PERFORMANCE CHARACTERISTICS OF MnO_2 HEATED AT VARIOUS TEMPERATURES. AN IMPEDANCE STUDY WITH HEATED MnO_2 ON Li-MnO_2 CELL

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SUMMARY

Manganese dioxide exists in several crystalline forms. Heating MnO_2 in air or vacuum brings about changes in crystallinity. Heat-treated samples of MnO_2 at 373, 573, 723 and 1023 K were used in fabricating Li-MnO_2 cells. These cells were subjected to impedance measurements at 283, 293, 303 and 313 K temperatures. The R_{ct} and i_o values were calculated after subjecting to C_{dl} and R corrections. Tehse results are discussed.

INTRODUCTION

Manganese dioxide exists in several crystalline modifications. It is known to contain occluded water which influences its performance. Heating MnO_2 in air or vacuum brings about changes in its crystallinity and occluded water content [1]. The effect of heating MnO_2 on the impedance parameters of the Li/MnO_2 button cells have been investigated by us [2]. In a commercial energy storage cell, the system is far removed from the precise conditions of usual laboratory electrochemical cells, where each electrode could be studied individually. In a battery, the porosity of the electrode, the limited availability of electrolyte solution, presence of separator mterial and the roughness as well as the changing area of the electrodes make much difference. When we study the impedance response behaviour of a battery, we have to study in a two electrode system. The possible inclusion of a third electrode will alter the system.

Interpretation of impedance data on battery systems done so far have utilized the already established cell reactions. Butler-Volmer equation has been used to derive kinetic factors [3].

EXPERIMENTAL

Portion of Indian EMD [4] were heated in a furnace in air for 24 hours at 100°C (373 K), 300°C (573 K), 450°C (723 K) and 750°C (1023 K) respectively. Fused lithium perchlorate was used to prepare solutions in purified propylene carbonate [PC] and 1,2 Dimethoxy ethane (DME) of 1 M concentration , 3:1 and 1:1 ratios of PC:DME containing $LiClo_4$ (1 M) were prepared. Button cells were fabricated inside a dry box using pure lithium metal as anode and various EMD samples as cathodes. Several cells with each electrolyte composition were fabricated using cellulose separators.

Impedance measurements of these cells at frequencies ranging from 1 mHz to 20 KHz with a Solartron Frequency Response Analyser 1174 were conducted at different temperatures. Sluyter's plots were constructed and from these the solution resistance, R_{sol} and the charge transfer resistance, R_{act} were calculated. The exchange current density, i_o, and the double layer capacitance C_{dl} were also calculated from these data.

DISCUSSION

Impedance analysis of Li/MnO_2 system has been carried out recently [5].

The impedance parameters calculatd for the various cells are given in Tables 1 and 2. The general shape of the semi-circles were distorted owing to the changing area of the electrode and surface roughness. It is observed that the increase in temperature of experiment favours high i_o values and low R_{act} values. Higher i_o values are observed for the PC-DME mixture cells in comparison with our earlier work [2,6] where PC alone was used. The values of course show some variations. Higher temperature of experiments also favour better exchange characteristics, PC:DME of 3:1 composition has a better performance than the 1:1 composition. This is presumably due to the presence of more PC which has a good dielectric constant. But the addition of DME

TABLE 1

VARIATION OF R_{act} VALUES WITH SOLVENT COMPOSITION

Heating Temperature (K)	PC/Ohms	PC-DME/Ohms 3:1	PC-DME/Ohms 1:1
283 K			
373	450	260	425
573	370	580	700
723	520	850	320
1023	550	320	400
293 K			
373	255	170	260
573	180	325	325
723	310	135	200
1023	400	270	260
303 K			
373	260	300	300
573	280	220	200
723	550	150	325
1023	450	350	250
313 K			
373	200	135	115
573	115	100	140
723	300	70	115
1023	280	105	100

R_{act} = Charge transfer resistance
PC = Propylene Carbonate
DME = Dimethoxy ethane

TABLE 2

VARIATION OF i_o VALUES WITH SOLVENT COMPOSITION

Heating Temperature (K)	PC i_o (mA cm^{-2})	PC-DME i_o (mA cm^{-2})	PC-DME i_o (mA cm^{-2})
283 K			
373	0.035	0.061	0.037
573	0.043	0.027	0.022
723	0.031	0.018	0.049
1023	0.030	0.049	0.039
293 K			
373	0.063	0.096	0.063
573	0.092	0.051	0.051
723	0.053	0.120	0.082
1023	0.041	0.061	0.063
303 K			
373	0.065	0.100	0.057
573	0.060	0.078	0.084
723	0.031	0.111	0.053
1023	0.037	0.049	0.067
313 K			
373	0.087	0.129	0.153
573	0.150	0.175	0.120
723	0.059	0.240	0.153
1023	0.063	0.170	0.175

i_o = Exchange current density : DME = Dimethoxy ethane
PC = Propylene Carbonate

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