CARBON FILAMENTS AS A CONDUCTIVE ADDITIVE IN MnO_2 ELECTRODES

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INTRODUCTION

The MnO_2 cathode is a composite electrode which uses carbon as an additive primarily to enhance electrical conductivity, because cathode electrical conductivity is thought to be the main factor influencing the Li/MnO_2 battery performance [1]. Studies conducted relative to the contribution of the conductive additive have, in general, been focused on carbon black because of its high conductivity. The scope of these studies have been limited to the type of carbon black and the volume fraction required to reach optimum MnO_2 cathode conductivity. The contribution of cathode electrolyte absorption, compressibility and elasticity have not been studied, and no correlation has been made between the cathode electrolyte absorption and the Li/MnO_2 cell capacity. There have been essentially no comparative studies of carbon black with other carbon materials using the Li/MnO_2 system, and 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. This work shows that carbon filaments, because of their high aspect ratio and their shape, greatly improve MnO_2 cathode absorptivity, while acting as the binder for the cathode. The improved cathode absorptivity, as opposed to cathode conductivity, was found to result in significant increases in capacity in the Li/MnO_2 cell with the added bonus of a gently sloping discharge curve. The latter makes the Li/MnO_2 system available for use in applications requiring end-of-life indication, such as the cardiac pacemaker.

EXPERIMENTAL

A laboratory plate-to-plate discharge test cell was used to study the impact of the carbon additive on the performance of the Li/MnO_2 cathode. Electrodes were made by placing the carbon material mixed with MnO_2 in a stainless steel cup made by cutting down a AA size battery case and pressing in the case at 21 MPa. An insulative separator was placed on top of the carbon followed by a lithium/nickel screen anode assembly. The layered electrodes were covered with a polymer insulator and a glass slide. The assembly was held together using a metal clip, immersed in an electrolyte comprised of lithium hexafluoroarsenate in propylene carbonate mixed with dimethoxyethane, then discharged at 0.3 mA/cm^2. Data were evaluated at three cut-off voltages, 2.5, 2.0 and 1.5 V. Carbon filament electrodes were compared with electrodes fabricated using conventional carbon black. No binder was used with the carbon filaments, as the filaments provided binding. However, a binder (teflon) was necessary for carbon black.

RESULTS AND DISCUSSION

Carbon filaments (0.15 μm diameter, Grade ADNH, from Applied Sciences Inc., Cedarville, Ohio) used in place of carbon black as the conductive additive to MnO_2 cathodes resulted in capacity improvements over cathodes fabricated with conventional carbon blacks due to the cathode's increased electrolyte absorption capability and rate of electrolyte absorption and not the cathode conductivity (Table 1). Cleansing of the filaments in acetone, whether (i) followed by chopping in water and then drying, (ii) followed by chopping in water containing Pluronic (a surfactant), 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

TABLE 1 - DISCHARGE CHARACTERISTICS OF MnO2 CATHODES

Carbon type	Carbon treatment	Capacity ($mAh/g\ MnO_2$) for a cut-off voltage of 2.0 V ± 25	Absorptivity (g electrolyte /g cathode) ± 0.5	Rate of absorption (g electrolyte /g cathode/15s) ± 0.5	Resistivity (Ω•cm) ±5	Packing density (g/cm^3) ± 0.02
Filaments	As received	139	10.5	36.1	78	0.95
Filaments	Acetone cleansed /chopped in water	140	10.9	41.8	26	1.07
Filaments	Acetone cleansed /chopped in water /oven dried	206	60.0	199.1	46	2.31
Filaments	Acetone cleansed /Pluronic treated	213	50.9	201.9	8	1.74
Filaments	Acetone cleansed /chopped 1 min	207	61.5	214.8	58	1.09
Filaments	Acetone cleansed /chopped 3 min	191	46.6	177.9	63	1.05
Carbon black	As-received	136	10.2	34.6	6	1.55
Carbon black	Pluronic treated	203	52.6	209.9	3	1.59

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 open circuit voltage, OCV, and the closed circuit voltage, CCV), due to excessive shortening of the filaments. The substitution of carbon black with carbon filaments also produced a discharge curve with a gentle slope at end-of-life. The end-of-life was abrupt when carbon black (whether as-received or Pluronic treated) was used. Furthermore, discharge capacities exceeded those achieved by as-received carbon black when the filaments were used. The primary factor contributing to the gradual end-of-life when filaments were used is associated with the high 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 faster. 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 the governing factors for carbon black containing cathodes.

CONCLUSIONS

Substitution of carbon black as the conductive additive to 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. 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. 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.

REFERENCES

1. H. Dietz, J. Garche and K. Wiesener, *J. Power Sources*, 14 (1985) 305.