

CATHODIC POLARISATION OF MANGANESE DIOXIDE IN NONAQUEOUS MEDIA

A O SURENDRANATHAN, R GANGADHARAN and KI VASU

Central Electrochemical Research Institute, Karaikudi-623 006

ABSTRACT

Cathodic polarization of gamma-manganese dioxide in propylene carbonate, dimethoxyethane, dimethyl formamide and their mixtures was carried out. Experiments were also conducted for various current densities in propylene carbonate. It is concluded that for a given current density, manganese dioxide is more efficient as a depolariser in the mixture of solvents and that for a given solvent, the efficiency increased with decrease in current density.

Key Words: MnO_2 , Cathodic polarisation, Non aqueous media

INTRODUCTION

Manganese-dioxide is used as a cathode material for aqueous, alkaline and non-aqueous batteries. It occurs naturally (NMD) and also it can be synthetically produced in large quantities, both chemically (CMD) and electrolytically (EMD). The natural manganese dioxide (NMD) is not very efficient as a depolariser. Therefore, the synthetic varieties are generally considered for commercial battery purpose. Of the synthetic varieties, gamma-manganese dioxide obtained through chloride route by electrolysis is found to be the most suitable depolariser in the commercial world.

Zinc-manganese dioxide couple in alkaline and neutral media is used for fabricating cells which normally show voltages in the range 1.4 to 1.5 V [1]. These cells have low shelf life (2 to 3 years), high corrosion problems and poor efficiency. The reason for high corrosion and low efficiency is due to the need to use aqueous solutions in the cell.

In order to obviate the above difficulties, nonaqueous solvents are

Electrolyte

Lithium perchlorate (AR) was fused in vacuum for more than 48 hours [10]. This sample was used as the solute for preparing the electrolytic solution. Solutions of 1M concentration were used for the experiments.

Reference electrode

Lithium electrode has been extensively investigated in the course of battery development and appears to be stable and reversible in most highly purified aprotic solvents [3,11-17]. Lithium metal was cut into shape in dry box and then the electrode was prepared. This was used as the reference electrode for measuring the potentials of the manganese dioxide electrode.

The working electrode

The process of EMD production through chloride route had been developed successfully [18]. This was used as the cathode material. The bulk of the sample was sieved through a 200 mesh sieve and the -200 portion was used for experiments. SEM photographs of the sample

range of operation. For example, lithium-manganese dioxide cells in nonaqueous media show voltages around 3.2 V and their shelf life normally exceeds 5 years [2].

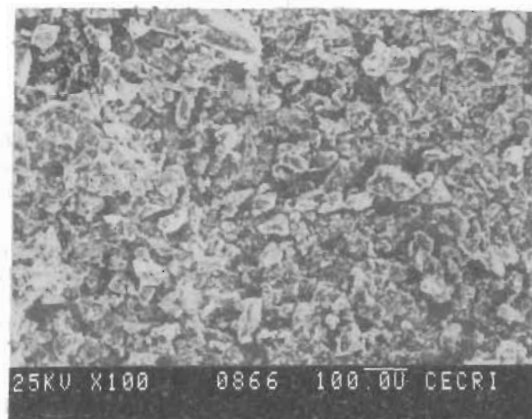
The purpose of this work is to find out the efficacy of gamma-manganese dioxide prepared through chloride route (F-type) when it is cathodically polarised using various nonaqueous solvents both in pure form as well as their mixtures at various current densities. Considerable amount of work has been done in aqueous solutions regarding the polarisation behaviour of manganese dioxide. But this work has now been extended to nonaqueous solutions.

EXPERIMENTAL

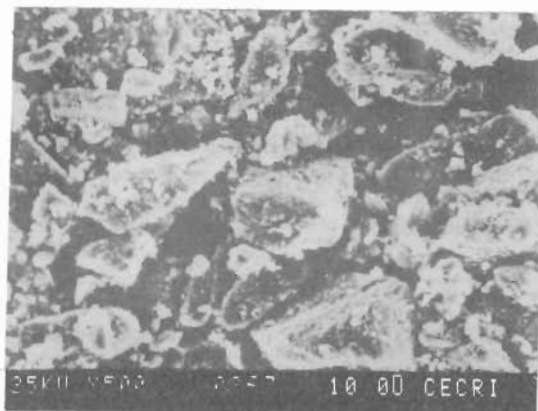
Organic solvents

Basically, three organic solvents were used for the experiments, namely, propylene carbonate (CPC), 1,2-dimethoxyethane (DMC) and N,N-dimethyl formamide (DMF). Since all the solvents are thermally unstable [3], they were purified by distillation under vacuum [4,5] in a three-stage distillation unit. The distilled solvents collected over molecular sieves [6-8] (Linde 4A) were carefully stored. The final drying was carried out using lithium metal [9].

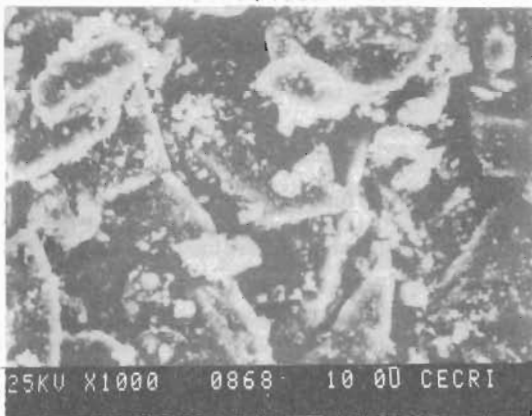
Fig. 1: (a,b,c). SEM Photographs of γ -EMD at 100X, 500X and 1000X



(a)



(b)



(c)

The manganese dioxide was dried in an air oven and mixed with acetylene black in the ratio 9:1 by weight. To this mixture was added a suitable binder to make pellets of dimensions 11 mm dia and 2 mm height to fit into the electrode end. Proper electrical contacts were made from the manganese dioxide pellet. One each of this kind of electrode was used as the working electrode. The amount of manganese dioxide had been noted before each experiment.

Auxiliary electrode

A circular portion of sufficient area was cut from a thin platinum sheet. This was fixed in the electrolytic cell and electrical contact was made. This served as the auxiliary electrode.

The experiments

All the experiments were carried out in a dry box.

Sufficient quantity of propylene carbonate containing lithium perchlorate of 1M concentration was taken in a dried electrolytic cell. The above mentioned electrodes were placed in it in such a way that the interfacial distance was at a minimum. The connections for electric current were made as shown in Fig. 2.

Keeping the current constant, potentials at various times were noted from the printing voltmeter. Readings were taken for currents of 12, 10, 8, 6, 4, 2 and 1mA and also for 750, 500 and 250 μA. Experiments were repeated for reproductivity. For each experiment, the potential versus time curves were drawn. From these graphs, the ampere-hr and watt-hr efficiencies were calculated.

Similar experiments were carried out in 1,2-dimethoxyethane (DME) and N,N-dimethyl formamide (DMF) as solvents for 1mA current. The solutions were then mixed in 1:1 proportion by volume and with the

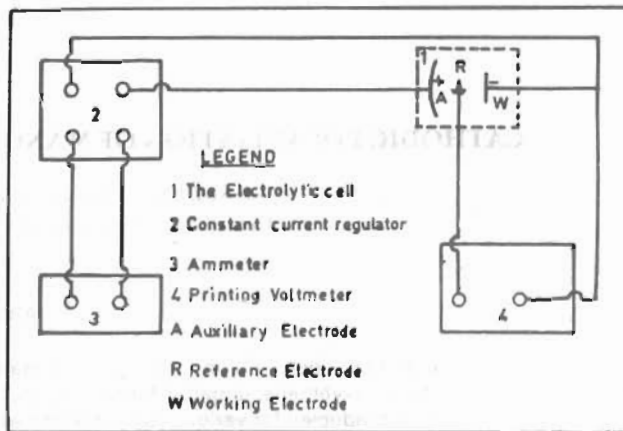


Fig. 2: Electrical circuit diagrams for polarization measurements mixture of solvents, again the experiments were repeated at 1mA current.

RESULTS AND DISCUSSION

Potential-time curves for PC

Discharge studies using gamma-manganese dioxide were carried out at low and high currents in order to understand the behaviour of the depolarisation action of manganese dioxide in LiClO₄ solution. Fig. 3 shows the potential-time curve in the mA range and Fig. 4 shows that in the μA range. At low current densities, the potential-time curves are

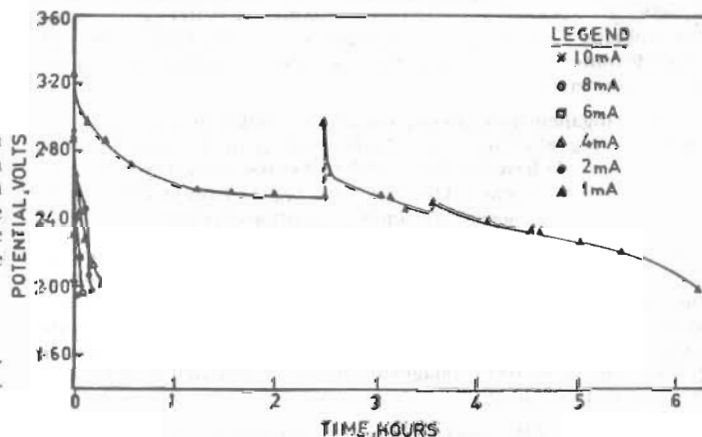


Fig. 3: Galvanostatic cathodic polarization of γ-EMD

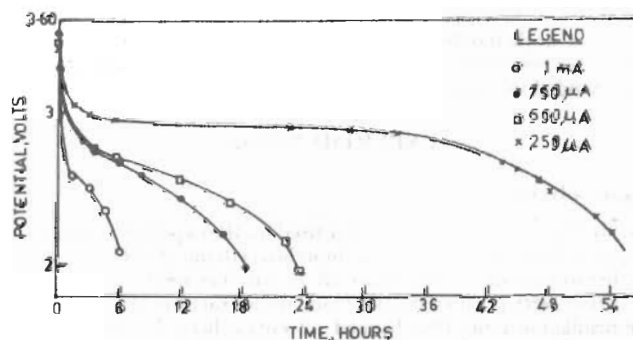


Fig. 4: Cathodic polarization of γ-EMD in 1M LiClO₄ in PC

fairly flat and at high current densities, they fall off considerably with time. Therefore, it can be concluded that the discharge behaviour of manganese dioxide is highly efficient at low current densities. This is in agreement with an earlier work [19] where the discharge current densities and the rate of cathodic utilization of manganese dioxide were related. It was shown that lower current densities gave better utilization.

The ampere-hr and watt-hr efficiencies obtained are given in Table I. The low ampere-hr efficiencies obtained for high current rates are attributed to the inefficiency for reduction at these rates.

Table I: Ampere-hr and watt-hr efficiencies for various current densities

Solvent	Current	Ah. efficiency (percent)	Wh. efficiency for 2 V cut off (percent)
PC	12 mA	3.2	65.1
PC	10 mA	3.6	62.1
PC	8 mA	6.0	72.6
PC	6 mA	5.1	72.8
PC	4 mA	3.8	72.5
PC	2 mA	3.3	75.7
PC	1 mA	8.5	75.2
PC	750 μA	17.7	70.1
PC	500 μA	46.2	74.3
PC	250 μA	51.7	80.0
DME	1 mA	16.0	72.8
DMF	1 mA	9.2	65.5
1:1::PC:DME	1 mA	52.3	85.5
1:1::PC:DMF	1 mA	20.0	76.3

Potential-time curves for various solvents

The results obtained for polarisation studies in various solvents are plotted in Fig. 5. The pure solvents containing LiClO₄ show shorter plateau compared with the mixture of solvents. PC + DME combination showed excellent result because the plateau is found to be twice that of PC + DMF combination. This may be due to the higher conductivity of PC + DME combination. Since the dielectric constants of DME and DMF are

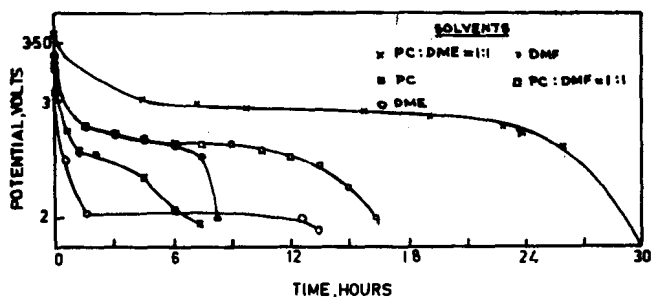


Fig. 5: Cathodic polarization of γ -EMD at 1 mA current

comparatively low as compared with that of PC, DME + DMF combination was not tried. Dielectric constant of a solvent is one of the factors that governs its conductivity [3]. The advantages of solvent mixtures for preparing the battery electrolyte have been indicated in an earlier communication [20].

The ampere-hr and watt-hr efficiencies obtained for these experiments are also shown in Table I. From this, it can be stated that PC + DME combination must perform well in lithium-manganese dioxide cells.

Current-ampere-hr efficiency curves

From Table I, the values of ampere-hr efficiency for different current

values in the case of PC were taken to plot the current-ampere hour efficiency curve (Fig.6). It is seen from the curve that the ampere-hour effi-

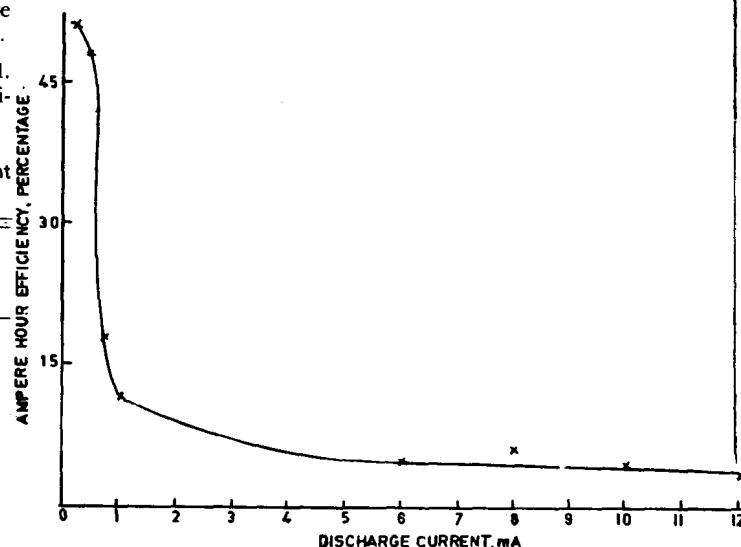


Fig. 6: Cathodic polarization of γ -EMD: Ah-efficiency vs discharge current solvent = PC. Electrolyte = LiClO₄

ciency is maximum at low currents whereas at high current values, it is minimum. The Faradaic inefficiency to reduce manganese dioxide begins above 1 mA current.

CONCLUSION

From these investigations, the following conclusions can be drawn:

1. The efficiency of gamma manganese dioxide (F type) decreases with current density for a given solvent
2. Suitable mixture of solvents gives better performance in a cell when the electrolyte is prepared out of it
3. 1:1::PC:DME mixture can be recommended for lithium-manganese dioxide cells.

REFERENCES

1. R Gangadharan, *Batteries Bulletin*, 1-1 (1983)
2. H Yamin and E Peled, *Proc Symp Lithium Batteries*, A N Dey, Ed. Washington (1983)
3. *Advances in Electrochemistry and Electrochemical Engineering*, Vol. 7, Eds. Paul Delahay and Charles W Tobias, Wiley-Interscience (1971)
4. R J Jaisinski, *High Energy Batteries*, Second Quarterly Report on Contract No-66-0621-C, Sept. (1966)
5. E I Du Pont Company, *Dimethyl Formamide Technical Bulletin*, (1960)
6. G H Aylward, J L Garnett and J H Sharp, *Anal Chem*, **39** (1967) 457
7. S B Brummer, *J Chem Phys*, **42** (1965) 1636
8. *Lithium Battery Technology*, H V Venkatesetty, John Wiley & Sons (1984)
9. A Morita, T Iijima, T Fujii and H Ogawa, *J Power Sources*, **5** (1980) 111
10. T W Richards and M Cox, *J Am Chem Soc* **36** (1914) 819

Surendranathan etal — cathodic polarization of MnO_2 in nonaqueous media

11. R G Selim, K R Hill and M L B Rao, *Research and Development of a High caapacity Nonaqueous Secondary Battery*, Final Report, Chem Abstr **66**, 121447
12. H F Banman, J E Chilton, W J Comer and G M Cook, *New Cathode-Anode Couples Using Nonaqueous Electrolytes*, Final Report, Contract No. AF 33 (616)-7957, Oct. 1963
13. D P Boden, H R Babner and V J Spera, *High Energy System (Organic Electrolyte)*; First Quarterly Report, Contract No. DA-28-043-AMC-0139(E), Oct. 1965
14. B Burrows and R Jasinski, *J Electrochem Soc* **115** (1968) 365
15. J E Chiton, *New Cathode-Anode Couples Using Nonaqueous Electrolytes*, Annual Report, Contract No. AF-33 (616) 7957, April (1962)
16. J E Chilton, W J Conner, G M*Cook and R W Holsinger, *Lithium-Silver Secondary Battery Investigation*, Final Report, Contract No. AF.33(615)-1195, Feb. (1965)
17. J E Chilton, and G M Cook, *New Cathode-Anode Couples using Nonaqueous electrolytes*, Annual Report, Contract No. AF.33(616)-7957, September 1962
18. V Aravamuthan, R Srinivasan, S C Chockalingam, S Kulandaswamy, C C Gopalakrishnan, J P R Raj, S Visvanathan and H V K Udupa, *Proc. 2nd Int Symp Industrial and Oriented Basic Electrochemistry*, Madras (1980) p 2.5.1
19. H Ikeda, *Lithium Manganese Dioxide Cells in Lithium Batteries*, J B Gabano, Ed. Academic Press, London (1983)
20. R Bates and Y Jumel, *Lithium cupric oxide cells on lithium batteries*, J B Gabano Ed. Academic Press, London