

improves diffusion. The MnO_2 heated to 575 K has the overall best performance. This is similar to the earlier work also. The presence of gamma-beta MnO_2 is responsible for this. The higher charge transfer resistance values indicate that the lithium has a surface film.

MnO_2 heated to 573 K and an electrolyte composition of PC:DME, 3:1 containing 1 molar concentration of lithium perchlorate seems to be the best for lithium button cells.

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PRELIMINARY STUDIES ON THE BEHAVIOUR OF MANGANESE DIOXIDE IN PROPYLENE CARBONATE BY CYCLIC VOLTAMMETRY - I

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SUMMARY

Heat treated electrolytic manganese dioxide is used as the cathode in lithium manganese dioxide primary batteries. Heat treatment at 400°C , removes the occluded water in the MnO_2 . Also, partial crystal change from pure gama to a mixture of gama- Beta occurs during this heat treatment. In this paper the reduction mechanism of heat treated MnO_2 in 0.5 M LiClO_4/PC - 2 M LiClO_4/PC have been studied by cyclic voltammetry. The mechanism of MnO_2 reduction varies with the concentration of electrolyte.

INTRODUCTION

Manganese dioxide has been used as a cathode for fabricating lithium/manganese dioxide cells in non-aqueous media [1,2,3]. One of the solvents used for this purpose is propylene carbonate (PC). MnO_2 used for the Li/ MnO_2 cells

is gamma MnO_2 or beta MnO_2 . Generally, occluded water in the above forms of MnO_2 is removed by heating the cathode material for more than 48 hours at 400°C . The sample thus obtained becomes suitable for the cathode of a lithium-manganese dioxide cell. The reduction behaviour of MnO_2 is not well understood in spite of several investigations conducted [1,4,5] by various research workers. This paper attempts to study in a detailed way the behaviour of MnO_2 in propylene carbonate containing LiClO_4 by cyclic voltammetric experiments.

EXPERIMENTAL

a] Apparatus

A Wenking potentiostat LB75 H, Scan Generator VSG 72 and a Digilog 2000 x-y recorder with module types 7 and 8 each having 17 ranges of sensitivity were used. An IR drop compensator was specially designed for these experiments to compensate the high resistance of the non-aqueous medium.

b] Cell

A three electrode cell was used for experiments. A Pt foil was used as an auxiliary electrode and Li metal as reference electrode. Provision was made for bubbling

Argon gas through the cell to have an inert atmosphere. The Argon gas was purified by means of a 'Rare gas purifier 4' supplied by M/s British Oxygen Ltd., London.

The experiments were conducted by keeping the cell in a glove box as described below. Silica gel (BDH) was used for indicating the relative humidity and P_2O_5 (Ranbaxy) was used for drying the atmosphere. Before introducing the cell Argon was flushed inside the glove box.

c] Electrodes

EMD obtained from Central Electrochemical Research Institute, Karaikudi, India, has been used for preparing the electrode. The EMD was washed several times to remove chloride impurities and then powdered and sieved. MnO_2 powder was sieved through a mesh size of 200. This was heated to 450°C for more than 48 hours to get beta MnO_2 [1]. This was mixed with 10% acetylene black and colloidal PTFE binder and dried at 110°C for two hours. Pellets were made at a pressure of 5000 kg/cm^2 . The substrate for the pellet was nickel mesh. Leads were taken from this mesh through a glass tube for electrical connections.

Platinum foil electrode was cleaned in nitric acid, washed with water followed by a wash in acetone and dried.

d] Electrolyte

PC supplied by Riedel, W. Germany was distilled under reduced pressure and dried over 4 A molecular sieves

(Linde). This sample was further distilled with Li metal powder (Foote, USA). Water content was brought down to 30 ppm and estimation of water content was done by an automatic Karl Fischer Titrimeter (Toshniwal, India). LiClO_4 sample (fluka) was dried under vacuum at 120°C for 48 hours. The solutions were prepared in a glove box.

Cyclic voltammograms for various concentrations ranging from 0.5 M to 2 M LiClO_4 in PC were obtained for sweep rate of 20 mV sec^{-1} . Potential scans were made from Rest potential (+ 3.2 V) up to + 2 V and back. All experiments were conducted after 15 minutes of immersion of the MnO_2 electrode in the electrolyte.

RESULTS AND DISCUSSION

Fig. 1 to 3 show the voltammograms for the beta MnO_2 . The non-stoichiometry of MnO_2 is in the ratio of 1:0.8. For a 0.5 M LiClO_4 concentration in PC, the reversibility of the MnO_2 is affected. This is due to the fact that the reduction of MnO_2 has not favourably occurred in this concentration. But on increasing the concentration to 1 M, a reversible voltammogram is obtained indicating that reduction of MnO_2 takes place at a peak potential of 2.65 with respect to lithium. The same condition is repeated for 2 M solution. However, there are two peaks at 2.85 V and 2.35 V indicating that the reduction is not taking place in a single stage and involves more detailed examination.

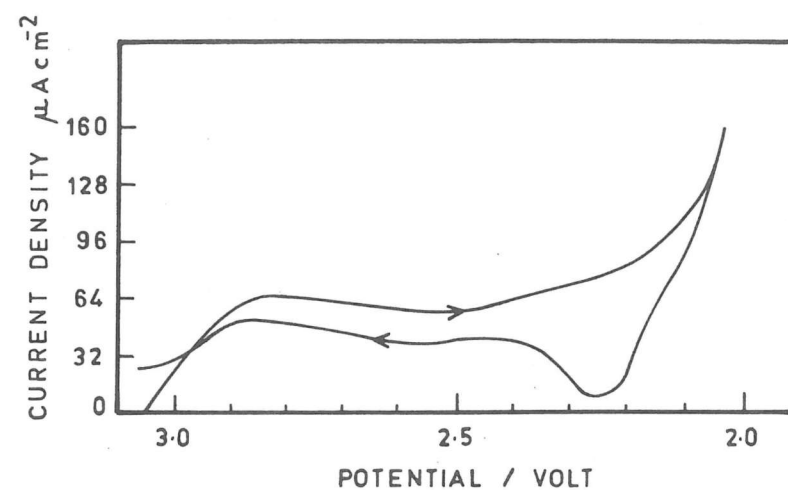


FIG.1. CYCLIC VOLTAMMOGRAM OF MnO_2 IN PC CONTAINING LiClO_4 (0.5 M) SWEEP RATE : 20 mV S^{-1}

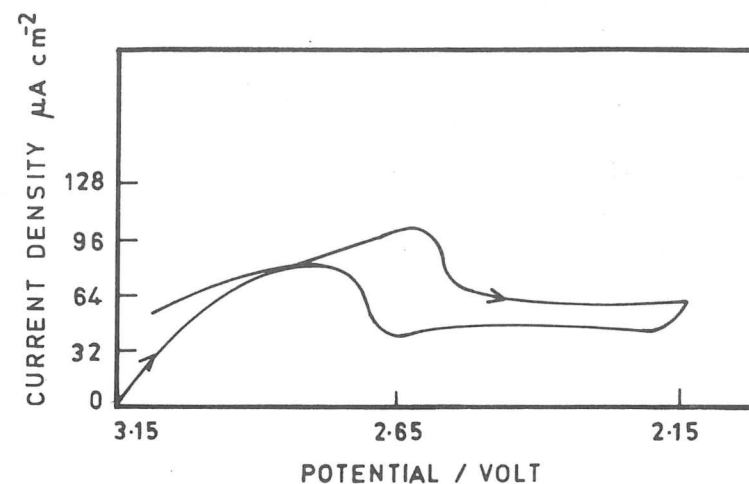


FIG.2. CYCLIC VOLTAMMOGRAM OF MnO_2 in PC CONTAINING LiClO_4 (1.0 M) SWEEP RATE : 20 mV S^{-1}

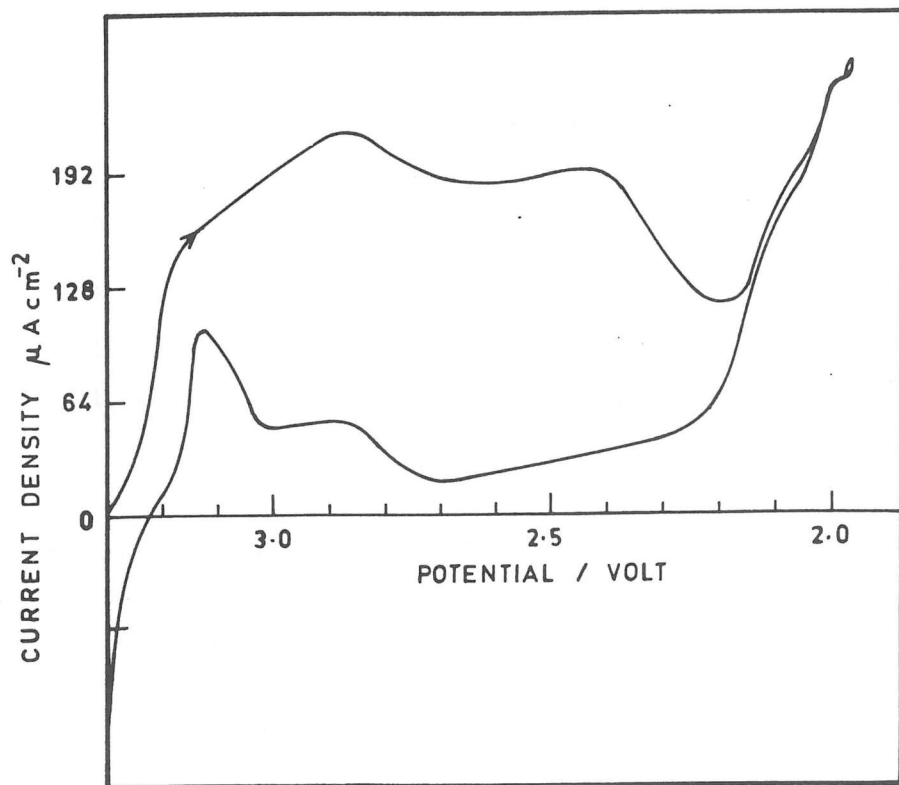


FIG.3. CYCLIC VOLTAMMOGRAM OF MnO_2 IN PC CONTAINING $LiClO_4$ (2.0M). SWEEP RATE : 20 mVS^{-1}

The possible mechanism of reduction MnO_2 in a lithium cell first predicted by Ikeda [1] is that the intercalation of Li into the pores of MnO_2 takes place and $Mn^{3+}(Li^+)O_2$ type of compound is formed. This has been further experimentally verified by Maria et al [4] in their chronopotentiometric studies. But in all these experiments the above authors have used Li as an auxiliary electrode and it is quite likely that the electronic reduction of MnO_2 is accompanied by the dissolution of Li ions. In this investigation experiments have been carried out using inert Pt electrode in the place of Li. In such a situation we expect that the possible electronic reduction of MnO_2 might be different from the one which has been predicted by Ikeda. It is evident from the changes of concentration, starting from 0.5 M to 2 M, the pattern of cyclic voltammogram vary from no peak to two peaks. As the concentration increases from 1 M to 2 M, the process of reduction of MnO_2 varies. Tikhonov and his coworkers [6] suggested that a chemical reaction might follow the reduction of MnO_2 . From the variation of concentration of the electrolyte the mechanism of the reduction varies. Hence, the observation made by Ikeda and Tikhonov for specific reduction of MnO_2 do not agree with the present results. We conclude that in presence of an inert electrode the reduction of MnO_2 depends on concentration of the electrolyte possibly varying from chemical to electrochemical reduction.

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A Voltammetric Study of Silver Electrodeposition Coupled
with Hydrogen Peroxide Oxidation and Reduction
on Carbon Microelectrodes

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ABSTRACT

Measurements are reported of the linear sweep voltammograms of silver on the presence of mixed catalytic oxidation/reduction of hydrogen peroxide on to vitreous carbon microdisk electrode. The catalytic rate constants were determined by performing theoretical simulations of the expected responses of the current-potential profiles and good agreement was found between these calculated profiles and the experimental responses in the cathodic branch for $k_2^0 = 2.5 \cdot 10^{-6} \text{ mol cm}^{-2} \text{ s}^{-1}$. The occurrence of a nonelectrochemical pathway reaction associated to the catalytic behaviour of hydrogen peroxide at silver substrates was observed experimentally and the density flux rate constant of this reaction was found to be $3.2 \cdot 10^{-6} \text{ mol cm}^{-2} \text{ s}^{-1}$.

INTRODUCTION

The coupled reduction and oxidation of hydrogen peroxide has been repeatedly investigated following the initial work towards the end of the last century [1]. The interest in this reaction has stemmed both from the view that it should be one of the simplest examples of catalytic processes (a view hardly born out by the results obtained experimentally) and, latterly, because of the participation of hydrogen peroxide as an intermediate in the technologically important