untreated fibers are used. The activation treatment does not degrade the tensile properties of the fibers.

Acknowledgements

Technical assistance by Weiming Lu of this University is appreciated.

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A comparative study of carbons for use as an electrically conducting additive in the manganese dioxide cathode of an electrochemical cell

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Received 18 February 2001; accepted 5 August 2001

Keywords: A. Carbon black; Carbon filaments; Electrodes; Mesophase pitch; D. Electrical properties

Due to the fact that some electrochemical electrode materials are not conductive electrically, a conductive additive is added to the electrochemically active species in forming the electrode [1–6]. An example is manganese dioxide (MnO_2), which is not conducting and serves as the cathode of various electrochemical cells, including lithium cells. Due to the chemically inert and electrically conductive nature of carbons, carbon is used as the conductive additive. Among the carbons, carbon black is particularly common for this purpose.

Other than the electrochemically active materials and the conductive additive, the electrode contains a binder, which is commonly a thermoplastic polymer, such as polytetrafluoroethylene (PTFE, or teflon) and polyvinylidenefluoride (PVDF) in the form of particles. The binder serves to bind the ingredients together to form a shaped object (such as a disc) that can be handled. The type and amount of binder are expected to affect not only the bindability, but also the distribution of the carbon additive.

The primary objective of this work is to investigate the effect of the type of carbon additive on the electrical resistivity of the MnO_2 cathode. The types of carbon include graphitized mesophase pitch, natural graphite, graphitized carbon filaments (0.1 μm diameter, as made catalytically from carbonaceous gases), carbon filaments without graphitization, and carbon black. These types of carbon differ in their particle size, aspect ratio and degree of crystallinity, so their dispersion, connectivity and effectiveness as a conductive additive are expected to differ.

The secondary objective of this work is to investigate the effect of binder content on the effectiveness of carbons as a conductive additive.

Previous work has shown that carbon black is more effective than submicron carbon filaments without graphitization as a conductive additive for the MnO_2 cathode [7], even though a carbon black compact without MnO_2 exhibits higher resistivity than a carbon filament compact without MnO_2 [8]. Thus, a low resistivity for a carbon compact does not imply a low resistivity for an MnO_2–carbon composite. This is because the resistivity of an MnO_2–carbon composite depends on the dispersion and connectivity of the carbon in the midst of MnO_2 particles.

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PII: S0008-6223(01)00233-0

In spite of the large aspect ratio of a carbon filament, the carbon black is superior as a conductive additive, because of the spreadability of carbon black between the MnO_2 particles [7]. Because of the difficulty of theoretical prediction regarding the effectiveness of a carbon additive as a conductive additive, an experimental comparative study of various carbons for this application is the focus of this work.

The MnO_2 cathode was prepared by (i) degassing the carbon additive in vacuum at 150°C for 1 h, (ii) mixing the carbon additive (5 wt.%), the binder (PVDF, 5-μm particle size, either 10 or 6 wt.%), MnO_2 powder (from Aldrich, Milwaukee, WI, 99+%, 60-μm particle size, 85 wt.% when PVDF amounted to 10 wt.%, 89 wt.% when PVDF amounted to 6 wt.%) and ethanol to form a paste, (iii) making a foil from the paste, (iv) cutting a disc from the foil, (v) pressing the disc at a pressure of 30 kg/cm^2, and (vi) drying the disk in a vacuum at 125°C. Step (i) is for removing the adsorbed moisture, oxygen and other volatile species from the surface of the carbon. The disc was of diameter 20 mm and thickness ranging from 3 to 4 mm. The thickness of each specimen was measured for the purpose of determining the resistivity.

Five types of carbon were used in this comparative study. They are listed in Table 1 and their basic characteristics are shown there as well. The mesophase pitch was from Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan, Shanxi, PR China. The natural graphite was from Superior Graphite, Chicago, IL. The carbon filament was from Applied Sciences, Cedarville, OH; its diameter was 0.1 μm; its length was at least 100 μm. The carbon black was Shawinigan acetylene black from Chevron, Houston, TX; it was made by decomposing a high purity acetylene gas at about 1500°C.

Graphitization was performed on the mesophase pitch and the carbon filaments, using a vacuum furnace at 2800°C. Both carbon filaments with and without graphitization were investigated.

The DC volume electrical resistivity of the MnO_2 cathodes with five different types of carbon additive and two different binder contents was measured in the direction perpendicular to the plane of the cathode disc by using the four-probe method. All four electrical contacts were in the form of silver paint in conjunction with copper wire. A current contact in the form of a loop and a voltage contact in the form of a dot at the center of the loop were applied to each of the two circular faces of a disc. Six specimens of each combination of carbon type and binder content were tested. A Keithley 2001 multimeter was used for resistance measurement.

As the resistivity of a disc is expected to decrease with increasing packing density, the density is a relevant attribute. The density of a cathode disc was determined by measuring the weight and volume of the disc.

Table 2 gives the resistivity and density of the 10 different compositions of the MnO_2 cathode. At a binder content of 10 wt.%, graphitized carbon filament and graphitized mesophase pitch gave the lowest resistivity, while carbon filament without graphitization gave the highest resistivity. The resistivity of the cathode containing natural graphite was quite low, in spite of the low density. The cathode containing graphitized carbon filament exhibited lower resistivity than that containing graphitized mesophase pitch, in spite of the lower density of the former. At a binder content of 6 wt.%, carbon black and graphitized carbon filaments gave the lowest resistivity, while natural graphite and graphitized mesophase pitch gave the highest resistivity.

At either binder content, graphitization of the carbon filaments decreased the resistivity of the MnO_2 cathode, while increasing the density slightly. At either binder content, carbon black gave a cathode of lower resistivity than carbon filaments without graphitization, as previously reported [7].

For all the types of carbon except carbon black, a decrease in binder content increased the resistivity. For all the types of carbon, a decrease in binder content increased the density slightly. Thus, except for carbon black, the resistivity increased in spite of an increase in density. This effect is attributed to the decrease in the degree of dispersion of the carbon as the binder content decreased. In other words, the binder helped the dispersion of the

Table 1
The basic characteristics of various types of carbon

	C (%)	d_{002} (Å)	BET-specific surface area (m^2/g)	Particle size (μm)
Graphitized mesophase pitch	99.90	3.369	5.23	12
Natural graphite	99.89	3.362	2.75	27
Graphitized carbon filaments	99.70	3.360	26.4	/
Carbon filaments	99.70	3.367	53.9	/
Carbon black[a]	/	/	2.8	0.05

[a] Pore size = 18.9 Å [7].

Table 2
Electrical resistivity and packing density of MnO_2 cathodes of various compositions

Carbon type	Binder content (wt.%)	Resistivity ($\Omega\cdot$cm)	Density (g/cm^3)
Graphitized mesophase pitch	10	1.7 (±5.2%)	2.27 (±1.2%)
Natural graphite	10	3.9 (±4.3%)	0.79 (±1.3%)
Graphitized carbon filaments	10	1.0 (±4.7%)	1.41 (±1.2%)
Carbon filaments (without graphitization)	10	21 (±4.2%)	1.36 (±1.2%)
Carbon black	10	10.2 (±5.2%)	1.61 (±1.2%)
Graphitized mesophase pitch	6	152 (±6.0%)	2.30 (±1.4%)
Natural graphite	6	213 (±5.6%)	0.82 (±1.5%)
Graphitized carbon filaments	6	9.2 (±5.7%)	1.44 (±1.4%)
Carbon filaments (without graphitization)	6	29 (±5.2%)	1.38 (±1.5%)
Carbon black	6	8.9 (±5.8%)	1.65 (±1.5%)

carbon, except for carbon black, the dispersion of which is related to the spreadability of the carbon black between the MnO_2 particles. In contrast, the other types of carbon could not spread upon squeezing and, so, their dispersion needed the help of the binder more.

A decrease in binder content from 10 to 6 wt.% increased the resistivity of cathodes with carbon filaments (whether graphitized or not), but not drastically. On the other hand, the resistivity increased drastically upon decreasing the binder content for the cases of graphitized mesophase pitch and natural graphite. This means that particulate carbon required the help of the binder for its dispersion more severely than filamentous carbon. This is reasonable, since the large aspect ratio of filamentous carbon enhanced connectivity and hence decreased the importance of dispersion.

Among the 10 compositions in Table 2, the cathodes containing 10 wt.% binder and graphitized carbon filaments gave the lowest resistivity. However, the cathode containing 10 wt.% binder and graphitized mesophase pitch gave almost as low a resistivity, and graphitized mesophase pitch is less expensive than graphitized carbon filaments. On the other hand, the low density of the cathode containing graphitized carbon filaments is attractive for electrochemical cells with a high energy density. For a low density, natural graphite is even more attractive, though the resistivity is higher. In general, the choice of a carbon type in practice depends on the resistivity, density and cost.

In summary, the effectiveness of carbon as a conductive additive in an MnO_2 cathode was evaluated by measuring the electrical resistivity of the composite cathode. Graphitized carbon filaments gave the cathode with the lowest resistivity. Graphitized mesophase pitch gave a slightly higher resistivity, but a much greater density. Without graphitization, the carbon filaments gave even higher resistivity than carbon black. The above conclusions were for a PVPF binder content of 10 wt.%. A decrease of the binder content to 6 wt.% increased the resistivity (due to a decrease in the degree of carbon dispersion), and the effect was larger for particulate carbons than filamentous carbon, except for carbon black, the spreadability of which enhanced the resistivity and decreased the need for a binder to help its dispersion.

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