On the Synthesis of CMD from Manganese-Ammonium-Carbamate and its Properties IV. Heating Properties of Densified CMD and Application of Its Dehydrated Product to Li-MnO₂ Cells*

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The heating and dehydration properties in both air and O₂ atmosphere for densified CMD were compared with those of EMD, and the discharge properties and packing capabilities of these dehydrated products for Li-MnO₂ cells were investigated as follows. 1) In the DTA tests, the peak indicative of conversion to Mn₂O₃ shifted to a higher temperature by about 30°C in O₂ atmosphere (at 560°C) than in air for both CMD and EMD, and the dehydrated products in O₂ atmosphere had slightly higher MnO₂ content and hydrazine index than did those in air. In O₂ atmosphere, this might be attributable to the suppression of decomposition of MnO₂ on dehydration. 2) For both CMD and EMD, the optimum dehydration temperature was found to be about 380°C by the discharge tests. The dehydrated products obtained in O₂ atmosphere were shown to be superior in discharge properties to those of the products obtained in air. 3) The dehydrated CMD whose MnO₂ ratio by chlorate reaction was 22% showed higher tapping density, packing capability and discharge properties compared with those of EMD as the cathode material in Li-MnO₂ cells.

1 Introduction

In recent years, the dehydration properties of electrolytic manganese dioxide (EMD) and application of its dehydrated product to Li-MnO₂ cells have been investigated by Ikeda *et al.*¹⁾ and Hirai *et al.*^{2,3)}. However, our survey of the literature showed that the heating properties of CMD, the properties of its dehydrated product and its application to Li-MnO₂ cells have not yet been studied. In our preceding papers, the synthesis of dense MnCO₃ from Mn-NH₄-carbamate⁴⁾, its oxidation⁵⁾ and the densification of crude MnO₂⁶⁾ were described. This paper describes the heating property of densified CMD, the properties of the dehydrated product, the packing capability and discharge properties in Li-MnO₂ cells utilizing dehydrated CMD, and the comparison of these properties with those of EMD. For both CMD and EMD, their heating properties in both air (used conventionally) and oxygen were compared each other. The reaction of conversion to Mn₂O₃ occurred at a higher temperature by about 30°C in oxygen than in air, showing a

greater contribution of oxygen atmosphere to the quality of the dehydrated products. The effect of oxygen atmosphere on both the quality of the dehydrated products and the discharge properties was investigated in detail. Discharge tests of coin type Li-MnO₂ cells having these dehydrated MnO₂ material as cathode were performed.

2 Experimental

2.1 CMD and EMD samples

As shown in Table 1, densified CMD samples were chosen and IC-1 (No. 7) was selected as the EMD sample. The No. 1 sample was obtained by further oxidation (in 3 atm wet O₂) of crude MnO₂ previously obtained by oxidation of dense MnCO₃ in wet air. No. 2~6 samples having various degree of densification were obtained by chlorate reaction of the No. 1 sample.

2.2 Heating property and dehydration treatment

Both DTA and TG were performed up to 600°C at a heating rate of 5°C/min in both air and oxygen atmosphere to evaluate the difference in their heating properties. Samples in this experiment include the lightest CMD (No. 1 sample which was not subjected to the densification Process), the densest CMD (No. 6) and EMD (No. 7). A 20 g sample was heated in an electric furnace at 200°C to 420°C for 4 h

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Table 1 Densified CMD by chlorate reaction

Kind	No.	MnO ₂ (%)	MnO ₂ ratio by chlorate reaction to total MnO ₂	H.I.	B.D. g/cm ³	T.D. g/cm ³	True. D. g/cm	Water adsorp. (%)	Ion exchange cap. Zn ²⁺ × 10 ⁻⁵ mol/g	Surf. A. m ² /g
CMD	1	91.0	0	57.2	1.53	1.74	4.69	38.5	35.5	57.4
	2	92.4	12.2	58.6	1.74	2.07	4.74	27.5	45.3	54.6
	3	92.2	20.5	57.9	1.92	2.25	4.71	24.5	42.5	48.5
	4	92.3	22.1	57.5	2.00	2.30	4.70	22.8	39.7	44.1
	5	92.3	24.6	56.5	2.06	2.42	4.65	20.2	38.0	39.2
	6	92.3	27.5	55.9	2.13	2.43	4.65	19.2	37.8	38.0
EMD	7	91.1	—	56.2	1.49	2.32	4.46	19.2	37.1	58.5

in both air and oxygen which were dried in Mg (ClO₄)₂, at a flow rate of 15 L/h. The residual water content in the dehydrated products at 110°C was determined by absorbing the water released at 750°C by Mg (ClO₄)₂ in N₂ as the carrier gas. The MnO₂ content and apparent density of the dehydrated products were determined in accordance with JIS, the hydrazine index (H.I.) by the Drotschmann⁷⁾ method, and the specific surface area by the BET process.

2.3 Shaping and packing capability of cathode mix utilizing the dehydrated products

As shown in the standard mixing ratio (CMD-1 and EMD-1) in Table 2, dehydrated MnO₂, acetylene black (A.B.), graphite and Teflon powder were thoroughly mixed together; a 250 mg sample weighed accurately was pressed into a cylindrical shape 17.2 mm in diameter at a pressure of 500 kg/cm² and dried *in vacuo* at 120°C. The thickness of the shaped product was measured. The electrolyte was 1 M LiClO₄, which was dried *in vacuo* at 120°C and dissolved in propylene carbonate which had been dehydrated by passage through a molecular sieve.

The absorption ratio of electrolyte in the cathode mix was measured; the cathode mix was immersed in the electrolyte for 5 hours and weighed after the solution adhering to its surface was wiped off with dry filter paper.

2.4 Discharge tests

As shown in Fig. 1, a test cell was made of nickel-plated brass with an effective electrode area of 2.3 cm² and was screwed into the framework. The discharge tests were carried out in a dried argon atmosphere at 20 ± 1°C, using the cathode mix in Table 2. The lithium

Fig. 1 Li-MnO₂ cell used for the experiment

Table 2 Composition of the cathode mix of CMD (22% MnO₂ by chlorate reaction to total MnO₂) and EMD

Kind	Combination No.	MnO ₂ (mg)	A.B. (mg)	Graphite (mg)	Teflon (mg)	Thickness of pressed cathode mix (mm)
CMD	1	175 (70)	18.8(7.5)	18.8(7.5)	37.5(15)	0.565
	2	186.4(70)	20.0(7.5)	20.0(7.5)	39.9(15)	0.60
	3	175 (70)	20.6(8.2)	20.6(8.2)	37.5(15)	0.595
EMD	1	175 (70)	18.8(7.5)	18.8(7.5)	37.5(15)	0.60

() : ratio

electrode of about 1 mm thickness (about 0.12g), as the anode material, was made of Li metal (99.9% purity, Rare Metallic Co.). The duration times of discharge down to 1.5 V at from 0.025 to 0.5 mA/cm² were measured and the discharge efficiencies were calculated.

3 Results and Discussion

3.1 Heating properties and the effect of oxygen atmosphere on the properties of the dehydrated products

Figures 2 and 3 show the results of TG and DTA in both air and oxygen for CMD No. 1, CMD No. 6 and EMD No. 7. It was noted that the temperature indicative of the conversion to Mn₂O₃ for both CMD and EMD shifted to the higher side by about 30°C in an oxygen atmosphere (at about 560°C) compared to that

ionally¹⁾ for MnO₂ in Li-MnO₂ cells was 350~400°C. A part of the MnO₂ was considered to decompose in view of the difference in both the MnO₂ content and the weight between before and after dehydration. Therefore, it was confirmed that the oxygen atmosphere suppressed the decomposition of MnO₂.

The dehydration of both CMD and EMD at from 200°C to 420°C was performed in both air and oxygen, and the residual water content, the MnO₂ content of the dehydrated products as well as the hydrazine index were determined.

The residual water content corresponding to each dehydration temperature are shown in Fig. 4. Although the residual water content in EMD is more than that of CMD at room temperature, it became almost the same as that of the dehydrated CMD obtained by treatment above 200°C for 4 h; it amounted to 0.5~0.6% at 380°C and dropped down to 0.35% at 420°C.

Fig. 2 Results of TG on both CMD and EMD in both dry air and dry O₂

Fig. 3 Results of DTA on both CMD and EMD in both dry air and dry O₂

in air, indicating the more favorable contribution of oxygen to their heat stability.

The dehydration temperature used convent-

Fig. 4 Relation between dehydration temperature and residual water content at 110°C

The variations in MnO₂ content and hydrazine index due to the dehydration temperature are shown in Fig. 5. For both CMD and EMD, the MnO₂ content of the dehydrated products in oxygen atmosphere was higher than that obtained in air by 0.3~0.7%, its difference increasing with the increase in dehydration temperature. It was noted that the MnO₂ content of EMD increased much more than that of CMD. The decrease in hydrazine index with the increase in dehydration temperature was especially significant for EMD in both cases. For both CMD and EMD, both the MnO₂ content and the hydrazine index of the

dehydrated products obtained in oxygen atmosphere were a little higher than those of the products obtained in air.

Fig. 5 Relation between dehydration temperature and both MnO_2 content and H.I. of the dehydrated products

*Calculated MnO_2 % from wt. loss by heating

The higher MnO_2 content and hydrazine index of the dehydrated products in oxygen as compared to air might be attributable to the suppression of decomposition of MnO_2 in the course of the dehydration. The difference in hydrazine index between the dehydrated products of both CMD and EMD might be mainly attributable to the significant difference in the specific surface area of the dehydrated products.

3.2 The degree of densification of CMD, properties and packing capability of its dehydrated products

Dehydration was performed in oxygen atmosphere at 380°C , the optimum dehydration temperature as described later, for samples No. 1~No. 6 in Table 1. The variation in MnO_2 content, residual water content and hydrazine index of the dehydrated products due to MnO_2 ratio by chlorate reaction to total MnO_2 are shown in Fig. 6. For various MnO_2 ratios by chlorate reaction to total MnO_2 , Fig. 7 shows the tapping density of the dehydrated products, the thickness of the cathode mixes having a standard mixing ratio and absorption ratio of electrolyte in cathode mix.

Fig. 6 Relation between MnO_2 ratio by chlorate reaction to total MnO_2 and properties of the dehydrated products (in O_2 atmosphere for 4 h at 380°C)

Fig. 7 Effect of MnO_2 ratio by chlorate reaction to total MnO_2 on T.D. of the dehydrated products at 380°C , thickness and absorption ratio of electrolyte in cathode mix after pressing (Cathode mix : Mix ratio was CMD-1 and EMD-1 in Table 2)

The slightly higher MnO_2 content of the dehydrated products of EMD compared to those of CMD might be due to the larger weight loss of EMD during dehydration. The hydrazine index decreased considerably with increasing MnO_2 ratio by the chlorate reaction when the ratio was above 23%; whereas, it decreased slightly when the ratio was below 22%. Therefore, it is considered that the dehydrated products, whose MnO_2 ratio by the chlorate reaction is above 23%, have undesirable discharge properties in Li- MnO_2 cells. It was

observed that the apparent density of the dehydrated product of CMD was larger than that of EMD when the MnO_2 ratio by the chlorate reaction to total MnO_2 was above 22%. It might be due to the smaller weight loss of CMD compared with EMD in the dehydration process. The thickness of the cathode mix utilizing the dehydrated CMD in the case of the 22% ratio was considerably smaller compared with that of EMD due to the higher compression ratio of CMD. The absorption ratio of the cathode mix utilizing the dehydrated CMD (22% ratio) was almost the same as that of EMD.

3.3 Crystal structure of the dehydrated products

The X-ray patterns of the dehydrated products for both CMD (No. 4 in Table 1) and EMD (No. 7) are shown in Fig. 8. EMD exhibited the γ -type peak at 200°C, a broad pattern similar to that of CMD (No. 1 in Table 1 at room temperature) at 300°C, the β -type peak at 350°C, and a higher β -type peak at 380°C. The CMD exhibited the β -type peak at 300°C, and its peak became a sharp pattern at 350°C indicating obviously that CMD decame β -type at a lower temperature by about 50°C compared with EMD. The difference in those temperatures between the dehydrated

Fig. 8 Effect of the dehydration temperature on X-ray diffraction patterns of both CMD No. 4 and EMD

*: γ -type peak, *: β -type peak

products of CMD and EMD might be mainly due to the difference in the residual water content. The dehydration temperature of those materials used in this experiment was higher than that used by Ikeda *et al.*¹¹. This difference might be attributable to the difference in the conditions of these experiments.

3.4 Discharge properties

3.4.1 The optimum dehydration temperature for discharge properties and effect of oxygen atmosphere

In order to obtain the optimum dehydration temperature for the longest duration time of discharge, discharge tests were performed at 0.25 mA/cm² on the dehydrated products obtained at various temperatures for both CMD (No. 4 in Table 1) and EMD (No. 7). Figures 9 and 10 show the results of discharge tests at 0.25 mA/cm² for both CMD and EMD. The dehydration tem-

Fig. 9 Results of 0.25 mA cm⁻² discharge tests of dehydrated products of No. 4 CMD in both O₂ and air atmosphere (Cathode mix: Mix ratio was CMD-1 in Table 2)

Fig. 10 Results of 0.25 mA cm⁻² discharge tests of dehydrated products of EMD in both air and O₂ atmosphere (Cathode mix: Mix ratio was EMD-1 in Table 2)

perature at which the duration time down to 1.5 V was the longest was determined as the optimum one. Thus, it was concluded that the considerably longer duration time of discharge was obtained in oxygen.

3.4.2 The degree of densification and discharge properties The relation between the MnO_2 ratio by the chlorate reaction to total MnO_2 and the discharge properties for their dehydrated CMD obtained in oxygen at 380°C was investigated. A cathode mix having a standard mixing ratio (CMD-1 in Table 2) was used in this experiment. This result was compared with that for dehydrated EMD as shown in Fig. 11. With increased MnO_2 ratio by the chlorate reaction, the duration time was only slightly decreased up to 22%; whereas, it was considerably decreased for more than 23%. It is noted that the dehydrated product of CMD whose MnO_2 ratio is 22% showed a considerably longer duration time compared with that of EMD obtained in both air and oxygen.

Fig. 11 Relation between MnO_2 ratio by chlorate reaction to total MnO_2 and performance in 0.1 mA/cm^2 discharge test (Cathode mix: Mix ratio was CMD-1 and EMD-1 in Table 2)

3.4.3 Discharge current density, packing capability and the composition of the cathode mix As shown in Fig. 12 for the dehydrated products of both No. 4 CMD obtained in oxygen and EMD (No. 7) obtained in both air and oxygen, respectively, discharge tests at $0.025\sim 0.5 \text{ mA/cm}^2$ were performed with a cathode mix having both a standard composition and packing quantity. The dis-

charge efficiency and duration time increased considerably with decreasing discharge current density. The dehydrated product of No. 4 CMD obtained in oxygen atmosphere was shown to be superior in discharge properties.

Fig. 12 Relation between current density and discharge performance

The superior packing capability of CMD (No. 4 in Table 1) compared with EMD of standard composition resulted in an increase in packing quantity of the cathode mix with the same thickness compared with dehydrated EMD having the standard packing quantity. This result (CMD-2 in Fig. 12) showed that the discharge efficiency was almost the same as that for the standard composition, the duration time being observed to increase in proportion to the weight of the MnO_2 in the cathode mix.

The quantities of both acetylene black and graphite were increased in the cathode mix with the same thickness as that of the dehydrated EMD having the standard packing quantity, with the quantities of MnO_2 and Teflon being unchanged. As shown in Fig. 12(CMD-3), it was shown that the increase in quantity of both acetylene black and graphite resulted in increased discharge efficiency, though the duration time did not increase so much as in the case of increased MnO_2 .

These results led to the conclusion that the dehydrated product of CMD No. 4 obtained in oxygen atmosphere showed a longer duration time than that of EMD in air due to its better

discharge efficiency and packing capability.

4 Conclusion

The heating and dehydration properties in both air and oxygen atmospheres for the densified CMD were compared with those of EMD, and the discharge properties and packing capability of these dehydrated products for Li-MnO₂ cells were investigated as follows.

1. In the DTA tests, the peak indicative of conversion to Mn₂O₃ shifted to a higher temperature by about 30°C in oxygen atmosphere (at 560°C) than in air for both EMD and CMD. For both CMD and EMD, the dehydrated products obtained in oxygen showed a definitely higher MnO₂ content and hydrazine index than did those obtained in air, though the effect of the oxygen atmosphere was small. It was considered that the oxygen atmosphere suppressed the decomposition of MnO₂ during dehydration.

2. The hydrazine index of the dehydrated CMD was considerably higher than that of EMD at the same dehydration temperature. The hydrazine index of the dehydrated product for CMD showed the same hydrazine index in spite of the increase in the MnO₂ ratio by the chlorate reaction when the ratio was less than 22%; whereas, for more than 23%, its value

decreased with increasing MnO₂ ratio.

3. For both CMD and EMD, the optimum dehydration temperature was estimated to be about 380°C from the discharge properties, and the dehydrated products obtained in oxygen atmosphere were shown to be superior in discharge properties to those of the products obtained in air.

4. The dehydrated CMD whose MnO₂ ratio by the chlorate reaction was 22% showed excellent packing capability and discharge properties compared with those of EMD as the cathode material in Li-MnO₂ cells.

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