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The role of particle size in cathode optimization in alkaline primary batteries

A. URFER, G.A. LAWRANCE* and D.A.J. SWINKELS
Department of Chemistry, The University of Newcastle, Callaghan NSW 2308, Australia
*(*author for correspondence)*

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Abstract

In the search for cathode mixes which show maximum discharge performance, cathode mixes with different electrolytic manganese dioxide (EMD) and graphite compositions have been investigated in a flooded test cell assembly. Variation in performance with particle size, both EMD and graphite, was observed. In general, performance improved with higher amount of graphite and finer particle size. Both lower open circuit potential and significantly better performance towards the lower potential range of the discharge occur with carbon black present. The influence of combinations of graphite and carbon black with high surface area has also been examined. The information gained can be used to better explain the influence of selected cathode materials in batteries.

1. Introduction

Primary alkaline test cells containing manganese dioxide as the active cathode material were investigated in this work. Electrolytic manganese dioxide (EMD) is well known as an excellent electrode material and has been found to be the form of manganese dioxide that is most suitable as the positive active material in alkaline cells [1]. EMD is inexpensive, can maintain high discharge rates, displays a good performance over a wide temperature range and has a long storage life. Consequently, EMD is the most widely used cathode material for alkaline batteries and has recently found application in rechargeable batteries [2].

EMD is not a single compound, but a rather large family of closely related compounds whose physical and chemical properties vary significantly upon changing the conditions of electrodeposition [3, 4]. A range of structural forms with mostly non-stoichiometric compositions MnO_x with $x < 2$ exist, and a typical EMD would have a chemical composition similar to $MnO_{1.96}H_{0.08}$ on a dry basis. It is generally accepted that manganese dioxide discharges by insertion of a proton from the concentrated potassium alkaline electrolyte and of an electron from an external circuit:

$$MnO_2 + H^+ + e^- \rightarrow MnOOH$$

The proton–electron pair formed during the discharge diffuses away from the EMD surface to the interior of the material [5]. The rate at which this proton–electron pair diffuses is limited by the ability of the proton to move through the solid and is a function of the structural, chemical, physical and electrochemical properties of the EMD. To improve the performance of a given EMD battery, the function and behaviour of each component of the alkaline manganese battery have to be understood.

Nagamine and Yoshida [6] have studied various parameters affecting the positive and negative electrodes, especially aimed to find out the optimum moisture content and mixing ratio of graphite to EMD in the cathode mix (also called 'black mix') as well as the optimum surface area of zinc powder used for the anode. In this work, the emphasis is only on the cathode. Its performance is largely affected by the graphite to EMD ratio, the amount of EMD in the battery, the compacting pressure and the conductivity of the electrolyte at a given discharge rate. The optimum values of these parameters are expected to change with the discharge conditions for a given cell size and possibly with the particle size of EMD and graphite used. Fischer and Wissler [7] studied the influence of graphite concentration and cathode compacting pressure on the alkaline performance. Their observation reveal an optimum cathode performance for a range between 0.08 and 0.10 for the graphite to EMD ratio, 3.05–3.10 g cm^{-3} for the cathode density and 1.5–3 ton cm^{-2} for compacting pressure.

In this paper, two sets of experiments are described where the discharge performance of cathodes containing graphite or graphite plus carbon black, respectively, have been investigated. The cells have been discharged at constant current at different rates and the discharge data have been recorded.

2. Experimental details

2.1. *Full factorial design*

Various factors can influence the discharge performance of batteries, for example, the starting materials EMD and graphite (quality, particle size), preparation of the cathode mix (concentration and volume of electrolyte, mixing ratio, mixing time, compacting pressure), preparation of the cells (compacting pressure, compacting time, cathode thickness, ageing time) or applied discharge current. To investigate all combinations with this amount of different factors is practically impossible and realistically not all of the combinations can be studied within a reasonable time frame. Therefore, only combinations of a few factors considered to be more important than the rest have been thoroughly investigated in the search for cathode mixes which show maximum discharge performances, and the emphasis has been placed on EMD and graphite particle size and cathode thickness. All other factors were kept constant, for example, EMD quality, concentration and volume of electrolyte used to make the cathode compacts, mixing time and compacting pressure in the preparation of the cathode mixes, compacting pressure, compacting time and ageing time in the preparation of the cells, temperature and applied current.

2.1.1.

In a first test series, cathode mixes with three factors at two levels each were investigated, as detailed in Table 1.

For a full factorial design without duplicates with factors A, B and C at two levels (0 and 1) each, $2^3 = 8$ assemblies were required. Cells were run in triplicate giving a total of 24 cells. The constant discharge current applied was 223 mA, equivalent to a current density of 50 mA cm^{-2} in the cell employed.

2.1.2.

In this test series, cathode mixes with two factors at three levels each were investigated, as detailed in Table 2.

For a full factorial design with factors A and B at three levels (0, 1 and 2) each, $3^2 = 9$ assemblies were required. With six replicates of each formation, 54 cells were discharged. Approximately 3.5 g of cathode mix was pressed into the can giving a pellet thickness of about 2.5 mm, which is similar to the dimensions in a commercial AA cell. The constant current applied was 120 mA, equivalent to a current density of 26.9 mA cm^{-2}.

Table 1. Experimental conditions selected, with two levels for three investigated factors

Factor	Level	
	0	1
A Type of TIMCAL graphite	KS 6	KS 44
B Amount of graphite (%)*	6	10
C Thickness of cathode pellet (mm)	~2	~10
Weight of cathode pellet (g)	~2.4	~12.0

* added to EMD on a dry weight basis before addition of 9 M KOH

Table 2. Experimental conditions selected, with three levels for two investigated factors

Factor	Level		
	0	1	2
A EMD particle size (μm)	−45	45–75	+75
B Amount of KS 44 (%)	7	5	3
plus	+	+	+
Amount of Ketjen Black (%)	0	2	4

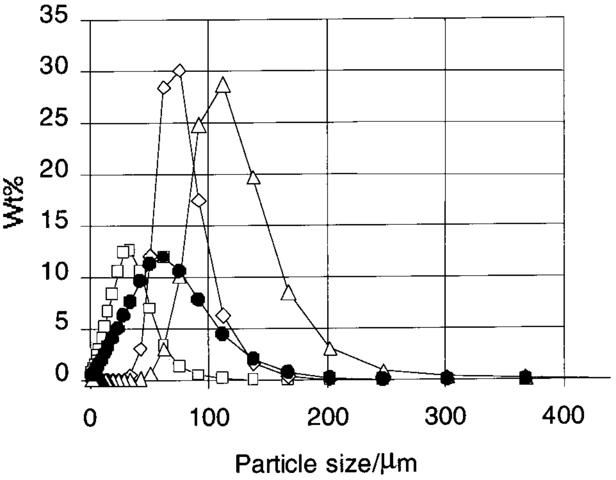

Fig. 1. Particle size distribution for parent and sieved EMD lot 291 sample fractions. Key: (□) −45 μm, (◇) 45–75 μm, (△) +75 μm and (●) lot 291.

2.2. *Preparation of the cathode mixes*

The same commercial EMD was utilised for all test cells: lot 291 as-received from Australian Manganese Co Pty (now Delta EMD Australia Pty). The −45 μm fraction was obtained by dry sieving the lot 291 through a sieve with a mesh of 45 μm, whereas the other two fractions, 45–75 μm and +75 μm, were sieved through a 75 μm mesh sieve and on a 45 μm mesh sieve, respectively. Their particle size distributions as determined using a Malvern Mastersizer are shown in Figure 1.

Timrex KS type graphite was obtained from Timcal Corp. The two grades of graphite mainly differed in their BET surface area. For KS 6 particles, this area was 20 m^2 g^{-1} whereas KS 44 particles had an area of 9 m^2 g^{-1}. The carbon black used (Ketjen Black) had a substantially higher BET surface area than graphite, about 1000 m^2 g^{-1}.

2.2.1.

The general method for preparing all four cathode mixes is given below:

(i) 100.0 g of EMD plus the desired amount of graphite were weighed into the tumbler.
(ii) 23 steel balls were added and the mix was tumbled at 43 rpm for two hours.
(iii) 6% of 9 M potassium hydroxide solution ($d = 1.316$ g ml^{-1}) was added to the EMD/graphite combination. The moistened mix was tumbled at 43 rpm for a further four hours. During the tumbling periods, the tumbling was regularly interrupted for a short amount of time and the material on the walls of the tumbler was loosened by scratching with a plastic spatula to assist a better mixing.
(iv) The mix was transferred to a sealed container and stored overnight.
(v) The cathode mix was compacted through a hand operated roller compactor with a spacing between the two cyclinders of 0.6 mm and 0.7 mm, depending on the blend, and the densified mix was then broken into small pieces.
(vi) This compacting process was repeated three more times.
(vii) Instead of crushing the material after the fourth compacting process, it was granulated through a sieve with a wire mesh of 1.18 mm. This gave the final cathode mix used for the preparation of test cells.

Depending on the amount of graphite (6.0 g or 10.0 g), each moistened cathode mix contained 89.0% or 85.7% of EMD, 5.3% or 8.6% of graphite (KS 44 or KS 6) and 5.7% of 9 M potassium hydroxide solution.

2.2.2.

For the test series described in Section 2.1.2., each moistened cathode mix contained 87.0% of EMD, 7.0% in total of graphite (KS 44) plus carbon black (Ketjen Black) and 6.0% of 9 M potassium hydroxide solution. The overall weight of each cathode mix was 100.0 g and the general method for preparing all nine cathode mixes is given below:

(i) 87.0 g of EMD and a combined total of 7.0 g of graphite (KS 44) plus carbon black (Ketjen Black) were weighed into the tumbler.
(ii) 20 steel balls were added and the mix was tumbled at 43 rpm for 30 min.
(iii) 6.0 g of 9 M potassium hydroxide solution ($d = 1.316$ g ml^{-1}) was added to the EMD/graphite/carbon black combination and the moistened mix was tumbled at 43 rpm for a further 60 min. During the tumbling periods, the tumbling was regularly interrupted briefly and material adhering to the walls loosened to assist mixing.
(iv) The mix was transferred to a sealed container and stored overnight.
(v) The cathode mix was compacted four times, and finally granulated through a sieve to give the final cathode mix used for the preparation of test cells as described in Section 2.2.1. above.

2.3. *Preparation of test cells*

2.3.1.

A thin graphite layer (~200 mg of KS 44) was pressed on the bottom of a new C-size can with a pressure of 6 tons (1.34 tons cm^{-2}). The inside wall of the can was then lined with teflon sheet (~0.25 mm thick) which left an inside area of 4.47 cm^2. The experimentally determined weight of cathode mix to produce the correct cathode pellet thickness was pressed into the can for about 10 to 15 s with 6 tons (1.34 t cm^{-2}). After the cathode mix had been pressed, the top of the cathode pellet was covered with two filter papers and the can was tilted about 45 degrees. 2 ml to 3 ml of electrolyte (9 M KOH) was very slowly added along the wall into the interior of the can and the cell was left in this tilted position overnight for ageing purposes. After the can had been arranged upright, it was filled up with 9 M KOH to about one third to one half of its total volume, checking that no air bubbles were trapped in the filter papers and in the cathode pellet.

2.3.2.

Alternatively, the inside bottom of a new C-size can was sprayed with a water based conductive graphite coating suspension, dispersed with a professional Paasche single-action air-brush, and the can was dried in an oven at 60 °C. The dried thin graphite layer weighed 34 mg ± 11 mg. The inside can wall was lined with an about 0.25 mm thick teflon sheet which left an exposed area of 4.47 cm^{-2} in the bottom of the can. 3.5 g of cathode mix was pressed into the can for 10–15 s with a pressure of six tons (1340 kg cm^{-2}) giving a pellet thickness of about 2.5 mm. The weight for the graphite layer as well as the pellet thickness is similar to the dimensions that can be found in a commercial AA cell. After the cathode pellet has been pressed, the top of the cathode pellet was covered with three filter separation papers. The can was tilted about 45° and 3 ml of electrolyte (9 M KOH) was added with a syringe. The can was placed upright again and it was left in this position overnight so the cathode could age. A 2 mm thin porous Perspex disc with a diameter of 23.9 mm and with 73 holes of 1.5 mm diameter each was placed on top of the filter papers before 4 ml of 9 M potassium hydroxide electrolyte was added.

In all cases, stainless steel anodes were inserted in the cells before the cells were arranged and wired in the discharge rig. Figure 2 is a schematic representation of one test cell ready to be discharged. The porous Perspex disc was not used in the first set of experiments.

2.4. *Constant current discharge set-up (hardware and software)*

The test facility comprised an IBM-compatible computer equipped with a high performance data acquistion card PC-LabCard PCL-818 (maximum input range of ±10V) which read up to eight differential analog input

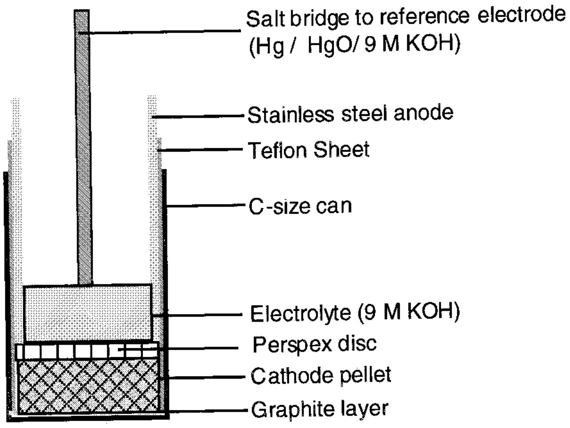

Fig. 2. Schematic diagram of the flooded discharge test cell.

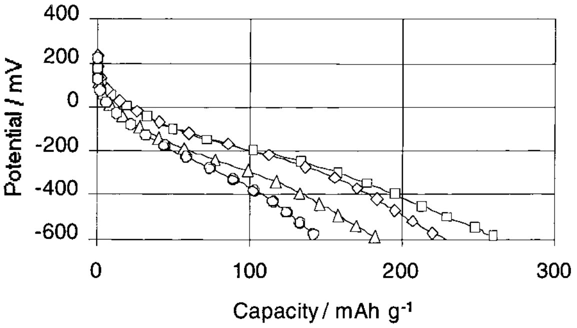

Fig. 3. Averaged discharge curves for 2 mm thick cathodes. $j = 50$ mA cm^{-2}. Key: (□) 10% KS 6, (◇) 10% KS 44, (△) 6% KS 6 and (○) 6% KS 44.

channels. Connection blocks for the PCL-818 were provided by the universal screw terminal daughter board PCLD-780 which was mounted in a protective instrument case. The control software was written in Microsoft Quick Basic 4.0 using the PCL driver version 1.0.

Up to seven test cells were simultaneously discharged under controlled conditions of continuous drain (constant current) at constant temperature using an EG&G Princeton Applied Research model 362 scanning Potentiostat. Their discharge data were recorded relative to mercury/mercury oxide/9 M potassium hydroxide reference electrodes. Readings of the PCL-818 data acquistion card were values between 0 and 4096 which had to be converted into potentials. These potentials were averaged over a user-defined period of time (typically 30 s) and the averaged potentials were periodically saved in data files as data pairs of the form [time (s), potential (mV)]. The analyses were conducted with Microsoft Excel. As soon as the desired end voltage of −600 mV has been reached, the recording of discharge data was stopped.

3. Results and discussion

3.1.1.

The results of the averaged discharge experiments of the full factorial test series with EMD lot 291, graphite with two different particle sizes (KS 6 and KS 44), two different graphite to EMD ratios (6% and 10%) and two different cathode pellet thicknesses (2 mm and 10 mm), discharged at the constant current of 50 mA cm^{-2}, are given in Figure 3 for the 2 mm thick pellets and in Figure 4 for the case of the 10 mm thick pellets.

It can be observed that the effects of different mixes were more pronounced for the thinner 2 mm cathodes and that these electrodes discharged more efficiently than the thicker 10 mm pellets. The following order for the mixture performance could be established: [10% KS 6] > [10% KS 44] > [6% KS 6] > [6% KS 44]. In other words, mixtures with 10% graphite were better than mixtures with 6% graphite and mixture with the same ratio of graphite to EMD discharged better when the smaller particle sized graphite (KS 6) was used. For the thinner electrodes this order was valid through the whole experimental range, whereas in the case of the thicker pellets this sequence was only applicable for potentials greater than approximately −450 mV. This order could be expected on the basis of improved conduction with both more graphite and finer particles, the latter permitting more intimate contact of EMD and graphite particles. More detailed cathode modelling is needed to understand the change in order for thick electrodes at low potentials.

The trends in open circuit voltage (OCV) are shown in Figure 5. The higher the graphite content and the finer the graphite particles the lower the open circuit potential: OCV (6%) > OCV (10%) and OCV (KS 44) > OCV (KS 6). This drop presumably relates to interactions of surface groups on the graphite with MnO_2.

The experimental set-up had some problems with reproducibility for cells with cathode mixes similar to cathode mixes found in commercial batteries. These reproducibility problems were most likely due to the absence of a porous rigid plastic cover on the EMD pellet which would have limited the cathode expansion during the discharge. This was introduced in following experiments.

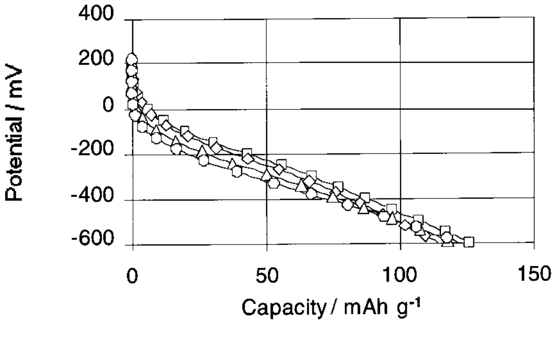

Fig. 4. Averaged discharge curves for 10 mm thick cathodes. $j = 50$ mA cm^{-2}. Key: (□) 10% KS 6, (◇) 10% KS 44, (△) 6% KS 6 and (○) 6% KS 44.

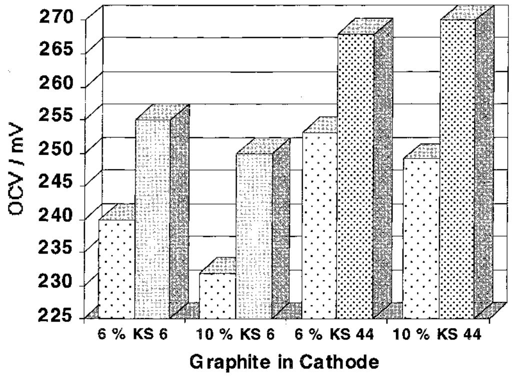

Fig. 5. Average open circuit voltage (OCV) of test cells. (For each set, 2 mm and 10 mm cathodes are on the left and right respectively.)

3.1.2.

Taking the averaged discharge curves from every cathode mix from the series defined in Section 2.1.2., there are two major ways to compare them with each other. The cathode mixes made up with the same EMD size fractions but varying ratios of graphite to carbon black can be put in relation as illustrated in Figure 6 for EMD with a fraction size of −45 μm, in Figure 7 for EMD with the 45 μm to 75 μm fraction size and in Figure 8 for EMD with a particle size of +75 μm.

These results showed that the discharge performances of test cells with carbon black compared to test cells without carbon black were worse at the beginning of the discharge but improved towards the end of the discharge and were considerably better at deeper levels of discharge. The higher Ketjen Black samples (4%) were consistently higher capacity than the lower samples (2%). There is an obvious trend, best viewed as the 'crossover' potential of the discharge curves with carbon black compared to the curve with only graphite present. This is presented in Table 3.

Improvement in relative overall discharge performance diminishes with EMD particle size and increases with amount of carbon black added. The less obvious effects with small EMD particles can be assigned to the high geometric surface areas of these particles, which presumably contact sufficiently well with the graphite particles. Large EMD particles make poor contact with the relatively large graphite particles, and the presence of small carbon black particles significantly enhances physical contact and conductivity, enhancing depth of discharge.

Table 3. 'Crossover' potential of discharge curves for samples containing carbon black with that of the parent curve containing only graphite

EMD size fraction/μm	2% KB + 5% KS	4% KB + 3% KS
−45	n/a*	−350 mV
45–75	−440 mV	−270 mV
+75	−410 mV	−200 mV

* not observed above −600 mV

Alternatively, the cathode mixes with the same graphite to carbon black ratio can be compared and the results are illustrated in Figures 9 and 10 for the two extreme cases. The expected and previously observed trend [8] amongst the cathode mixes with the same amount of graphite alone has been found, namely the finer the EMD size fraction was the better it performed (Figure 9). In the presence of large amounts of Ketjen Black (Figure 10), the effect of particle size is clearly less evident, as a result of the role played by the carbon

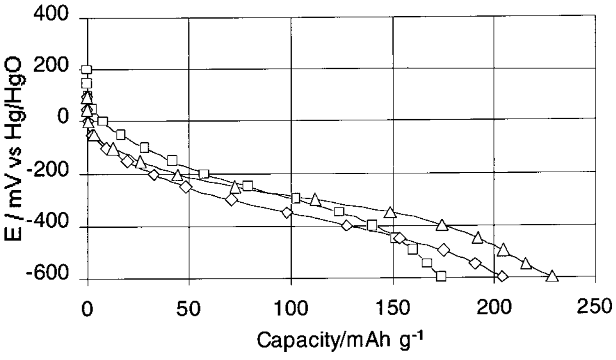

Fig. 7. Average discharge curves for cells with EMD size 45–75 μm, showing variation with graphite (KS) to carbon black (KB) percentages. Key: (□) 7% KS + 0% KB, (◇) 5% KS + 2% KB and (△) 3% KS + 4% KB.

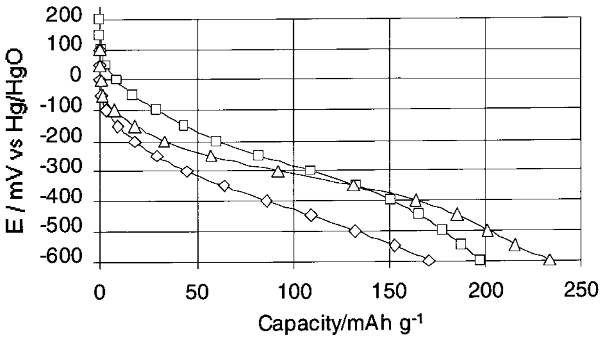

Fig. 6. Average discharge curves for cells with EMD size −45 μm, showing variation with graphite (KS) to carbon black (KB) percentages. Key: (□) 7% KS + 0% KB, (◇) 5% KS + 2% KB and (△) 3% KS + 4% KB.

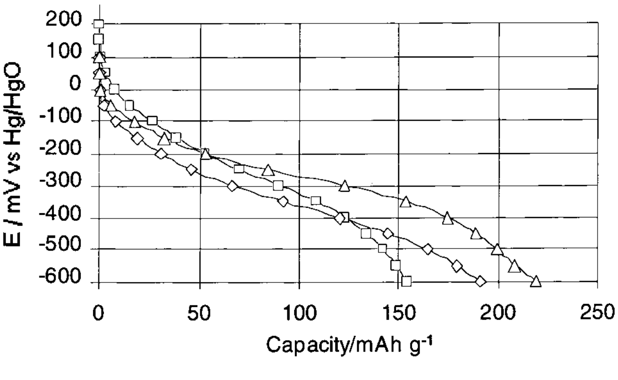

Fig. 8. Average discharge curves for cells with EMD size +75 μm, showing variation with graphite (KS) to carbon black (KB) percentages. Key: (□) 7% KS + 0% KB, (◇) 5% KS + 2% KB and (△) 3% KS + 4% KB.

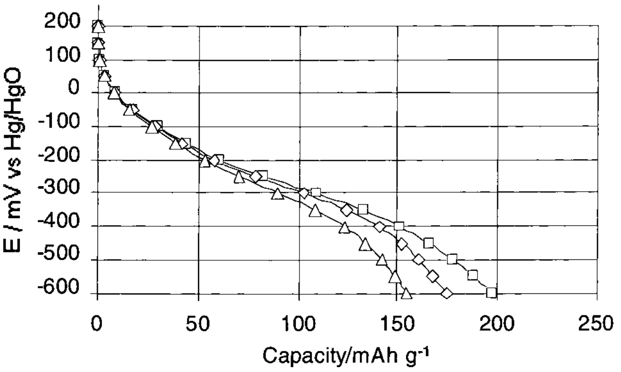

Fig. 9. Average discharge curves for cells with 7% KS 44 and no Ketjen Black. Key: (□) −45 μm, (◇) 45–75 μm and (△) + 75 μm.

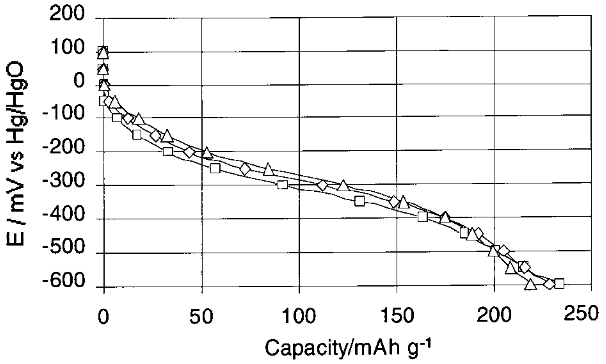

Fig. 10. Average discharge curves for cells with 3% KS 44 and 4% Ketjen Black. Key: (□) −45 μm, (◇) 45–75 μm and (△) + 75 μm.

black in promoting intimate contact to the EMD regardless of particle size.

In addition to the discharge data, the pellet thickness and its density, the open circuit voltage (OCV) and the discharge time have been measured for each test cell. Trends in pellet thickness (increasing with increasing percentage of carbon black) and pellet density (decreasing with increasing percentage of carbon black) reflect the lower density of carbon black compared with graphite or else reduced compressibility under the identical conditions employed. Although carbon black improved cell capacity, it is clear that its incorporation in a fixed volume device like a battery could also limit capacity by permitting less EMD to be employed. On balance, however, an overall improvement is anticipated.

The trends in open circuit voltage (OCV) are shown in Table 4. The higher the carbon black content the lower the open circuit potential, independent from the utilized EMD size fraction: OCV (0% KB) > OCV (2% KB) > OCV (4% KB). The drop on increasing carbon black content is substantial, and presumably relates to interactions of surface groups on the high surface area carbon balck with MnO_2.

Table 4. Average open circuit voltage/mV vs Hg/HgO of test cells for different EMD size fractions with various graphite (KS) and carbon black (KB) percentages

	−45 μm	45–75 μm	+ 75 μm
7% KS + 0% KB	246	254	257
5% KS + 2% KB	171	170	171
3% KS + 4% KB	152	148	149

Table 5. Average discharge capacity/mAh g^{-1} of test cells to −600 mV vs Hg/HgO, with various graphite (KS) and carbon black (KB) percentages

	−45 μm	45–75 μm	+ 75 μm
7% KS + 0% KB	197	175	154
5% KS + 2% KB	171	204	191
3% KS + 4% KB	234	229	219

Any conclusion about the discharge capacity therefore depend on the cut-off voltage. For an end potential of −600 mV versus the reference electrode, the trend is clearly shown in Table 5. Only the data set for −45 μm samples containing 2% carbon black appears anomalous, and it is clear that both smaller particle sizes of EMD and incorporation of carbon black affect capacity.

(a) For mixes with the same graphite to carbon black ratio, the discharge performance was the better the finer the EMD particles: Capacity (−45) > Capacity (45–75) > Capacity (+ 75). This trend holds at essentially any cut-off potential, but increases with depth of discharge. Small particles do not improve capacity by much more than 10 to 20%, at best, however.

(b) For mixes with the same EMD size fraction, the discharge performance was the better the more carbon black was present: Capactiy (4% KB) > Capacity (2% KB) > Capacity (0% KB). For the same particle size fraction EMD, improvement in capacity can range as high as 40% (+ 75 μm sample) for incorporation of 4% carbon black.

It should also be mentioned that the trends for other cut-off voltages (e.g., −400 mV) were not as distinctive as can be seen in Table 5. Nevertheless, the improvement in capacity by incorporation of fine carbon black in place of graphite is notable, and variations in discharge behaviour relate to the distinctly different particle sizes of the two carbon forms.

4. Conclusions

Cathode mixtures with a higher portion of graphite as well as finer graphite particle sizes performed better in constant current alkaline discharge tests. This trend is particularly true for thin cathodes. A sprayed graphite coating and a pressed graphite layer, respectively, in the can has been used to promote electrical conductivity, and a porous plastic disc has been introduced to confine the pellet and maintain a fixed volume. Small improvements in cell capacity observed in stepping from KS 44

(9 m^2 g^{-1}) to KS 6 (20 m^2 g^{-1}) were pursued by employing carbon black (Ketjen Black) with an extremely high BET surface area (about 1000 m^2 g^{-1}) along with the standard graphite KS 44. Two major effects were observed:

(i) The open circuit potentials (OCV) were considerably lower (80–1000 mV, depending on the added amount of carbon black) compared to reference cells with solely graphite. Interactions of surface groups on carbon black and graphite with MnO_2 are responsible for reduction of EMD and as soon as the two components were mixed together, the available capacity of the cathode mix at high discharge voltages was lessened. Addition of carbon black, which had a much higher surface area with more surface groups than graphite, reduced EMD even more, which explains the lower open circuit potentials.

(ii) Towards the lower potential range of the discharge, cathode mixes with carbon black performed significantly better than cells with graphite only. The product of the second electron reduction, $Mn(OH)_2$, is an insulator and causes the battery to fail as it coats particles, but through addition of carbon black with its high surface area and more interparticle contacts, more $Mn(OH)_2$ can be produced before the same consequence is encountered as with normal graphite.

Clearly, capacity enhancement at low discharge levels is advantageous. However, for commercial batteries, the loss in OCV is clearly unwanted especially for applications with high cut-off voltages. Nevertheless, it is not as important for use in low power situations. On the contrary, the improved discharge capacities would be ideal for latter usages. To be considered for battery applications, the initial EMD reduction should be reversed, e.g. through addition of an oxidising reagent such as potassium permanganate to the cathode mix. This needs to be addressed further in future investigations.

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