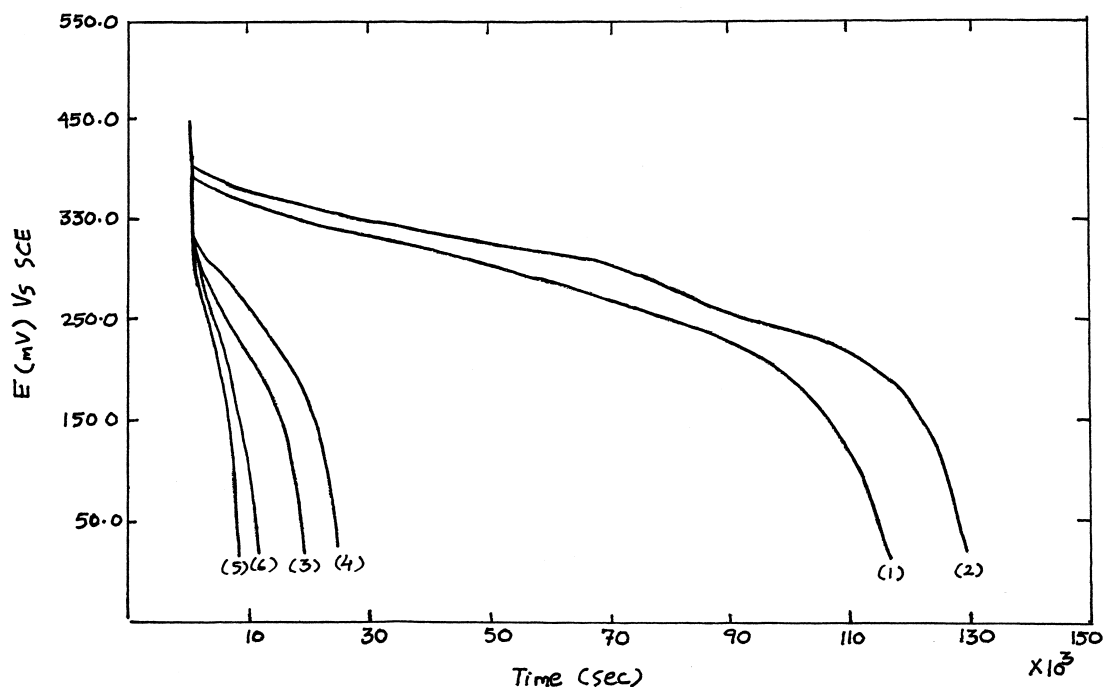

Fig. 3. Comparison of discharge characteristics of base and doped NMD samples at 25°C: (1,2) discharge plots of base and Mo-doped sample at 1 mA current drain, respectively; (3,4) discharge plots of base and Mo-doped sample at 5 mA current drain, respectively; (5,6) discharge plots of base and Mo-doped sample at 10 mA current drain, respectively.
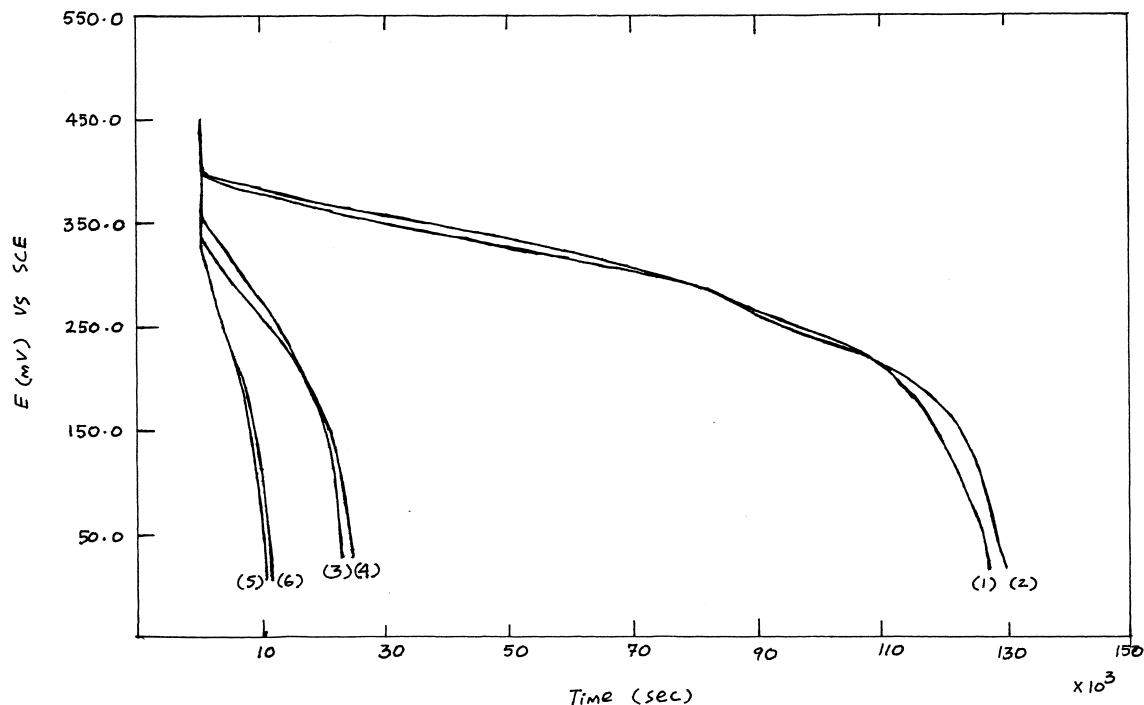
Fig. 4. Comparison of discharge characteristics of annealed and doped NMD samples at 25°C: (1,2) discharge plots of annealed and Mo-doped sample at 1 mA current drain, respectively; (3,4) discharge plots of annealed and Mo-doped sample at 5 mA current drain, respectively; (5,6) discharge plots of annealed and Mo-doped sample at 10 mA current drain, respectively.

given in Figs. 3 and 4, and the different parameters evaluated from the discharge plots are listed in Table 3.
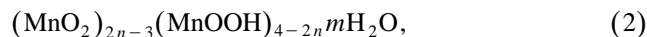
3. Results and discussion

3.1. Physico-chemical characteristics

As most of the MnO_2 lacks perfect stoichiometry, it is denoted by the formula MnO_{1+x}, where x lies preferably in the range of $0.93 < x < 0.98$ and is represented by the formula:

$$x = \frac{0.632(\%MnO_2)}{\%Mn}. \tag{1}$$

To make up this deficiency, either lower valent manganese (such as Mn^{+3}) should be present or some of the Mn^{+4} sites should be unoccupied. The Mn(IV) oxide with such

crystal defects is found to be highly active. The physical and electrochemical properties of such battery active manganese dioxides have been explained elsewhere through cation vacancy model [16]. According to this model, the general formulae of active manganese dioxide is given by:

$$(MnO_2)_{2n-3}(MnOOH)_{4-2n}mH_2O, \tag{2}$$

or in ionic form:

$$Mn^{4+}_{(1-x-y)}Mn^{3+}_y O^{2-}_{(2-4x-y)}OH^{-}_{(4x+y)} \tag{3}$$

where x is the fraction of Mn^{+4} missing from the MnO_2 lattice that results in Mn vacancies; y is the fraction of Mn^{+4} replaced by Mn^{+3}.

Since the cathodic reduction;

$$MnO_2 + H^+ + e^- \rightarrow MnOOH \tag{4}$$

involves insertion of protons into the MnO_2 lattice, the electrochemical activity should obviously depend upon the

Table 3
Discharge characteristics of MnO_2 in Leclanché electrolyte (5 M NH_4Cl + 2 M $ZnCl_2$) for different current regimes at 25°C

Sample	1 mA		5 mA		10 mA	
	Discharge duration (mA h)	Usable energy (J g^{-1})	Discharge duration (mA h)	Usable energy (J g^{-1})	Discharge duration (mA h)	Usable energy (J g^{-1})
NMD	32.47	321	26.60	199.7	22.92	167.5
Annealed NMD (at 450°C)	35.5	375.6	32.03	280.05	29.42	216.4
Mo-doped NMD	36.14	376.2	34.3	279.65	31.86	236

rate of proton transfer from the Mn vacancy. It has been established that the rate of proton transfer increases with the cation vacancy fraction x and attains a limiting value at $x = 0.25$.

Factors which influence the electrochemical behaviour of manganese dioxide other than cation fraction are crystal structure, surface area, pore volume, pore size distribution, morphological characteristics of the particles, density, presence of both surface and bulk impurities, and electrical conductivity.

3.2. Chemical composition

Table 1 shows that the purity of the annealed sample has increased compared with that of the base sample due to the loss of combined water by virtue of which the MnO_2 content has increased. In case of the doped sample, the purity is marginally lowered compared with that of the annealed sample. This is partially due to doping.

3.3. Structure

In order to evaluate the possible changes due to doping, the following samples were subjected to XRD analysis: (i) NMD (base sample); (ii) NMD annealed at 450°C for 48 h; and (iii) NMD doped with Mo at 450°C for 48 h.

From Fig. 1, it is confirmed that all MnO_2 samples are of β-phase with a tetragonal crystal structure. There is no fundamental change in phase due to doping. Similarly, due to the thermodynamic stability of the β-phase, there are no transition phases during the above temperature range. On comparing the XRD patterns of the above three samples, it is found that the crystallinity of the annealed sample has changed compared with that of the base sample. The peak intensity of the principal β peaks has been regained, however, after doping with molybdenum, as shown in Fig. 1. This basically confirms deformation of the structure due to heating and doping phenomenon.

3.4. Density

Density is an another important parameter which can be used to evaluate the quality of MnO_2. In the present study, the tapping density (apparent density) of the samples was measured. The results, given in Table 1, clearly indicate that, due to heating, the density decreases in the following order: NMD < annealed NMD < Mo-doped NMD. Given this trend, the surface area of the Mo-doped NMD sample increases considerably compared with annealed and base samples and, thereby, enhances the number of sites for reaction.

3.5. Resistivity

The resistivity of the samples was measured by the two-probe method. MnO_2 is a n-type semiconductor with a relatively high concentration of charge carriers (for β-MnO_2: $n = 10^{17}$ cm^{-3}). For electrochemical reduction, an electron as well as a proton must be available at the reaction site. In order to minimize the ohmic voltage drop and to achieve a uniform discharge profile, a high electronic conductivity is of advantage. Ruetschi's model [16] suggests that the electronic conductivity decreases with increase in water content. The resistivity of the samples increases in the following order (Table 1): NMD > Annealed NMD > Mo-doped NMD. Accordingly, the conductivity follows the opposite trend, which is in agreement with the Ruetschi's model.

3.6. Activity index

The activity index is a further important means to evaluate the activity of battery grade MnO_2. The reduction by ammonical hydrazine sulfate is believed to be identical to the first step of the electrochemical reduction. This step corresponds to the useful discharge range of a dry cell. The results presented in Table 1 show that the chemical activity index of either heated or doped samples shows no improvement in comparison with the base sample. It has been reported, however, that the electrochemical activity of MnO_2 is more dependent on the state of the surface than the particle size [17].

3.7. Electrochemical evaluation

It is evident from the data in Table 3 and Fig. 3 that the discharge performance in terms of mA h capacity and usable energy for the doped sample is significantly improved for all the three discharge regimes of 1, 5 and 10 mA, compared with that of the base sample. The improvement is not marked, however, compared with the performance of annealed NMD (Fig. 4). This enhanced electrochemical activity of doped and annealed samples may be due to the structural and physico-chemical changes that have taken place during the process of heating, such as a change in crystallinity, lowering of chemisorbed water content, and density, and increased conductivity. The improvement in the discharge performance of the doped sample compared with the annealed one, especially at heavy current drain, might be due to doping causing structural distortion, higher conductivity, and higher density.

4. Conclusions

An attempt has been made to study the feasibility of direct doping of thermodynamically most stable NMD, i.e., β-MnO_2. Such doping is possible at the softening tempera-

ture of NMD. Preliminary results show that there is considerable improvement in terms of discharge performance for Mo-doped samples compared with a sample. This clearly indicates that manganese dioxide can be enhanced in electrochemical activity by intentionally inserting dopants, and can be efficiently utilized at all discharge regimes, especially at high rate. The other related work such as an examination of the effect of ionic size on discharge, the effect of different electrolyte, etc., is in progress.

Acknowledgements

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