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Carbon filaments and carbon black as a conductive additive to the manganese dioxide cathode of a lithium electrolytic cell

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Abstract

Carbon filaments, when surface treated and used in stead of carbon black as the conductive additive to MnO_2 cathodes in lithium cells, produced a more gently sloping discharge curve (desirable for applications requiring end-of-life indication). These filament composite cathode plates also occupied less volume (higher packing density) and were handleable without the use of a binder, thus resulting in higher volumetric energy density than the carbon black counterpart. The Li/MnO_2 discharge capacity increased with the cathode's electrolyte absorptivity and rate of electrolyte absorption, as opposed to the cathode's electrical conductivity, whether carbon filaments or carbon black was used. The cathode's electrolyte absorption characteristics and packing density and the carbon's electron transfer rate were enhanced by surface treatment of the carbon. For carbon filaments, solvent cleansing, followed by either surfactant treatment or chopping plus drying, was effective; solvent cleansing also decreased the volume resistivity of both the carbon compact and the MnO_2/filament compact. For carbon black, surfactant treatment was effective and resulted in increases in test cell discharge capacity, open- and closed-circuit voltages (OCV and CCV), and cathode packing density. The volume electrical resistivity of the filament compact was lower than that of the carbon black compact, but the volume resistivity of the composite cathode was higher using carbon filaments instead of carbon black; the latter is due to the spreadability of carbon black between the MnO_2 particles.

Keywords: Manganese dioxide; Cathodes; Lithium; Carbon filaments; Carbon black; Conductivity; Batteries; Electrodes

1. Introduction

The use of carbon and graphite in commercial cells as a conductive additive to MnO_2 was first implemented by Leclanché [1]. The current zinc/carbon dry cell technology, which evolved from the original Leclanché battery, continues to use carbon black as the conductive additive to MnO_2. The electrical conductivity, electrolyte absorptivity, surface area, porosity and mechanical properties of these Leclanché-type cells are all affected by the type of carbon additive used [2–4]. Lahaye et al. [5] studied the effect of carbon black on the electrical properties of the MnO_2 cathodes of the current technology. Their study disclosed that the addition of carbon black to MnO_2 improved the conductivity of the composite electrode, enhanced the ability of the electrode to absorb and hold electrolyte, and provided compressibility and elasticity to the electrode. Researchers have also determined that the performance of composite electrodes for many electrochemical cells is dependent upon the particle size and shape of the carbon additive. Studies have shown that the conductivity of various composite electrodes significantly increases as particle size decreases [6–8]. Though carbon blacks are typically selected because they most closely satisfy the application requirements, graphite powders and carbon fibers have also been used as conductive additives [9–11]. The impact of different types of carbon black additives on electrolyte absorptivity of MnO_2 was also studied [12–15]. It was learned that the structure of carbon black significantly influences the absorption capacity of the composite cathode (high structure carbon blacks absorbing more electrolyte), and, in turn, influences the overall capacity of the cell (increased capacity with increased electrolyte absorption capability).

Solid cathodes of lithium cells are composite electrodes which also use carbon materials as an additive. In the case of Li/MnO_2 cells, carbon is added to the cathode primarily to enhance electrical conductivity, because cathode electrical conductivity is thought to be the main factor influencing battery performance [7,16–20]. Carbon black has been the only type of carbon additive studied for use in the Li/MnO_2 system precisely because it is highly conductive. The scope of these studies is limited to the type of carbon black and the

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volume fraction required to reach optimum MnO_2 cathode conductivity. Further, the correlation of cathode electrolyte absorption with the lithium cell capacity has not been made and comparative studies of carbon black with other carbon materials have not been conducted in the lithium system. This work shows that carbon filaments, because of their high aspect ratio and their shape, greatly improve MnO_2 cathode absorptivity. The improved cathode absorptivity, as opposed to cathode conductivity, was found to result in significant increases in capacity in the lithium/MnO_2 cell.

With the carbon black technology, binders such as Teflon™ are necessary to provide sheapeability and formability to the MnO_2 cathode. They are, however, passive and take up space which could be occupied by the active material, namely the MnO_2. The efforts toward improving the MnO_2 cathode for optimum lithium cell performance using carbon black as the conductive additive are lacking in depth relative to binder technology. In this work, carbon filaments, which replace the carbon black, also serve as the binder, so that the need for a conventional binder is eliminated. Further, the carbon black used in the current technology is highly structured as well as highly porous, so that composite MnO_2 cathodes using carbon black, although highly conductive, resist compaction. Therefore densification of composite MnO_2 cathodes is limited, which, in turn, limits energy density capability. As shown in this work, improvements in cathode compressibility, bindability and miniaturizability can be made by substituting carbon filaments for carbon black as the additive in the MnO_2 cathode.

Some battery applications, in particular medical implantable applications, require a characteristic discharge curve so that physicians have end-of-life indication early enough to explant and replace life-sustaining devices such as the cardiac pacemaker. The discharge curve may take the form of a stepwise running voltage, or it may have a gentle slope to end-of-life such that the decreasing running voltage as a function of capacity near end-of-life is long enough to allow time to make the explantation determination. In the MnO_2 system of the current technology (using the carbon black as the conductive additive), the characteristic discharge curve is too abrupt near end-of-life, due to the severe polarization of the composite cathode at end-of-life, that use as a medical implantable power source is impractical. In this work, carbon filaments were used as the conductive additive in stead of carbon black. Their use decreased cathode polarization and, in turn, favorably altered the appearance of the discharge curve at end-of-life, offering opportunity for use of the Li/MnO_2 system for applications requiring end-of-life indication.

Carbon filaments are a recent technological development offering potential for use in battery electrodes [21–24]. They are submicron in diameter (typically ~0.1 μm) and are grown catalytically from carbonaceous gases [25–27]. They are commercially available through Applied Sciences Inc. (Cedarville, OH). The carbonaceous gas for growing carbon filaments is usually carbon monoxide or a hydrocarbon, such as methane, various aliphatics, olefins and aromatics [28–34]. Since carbon filaments are small in diameter and exhibit high aspect ratio and high electrical conductivity, fabrication of dense electrodes with high surface area, good electrolyte absorptivity, high electrical conductivity, and good mechanical integrity is possible, as shown in this work. Further, as shown in this work, the high aspect ratio of carbon filaments provides mechanical connectivity within the electrode, allowing them to substitute passive electrode binders, such as Teflon™, that are currently used in composite electrodes. An objective of this paper, therefore, is to improve the state-of-the-art Li/MnO_2 cell (which uses carbon black as the conductive additive in the MnO_2 cathode) by increasing the energy density (i.e., increasing the cathode packing density) and making the drop in potential toward the end-of-discharge life more gradual (for implantable and other applications requiring end-of-life indication). A related objective is to investigate the use of carbon filaments in stead of carbon black as the conductive additive in the MnO_2 cathode, and simultaneously in stead of Tefon™ as the binder in the MnO_2 cathode. Another related objective is to compare carbon black and carbon filaments in terms of their mechanical and electrical connectivity when in the form of a compact with MnO_2. A final objective of this paper is to determine the material parameters that govern the discharge performance of the Li/MnO_2 cell with carbon as the conductive additive in the MnO_2 cathode.

Since the main purpose of the carbon material in Li/MnO_2 cells is to enhance the conductivity of the cathode, the electrical properties of the carbon material are important. The contact resistivity between adjacent units of the carbon and between carbon and the cathode material must be low. For this purpose, the surface of the carbon should not be covered by contaminants which are not good conductors. Carbon filaments, because of their manufacturing process, are covered with a tarry contaminant (mostly aliphatic hydrocarbons) that affects their electrical properties. Solvents are effective in removing filament contaminants [35]. The impact of solvent cleansing on cell discharge performance, however, requires investigation. This work demonstrates dramatic improvements in discharge capacity by using solvent cleansed carbon filaments as the conductive additive to MnO_2.

Surfactants are another means by which to treat materials when attempting to enhance wetting by an electrolyte. The term 'surfactant' is generally understood to refer to long-chain molecules containing hydrophilic and lipophilic moieties, that is, amphiphilic or soap-like structures [36]. In this case, the surfactant is adsorbed onto filaments during the chopping process, serving to significantly modify interfacial properties at low bulk solution concentrations. Consequently, the surface energy of the filaments is lowered, allowing better wettability by the electrolyte, and therefore absorptivity of the cathode. Pluronic, which was used in this work to treat the carbon conductive additives, is a difunctional block copolymer surfactant terminating in primary hydroxyl groups. It is nonionic and is 100% active. Surfactant treatment of carbon conductive additives is virtually unstudied, even in the current carbon black technology. This work demonstrates substantial improvements in not only the new carbon filament conductive additive application, but also to the state-of-the-art carbon black technology. Therefore, another objective of this paper is to investigate the effect of surface treatment of the carbon conductive additive on Li/MnO_2 cell performance and on the MnO_2 cathode's packing density (which relates to energy density), electrolyte absorptivity and electrical resistivity.

Since carbon is the conductive medium in the MnO_2 cathode, its volume resistivity, which decreases with increasing crystallinity, must be low. Just enough carbon must be present to provide the necessary conduction to the composite cathode and yet prevent polarization of the MnO_2 particles. Polarization is known to occur at too high a carbon content [3–6,13]. To achieve a continuous electrical network, the size, aspect ratio and degree of dispersion of the carbon and the amount of the carbon added to the cathode material are important as well. Continuity is enhanced by a small size, large aspect ratio, high degree of dispersion and large carbon volume fraction. Chopping of the filaments is a means of controlling these parameters [35]. Various media can be used to chop the filaments, but the effects of the chopping medium on cell discharge performance need to be studied. This work demonstrates that different capacities are achieved using different chopping media primarily because the absorptivity of the composite MnO_2 cathode is related to the chopping medium used.

The MnO_2 cathode material was chosen for study because it is well characterized due to its use in commercial cells prior to its use in lithium cells. MnO_2 exists as a natural ore and as a synthetic material. Since the supply of high quality natural ore MnO_2 is decreasing, battery manufacturers are relying heavily on the synthetic version which is produced either by chemical or electrolytic means. The physical, chemical and electrical properties of MnO_2 are dependent upon the manufacturing process. For example, electrolytic production results in good porosity and high depolarizing characteristics, while chemically produced MnO_2 has high activity.

The Li/MnO_2 discharge process has been studied by Ikeda and co-workers who proposed that MnO_2 is reduced from the tetravalent to the trivalent species as follows:

$$Li^+ + e^- + MnO_2 \rightarrow MnO_2(Li) \qquad (1)$$

The indication is that, upon discharge, lithium cations diffuse into the MnO_2 lattice [37]. Performance is dependent upon the crystalline state, level of hydration and activity of the MnO_2 [38]. Today, Li/MnO_2 cells, in flat button or cylindrical shapes, are sold commercially for use in watches, calculators, cameras and for applications requiring memory back-up. Improvements in energy and cell reliability have contributed to their introduction into the implantable device industry [39]. Researchers, however, are still working to resolve the abrupt end-of-life for this system. Typically, MnO_2 cathodes use carbon black (mean particle size of 500 Å and an aspect ratio of 1) as the conductive additive (optimized concentration between 30 and 40% by volume) [11]. The composite cathode may be fabricated in either of two ways. One method (used in this study to assess the effect of the conductive additive on discharge performance) is to dry mix the cathode constituents followed by pressing to form plates or pellets. The second (used in this study to assess the impact of conductive additive on cathode absorptivity) is to prepare a paste from the cathode mix and then pressing the mixture onto a current collector which also serves as a support. This method is commonly used to produce rolled anode and cathode assemblies. The advantages of the Li/MnO_2 technology include high energy density and high voltage, excellent discharge characteristics, wide operating temperature range, superior storage characteristics and a high degree of stability and safety [40].

The effective use of carbon as an additive to MnO_2 cathodes of lithium cells requires proper choice of numerous material parameters, particularly electrical conductivity, electrolyte absorptivity and compactability. The relative importance of these parameters have not been assessed for any form of carbon in the MnO_2 cathode used in the lithium cell. This paper provides carbon filament surface treatment and chopping techniques that are important for the effective use of carbon filaments in solid cathode lithium cell applications. Of practical significance is the finding that the use of carbon filaments in stead of carbon black provides increased discharge capacities for an MnO_2 cathode and with a more gently sloping discharge curve for use in applications requiring end-of-life indication. This work discloses that the main origin of the increased capacity was the increased electrolyte absorptivity and not the cathode electrical conductivity.

2. Experimental

Two types of carbon filaments were obtained from Applied Sciences Inc.: (i) ADNH of filament diameter 1500 Å and density 2.0 g/cm^3, and (ii) H79 of filament diameter 500 Å and density 2.0 g/cm^3. Both as-received filament types display lengths in excess of 100 μm. The carbon filaments were evaluated (i) as-received, (ii) after cleansing and chopping in a solvent, (iii) after cleansing in a solvent and then chopping in water, and (iv) after cleansing in a solvent and then chopping in water containing a surfactant. Cleansing was accomplished by immersing in either acetone or methylene chloride (reagent grade) while stirring using a stirring plate [35]. Chopping was achieved by blending using a rotary blade blender. Surfactant treatment was performed by dissolving 0.029 g of Pluronic obtained from BASF Corporation (Parsippany, NJ) in one liter of water. A portion of the solution was used to chop the filaments, whereas the carbon black was immersed in another portion of the solution while stirring using a stirring plate. The carbon black studied was Shawinigan acetylene black obtained from Chevron (Houston, TX) and of mean particle size 500 Å and density 2.05 g/cm^3. The effects of surfactant treatment of carbon black were compared to the current technology. Cleansing and surface treatment of the carbon additives were conducted prior to mixing with MnO_2. Except for the acetone cleansed ADNH chopped in water (which was allowed to air dry in a low humidity environment of less than 1% RH overnight), the cathodes were dried at 140 °C after pressing for a minimum of 6 h.

For discharge testing, the carbon filaments (the conductive additive) were dry mixed with the cathode material MnO_2 (an International Common Sample, Japan, I.C. No. 21, electrolytic MnO_2, particle size ranging between 2 and 10 μm, density of 5.0 g/cm^3) in a capped glass vial (25.4 mm diameter by 76.2 mm length) for 1 min using a Crescent Wig-L-Bug shaker prior to compaction at 21 MPa to form a plate (11.68 mm diameter). The volume fractions achieved ranged between 10 and 25% depending on filament treatment. Filament/MnO_2 cathodes were fabricated and discharged with and without a Teflon™ binder. All carbon black/MnO_2 cathodes were fabricated and discharged with Teflon™ binder. (Carbon black/MnO_2 cathodes without Teflon™ were not handleable.) In the Teflon™ containing cathodes, 8.2 wt.% carbon, 9.8 wt.% Teflon™ and 82 wt.% MnO_2 (a ratio of 1:10:0.8 carbon:MnO_2:Teflon™) were used. Those without Teflon™ contained 9.09 wt.% carbon and 90.9 wt.% MnO_2 (a ratio of 1:10 carbon:MnO_2). Note that for the sake of comparing the performance of the carbon material, the carbon weight in both the Teflon™ and no Teflon™ cases was fixed at 1/10 that of the MnO_2 cathode material. During dry mixing using the Wig-L-Bug shaker, the vial containing the carbon and the MnO_2 was placed horizontally in the shaker arm and rocked along the longitudinal axis of the vial forming a ± 120° angle. The vial was allowed to settle before opening to prevent particles from becoming airborne. (Since the carbon filaments are of such small size, researchers have expressed concern regarding their potential health hazard if inhaled.)

Effectiveness of the filaments as electrode materials was assessed by constant current, plate-to-plate discharge testing in an electrolyte comprising one molar lithium hexafluoroarsenate salt in a 50:50 solution of propylene carbonate/dimethoxyethane solvent. Apparatus and discharge parameters are described in a companion paper [41]. The discharge capacity was calculated per gram of MnO_2. Discharge data were collected and evaluated on two samples for each trial except for the as-received ADNH (six trials), as-received H79 (three trials) and chopping duration studies (one trial).

Electrolyte absorptivity was measured as described in Ref. [41]. The cathodes were fabricated using 8 wt.% carbon, 10 wt.% Teflon™ and 82 wt.% MnO_2 from a wet slurry of isopropyl alcohol in water containing a suspension of Teflon™ particles.

The electrical resistivity of the composite cathode (as a function of the carbon additive used) was measured using the four-point probe method [41,42]. The test fixture is shown in Fig. 1. Current (I) was applied using a Lakeshore power source. Voltage (V) was measured with a Keithley electrometer. The design incorporates a perforated plastic surface mount through which four wires were secured. Attached to the ends of the wires were alligator clips for connecting to the power source and the electrometer. The two inner wires were placed a known distance (l) apart. The potential developed across these two wires was measured as current was passed through the end wires. The electrical resistivity was measured by placing the cathode on the four wires and weighing it with a Mylar® insulated steel block to ensure good contact between the cathode and the wires.

The density of the cathode was determined by dividing the weight of the cathode by the volume of the cathode. Cathode thickness (used to calculate volume) was measured using a displacement transducer (Mitutoyo Digimatic) affixed with an arm to which is mounted a flat disk (diameter 8 mm), as shown in Fig. 2. The empty case was placed under the transducer with disked arm to zero. The case was removed from the transducer support surface, filled with cathode material, and the cathode was pressed inside the case at 21 MPa. The

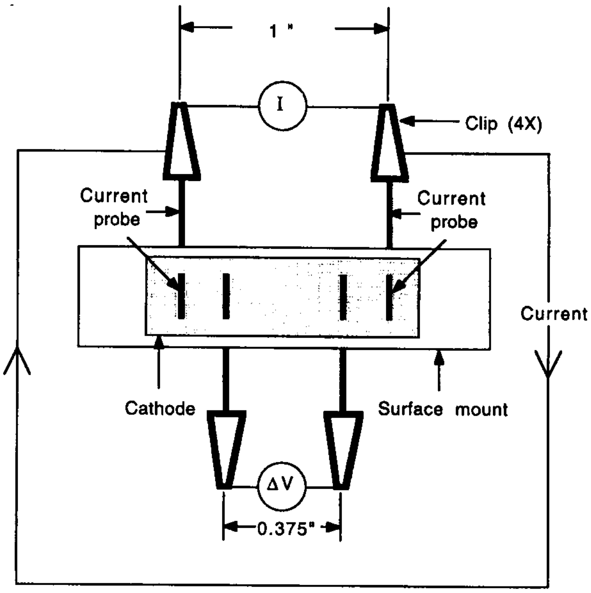

Fig. 1. Setup for the four-point probe method for measuring electrical resistivity of MnO_2 composite cathode plates.

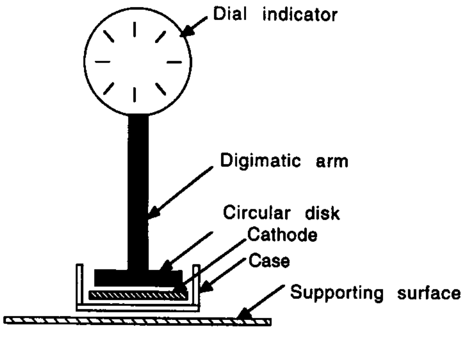

Fig. 2. Setup for packing density measurement of MnO_2 composite cathode plates.

assembly was returned to the transducer, the disked arm lowered to the cathode surface (no pressure was applied by the transducer) and the thickness of the cathode recorded.

Carbon material electrochemical performance was assessed by cyclic voltammetry (CV) using the method described in Ref. [35]. The carbon filaments were packed into the cavity of a purchased BAS holder normally used for carbon paste at a pressure of 10 MPa without the use of any binder, whereas carbon black was packed into the holder with mineral oil as the binder. (Without the binder, the carbon black dislodges from the electrode cavity during CV.) The circular carbon filament electrode had a surface area of 0.0792 cm^2. The rate constant for electron transfer (k_s) was used to compare the electrochemical performance of the carbon additives [35]. An aqueous solution was selected over an organic solution for this phase of study because aqueous systems are, in general, more conductive than organic systems allowing faster scan rates and, in turn, more efficient experimentation and evaluation of results. Even though the electrochemical response may be different in aqueous solutions than in organic solutions, the comparative information obtained relative to the effect of carbon type and treatment on electrochemical performance can be used to interpret performances achieved in electrochemical cells (such as battery electrodes) regardless of the electrolyte used.

3. Results

The two types of carbon filaments, H79 and ADNH, were obtained from Applied Sciences Inc. The differences in filament shape and size are given in Ref. [41]. (ADNH filaments were relatively straight, substantially larger in diameter, ~ 1500 Å, and less crystalline in nature in comparison to the H79 filaments which were more curved, twisted and smaller in diameter, ~500 Å.) Carbon black, with which the filaments were being compared, was spherical in nature with a mean diameter of 500 Å. X-ray diffraction demonstrated that, in contrast to the carbon filaments, the carbon black used to complement this study was absent of the 002 graphite peak.

MnO_2 cathode plates fabricated with ADNH carbon filaments as the conductive additive in stead of carbon black generally displayed a higher cathode resistivity (Table 1), even though filament compacts without MnO_2 displayed resistivities lower than those achieved by the carbon black compacts (Table 2). The higher filament/MnO_2 cathode resistivities, however, did not compromise discharge performance. Rather, under certain conditions, significantly higher capacities than those using carbon black were achieved, while the OCV and CCV of the test assemblies were equivalent to or higher than those with carbon black.

Because of their clinginess, the filament clusters were difficult to separate into individual filaments, thus affecting filament distribution in the MnO_2 cathode. A previous study demonstrated that chopping of the filaments in a liquid medium using a rotary blade blender shortened the length of the ADNH filaments [35]. In the case of ADNH, cleansing of the filaments in acetone, whether (i) followed by chopping in water and then drying, (ii) followed by chopping in water containing Pluronic, or (iii) followed by chopping in acetone, significantly increased the cathode's electrolyte absorptivity and absorption rate, which, in turn, resulted in a significant increase in the discharge capacity (Table 1). Acetone cleansing followed by chopping in water (but without oven drying), lowered the cathode volume resistivity, although it had little effect on the absorptivity, rate of absorption or capacity (Table 1). A chopping duration of 1 min in acetone was found to be better than 3 min for attaining high absorptivity and high rate of absorption and hence high capacity. Excessive chopping (as for 3 min of chopping in acetone) decreased absorptivity and rate of absorption (and hence decreased capacity), while increasing resistivity (and hence decreasing the OCV and the CCV) due to excessive shortening of the filaments. Cleansing and chopping ADNH in methylene chloride was not as effective as doing the same in acetone.

In the case of H79, cleansing and chopping in methylene chloride for 1 min resulted in equivalent absorptivity and rate of absorption (and hence equivalent capacity) compared to as-received carbon black and as-received ADNH cathodes. (A previous study disclosed cleansing in acetone to be ineffective for H79 [35].) The OCV and CCV values of the 1 min methylene chloride chopped H79 were significantly lower than those of the 3 min methylene chloride chopped H79; this is related to the higher resistivity of the former. Increasing the chopping time from 1 to 3 min is believed to facilitate filament distribution throughout the cathode, which, in turn, resulted in lower cathode resistivity and increased OCV and CCV. The absorptivity and absorption rate, however, were decreased (due to the reduced aspect ratio of the filaments), and therefore capacity also decreased.

The composite cathodes using cleansed H79 carbon filaments (chopped for 1 min) gave capacity that was comparable to the as-received carbon black counterpart, due to their comparable electrolyte absorptivity and rate of absorption (in turn, due to their similar unit size, 500 Å, and hence pore size). However, the capacity was lower than as-received carbon black when chopped for 3 min due to a decrease in cathode absorptivity and rate of absorption; in spite of this, OCV and CCV were higher than as-received carbon black when chopped for 3 min, due to the decreased resistivity, presumably resulting from more homogeneous distribution of the H79 filaments attained with 3 min chopping than with 1 min chopping. Use of H79 in stead of carbon black had no effect on cathode packing density. Capacities for the H79 containing cathodes were lower compared to cleansed and treated ADNH because of the lower cathode absorptivity and rate of absorption of the H79 cathodes.

Pluronic treatment of carbon black greatly increased the cathode's electrolyte absorptivity and rate of absorption, and hence the capacity, while the resistivity was decreased, thus causing OCV and CCV to increase (Table 1). Acetone

Table 1
Discharge results and cathode characteristics of MnO_2 cathodes with Teflon [a]

Carbon type	Carbon treatment	CCV(V) ±0.002	CCV(V) ±0.002	Capacity to 2.0 V (mAh/g MnO_2)(±25)	Cathode absorptivity (g/g cathode) (±0.5)	Rate of absorption (g/g cathode in 15 s)(±0.5)	Cathode resistivity (Ω cm)(±5)	Cathode packing density (g/cm^3) (±0.02)	Volume percent carbon (%)(±0.2)
ADNH	As-received	3.848	3.796	139	10.4	36.1	78	0.95	9.1
ADNH	Acetone cleansed, chopped in water [b]	3.875	3.843	140	10.9	41.8	26	1.07	10.3
ADNH	Acetone cleansed, chopped in water	3.853	3.835	206	60.0	199.1	46	2.31	22.1
ADNH	Acetone cleansed, chopped in Pluronic	3.879	3.843	213	50.9	201.9	8	1.74	16.6
ADNH	Acetone cleansed, chopped 1 min	3.986	3.967	207	61.5	214.8	58	1.09	10.5
ADNH	Acetone cleansed, chopped 3 min	3.853	3.745	191	46.6	177.9	63	1.05	10.0
ADNH	Methylene chloride cleansed, chopped 1 min	3.867	3.843	192	47.8	179.2	61	1.09	10.5
H79	As-received	3.865	3.799	73	7.4	22.3	64	0.99	9.5
H79	Methylene chloride cleansed, chopped 1 min	3.677	3.459	139	10.5	34.2	88	1.53	14.6
H79	Methylene chloride cleansed, chopped 3 min	3.884	3.857	95	8.2	28.7	48	1.56	14.9
Carbon black	As-received	3.857	3.826	136	10.2	34.6	6	1.55	14.8
Carbon black	Pluronic treated	3.882	3.843	203	52.6	209.9	3	1.59	15.2

[a] Theoretical OCV = 3.5 V; nominal CCV = 3.0 V, from Ref. [38].

[b] Dried overnight in an environmentally controlled room with < 1% RH. All others dried at 140 °C for a minimum of 6 h.

Table 2
Electrical resistivity of carbon filaments at 7 MPa pressure, from Ref. [35].

Filament type	Condition	Density (g/cm^3)	Resistivity (Ω cm)
ADNH	As-received	0.562	0.041
ADNH	Acetone cleansed	0.632	0.020
ADNH	Acetone cleansed, Pluronic treated	0.747	0.066
H79	As-received	0.795	0.106
H79	Acetone cleansed	0.733	0.109
H79	Methylene chloride cleansed	0.889	0.086
Carbon black	As-received	0.618	0.069
Carbon black	Pluronic treated	0.615	0.046

cleansed ADNH carbon filaments chopped for 1 min in acetone produced higher OCV and CCV than carbon black (as-received or Pluronic treated), but lower cathode packing density.

Surface cleansing and chopping of the filaments favorably impacted achieved capacities. The effect, however, is related to the increased electrolyte absorptivity and rate of electrolyte absorption of the cathode and not the decreased cathode resistivity. For example, the electrical resistivity of the cathode using ADNH chopped 3 min in acetone was ten times greater than the as-received carbon black counterpart, yet achieved almost 60 mAh/g MnO_2 more capacity than the as-received carbon black counterpart (Table 1). Only in the case of surfactant treatment of the carbon filaments was composite cathode electrical resistivity low and absorptivity high. Almost 80 mAh/g MnO_2 more capacity was achieved with surfactant treatment of the filaments than that achieved with the as-received carbon black counterpart (Table 1). The relationship between achieved capacity and electrolyte absorption and that between achieved capacity and electrolyte absorption rate are shown in Fig. 3 for all the carbon types studied. Table 1 and Fig. 3 clearly demonstrate that the main factors related to a high capacity are cathode electrolyte absorptivity and electrolyte absorption rate, not cathode conductivity.

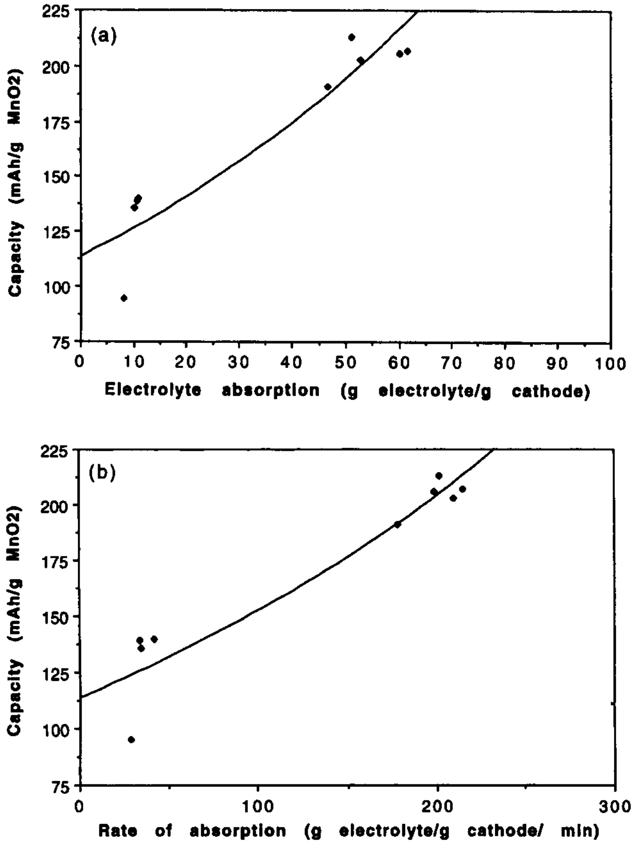

Fig. 3. Plot of cathode electrolyte absorption characteristics: (a) Capacity vs. cathode electrolyte absorption, and (b) capacity vs. cathode electrolyte absorption rate.

There are other advantages than just capacity improvements associated with using carbon filaments in place of carbon black as the conductive additive to MnO_2 cathodes. Both end-of-life indication and energy density are improved. With respect to end-of-life indication, Table 3 and Fig. 4 show that the discharge curve displays a more gentle slope near end-of-life with carbon filaments compared to carbon black. This means that cathodes using carbon filaments are conducive for use in applications requiring end-of-life indication, such as the implantable cardiac pacemaker. The end-of-life character of the discharge curve is shown in Table 3 in terms of the change in capacity upon changing the cutoff voltage from 2.5 to 1.5 V. The change in capacity for ADNH carbon filaments ranged between 40 and 90 mAh/g MnO_2 (Table 3). Carbon black containing cathodes, even with treatment, displayed capacity changes below 25 mAh/g MnO_2 (Table 3 and Fig. 5). However, for both ADNH and H79, the change in capacity decreased when the chopping time increased from 1 to 3 min. Thus, it is concluded that a large aspect ratio for the carbon additive unit is one factor desirable for achieving good end-of-life indication. A second factor, and probably the more important, is the electron transfer rate of the conductive additive. As shown by the CV data in Table 4 and Fig. 6(a), as-received ADNH displayed irreversible electrochemical behavior. After acetone cleansing and chopping in acetone (Fig. 6(b)), a more reversible electrochemical response was obtained with a calculable reaction rate constant. Carbon black, on the other hand, displayed irreversible performance even with Pluronic treatment, though the Pluronic treatment helped (Table 4 and Fig. 7). The ability to transfer electrons rapidly prevents charge build-up by the cathode and therefore inhibits abrupt end-of-life. A

Table 3
Discharge end-of-life characteristics of MnO_2 cathodes with Teflon

Carbon type	Carbon treatment	Capacity (mAh/g MnO_2) (±25)			Change in capacity for cutoff voltages between 2.5 to 1.5 V (mAh/g MnO_2) (±5)
		to 2.5 V	to 2.0 V	to 1.5 V	
ADNH	As-received	103	139	155	52
ADNH	Acetone cleansed, chopped in water [a]	112	140	153	41
ADNH	Acetone cleansed, chopped in water	165	206	228	63
ADNH	Acetone cleansed, Pluronic treated	171	213	237	66
ADNH	Acetone cleansed, chopped 1 min	147	207	236	89
ADNH	Acetone cleansed, chopped 3 min	143	191	218	75
ADNH	Methylene chloride cleansed, chopped 1 min	163	192	207	44
H79	As-received	52	73	79	27
H79	Methylene chloride cleansed, chopped 1 min	102	139	152	50
H79	Methylene chloride cleansed, chopped 3 min	79	95	103	24
Carbon black	As-received	130	136	139	9
Carbon black	Pluronic treated	190	203	214	24

[a] Dried overnight in an environmentally controlled room with < 1% RH. All others dried at 140 °C for a minimum of 6 h.

high absorptivity or a high rate of absorption per se (as in the case of Pluronic treated carbon black) did not necessarily result in good end-of-life indication (Tables 1 and 3). The cathode resistivity did not correlate with the end-of-life character (Tables 1 and 3).

Of the treatments to ADNH that resulted in dramatic capacity improvements, (i) acetone cleansing and chopping in water with Pluronic, and (ii) acetone cleansing and chopping in water plus drying, additionally increased the packing density of the MnO_2 cathode (11% and 33% higher respectively, Table 1). Only a slight increase in packing density (2%) was realized with the Pluronic treated carbon black. The resistance to compaction due to the structure of the carbon black overshadowed any significant densification that might be realized by the surfactant treatment of the carbon black. Acetone cleansing and chopping in water with Pluronic and acetone cleansing and chopping in water plus drying also made possible the fabrication of cathodes with higher carbon volume fractions. A higher carbon volume fraction contributed to lowering the cathode resistivity. In the case of ADNH that had been acetone cleansed and Pluronic chopped, the cathode resistivity was near to that achieved by using as-received carbon black (8 Ω cm ADNH and 6 Ω cm for as-received carbon black).

With respect to the energy density, the appropriately treated ADNH filament/MnO_2 cathodes consistently dis-

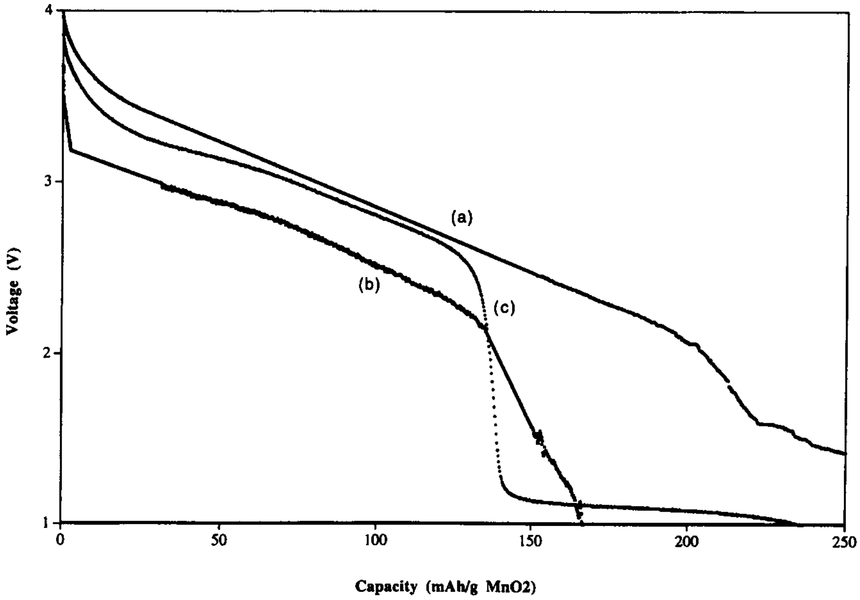

Fig. 4. Discharge results comparing composite cathodes made with: (a) ADNH filaments cleansed and chopped 1 min in acetone; (b) H79 filaments cleansed and chopped 1 min in methylene chloride, and (c) as-received carbon black as the conductive additive.

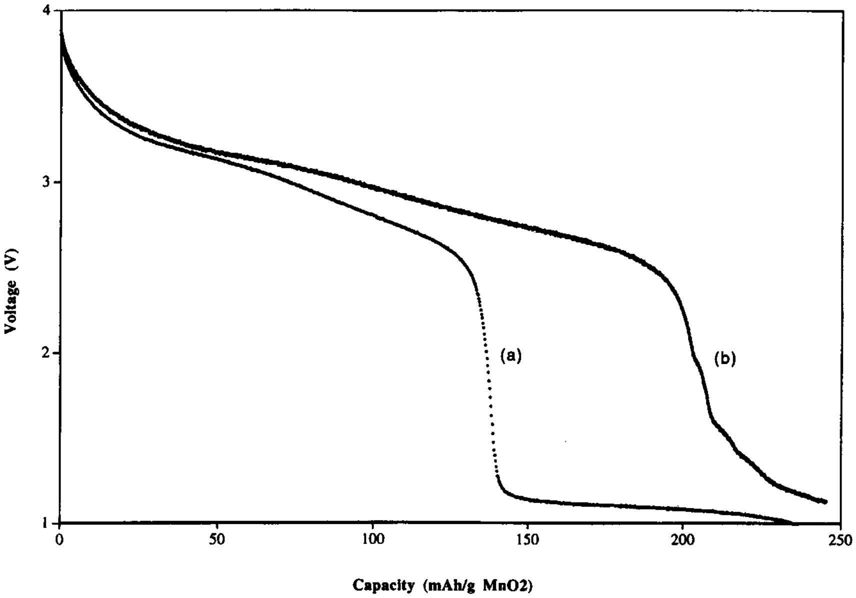

Fig. 5. Discharge results comparing composite cathodes made with: (a) as-received carbon black, and (b) surfactant treated carbon black as the conductive additive.

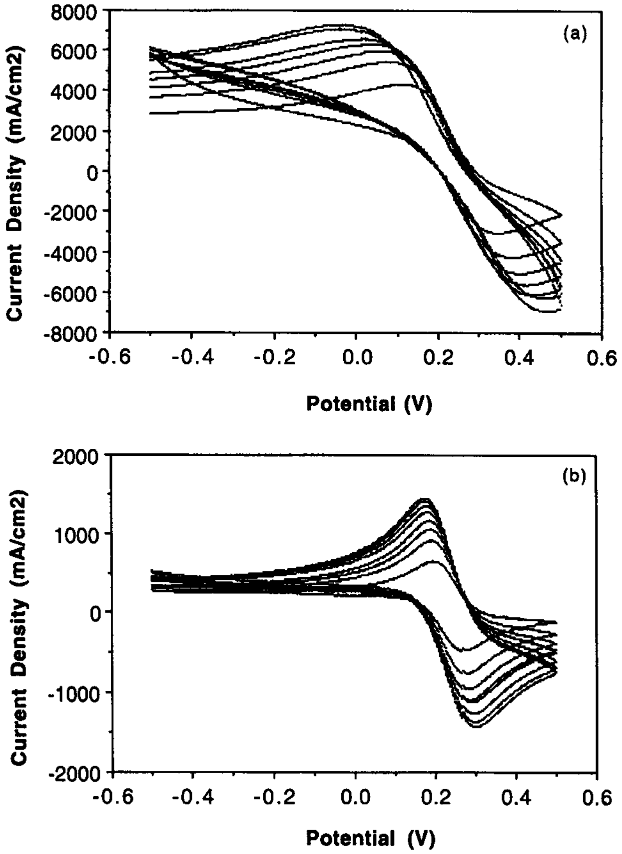

Fig. 6. Cyclic voltammetry results for carbon filaments: (a) as-received, and (b) acetone cleansed and chopped.

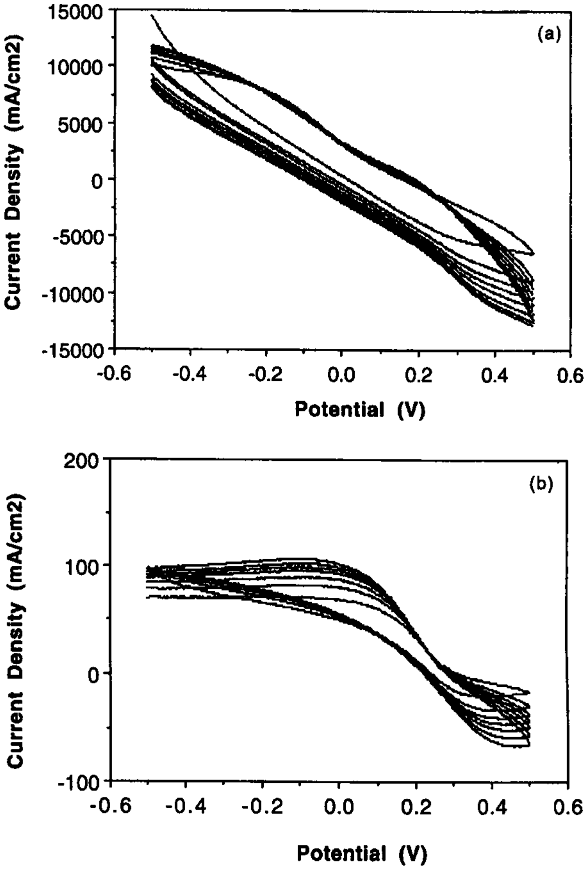

Fig. 7. Cyclic voltammetry results for carbon black: (a) as-received, and (b) Pluronic treated.

played higher gravimetric energy densities than those utilizing as-received carbon black, and the carbon black electrodes approached the gravimetric energy densities achieved using the treated ADNH filaments when treated with Pluronic (Table 5). The volumetric energy density of the ADNH filament/MnO_2 cathodes were dramatically improved by treat-

Table 4
Carbon material cyclic voltammetry results obtained at a potential scan rate of 200 mV/s

Filament type	Treatment	Anodic peak current density, I_a (mA/cm^2) (± 25)	Cathodic peak current density, I_c (mA/cm^2) (±25)	I_a/I_c (±0.2)	Peak separation, ΔE (mV) (±10)	Rate constant, k_s (cm/s) (±0.0005)
ADNH	As-received	7800	1650	4.7	530	Irreversible
ADNH	Acetone cleansed/ chopped	1680	1450	1.2	130	0.0082
Carbon black	As-received	9000	8300	NA	NA	Irreversible
Carbon black	Pluronic treated	89	13	6.8	556	Irreversible

Table 5
Energy densities with percent of theoretical value

Carbon type	Carbon treatment	Gravimetric energy density [a] (Wh/g)(±0.02)	% of theoretical value	Volumetric energy density [b] (Wh/cm^3) (±0.02)	% of theoretical value
ADNH	As-received	0.04	4	0.45	15
ADNH	Acetone cleansed, chopped in water [c]	0.33	33	0.84	27
ADNH	Acetone cleansed, chopped in water	0.48	48	2.65	86
ADNH	Acetone cleansed, Pluronic treated	0.45	45	1.86	60
ADNH	Acetone cleansed, chopped 1 min	0.48	47	1.24	40
ADNH	Acetone cleansed, chopped 3 min	0.43	43	1.08	35
ADNH	Methylene chloride cleansed, chopped 1 min	0.46	46	1.19	39
H79	As-received	0.18	18	0.43	14
H79	Methylene chloride cleansed, chopped 1 min	0.31	31	1.13	37
H79	Methylene chloride cleansed, chopped 3 min	0.23	23	0.85	28
Carbon black	As-received	0.42	42	1.57	51
Carbon black	Pluronic treated	0.49	49	1.87	61

[a] Theoretical gravimetric energy for Li/MnO$_2$ is 1.001 Wh/g for a theoretical voltage of 3.5 V, from Ref. [38].
[b] Theoretical volumetric energy density for Li/MnO$_2$ is 3.084 Wh/cm^3 for a theoretical voltage of 3.5 V, from Ref. [38].
[c] Dried overnight in an environmentally controlled room with < 1% RH. All others dried at 140 °C for a minimum of 6 h.

ing the filaments with a surfactant or acetone cleansing followed by chopping plus drying (Table 5). The improvement in volumetric energy density is attributed to the improved cathode packing density (Table 1) obtained with these treatments. In the case of acetone cleansing with chopping plus drying of the filaments, 25% more energy density by volume was achieved over even the Pluronic treated carbon black technology (Table 5). Further, the volumetric energy density achieved with ADNH that had been cleansed in acetone, chopped in water and then dried was 86% of theoretical (Table 5), whereas that of the as-received carbon black containing cathode was 51% of theoretical, and the Pluronic treated carbon black containing cathode was 61% of theoretical.

An added bonus to the carbon filament technology is that MnO$_2$ cathode plates using ADNH did not require binders for handleability and shapeability. Because of the filaments' clinginess to each other and their high aspect ratio, MnO$_2$ particles were held in place by the random orientation of the carbon filaments, which formed a web, effectively entrapping the MnO$_2$ particles between them. This is shown in Fig. 8(b). The highly structured, porous carbon black, although spreadable, thus providing better electrical connectivity, was unable to hold the MnO$_2$ particles in place. A binder, such as Teflon™, was required to provide a sticky backbone to which the carbon black and MnO$_2$ particles cling. Fig. 8(a) shows the carbon black/MnO$_2$/Teflon™ cathode. The end-of-life appearance of the discharge curve using carbon filaments and no Teflon™, as shown in Fig. 9, is unaffected by the absence of the Teflon™ binder. Additionally, as shown in Table 6 cathode packing density and volumetric energy density were increased an additional 10% by using no Teflon™.

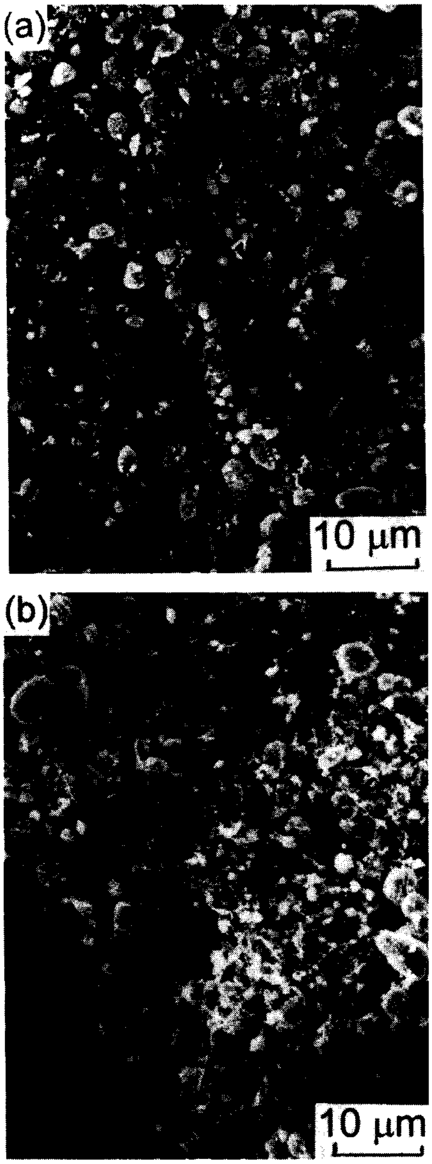

Fig. 8. Scanning electron microscope photographs of composite cathodes made with: (a) as-received carbon black, and (b) ADNH carbon filaments as the conductive additive.

4. Discussion

To be useful for applications requiring end-of-life indication, battery discharge curves must display a gradual change in voltage as a function of time so as to alert users of a time interval within which replacement can be made. The change in voltage can display itself as a series of declining running voltages so as to create steps in the discharge curve or the voltages near end-of-life can show a gradual decline in running voltage over a long period of time (for implantable devices, 6 months is the accepted time interval to replacement). In the Li/MnO_2 system, where carbon black is typically used as the cathode conductive additive, the abrupt and rapid decline in running voltage at end-of-life precludes its use for these applications. In this work, substitution of carbon black with ADNH carbon filaments produces a discharge

Table 6
Discharge capacity comparison for ADNH filament/MnO_2 cathodes with and without Teflon

Carbon type	Carbon treatment	Capacity to 2.0 V (mAh/g MnO_2) (± 25)	Gravimetric energy density [a] (Wh/g) (± 0.02)	Volumetric energy density [b] (Wh/cm^3) (± 0.02)	Cathode packing density (g/cm^3) (± 0.02)	Volume percent carbon (%) (± 0.2)	Cathode resistivity (Ω cm) (± 5)	Cathode absorptivity (g/g cathode) (± 0.5)	Rate of absorption (g/g cathode in 15 s) (± 0.5)
ADNH	Acetone cleansed, chopped 1 min with Teflon	207	0.48	1.24	1.09	10.5	58	61.5	214.8
ADNH	Acetone cleansed, chopped 1 min no Teflon	203	0.52	1.66	1.22	11.6	60	66.6	217.9

[a] Theoretical gravimetric energy density for Li/MnO_2 is 1.001 Wh/g for a theoretical voltage of 3.5 V, from Ref. [38].

[b] Theoretical volumetric energy density for Li/MnO_2 is 3.084 Wh/cm^3 for a theoretical voltage of 3.5 V, from Ref. [38].

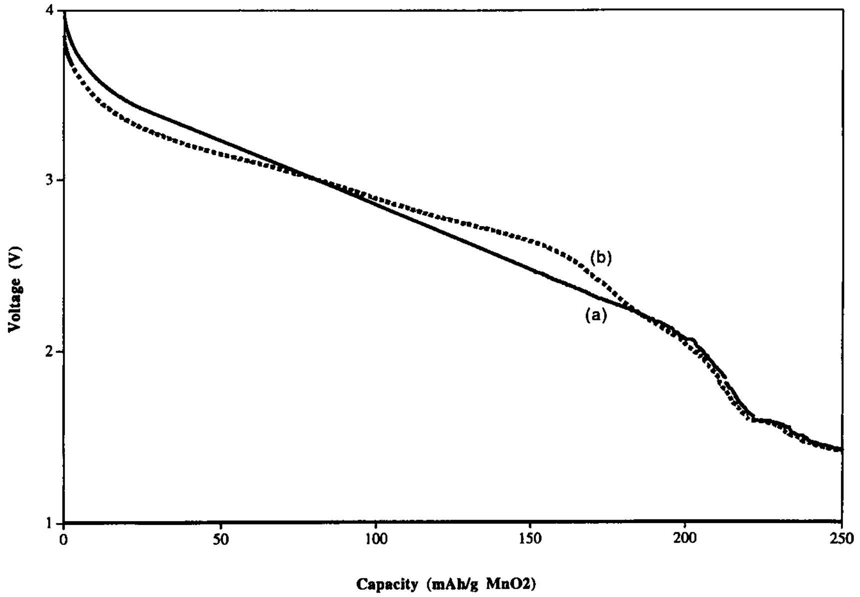

Fig. 9. Discharge results comparing composite cathodes made with acetone cleansed ADNH carbon filaments chopped 1 min: (a) with teflon, and (b) without Teflon binder.

curve with a gentle slope at end-of-life. Furthermore, discharge capacities exceed those achieved by the state-of-the-art carbon black technology. The primary factor contributing to these results is associated with the electron transfer rate of the carbon filaments with some contribution being made by the shape of the carbon filaments. Their high aspect ratio produces a channel-like pore structure within the MnO_2 cathode that facilitates flowability of electrolyte into the cathode. This easier flow of electrolyte allows a larger quantity of electrolyte to be held by the cathode and the rate of absorption of the electrolyte into the cathode to be higher. The availability of electrolyte to promote ionic conduction and the ability of the carbon filament to rapidly transfer electrons decrease the degree and rate of cathode polarization, thereby extending the usable life of the cathode and yielding a discharge curve with a gently sloping end-of-life. The importance of electrolyte absorptivity and rate of electrolyte absorption is in contrast to the currently accepted belief that cathode conductivity is the overriding factor contributing to the Li/MnO_2 cell performance. Cathode absorptivity and rate of absorption also proved to be governing factors for carbon black containing cathodes.

The performance of the Li/MnO_2 cell is described by the OCV, CCV, capacity, energy density (gravimetric and volumetric) and gradualness of the discharge curve toward end-of-life. This work shows that the use of appropriately treated ADNH carbon filaments in stead of as-received carbon black (state-of-the-art carbon black) resulted in comparable OCV and CCV, higher capacity, higher energy density (both gravimetric and volumetric) and improved gradualness of the discharge curve toward end-of-life. The improved gradualness toward end-of-life makes possible the use of the Li/MnO_2 cell for applications (such as implanted medical applications) that require an indication of the approach to end-of-life. Even with Pluronic treated carbon black, this is not possible. However, with appropriately treated ADNH carbon filaments this is possible.

The origin of the high volumetric energy density achieved by using the ADNH carbon filaments is in the high packing density of the cathode and the high capacity. The origin of the high capacity is the cathode's high electrolyte absorptivity and rate of electrolyte absorption. The good absorption characteristics are in turn due to the channel-like shape and large size of the pores in the cathodes. The origin of the high packing density is the small diameter of the carbon filaments (0.15 μm for ADNH) compared to a particle size of 2–10 μm for the MnO_2, and the effectiveness of the filament surface treatment in removing surface contaminants (polyaromatic hydrocarbons [35]) and filament length reduction (clustering tendency reduction).

The origin of good end-of-life indication is the alleviation of polarization in the cell. The polarization alleviation is in turn due partly to a high electron transfer rate at the carbon surface and partly to the cathode's high rate of electrolyte absorption and high electrolyte absorptivity, as the ease of electron transfer and of electrolyte flow avoids local charge build-up. For Pluronic treated carbon black, the absorption characteristics are as good as those of the filament cathodes, but the electron transfer rate is too low for avoiding polarization, so good end-of-life indication is not possible. There may still be other factors that govern the end-of-life character, but the cathode resistivity is not a major factor (in contrast to the common belief that a low resistivity helps reduce polarization). This work provides some but not all the factors.

The surface treatments that gave best overall performance to the Li/MnO_2 cell with ADNH carbon filaments were (i) acetone cleansing followed by chopping in water containing Pluronic, (ii) acetone cleansing followed by chopping in water and then oven drying, and (iii) acetone cleansing and chopping in acetone for 1 min. The second treatment is attractive in giving the highest volumetric energy density; the third treatment is attractive in giving the best end-of-life indication and the highest OCV and CCV; the first treatment is attractive in giving the next-to-highest volumetric energy density as well as the next-to-best end-of-life indication. All three treatments are similar in terms of cost and in the step of acetone cleansing and the step of chopping, though they differ in the acetone for chopping. Acetone cleansing serves to remove the surface contaminants (polyaromatic hydrocarbons [35]). Chopping serves mainly to help break up the filament clusters and reduce filament length, particularly if it is done for too long. The use of water as a chopping medium requires subsequent oven drying. The use of surfactant changes the surface functional groups on the carbon filaments, thereby allowing the filaments to pack more intimately with the MnO_2. This intimacy not only serves to increase the packing density, but serves to decrease the contact resistivity between carbon and MnO_2, thus enhancing the ease of charge transfer. If acetone is used as the chopping medium, no drying or surfactant use is needed.

The use of H79 instead of ADNH carbon filaments gave lower capacity (due to much lower absorptivity and much lower rate of absorption) and poorer end-of-life indication (due to a low electron transfer rate and poor absorption characteristics). The poor absorption characteristics are due to the small pore size, which is due to the small diameter of H79 compared to ADNH. Methylene chloride cleansing of H79 serves to remove the contaminant (polyaromatic hydrocarbons) on the filament surface [35]; acetone cleansing is not effective for H79 [35]. In spite of the cleansing and chopping in methylene chloride, H79 performed poorly.

This work shows that Pluronic treatment of carbon black greatly improves the Li/MnO_2 cell performance for cells that use carbon black as the conductive additive. The improvement is in terms of increased OCV, CCV, capacity and energy density (both gravimetric and volumetric). The increased OCV and CCV are due to the decreased resistivity. The increased capacity is due to the cathode's increased electrolyte absorptivity and rate of electrolyte absorption. The increased energy density is due to the increased packing density and increased capacity.

A low cathode resistivity is valuable not only in increasing OCV and CCV, but also for reducing the Joule heating of the cell during use. The heating reduction is desirable for enhancing the safety of the cell.

The electrical resistivity of the cathode is governed by the volume electrical resistivities of the cathode components (i.e., MnO_2 and carbon, particularly the latter), the contact electrical resistivity between the carbon and MnO_2, and the connectivity of the carbon. Table 2 shows that the carbon compact without MnO_2 is more conductive when the carbon consists of carbon filaments than when the carbon is carbon black. However, Table 1 shows that the compact with MnO_2 is more conductive when the carbon is carbon black than when the carbon is consisting of carbon filaments. The effect in Table 2 is due to the high aspect ratio and high volume fraction of the carbon filaments; percolation necessarily occurred since the filaments were the only phase present, thereby resulting in a low resistivity for the carbon compact. In contrast, the MnO_2/carbon compact of Table 1 contained up to only 22 vol.% carbon. The connectivity of the carbon depends on the ability of the carbon to spread itself between the adjacent MnO_2 particles. The result of Table 1 implies that carbon black has better spreadability than the carbon filaments, due to the porous nature of each carbon black particle. Table 1 also shows that appropriate treatments of the ADNH carbon filaments decreased the resistivity of the MnO_2/carbon compact. The most effective treatment involves acetone cleansing followed by chopping in water containing Pluronic. This treatment also decreased the resistivity of the carbon compact without MnO_2 (Table 2). These effects are because the surface treatment improved the dispersion of carbon filaments.

For the sake of comparison, this work fixed the carbon weight at 1/10 that of the MnO_2 cathode material for both carbon black and carbon filaments. Volume fractions varied. The optimum carbon volume fraction was not determined and may be different for cathodes with carbon black and those with carbon filaments.

In general, the filament/MnO_2 cathodes maintained handleability and shapeability without the use of binders, in contrast to carbon black containing cathodes. The filaments themselves are the binder, effectively entrapping the MnO_2 between the weblike structure formed by their random distribution throughout the cathode. The absence of binder further improves cathode packing density, and therefore volumetric energy density (Table 6).

5. Conclusions

Substitution of carbon black as the conductive additive to the MnO_2 cathode plates with ADNH carbon filaments that had been acetone cleansed and chopped in water with Pluronic surfactant, or acetone cleansed and chopped in water followed by drying, resulted in a gradual (not abrupt) decline in running voltage near cell end-of-life, and required less cathode volume and no binder for shapeability and handleability. Less cathode volume translated into higher volumetric energy density. The factors governing the capacity of the Li/MnO_2 system were determined to be electrolyte absorptivity and rate of electrolyte absorption rather than cathode electrical resistivity, regardless of the carbon additive used. The factors governing the gradualness toward end-of-life include a high electron transfer rate across the carbon surface and a high rate of electrolyte absorption. The MnO_2 cathode's electrolyte absorptivity, rate of absorption, packing density, and volumetric and gravimetric energy densities were, in turn, governed by the surface treatment of the carbon additive. In the case of carbon black, surfactant treatment was effective in improving electrolyte absorptivity, rate of absorption, and gravimetric and volumetric energy densities. Cathode compaction and carbon surface electron transfer rate, however, were only slightly improved. For ADNH carbon filaments, solvent cleansing, followed optionally by either chopping using a surfactant or chopping in water plus drying, was effective in improving absorptivity characteristics, carbon surface electron transfer rate and energy densities. Much higher cell discharge capacities were achieved using ADNH carbon filaments than by using H79 carbon filaments due to the former's higher electrolyte absorptivity and rate of electrolyte absorption. Though the carbon black compact without MnO_2 displayed a higher volume resistivity than the ADNH carbon filament compact, the carbon black/MnO_2 compact exhibited an electrical resistivity lower than or equivalent to that of the carbon filament/MnO_2 compact. This is attributed to the spreadability of the carbon black between adjacent MnO_2 particles when compressed.

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