Synergistic Effects and Conductivity Dispersions in MnO_2

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Electrochemical characteristics of MnO_2 mixtures were investigated in 30 w/o KOH. Discharge capacity of some of the mixtures are remarkably higher than that of individual samples. The results are discussed in terms of the difference in electrical conductivity between the constituent samples. Encapsulation of most active MnO_2 by less active but relatively more conducting MnO_2 appears to play an important role in electron transfer from cathode material.

Manganese dioxide is a material which has aroused considerable interest because of its importance in the battery industry [1-4]. Manganese dioxide for battery applications is seldom stoichiometric. It is a well known fact that the so-called *Electrochemical activity* of a manganese dioxide sample is a complex concept to define, particularly in alkaline electrolytes for fast recuperating periods [5]. The non - equilibrium nature is the main reason for difference in activity from sample to sample. Amongst the interesting phenomenon seen in this interesting material, is the synergistic effect [6]. Synergistic effect is the strange improvement in activity of two different samples when combined together. Some studies have been made in this context dealing with synthesized samples of academic importance and natural ores [7]. However, commercial technological materials of interest have not received much attention. Also an elegant and a clear theoretical picture (which could account for the observed synergistic effect in MnO_2) has not yet emerged. It is with this view in mind that the present work was undertaken. The main purpose of this paper is to investigate the effect of electrical conductivity of constituent samples on the performance of MnO_2.

EXPERIMENTAL

Materials

Three MnO_2 samples of different activity - A (of Australian origin), B (of Indian origin) and C (of Japanese Origin) were used as the study materials. The

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graphite powder used was a commercial KS 44 variety. Teflon suspension was used as the binder. *Kuralon* separator was used to isolate cathode and anode. A commercial perforated zinc electrode was used as the anode.

Preparation of Cathode

The cathodes were prepared by admixing 0.4g of MnO_2 with 0.1g of graphite powder and compacting on expanded nickel mesh with teflon binder. The electrodes were subsequently dried for 12 hrs at 30°C. The dimensions of the electrode were 2.5 cm X 2.5 cm. For the determination of synergistic effect, MnO_2 mixtures prepared from A&B, A&C and B&C each with ratios 3:1, 1:1, 1:3 were loaded on the substrate.

Electrochemical Activity

The cells were assembled by sandwiching a separator covered cathode between two zinc electrodes and fastening with a nylon thread. The cell was immersed in a 50 ml beaker containing electrolyte. Aqueous solution containing 30 wt% KOH was employed as the electrolytic solution. The cells were discharged at 30 mA to an end voltage of 0.7 V.

Physical Characterization

The X-ray powder diffraction analysis was performed on individual MnO_2 samples with a JEOL X-ray diffractometer. Electrical conductivity measurements were made on individual MnO_2 samples pressed at 5 tons.cm^{-2} using a Solartron impedance analyzer model 1260 at 300°K.

RESULTS

Electrochemical Study

The discharge curves of individual MnO_2 samples are presented in Fig 1. Sample A showed a much higher alkaline battery activity. The values of activity for the electrolytic MnO_2 (sample B) and chemically precipitated variety (sample C) are appreciably lower. It is well known

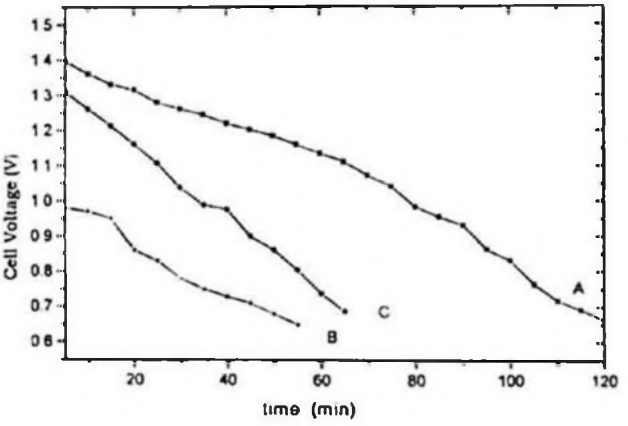


Fig 1 Discharge Characteristics of Individual MnO_2 Samples

that γ MnO_2 performs well in alkaline electrolytes. The activity can be in this order only based on γ phase content. The value of $h_{4.00}$ / $h_{2.12}$ gives an idea about the extent of γ phase. (The sample with a higher value of $h_{4.00}$ / $h_{2.12}$ has a greater γ phase content.)

The galvanostatic discharge curves of MnO_2 mixtures are presented in Fig 2. Both in case of A&B and A&C mixtures, the specific capacity recoverable lie in the order 1:1 > 3:1 > 1:3 (Table 1). Faradaic

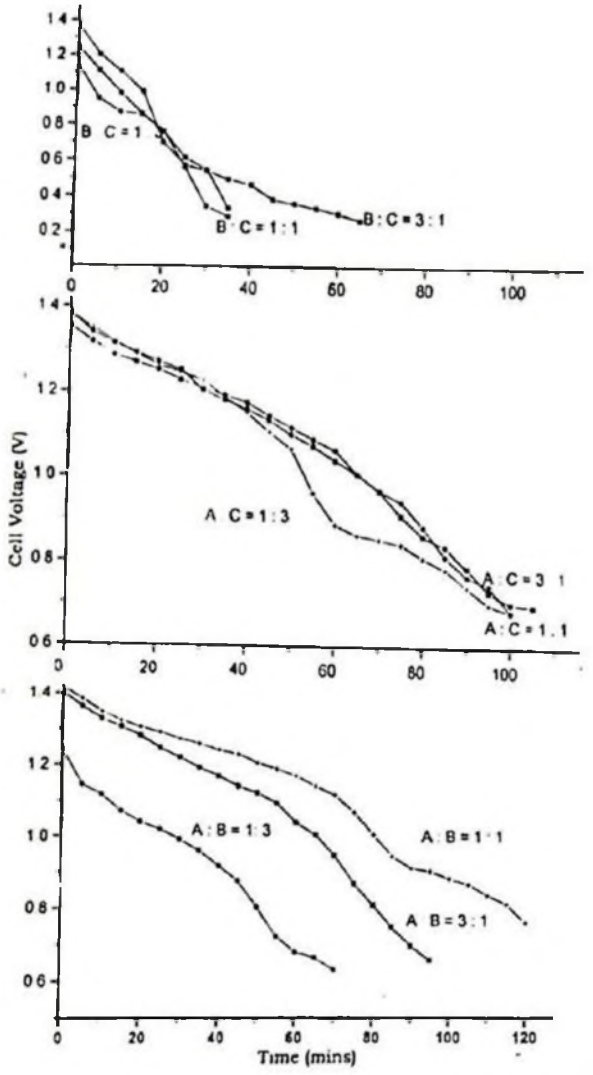


Fig 2 Discharge Characteristics of Mixtures

yield in case of 1:1 mixture (with A as one component) is better than the value expected for a simple mixture. Indeed in both cases, a superior Faradaic yield is obtained in the 1:1 composition by mixing active and inferior MnO_2 samples. However no significant improvement in discharge performance can be achelved by using mixtures of less active samples B and C (Table 1 and Fig 2).

Table 1

Discharge Performance of Manganese Dioxide Mixtures

Observed Capacity of Individual Samples [$mAh.g^{-1}$];
A = 150; B = 41.8 & C = 81

Mixture	Capacity in $mA.h.g^{-1}$ observed	Theoretical
A + B as 3:1	112.5	124
A + B as 1:1	162.5	95
A + B as 1:3	75.0	68
A + C as 3:1	125.0	134
A + C as 1:1	131.25	115
A + C as 1:3	131.25	98
B + C as 3:1	36.04	51.6
B + C as 1:1	31.25	61.4
B + C as 1:3	72.9	71.2

Physical Characterization

The experimental values of electrical conductivities for the three samples are A =1.59914 X 10^{-4}; B = 4.28471 X 10^{-4} and for C = 4.34862 X 10^{-4} $ohm^{-1}.cm^{-1}$. The XRD pattern of γ type MnO_2 is observed for all the samples as shown in Fig 3. However the presence of δ MnO_2 can also be identified in sample A. The γ phase contents for the studied samples are in the order A > C > B as seen from the value of $h_{4\,00}$ / $h_{2\,12}$: (The values for samples A,B and C are 1.80, 1.03 and 1.37 respectively).

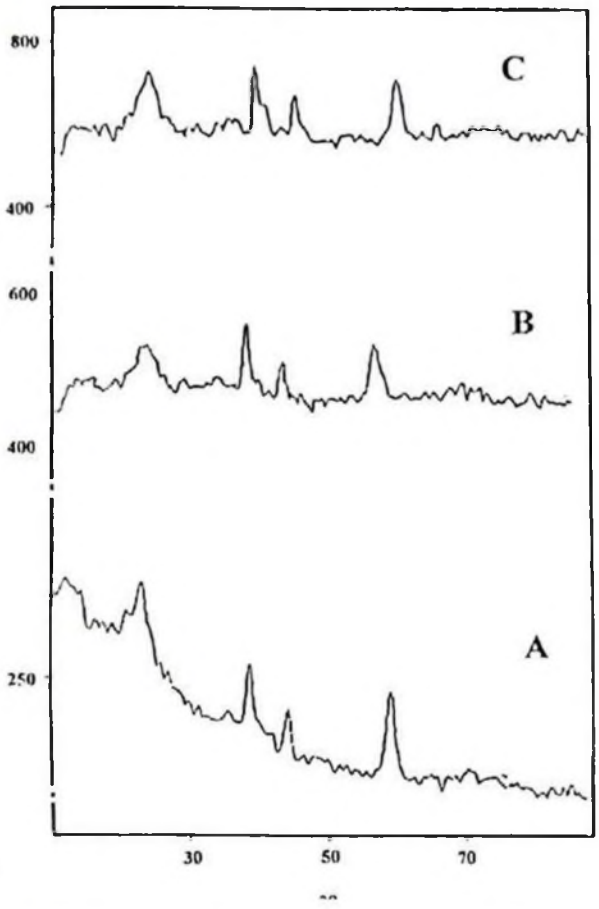


Fig 3. X-ray Diffraction Patterns of MnO_2 Samples

DISCUSSIONS

The capacity values obtained in the discharge experiments are a good indicator of the synergistic effects existing in MnO_2. A comparison of the results got in the case of both types of MnO_2 mixtures (A+B and A+C) show that the activity for 1:1 mixture is far higher than theoretically expected value and the best amongst the combinations studied. Based on the differences in electrical conductivity between two members of widely different electrochemical activity, we propose to give a theoretical model explaining the synergistic effect seen in our study.

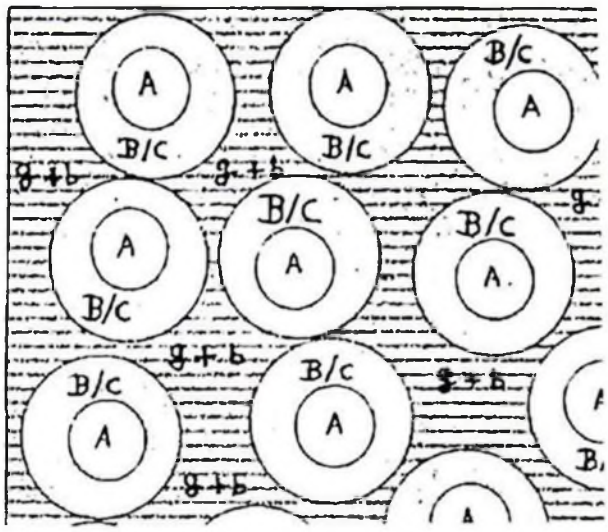


Fig 4. Model for Explaining the Synergistic effect in MnO_2
g+b is graphite and binder matrix

Among the three samples, A (with higher γ phase content) is very good, whereas the other two samples are only of an inferior battery activity. But, B and C are almost thrice more conducting than A. The observed synergistic effect can be explained in terms of the model shown in Fig 4. The superior activity of sample is being facilitated by electron transfer from the material through the surrounding comparatively less active but highly conducting MnO_2 samples. The surrounding comparatively highly conducting MnO_2 (samples B or C) facilitated electron tranfer from the comparatively less conducting but highly active sample A. Since the MnO_2 agglomerates (A+B or A+C) are surrounded by highly conducting graphite, the electron transfer from less conducting MnO_2 layer is easily accomplished through graphite.

The maximum effect in 1:1 combination confirms this as all active MnO_2 particles are equally surrounded by comparatively highly conducting MnO_2 particles. At compositions with higher content of A than 1:1, the coverage by A or C layer becomes inadequate thereby decreasing the performance, despite higher A content. At compositions of A less than that in 1:1 combination, the availability of active A sample is inadequate resulting in reduction in Faradaic yield. The absence of any distinct improvement in battery activity by discharging mixtures of highly conducting and less active samples (B and C) support this theory.

CONCLUSION

(1) Electrical conductivity dispersions play a crucial role in achieving an efficient electron transfer and

(2) by emlpoying proper combinations of samples of different electrochemical activity, high performances can be obtained. The surrounding less active MnO_2 encapsulated inside plays a decisive role in optimizing the charge transfer process and economy of materials. The finding that **a uniform encapsulation imparted to the active MnO_2 by the highly conducting inferior MnO_2 results in maximum discharge capacity** is the most important and interesting finding in this study.

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