Impedance studies on lithium manganese dioxide cells

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Electrolytic manganese dioxide (EMD) samples were heated to 373K, 573K, 723K and 1023K. Li/MnO_2 button cells were fabricated using these EMD samples as cathode materials. These cells were investigated for impedance response. Kinetic parameters were calculated.

Key words: Impedance, lithium cell, electrolytic MnO_2

INTRODUCTION

It has been proved that heating MnO_2 in air or vacuum brings about changes in its crystallinity and occluded water content [1]. The effect of heating electrolytic manganese dioxide (EMD) on the impedance parameters of the Li/MnO_2 button cells has been studied. Butler-Volmer equation [2] has been used earlier to derive kinetic factors. Similar calculations were also made.

TABLE-I: Variation of kinetic parameters of heated MnO_2 samples with concentration of PC ($LiClO_4$)

	0.5M PC		1M PC		1.5M PC		2M PC	
MnO_2 heating Temp. K	R_{act} (ohm)	i_o ($mA.cm^{-2}$)	R_{act} (ohm)	i_o ($mA.cm^{-2}$)	R_{act} (ohm)	i_o ($mA.cm^{-2}$)	R_{act} (ohm)	i_o ($mA.cm^{-2}$)
At 283K								
373	165	0.096	450	0.035	1060	0.015	175	0.090
573	120	0.030	370	0.043	700	0.022	520	0.031
723	320	0.049	520	0.031	390	0.041	350	0.045
1023	250	0.063	550	0.030	1440	0.010	320	0.049
At 293K								
373	140	0.116	255	0.063	1030	0.016	180	0.090
573	82	0.020	180	0.092	360	0.045	200	0.082
723	105	0.150	310	0.053	250	0.065	190	0.086
1023	175	0.094	400	0.041	740	0.022	150	0.110
At 303K								
373	190	0.090	260	0.060	270	0.041	170	0.010
573	30	0.570	280	0.060	270	0.063	225	0.076
723	325	0.053	550	0.031	90	0.190	150	0.110
1023	275	0.061	450	0.037	1600	0.010	135	0.120
At 313K								
373	45	0.390	200	0.087	240	0.073	90	0.194
573	25	0.700	115	0.150	230	0.075	140	0.120
723	140	0.124	300	0.059	100	0.175	100	0.175
1023	140	0.120	280	0.063	400	0.043	50	0.350

EXPERIMENTAL

Details on heating EMD, purification of materials and cell fabrication have been reported earlier [3]. Impedance measurements of these cells at frequencies ranging from 1 mHz to 20 KHz with a Solartron FRA1174 were conducted at different temperatures. The cell was connected galvanostatically across 100 kilo ohms resistance and an a.c. signal of 100 mV was applied. Sluyter's plots were constructed and from these the solution resistance R_{sol}, charge transfer resistance R_{act}, exchange current density, i_o and double layer capacitance C_{dl} were calculated.

RESULTS AND DISCUSSION

The R_{act} and i_o values for these cells are given in Table I. Values of i_o observed in these experiments are from 1×10^{-2} mA.cm^{-2} to 7×10^{-1} mA.cm^{-2}. The heating of MnO_2 samples has altered the crystalline nature of the sample and hence the diffusion of lithium ions into the lattice would be altered. The highest i_o values are for the MnO_2 sample heated to 573K. At 313K, the cell with 0.5M propylene carbonate (PC) $LiClO_4$ solution and MnO_2 heated to 573K has an i_o value of 0.7 mA.cm^{-2} and at 303K the cell of the same composition has an i_o value of 0.57 mA.cm^{-2}. The R_{act} values are minimum for this sample. It is obvious that high temperature and low viscosity support good exchange behaviour. The R_{sol} also increases with concentration. Ion association, high viscosity and diffusion problems are probably enhanced at high concentration. The i_o value decreases with increase in concentration of electrolyte for the cell with MnO_2 (573K), the i_o values at 293K for 0.5M, 1M, 1.5M and 2M are 0.20, 0.092, 0.045 and 0.082 mA.cm^{-2} respectively. There is some deviation at 2M concentration . At 313K,i_o values are uniformly good at all concentrations. The i_o values are in the 10^{-2} level at 283K. Only from 293K onwards it starts increasing. I_o increases with increase in temperature and R_{act} decreases. The diffusion phenomenon which is very essential in electrolytic conduction is favoured at these higher temperatures.

CONCLUSION

It is clear that MnO_2 (573K) and 1M PC/$LiClO_4$ solution is the ideal composition for Li/MnO_2 cell for best performance.

REFERENCES

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