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Synthesis of carbon/EMD composite from carbon-suspended sulfuric acid and manganese sulfate bath

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Abstract

A study has been made of the electrodeposition of MnO_2 on a titanium anode from a carbon or carbon/MnO_2 composite suspended in a H_2SO_4–$MnSO_4$ bath. Electrolytic manganese dioxide (EMD) containing acetylene black or vapour-grown carbon fibre shows excellent alkaline battery performance and good grindability. Nevertheless, passivation of the titanium anode sometimes occurs during electrolysis at a current density of 1 A dm^{-2}. This problem is successfully resolved without loss of battery performance, by using carbon/δ-MnO_2 as suspension particles. Apart from producing EMDs with good grindability and excellent battery performance, this bath has several other advantages, namely: easy maintenance of the dispersion; good reproducibility; low anode potential during electrolysis, and higher carbon content. It is proposed that a close relationship exists between battery performance and the surface characteristics of EMDs such as BET surface area and pore size.

Introduction

Electrolytic manganese dioxide (EMD) is usually produced by anodic oxidation of manganese ions from a bath of $MnSO_2$ that contains H_2SO_4 at 90 to 98 °C. At present, titanium plate is used for the anode because its good resistance to passivation extends the service life to several years. A low current density (i.e., 0.6 to 0.7 A dm^{-2}) is normally used for the preparation of EMD for application as cathode material in alkaline MnO_2 batteries. The production cost of EMD is increased, however, on lowering the current density. Moreover, the hardness of the EMD is increased and this causes harmful impurities (e.g., iron) to become incorporated during the subsequent crushing process. That is, the quality of the EMD is lowered.

Significantly higher current densities can be applied with a manganese oxide suspension bath [1–3] without suffering passivation of the titanium anode. This lowers the cost of EMD production. Unfortunately, however, the EMD obtained by this method shows low battery performance in alkaline batteries at high discharge rates.

A carbon/EMD composite is expected to have high grindability, and to give high performance because the resistivity of EMD is lowered by the presence of carbon. Given this possibility, Matsuki *et al.* [4] have tried co-deposition of carbon with EMD (carbon/EMD) from a bath that contained sulfonated acetylene black (AB) as suspended particles in a sulfuric acid–manganese sulfate solution.

In this study, carbon materials have been suspended in a sulfuric acid and manganese sulfate bath by using surface-active agents, instead of sulfonation, in order

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to avoid the lower conductivity of the sulfonated carbons. Excellent carbon/EMDs for alkaline batteries have been obtained by this method but, at times, the titanium anode exhibits high potential during electrolysis because of passivation effects. It has been found that the presence of a dispersed carbon/δ-MnO_2 composite in the electrolyte can successfully protect the titanium anode against passivation without affecting the electrochemical properties of the resulting carbon/EMD composite.

Experimental

The following carbon materials were used as the suspended particles: acetylene black (AB) (Denki Kagaku Co.) with surface area 30 (AB-30) and 130 (AB-130) m^2 g^{-1}; Ketjenblack (Japan EC); graphite (Toyoh Carbon Co.), and vapour-grown carbon fibres (VGCF).

The VGCFs were synthesized from benzene by the CVD method [5] and used ferrocene and thiophene as catalysts. The resulting carbon fibre, produced at 1170 °C, was washed in a diluted H_2SO_4 solution (0.1 M) that contained 0.5 g of Triton X-100 to remove iron impurities.

A composite of carbon and δ-MnO_2 was prepared as follows. A sample of 3 g of AB-30 was dispersed in 1 l of distilled water that contained 100 mg of trimethylstearyl ammonium chloride. Next, 22.75 g of $MnCl_2 \cdot 5H_2O$ was dissolved in the solution, and then 1 l of 1.1 M KOH was added [6]. Oxidation of the Mn^{2+} ions was carried out with oxygen gas at ambient temperature. The resulting AB-30/δ-MnO_2 composite was filtered and dried at 120 °C for 2 h.

The electrolysis procedure was performed in a cylindrical Pyrex cell (500 cm^3). Carbon counter electrodes were placed on both sides of a titanium anode. A reflux condenser was attached at the top of the cell to prevent any water loss during electrolysis.

Anodic deposition of EMDs was carried out from a bath of 1.0 M $MnSO_4$ and 0.4 M H_2SO_4 that contained a suspension of carbon dispersed by a surface-active agent (SSA) at 98 ± 1 °C. A constant current density of 1.0 A dm^{-2} was applied for 20 h. Homogeneous dispersion of AB was carried out by mechanical mixing using a homogenizer (Silverson L4R) in the presence of the SSA.

The given EMD was removed from the bath and washed with distilled water. The deposit was dried at 80 °C and ground to a fine powder (less than 20 μm). The powder was neutralized to a pH of 6.5 with 25% NaOH solution. The EMD samples were analysed by X-ray diffraction. The percentage of MnO_2 and the surface area were measured by the ferrous sulfate [7] and the BET [8, 9] methods, respectively.

The deposited EMD was cut to rectangular plate, and the conductivity was determined by the four-probe method.

The nitrogen-absorption isotherm for each EMD was measured with a Quantachrome-1 instrument. Samples were outgassed at 200 °C for 20 min.

The discharge test of the EMD was essentially the same as that reported in ref. 10. The use of the conductive binder (CB), however, was different [11]. In this study, 100 mg of powdered EMD was mixed with 30 mg of conductive binder (polytetrafluoroethylene–AB composite). A ceramic motor was then used to fabricate the mixture into a sheet. This sheet was pressed on a stainless-steel screen at 800 kg cm^{-2}. The electrode was discharged at 50 mA per g of EMD in a glass jar containing 9 M KOH. The counter and reference electrodes were platinum and Hg/HgO/9 M KOH, respectively. The measurements were conducted under a flow of nitrogen ($\sim$30 cm^3 min^{-1}) to remove dissolved oxygen.

Polarization measurements were performed at the 10 mAh discharge stage. An electrode containing 100 mg of powdered EMD was discharged continuously at 2 mA for 5 min and at 5 mA for 2 min after a 10 h discharge at 1 mA. Then, the electrode was relaxed for more than 24 h until its potential reached constant equilibrium value [10]. The difference between the equilibrium and final values of the potential at the individual discharge current was taken as the polarization value at the 10 mAh discharge stage.

Results and discussion

Deposition of EMDs from carbon suspension bath

A scanning electron micrograph of VGCF is presented in Fig. 1(a). The diameter is 0.05 to 0.30 μm. The surface of the EMD obtained from the VGCF suspended bath shows that the EMD grows on the fibres and that these fibres are in close contact with each other, as revealed by the micrograph given in Fig. 1(b).

The VGCF fibres display a colloidal character because of their fineness. They partially aggregate in the electrolyte, even at room temperature. The ability of various surface-active reagents (20 to 100 mg per l of electrolyte) to the VGCF fibers is summarized in Table 1. Cationic type reagents, such as cetyltrimethyl ammonium chloride, trimethylstearyl ammonium chloride, benzyldimethylcetyl ammonium chloride, and cetylpyridinium bromide, are effective in maintaining a homogeneous dispersion of the VGCF fibres in the electrolyte, even at 100 °C.

Figure 2 shows the voltage–time relation of the titanium anode during deposition of EMD in 1 M $MnSO_4$+0.4 M H_2SO_4 electrolyte (98 °C) that contains various kinds of suspended carbons (0.6 g l^{-1}) in the presence of trimethylstearyl ammonium chloride (20 to 100 mg l^{-1}). It can be seen that the anode potential during electrolysis is lowered in the presence of carbons (0.6 g l^{-1} of VGCF and AB-130, over 0.3 g l^{-1} of AB-30). This is roughly consistent with the reported behaviour of a suspension bath that contains MnO_2 particles [1–3].

The physicochemical properties of the carbon/EMD composites are listed in Table 2. The BET surface areas of VGCF/EMD and AB-30/EMD are much lower than that of the EMD obtained from a conventional bath at a current density of 1.0 A dm^{-2}.

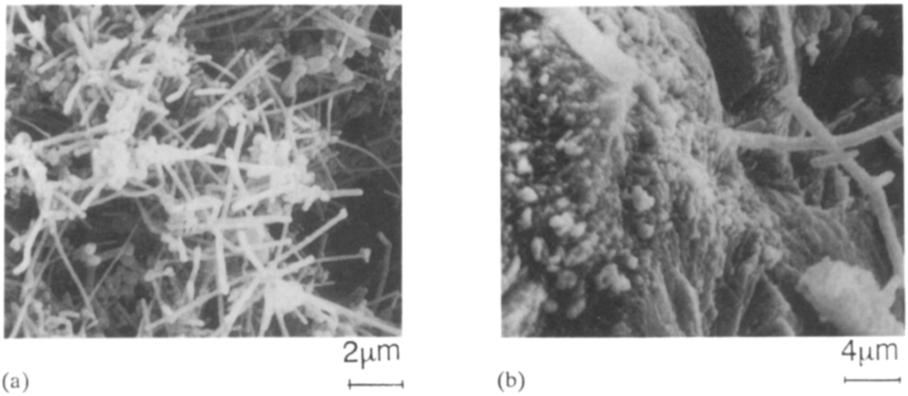

Fig. 1. Electron micrographs of: (a) VGCF, and (b) surface of EMD obtained from VGCF suspension bath.

TABLE 1

Effect of addition of surface active agents (20 to 100 mg l^{-1}) to 0.4 M H_2SO_4+1 M $MnSO_4$ solution containing vapour-grown carbon fibres (VGCFs) on the dispersion of VGCF; (○) good dispersion; (a) aggregation

	Surface-active agent	Temperature (°C)				
		RT[b]	40	60	80	100
Cationic	Cetyltrimethyl ammonium chloride	○	○	○	○	○
	Trimethylstearyl ammonium chloride	○	○	○	○	○
	Benzyldimethylcetyl ammonium chloride	○	○	○	○	○
	Cetylpyridinium bromide	○	○	○	○	○
	n-Dodecyltrimethyl ammonium chloride	○	a	a	a	a
	Distearyl ammonium chloride	○	a	a	a	a
	1-Laurylpyridinium chloride	a	a	a	a	a
	Tetra-n-butylammonium chloride	a	a	a	a	a
Neutral[a]	Polyethylene gylcol monostearate ($n = 25$)	○	○	○	a	a
	Triton X-100	○	○	a	a	a
	Polyethylene gylcol monooleyl ether ($n = 10$)	○	○	a	a	a
	Polyethylene gylcol mono-*p*-nonylphenyl ether ($n = 10$)	○	○	a	a	a
	Polyethylene gylcol monostearate ($n = 40$)	○	○	a	a	a
	Polyethylene gylcol monostearate ($n = 2$)	a	a	a	a	a
Anionic	Sodium dodecylsulfonate	○	○	○	a	a
	Sodium dodecylbenzenesulfonate	○	○	a	a	a
	Sodium hexadecylsulfonate	○	a	a	a	a

[a] The symbol *n* means the number of oxyethylene units (OCH_2CH_2).
[b] Room temperature: 15 to 20 °C.

By contrast, the surface areas of graphite/EMD and KB/EMD are roughly the same as that of EMD.

AB-30/EMD shows the highest carbon content, viz., 0.44 wt.%. The BET surface area of the EMDs are strongly related to the content of the carbon. The incorporation of carbon into EMD reduces the BET surface area. This is a common phenomenon with deposits prepared from a carbon and MnO_2 suspension bath.

The conductivities of VGCF/EMD and KB/EMD are higher than that of carbon-free EMD. Nevertheless, because KB/EMD contains only a trace amount of carbon, the reason for the improvement in conductivity of EMD by carbon incorporation is not clear.

The XRD patterns for the EMDs are given in Fig. 3. A typical XRD pattern for γ-type MnO_2 is observed for all EMDs. AB-30/EMD and VGCF/EMD show higher (110) diffraction lines than graphite/EMD, KB/EMD and EMD without carbon. The *Q* value [2] of AB-30/EMD (1.13) and VGCF/EMD (1.20) are very close to that of IC 17 (1.11). (Note, the *Q* value is the intensity ratio of the reflections at $2\theta = 28°$ ((110) plane) and 47° ((021) plane [3].)

The effect of electrolysis current density on the *Q* value of EMDs obtained from a carbon or γ-MnO_2 suspension bath and a conventional bath are shown in Fig. 4. VGCF/EMD and AB-30/EMD show higher (110) peak heights than EMD obtained from a conventional bath. The effect of a carbon suspension on the increase in the (110) peak height is not as strong as that of a MnO_2 suspension.

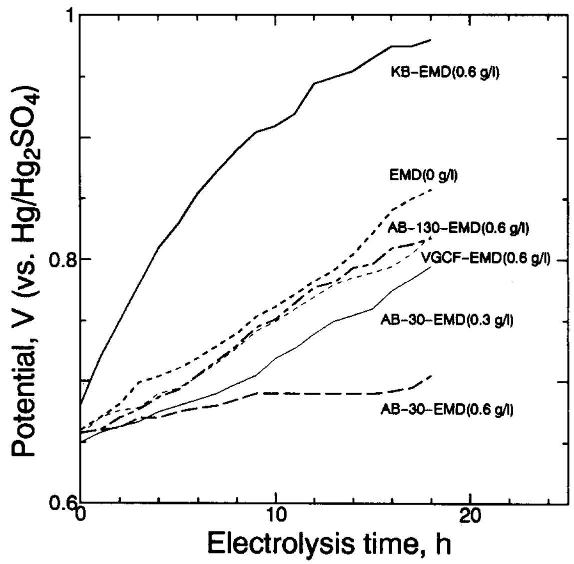

Fig. 2. Time dependence of anode potential in electrodeposition of MnO_2 from either suspension baths with various types of carbon or conventional bath at current density of 1.0 A dm^{-2}.

TABLE 2

Physicochemical properties of IC 17[a] or EMDs obtained from 0.4 M H_2SO_4 + 1 M $MnSO_4$ bath (98 °C) at current density of 1.0 A dm^{-2} with or without suspension particles (0.6 g l^{-1})[b]

EMD	x in MnO_x	BET surface area ($m^2\ g^{-1}$)	Conductivity ($\Omega^{-1}\ cm^{-1}$)	Carbon content (wt.%)	Water content (wt.%)	Grindability
VGCF/EMD	1.95	37.8	2.6×10^{-2}	0.39	1.54	Easy
AB-30/EMD	1.94	36.5	1.0×10^{-2}	0.44	1.75	Easy
KB/EMD	1.93	59.1	2.5×10^{-2}	Trace	1.76	Easy
Graphite/EMD	1.94	55.9	9.1×10^{-3}	Trace	1.95	Easy
EMD	1.94	50.1	1.2×10^{-2}		1.10	Difficult
IC 17	1.95	40.0			1.71	

[a] IC 17 = International common MnO_2 sample no. 17 [12].

[b] VGCF, AB-30, KB and graphite give suspended particles in the electrolyte.

The relation between the oxygen distortion parameter, a''/a', and the lattice parameter, b_0, of orthorhombic γ-MnO_2 is displayed in Fig. 5. The a''/a' value is calculated from the following expression [13]:

$$a''/a' = 0.5(1+(b_o)^2/(4c_o^2))^{1/2} \qquad (1)$$

where c_o is the lattice parameter of orthorhombic γ-MnO_2. A linear relationship between a''/a' and b_o is observed. The a''/a' values of VGCF/EMD and AB-30/EMD are intermediate between those for EMDs obtained from a γ-MnO_2 suspension bath and a conventional bath. The a''/a' values of 0.99 for VGCF/EMD and AB-30/EMD indicate that the oxygen atoms in both EMDs have an ideal hexagonally closed-packed array.

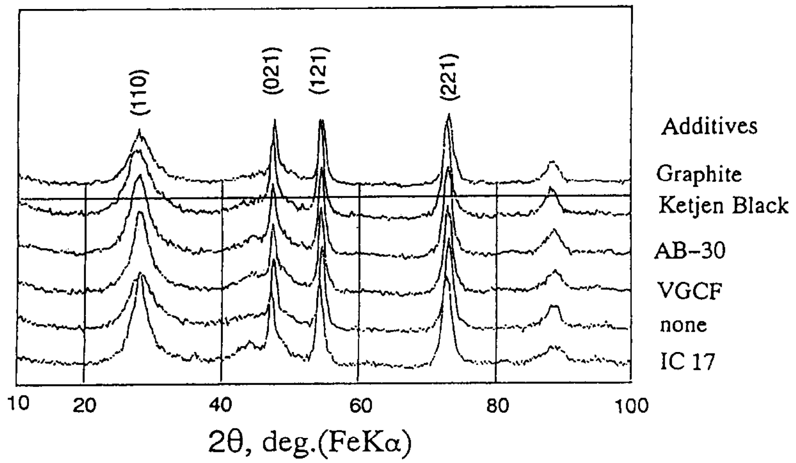

Fig. 3. X-ray diffractions patterns of IC 17 and EMDs obtained with or without carbon suspension.

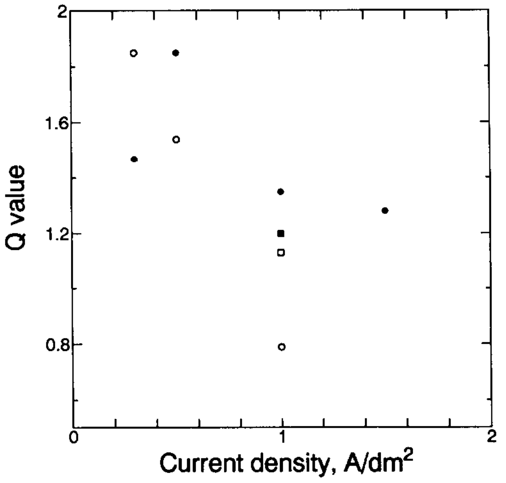

Fig. 4. *Q* value of EMDs obtained at various current densities from (○) conventional, (●) γ-MnO_2 (0.2 g l^{-1}) suspension, or carbon (0.6 g l^{-1}) suspension ((■) VGCF, and (□) AB-30) baths.

The discharge curve of VGCF/EMD at a discharge rate of 50 mA g^{-1} in an alkaline battery is presented in Fig. 6. The capacity of reduction from MnO_2 to MnOOH is 27.5 mAh. This is the theoretical capacity after taking the purity of MnO_2 (93%) into consideration. The discharge capacities of the EMDs at −200 and −400 mV are summarized in Table 3. The discharge capacities of VGCF/EMD and AB-30/EMD at −200 mV are roughly the same as that of IC 17, even though they were obtained at a higher current density of 1.0 A dm^{-2}. By contrast, their capacities at −400 mV are 5% higher than that of IC 17. This result shows that EMDs containing carbon are excellent cathode materials for alkaline batteries. EMDs with high carbon content, such as VGCF/EMD and AB-30/EMD, yield higher capacities than those with a low

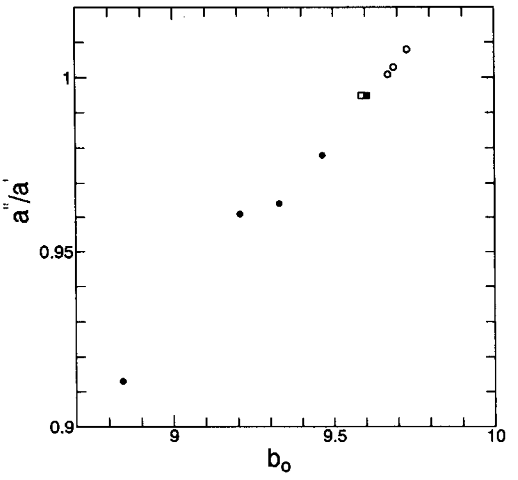

Fig. 5. Relationship between oxygen distortion parameter, a''/a', and orthorhombic lattice parameter, b_o of EMDs. Symbols denote the same baths as in Fig. 4.

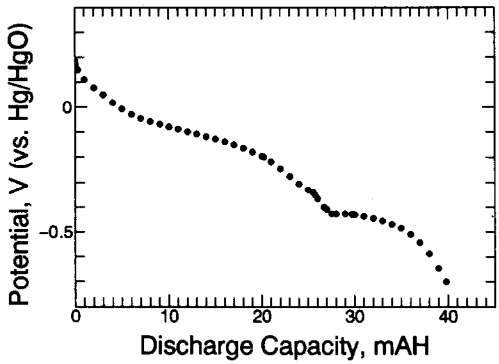

Fig. 6. Continuous discharge curve of VGCF/EMD obtained at 1.0 A dm^{-2} in alkaline cell at a discharge rate of 50 mA per g MnO_2.

content of carbon. Thus, the incorporation of carbon is considered to be important for improving the performance of alkaline batteries.

The polarization of various kinds of MnO_2 at 1, 2, and 5 mA in alkaline batteries is given in Fig. 7. Both VGCF/EMD and AB-30/EMD exhibit an extremely lower polarization than either EMDs (IC 1, IC 17 and IC 32)* or chemically prepared manganese dioxides, CMDs (IC 12 and IC 22). This is the reason for the high capacities of EMDs containing carbon at high discharge rates. Thus, because of its lower polarization, the carbon/EMD composite would be suitable for high-rate discharge in an alkaline cell.

Direct proof of increased conductivity of EMDs with carbon incorporation could not be obtained from conductivity measurements. Nevertheless, the lower polarization

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*IC 1, 17 and 32 = International common MnO_2 sample nos. 1, 17 and 32.

TABLE 3

Discharge capacities of IC 17 or EMDs obtained from 0.4 M H_2SO_4+1 M $MnSO_4$ bath (98 °C) at a current density of 1.0 A dm^{-2}, with or without suspended particles (0.6 g l^{-1}); cutoff voltage −200 mV or −400 mV vs. Hg/HgO/9 M KOH; discharge rate: 50 mA per g EMD

EMD[a]	Discharge capacity (mAh g^{-1})	
	−200 mV	−400 mV
VGCF/EMD	202	267
AB-30/EMD	203	266
KB/EMD	190	262
Graphite/EMD	188	257
EMD	170	237
IC 17	204	249

[a] The same symbols are used as in Table 2.

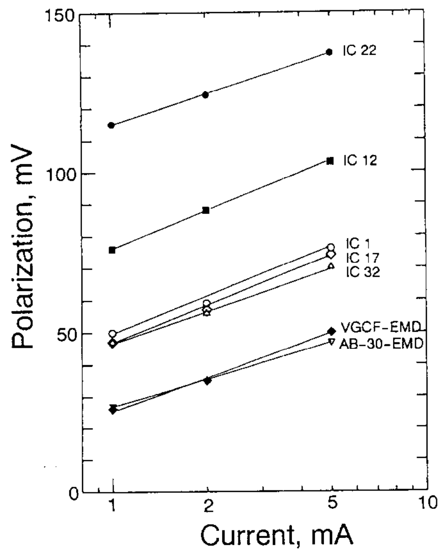

Fig. 7. Relation between polarization and current of various MnO_2 in alkaline cells at 10 mAh discharge stage.

of EMDs containing carbon is a demonstration of the increased conductivity of the carbon/MnO_2 composite.

Deposition of EMDs from a AB-30/δ-MnO_2 composite suspension bath

The carbon/EMD composite is an excellent cathode material in terms of battery performance and grindability, as described above. Unfortunately, however, its low mechanical strength sometimes causes a rapid increase in anode potential due to the passivation of the titanium substrate electrode, as shown in Fig. 8. Since it is well known [1–3] that dispersed MnO_2 is effective in decreasing the anode potential, an attempt was made to prepare a composite of carbon with MnO_2. The AB-30/δ-MnO_2

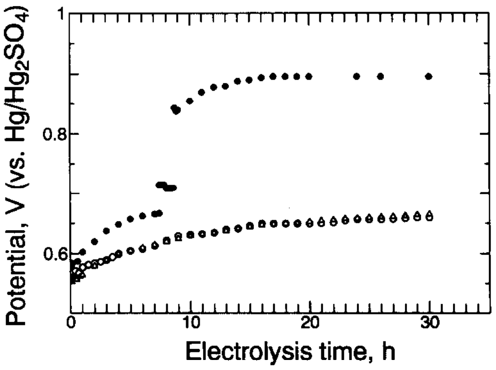

Fig. 8. Time dependence of anode potential in the electrodeposition of MnO_2 from a suspension bath with (●) 0.5 g l^{-1} AB-30, (○) AB-30/δ-MnO_2 or (△) δ-MnO_2 at 1.0 A dm^{-2}.

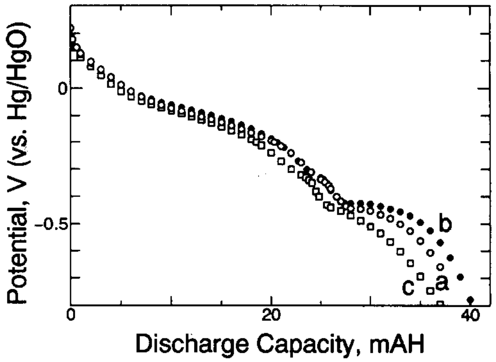

Fig. 9. Discharge behaviour of EMDs obtained from suspension bath with (a) 0.5 g l^{-1} AB-30, (b) AB-30/δ-MnO_2 or (c) δ-MnO_2 at 1.0 A dm^{-2} in alkaline cells at discharge rate of 50 mA per g MnO_2.

composite was selected in order to avoid oxidation of the carbon surface, a process proceeds under mild conditions. A low, stable and reproducible potential–time curve was obtained for electrolysis from the AB-30/δ-MnO_2 suspension bath. The anode potentials of the δ-MnO_2 and AB-30/δ-MnO_2 composite suspension baths during the electrolysis were similar. In both cases, the anode potential was controlled strongly by the δ-MnO_2.

Figure 9 shows the discharge behaviour of the above EMD samples in alkaline batteries. The EMDs obtained from an AB-30 and AB-30/δ-MnO_2 suspension bath show superior battery performance to that obtained from a δ-MnO_2 suspension bath. This result indicates that not only is the presence of the carbon/MnO_2 composite in the electrolyte important for obtaining MnO_2 cathode material of excellent quality for alkaline batteries, but also the method has the potential to become an industrial production method because a higher current density of 1.0 A dm^{-2} can be applied in the electrolysis.

The relation between anode potential and electrolysis time at various electrolysis current densities is given in Fig. 10. Very low anode potentials at current densities less than 1.0 A dm^{-2} are measured during the electrolysis time of 20 h. The anode

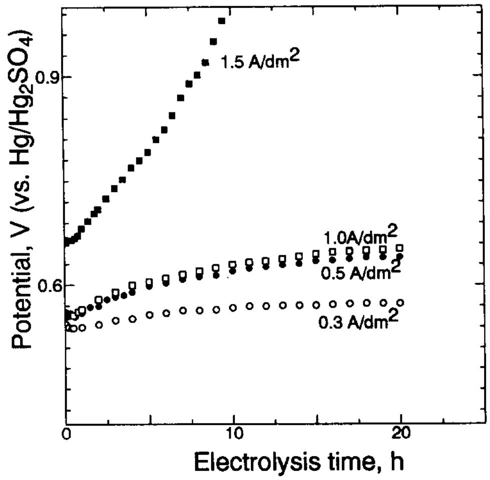

Fig. 10. Effect of current density on anode potential during electrolysis from AB-30/δ-MnO_2 composite suspension bath.

potential at 1.0 A dm^{-2} remains within only 740 mV during a prolonged electrolysis time of 120 h. Electrolysis at 1.5 A dm^{-2} causes the titanium substrate to become passivated and the anode potential to increase to over 1 V.

The anode potential is also influenced by the H_2SO_4 concentration of the electrolysis bath. The passivation of the titanium substrate proceeds even at 1.0 A dm^{-2} with a higher H_2SO_4 concentration of 0.5 M. The electrolysis from 0.35 M H_2SO_4+1 M $MnSO_4$ at 1.0 A dm^{-2} current density is recommended for a practical production process.

The physicochemical properties of EMDs obtained from an AB-30/δ-MnO_2 composite suspension bath under various electrolysis conditions are summarized in Table 4. All EMDs obtained contain 1.8 to 2.1 wt.% carbon. Since the carbon content of EMD obtained from an AB-30 suspension bath is only 0.44 wt.%, co-deposition of carbon is enhanced markedly in the electrolysis from an AB-30/δ-MnO_2 composite suspension bath. This result also shows that suspended MnO_2 is easily incorporated into EMD.

Although EMDs containing carbon yield excellent battery performance in alkaline cells, higher H_2SO_4 concentrations (>0.4 M) and a higher current density of 1.5 A dm^{-2} decrease the discharge capacity of the EMD deposit. When the BET surface area is less than 33 m^2 g^{-1}, the EMDs display excellent battery performance. For example, excellent EMDs obtained from a carbon suspension bath have low BET surface areas of 36 to 38 m^2 g^{-1}. Since the surface character of EMD strongly affects battery performance, this parameter has been examined in detail for the carbon/EMD composite. Figure 11 shows the nitrogen adsorption isotherm for IC 17 and for EMDs obtained from an AB-30/δ-MnO_2 composite suspension bath at current densities of 0.3, 1.0 and 1.5 A dm^{-2}. The isotherm for IC 17 shows distinct hysteresis around $P/P_0=0.5$. This is a typical characteristic of EMDs [14]. The hysteresis of EMDs obtained at current densities of 0.3 and 1.0 A dm^{-2}, however, is reduced and these EMDs adsorb a large quantity of nitrogen gas at around ambient pressure. It is concluded that the presence of large pores in the EMDs is important for excellent battery performance at a high discharge rate of 50 mA g^{-1}.

TABLE 4

Physicochemical properties of IC 17 or EMDs obtained from an AB-30/δ-MnO_2 composite (0.5 g l^{-1}) suspension bath (98 °C) with various H_2SO_4 concentrations

Electrolysis conditions		x in MnO_x	MnO_2 (wt.%)	Carbon content (wt.%)	BET surface area (m^2 g^{-1})	Water content (wt.%)	Grindability
Current density (A dm^{-2})	H_2SO_4 (M)						
0.3	0.35	1.95	91.2	2.06	27.0	1.76	Easy
0.5	0.35	1.94	92.5	2.06	28.9	2.07	Easy
1.0	0.35	1.97	93.3	2.08	32.3	2.22	Easy
1.5	0.35	1.94	91.1	2.09	55.1	2.89	Easy
1.0	0.10	1.95	92.6	1.83	27.3	1.83	Easy
1.0	0.25	1.94	91.5	1.90	28.8	1.86	Easy
1.0	0.40	1.94	91.3	2.00	41.6	2.25	Easy
1.0	0.50	1.95	92.2	1.85	50.4	2.36	Easy
IC 17		1.95	90.9		40.0	1.71	

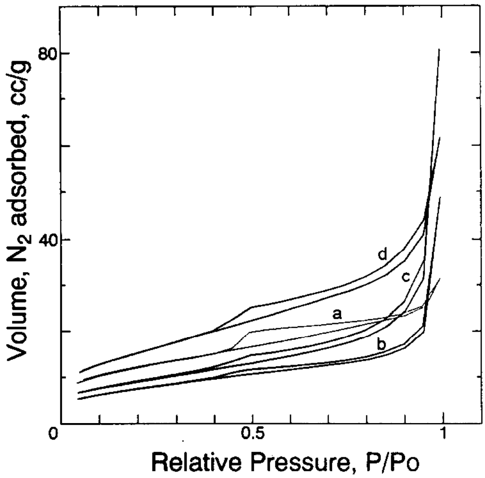

Fig. 11. Nitrogen isotherm at −195 °C for (a) IC 17; EMDs obtained from AB-30/δ-MnO_2 composite suspension bath at current densities of (b) 0.3, (c) 1.0, and (d) 1.5 A dm^{-2}.

Conclusions

The electrodeposition of MnO_2 on a titanium anode from a carbon suspended H_2SO_4–$MnSO_4$ bath has been studied in detail. EMDs obtained from an AB-30 and VGCF suspension bath contain 0.4 wt.% carbon. Those EMDs show excellent alkaline battery performance, good grindability, and low BET surface area. Nevertheless, this bath has a defect in that passivation of the titanium anode sometimes occurs during electrolysis because of weakness in the mechanical strength of the deposit. This problem is successfully resolved without loss of battery performance by using carbon composite

δ-MnO_2 as the suspension particle. In addition to yielding excellent alkaline battery performance and good grindability, such a bath has several other advantages, namely: easy maintenance of good dispersion; good reproducibility; low anode potential during the electrolysis, and higher carbon content.

The battery performance is closely related to the surface characteristics of EMDs, such as the BET surface area and pore size.

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