Electrochemical Activity of the International Common Samples of Manganese Dioxide

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The depolarising capacity or the electrochemical activity of twelve International common samples of manganese dioxide has been determined according to the method developed earlier. It has been shown that the results obtained by this method can satisfactorily be correlated within experimental limitations with the actual performance data of these samples in dry cells. The activity data obtained by the author has been correlated with the well-known "hydrazine number" and also the number of coulombs exchanged during electrochemical reduction as determined by the potentiodynamic method. These correlations suggest that the method developed by the author and his co-workers can be used for quick evaluation of MnO_2 for dry cells.

Manganese dioxide is considered to be the life-blood of battery industry. It is widely used in the manufacture of 'Leclanche' type dry cells, alkaline cells, Li-MnO_2 non-aqueous miniature cells, etc. For all these primary cells, activity of MnO_2 is the most important factor in determining their satisfactory performance. The battery manufacturers therefore have to evaluate a large number of samples in order to assess their suitability for use in dry cells. A considerable amount of work has been carried out for quick determination of electrochemical activity and as a result, several method have been proposed. These may be broadly classified as direct(1-6) and indirect(3,7-9) methods. The direct methods are based on discharging a mixture of small amount of MnO_2 and carbon in the laboratory test cells under suitable conditions of current and load. Indirect methods are based on the determination of the rate of oxidation of some chemicals like hydrazine hydrate, hydrogen peroxide, sodium oxalate, potassium iodide etc. by MnO_2. But the success achieved appears to be somewhat limited because of various inherent complexities involved in studying the reactivity of MnO_2. As a result, even today the only reliable method for evaluating a given type of MnO_2 is to determine the life of a standard dry cell under actual operating conditions. The authors have developed a method(10) for determination of discharge characteristics. Here activity data obtained by this method is correlated with actual discharge performance data as published earlier by different authors for standard size dry cells made from International common samples of manganese dioxide.

EXPERIMENTAL

The following International Common Samples of MnO_2 were used in this investigation.

No.1	Electrolytic MnO_2 (Ti anode)	Japan
No.2	Electrolytic MnO_2 (pb anode)	Japan
No.3	Electrolytic MnO_2 (C anode)	Japan
No.4	Electrolytic MnO_2	La Pile leclanche' (France)
No.5	Chemical MnO_2	Japan Metals & Chemicals Corporation (Japan)
No.6	Reagent grade β-MnO_2	Fischer (U.S.A)
No.7	Natural MnO_2	Ghana, west Africa
No.8	Chemical MnO_2	Sedema (Belgium)
No.9	Electrolytic MnO_2 (Coarse grade)	Kerr-McGee Corpn. (USA)
No.10	Electrolytic MnO_2 (regular grade)	Kerr-McGee Corpn. (USA)
No.12	Chemical MnO_2 (Faradiser M)	Sedama (Belgium)
No.13	Natural MnO_2	Gabon, Africa

DISCHARGE CAPACITY IN TEST CELL

The design of the test cell developed in this laboratory and the method of determining discharge or depolarising capacity have been described earilier(10). All the measurements have been carried out by discharging a pelletised mixture of 0.15g MnO_2 sample and 0.015g acetylene black in an electrolyte mixture containing 20% NH_4Cl and 27% $ZnCl_2$ in water at a constant current of 15mA.

For discharge in alkaline medium (7.0M KOH) a higher current strength (30 mA) was used. The discharge capacity of the samples was obtained in term of the time required to reach the arbitrary cut-off voltage of either 1 volt or 0.8 volt. All other conditions were same as these used for NH_4Cl-$ZnCl_2$ medium. All the measurements were carried out at 27 - 28°C. At the current strength used no appreciable iR drop was observed.

HYDRAZINE NUMBER

Accurately weighed 0.2 gm of finely ground MnO_2 sample was taken in a 100 ml stoppered Erlenmayer flask in which 20 ml of 0.2N NH_4OH and 10 ml of 0.1N hydrazine hydrate were added. The reaction mixture was allowed to equilibrate at 27 - 28°C for 2 hrs with intermittent shaking, filtered through sintered glass crucible of porosity 4 and washed with a little (25-30 ml) 0.2 NH_4OH. The filtrate was acidified to methyl orange with 0.5 N HCl. About 2 gm of powdered sodium bicarbonate was added, diluted with water to about 150 ml. The residual hydrazine in the filtrate was then titrated against N/5 iodine solution in presence of starch solution as indicator. Let this titre value be A ml. A blank titration was carried out under similar condition. Let this titre value be B ml. The hydrazine number (or index) is given by Hydrazine Number = [(B-A) x 100] / B

DISCHARGE PERFORMANCE IN DRY CELL

Actual performance data of some International common samples of manganese dioxide in 'C' size dry cells has been obtained from the following methods.

1) Leclanche' type dry cells(11-12)
2) Alkaline - MnO_2 cells(13)

In addition to the above, the activity data obtained by Brenet et al(14) from potentiodynamic method has also been considered for correlation.

RESULTS AND DISCUSSION

Typical behaviour of some International common samples of MnO_2 under continuous discharge in different electrolyte media is shown in Figs.1 and 2. The results show that although the majority of the samples belong to γ-variety(14) there are considerable differences in their discharge characteristics. Thus although the initial drop in voltage of some samples like 5 and 12 (Chemical MnO_2) are higher than those of electrolyte MnO_2, their activity in terms of time required to reach either 0.8 V or 1.0 V is nearly same or even higher than those of electrolytic MnO_2 samples. Similarly, natural γ-MnO_2 samples from Ghana and Gabon which are known for their battery activity appear to be much poorer in comparison with synthetic samples. Our results therefore indicate

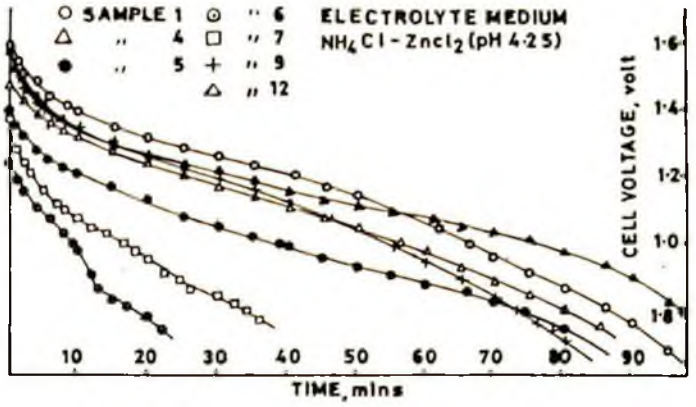


Fig. 1 Continuous discharge characteristics of some I.C. samples in NH_4Cl-$ZnCl_2$ medium at 15mA current.

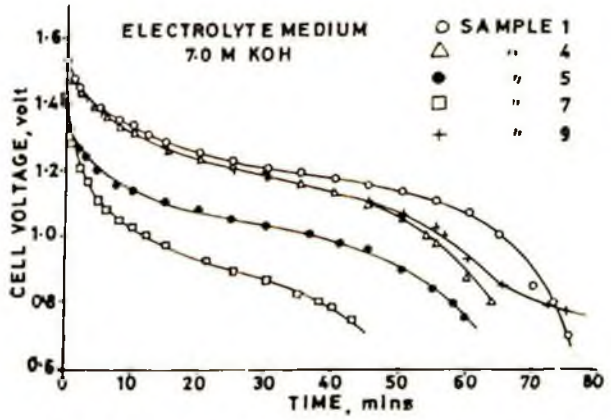


Fig. 2 Continuous discharge characteristics of some I.C. Samples in 7M KOH medium at 30mA current.

that CMD can give as good service life in dry cells as EMD.

Fig. 3 illustrates the relationship between the activity of I.C. samples determined according to our method and the cell performance data obtained by Ohata et.al(11) in both NH_4Cl and $ZnCl_2$ as

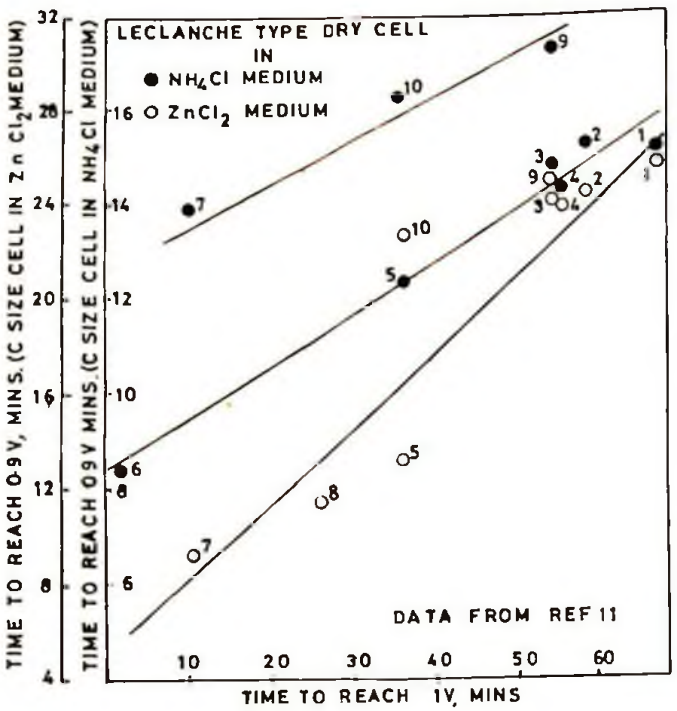


Fig. 3 Correlation between activity in the test cell(10) and the performance data of I.C. samples in 'C' size dry cells according to Ohata et.al(11). Superscripts donate the sample numbers.

electrolyte media. The figure shows that in general there is a direct relationship between the two methods of evaluation. However, for NH_4Cl medium two different straight lines are necessary for such correlation. In the case of discharge performance of the dry cells in $ZnCl_2$ medium considerable deviation is observed for sample Nos. 5 and 10. Such deviation is not unexpected as we have determined the depolarising capacity of the samples in the buffered medium of NH_4Cl-$ZnCl_2$ (pH 4.25). In order to substantiate this view, we have taken the data of Schewigart(12) who has determined the continuous discharge capacity of some I.C.samples in an electrolyte medium containing 10% $ZnCl_2$, 20% $NH^{\circ}v4Cl$ and 70% water. When the data is plotted against our results, a much better correlation is obtained as shown in Fig.4. Nevertheless, some deviation is also observed for sample Nos. 5 and 10.

As far as alkaline-MnO2 cells are concerned, activity data of the International common samples obtained by our method are well-correlated (Fig.5) with those obtained for 'C' size cell by Touchida(13). However, the author has expressed his activity data in terms of service output per unit gram of MnO_2 for continuous discharge under 4 Ohm load.

The above results demonstrate that for both

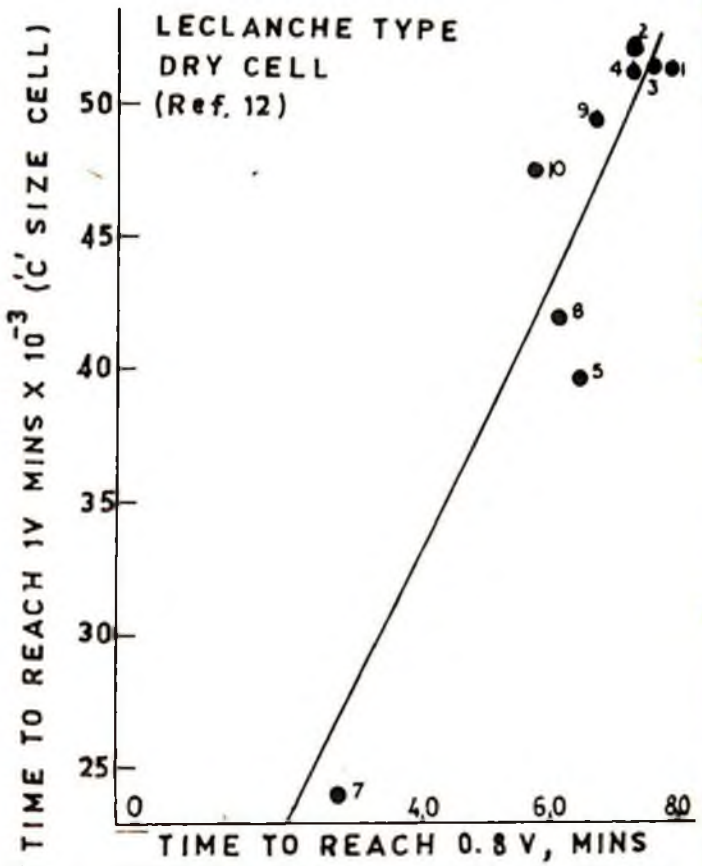


Fig. 4 Correlation between activity in the test cell(10) and the performance data of I.C. samples in C size dry cells according to Schweigart(12). Superscipt denote the sample numbers.

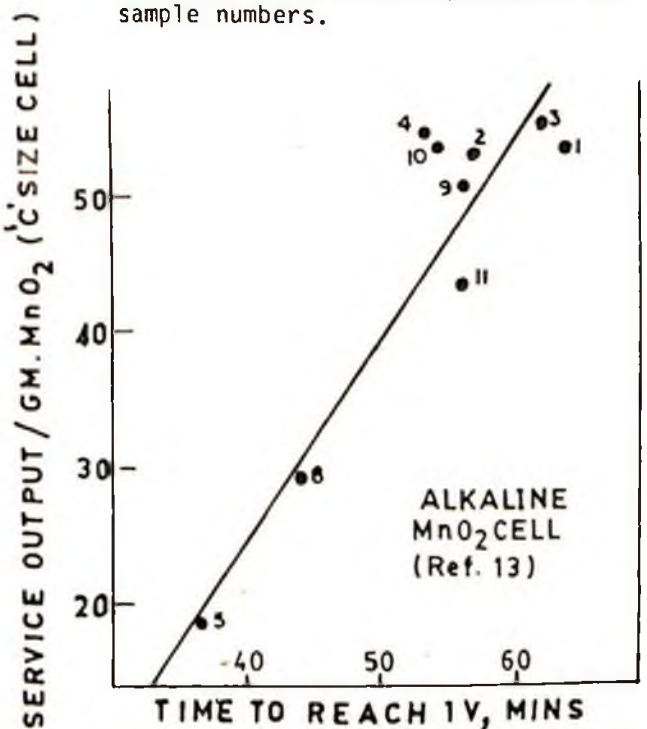


Fig. 5 Correlation between activity in test cell(10) and the performance data of I.C. samples in alkaline cells by Touchida(13). Superscripts denote the sample numbers.

Leclanche type dry cells and alkaline- MnO_2 cells, actual performance data as obtained by various investigators can be correlated well with the activity data determined by us using a small quantity of pelletised sample. Brenet et al(14) have determined the electrochemical reactivity of I.C. Samples of MnO_2 by reducing a mixture of the sample (85%) and graphite (15%) potentiodynamically in a saturated $NH^{\circ}v4Cl$ solution. The electrode potential although measured with respect to SCE was finally converted to normal hydrogen electrode (NHE), Brenet et al have observed that the potential of +100 mV/NHE corresponds well on the average with the cell voltage of 0.9 V which is usually considered as the cut-off voltage for leclanche type dry cell. The number of coulombs exchanged per gram of MnO_2 under this condition, when plotted against the activity data determined by our method shows a good linear relationship as shown in Fig.6, even though the electrolyte medium is different.

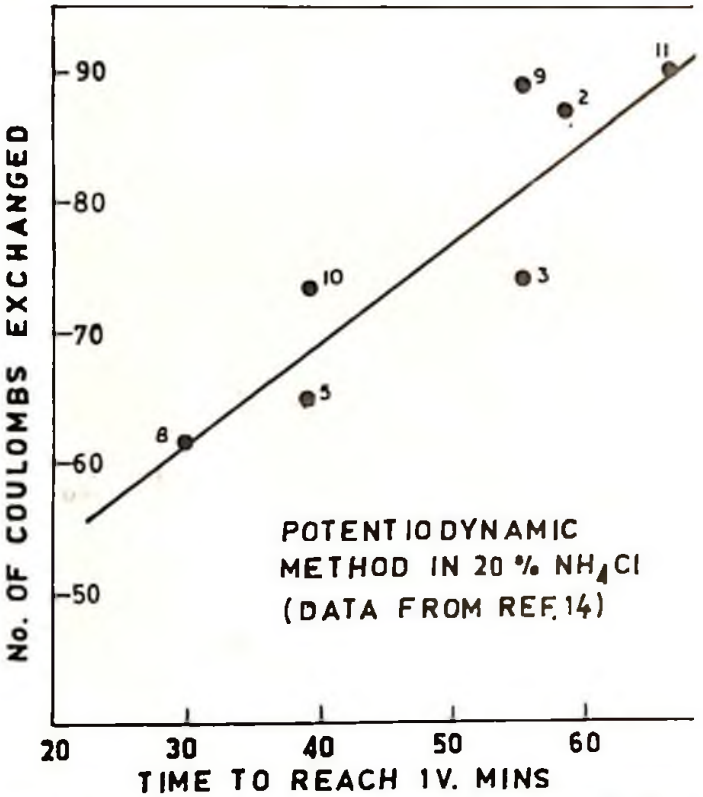


Fig. 6 Correlation between activity data in the test cell(10) and the coulombs exchanged per gram determined by Brenet et al(14). Superscripts denote the sample numbers.

Since hydrazine reduction has been extensively used by the battery manufacturer for evaluation of MnO_2, we have also determined the hydrazine number of the samples. Fig.7 shows the relationship between our activity data in test cell and the hydrazine number of the I.C. samples. It is now

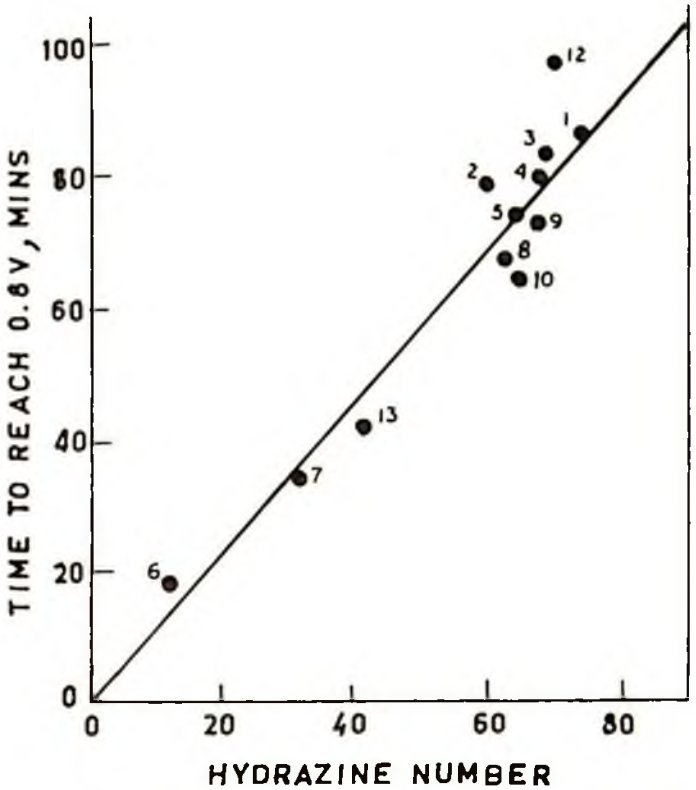


Fig. 7 Relationship between activity data in the Test cell(10) and hydrazine number of the I.C. samples. Superscripts denote the sample numbers.

well-established that unless drastic conditions are employed, dilute solution of ammoniacal hydrazine reduces Mn^{4+} to Mn^{3+} and seldom to Mn^{2+}. This is within the range of the following homogeneous phase reduction of MnO_2 during the discharge.

$$MnO_2 + H^{+} + e^{-} = MnOOH$$

During this homogeneous phase reduction cell, voltage drops from 1.6V and 0.9V and our activity data fulfils this condition.

All these results demonstrate that discharge of a small quantity of the intimate mixture of MnO_2 and carbon in pelletised form can be used to evaluate various MnO_2 for use in dry cell. Such an experimental procedure not only saves considerable amount of time required for evaluating dry cells, but also avoids complicated procedure of making dry cells just for the purpose of evaluation. Besides, the quantity of MnO_2 required for this is also very small in comparison with 20-25 g required for making a dry cell.

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