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Journal of Power Sources 58 (1996) 55–66

# Use of carbon filaments in place of carbon black as the current collector of a lithium cell with a thionyl chloride bromine chloride catholyte

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Received 10 July 1995; revised 6 November 1995

## Abstract

Submicron carbon filaments (ADNH, Applied Sciences Inc.) used in place of carbon black as porous reduction electrodes (i.e., current collectors) in plate and jellyroll configurations in carbon limited lithium batteries with the BCX (bromine chloride in thionyl chloride) catholyte gave a specific capacity (at 2 V cut-off) of up to 8700 mAh/g of carbon, compared with a value of up to 2900 mAh/g of carbon for carbon black. The high specific capacity for the filament electrode is partly due to the filaments' processability into sheets as thin as 0.2 mm with good porosity, acceptable mechanical properties and without binder, and partly due to the high catholyte absorptivity and high rate of catholyte absorption of the filament electrode. Use of solvent-cleansed filaments in place of as-received filaments in making electrodes increased the packing density, thus decreasing capacity per g of carbon. The BCX catholyte acted as a cleanser anyway, due to the thionyl chloride in it. The specific capacity per $cm^3$ of carbon and that per unit density of carbon were also increased by using carbon filaments in place of carbon black, provided that the filament electrode was not pressed after forming by slurry filtration. Though no binder was needed for the filament plate electrode, it was needed for the filament jellyroll electrode. The Teflon™ binder increased the tensile strength and modulus, but decreased the catholyte absorption and rate of absorption. The filament electrode exhibited 40% less volume electrical resistivity than the carbon black electrode, both without a binder.

*Keywords:* Carbon filaments; Carbon black; Thionyl chloride; Bromine chloride; Lithium; Catholyte; Electrodes

## 1. Introduction

Battery electrodes are one among several electrochemical applications using carbon and graphite materials. For porous electrodes in lithium/oxyhalide primary cells, carbon and graphite materials act both as a current collector and as a catalyst for the reduction of the depolarizer. Extensive studies using carbon and graphite have been conducted, primarily because it is the porous electrode that usually limits the lithium/oxyhalide cell performance [1–19]. The investigations conducted focused on the impact of the carbon material, the carbon treatment, and the porous electrode fabrication process on battery performance. Carbon blacks, graphite powders, charcoal, activated carbon, and carbon fibers have been studied as possible porous electrode materials [19–21]. Battery manufacturers, however, tend to use carbon black because it is carbon black that most closely satisfies performance requirements. The material parameters important for lithium/oxyhalide cell performance include the carbon's crystalline structure, the morphology (surface area, porosity, particle shape), particle size, distribution and purity [22]. Also important are the surface area, electrode porosity and dibutyl phthalate (DBP) absorption number (which is associated with surface area) of the carbon. Studies have shown that cell capacity increases as surface area, porosity and DBP absorption increase [1–4], [7,8], [11–13]. Though carbon black is the usual material of choice for porous electrodes, efforts continue to be directed toward identifying factors for performance improvement. For example, chemical pretreatment of carbon black using solvents such as acetone and methanol [13], evaluation of the binder material (such as chlorinated polyethylene or Teflon™ [23]) effect in carbon black electrodes, and study of the effect of additives (such as platinum, copper, or palladium [24–35]) to the carbon black porous electrode have all been attempts at improving the porous carbon electrode, and ultimately, the performance of the lithium/oxyhalide cell.

The Li/BCX (bromine chloride in thionyl chloride) electrochemical system, which belongs to a family of lithium soluble cathode cells, was used for this work. Discharge initially comprises reduction of the interhalogen BrCl, and the halogens chlorine and bromine, with which it is in equilibrium

0378-7753/96/$15.00
*SSDI* 0378-7753(95)02292-9

[36]. Then, the $SOCl_2$ is discharged until cell end-of-life. The accepted mechanism for the discharge of $SOCl_2$ is [37]:

$$2Li + SOCl_2 \rightarrow 2LiCl + 1/2S + 1/2SO_2 \quad (1)$$

Note that carbon is not part of the overall discharge reaction. Rather, the carbon serves as a catalyst for the reduction of the depolarizer. In addition to catalyzing the reduction reaction, however, the solid discharge products, sulfur and lithium chloride, are collected within the porous carbon. The discharge capacity of the conventional carbon black electrode has been correlated to the physical properties of the particular carbon black utilized [1–4], [7,8], [10–14]. To be effective then, the carbon material from which the electrode is made must have a high surface area so that reduction sites are maximized [12]. The porous electrode must also have a pore structure of sufficient size in order to accommodate adequately the solid discharge product yet maintain resilience to allow expansion of the electrode when discharge product accumulates. Finally, the distribution of the pore size must be homogeneous so that the electrode does not prematurely polarize, effectively shutting down the cell.

Even with all the effort undertaken with carbon materials, and specifically, with carbon black, there are still shortcomings in this technology. For example, binders are necessary with carbon black to provide shapeability and handleability of the electrode. The binders evaluated to date are all passive and take up space that could be occupied by the catalyzing (or active) carbon. With the current carbon black technology, fabrication of porous carbon black electrodes of thicknesses less than 0.50 mm is expensive due to the need for excessive solvent. It is an objective of this work to demonstrate that by using carbon filaments in place of carbon black, porous electrodes of less than 0.25 mm are possible using simple electrode fabrication methods and without the need of a binder for shapeability and handleability. The investigations were conducted in carbon-limited cells (with excess catholyte and lithium) to focus on the impact of the carbon material, carbon treatment, and the porous electrode fabrication process on battery performance.

The use of carbon filaments for battery electrode applications have been a recent area of research [38–42]. Carbon filaments are small in dimension (<0.1 μm in diameter), and have high aspect ratio and high electrical conductivity. Their high aspect ratio provides connectivity within the electrode, thus allowing them to substitute passive electrode binders, such as Teflon™, that are currently used for carbon black electrodes. They are grown catalytically from carbonaceous gases [43–45], and are commercially available through Applied Sciences Inc. (Cedarville, OH, USA). The surface of vapor-grown carbon filaments, however, was found to be covered with a layer of tarry substance which degraded the electrochemical performance, increased the filament-to-filament electrical contact resistivity in a binderless filament compact and decreased the filaments' compactability [41]. The tarry substance comprises polyaromatic hydrocarbons which condense on the filament surface as a result of the filament growth process (a vapor–liquid–solid process in which the catalyst is sprayed into the growing chamber and carbon filament growth is initiated at the suspended catalyst) [46]. Solvent cleansing (acetone or methylene chloride) removed the tarry coating from the ADNH filaments (found to yield higher carbon efficiency in the Li/BCX system compared with carbon black), thereby exposing oxygen-containing functional groups. But solvent cleansing increased the filament packing density [41] which is expected to negatively impact on discharge performance in the Li/BCX system given the importance of pore size, structure and distribution. It is another objective of this paper, therefore, to demonstrate that the BCX catholyte serves as a cleanser for the filaments, and that this approach to cleansing is preferred to acetone or methylene chloride solvent cleansing because electrode kinetics are improved without compromising electrode pore structure or distribution.

## 2. Experimental

Applied Sciences Inc. provided two types of carbon filament for study, ADNH of filament diameter: 1500 Å and density: 2.0 g/cm$^3$, and H79 of filament diameter: 500 Å and density: 2.0 g/cm$^3$. Both types as-received display lengths in excess of 100 μm. Results obtained with the carbon filaments were compared with those obtained with Shawinigan carbon black from Chevron (Houston, TX, USA) of mean diameter: 500 Å and density: 2.05 g/cm$^3$.

To remove the tarry residue from the surface, the filaments were immersed in either reagent grade acetone or methylene chloride (contained in a beaker) and stirred for 10 min using a Fisher Scientific Model 210T stirring plate [41]. This caused the solvent to change in appearance, from clear to dark, indicating the cleansing action of the medium. The filaments were separated from the solvent by pouring the mixture through filter paper. This was repeated four times or until the solvent remained clear. After filtration, the cleansed filaments were chopped by blending using a stainless-steel rotary blade blender [41]. After chopping, the filaments were air-dried in a low humidity environment (RH < 1%) overnight or oven-dried at 140 °C for a minimum of 6 h before testing [41]. To assess the cleansing action of the BCX catholyte, a systematic study involving the catholyte constituents was conducted. The treatments applied to the filaments involved BCX catholyte, neat thionyl chloride (i.e., without electrolyte salts) and neat thionyl chloride with bromine chloride. The filaments were immersed in a beaker of the test solution and the mixture was stirred with a glass stirring rod for 3 min. The filaments were allowed to settle to the bottom of the beaker then the test solution was poured from the beaker being careful not to agitate the filaments. The wet filaments were poured onto a glass fiber separator paper (the same type used in the discharge testing because of its compatibility with the catholyte constituents) to absorb any remaining solution and to allow any residual solution to evaporate from the surface of the filaments (~1 h). The filaments were then chopped in deionized water for 1 min using a stainless-steel blender before drying as described for solvent cleansing.

To assess the impact of the filament cleansing methods, electrochemical performance was assessed by cyclic voltammetry (CV) [41]. A Bioanalytical Systems (BAS) CV cell was used along with the Head Start electrochemistry software as developed by EG&G Princeton Applied Research, a potentiostat and an IBM personal computer. The test solution in CV comprised 6 mM potassium ferricyanide (or potassium hexacyanoferrite(III) in IUPAC nomenclature) ($K_3Fe(CN)_6$), the electroactive species, in 1 M potassium nitrate ($KNO_3$) in water, the supporting electrolyte. The solution was purged with argon prior to electrochemical testing through a gas inlet tube. A saturated calomel electrode served as the reference and a platinum wire as the auxiliary electrode. The working electrode was a purchased BAS holder normally used for carbon paste. The carbon filaments were packed into the holder cavity at a pressure of 10 MPa without the use of any binder. The circular carbon filament electrode had a surface area of 0.0792 $cm^2$. The CV current densities were calculated by dividing the measured current by the area of the electrode outer surface. Voltammograms began sufficiently negative of the ferricyanide potential to allow reduction of the electroactive species in solution to ferrocyanide. Cycling then began with the oxidation half cycle at scan rates of 20, 50, 75, 100, 125, 150, 175 and 200 mV/s.

The carbon filament electrode plates were fabricated in two ways. Method 1 used filter paper, shaped to resemble a flat, glass Petri dish and fitted to the rim of a glass funnel. The funnel was placed into the mouth of a flask and the flask was affixed to a vacuum hose. The chopped filaments were separated from the chopping medium by pouring the filament slurry through the filter paper and vacuum filtering. The filter paper and filaments were removed from the funnel and dried at 140 °C for a minimum of 6 h. The filaments were removed from the filter paper in the form of a continuous sheet. Test electrodes were obtained by using an 11.70 mm diameter cutting tool to cut the carbon electrode from the carbon sheet. Method 2 involved placing the carbon filaments into the cavity of a cut-down AA stainless-steel battery case (12.45 mm internal diameter) and compacting at a pressure of 4.2 MPa. For flat electrodes to be used as a wound jellyroll assembly with the lithium anode, the carbon filaments were chopped in isopropyl alcohol in water to which was added a suspension of Teflon™ particles (10 wt.%). The chopped filaments with Teflon™ binder were vacuum filtered to form a sheet, as described above. The sheet was removed from the filter paper, placed on a Mylar sheet and cut into two 50.8 mm × 10.80 mm rectangular strips. The carbon filament strips were placed on either side of an expanded nickel screen (the support structure for the electrode, 44.45 mm × 6.35 mm), the end of which had spotwelded to it a nickel lead (for electrical connection, 76.20 mm × 3.20 mm × 0.13 mm). The carbon filament strips and screen were placed between two Mylar sheets and rolled between two steel rollers to press the carbon into the open structure of the nickel screen, forming an electrode assembly. After rolling, the electrode assembly was sintered in air at 300 °C for 1 h. Carbon black electrodes were prepared in the conventional manner, from a wet slurry of isopropyl alcohol in water containing a suspension of Teflon™ particles (10 wt.%). For the test plate electrode, the carbon black/Teflon™ mixture, obtained after evaporation of most of the alcohol from the slurry, was spread between two Mylar sheets without an expanded nickel screen and rolled between two steel rollers to compact into a sheet. The carbon sheet was peeled from between the Mylar sheets. Following removal of the carbon black sheet, sintering was conducted as for the carbon filament with Teflon™ electrode assembly. The same cutting tool used for the carbon filament disk electrodes was used to cut the carbon black disk electrodes. The carbon black flat electrode was prepared by placing the carbon black/Teflon™ mixture onto the Mylar sheet. On top of the carbon black/Teflon™ mixture was placed the expanded nickel screen with lead. A second charge of the carbon black/Teflon™ mixture was placed on top of the screen and lead assembly. A second sheet of Mylar was placed on the very top, and the combination was rolled through the steel rollers to press the carbon into the open spaces of the screen. The dimensions of the carbon black flat electrode were the same as that of the carbon filament flat electrode. A jellyroll wound assembly was fabricated using a lithium anode, glass fiber separator paper and porous carbon electrode, as shown in Fig. 1.

Discharge testing of the carbon plate electrodes was conducted using the setup shown in Fig. 2. The cut-down AA stainless steel battery case served as the carbon electrode current collector. The carbon electrode was separated from the lithium anode by a nonconductive glass fiber separator paper. The assembly was held together with a metal clip and immersed in the BCX catholyte. Fig. 3 shows the setup used to discharge the jellyroll test assemblies. In this case, the

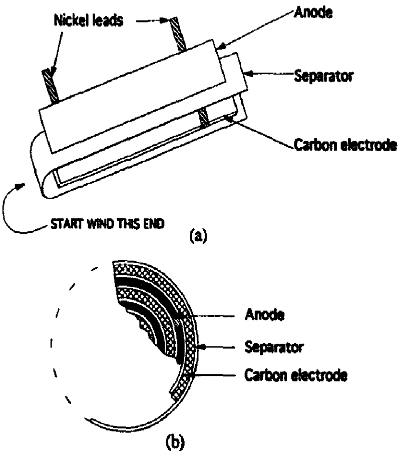

Fig. 1. Jellyroll wound assembly.

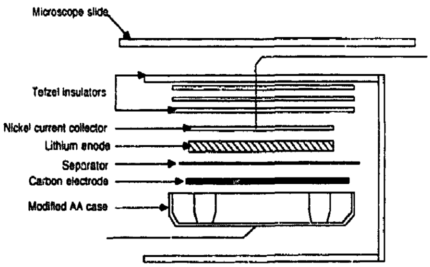

Fig. 2. Setup for plate-to-plate discharge testing of Li/BCX test cells.

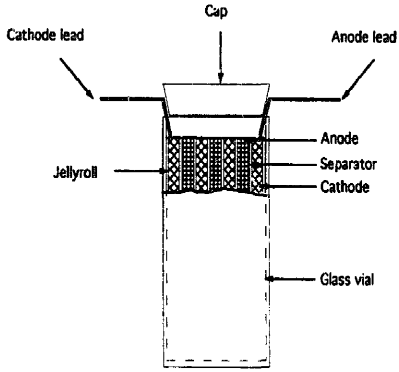

Fig. 3. Setup for jellyroll discharge testing of Li/BCX test cells.

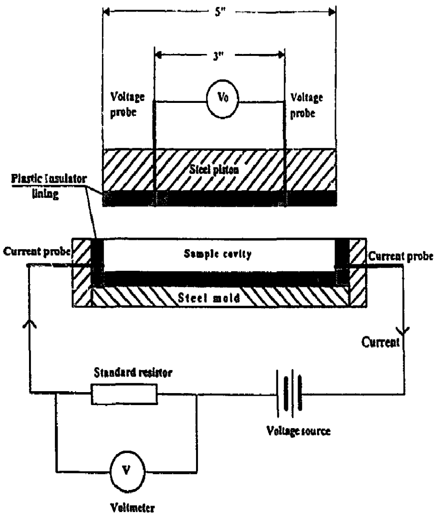

Fig. 4. Setup for the four-point probe method for measuring electrical resistivity of porous carbon plates.

jellyroll was wrapped with a final wrap of separator paper and inserted into a glass vial of internal diameter 15.90 mm. The glass vial was capped with a Teflon™ plug, allowing the anode and cathode leads to exit between the plug and the glass vial wall. The mouth of the capped glass vial was tightly wrapped with Teflon™ tape to prevent catholyte leakage during testing. A Keithley power source was used to apply a constant current of 3.0 mA. The current density was 5.9 mA/cm$^2$ for the plate electrode and 0.55 mA/cm$^2$ for the jellyroll electrode. All data were collected using a Tandy computer.

Electrical resistivity measurements of compacted carbon were performed using the four-point probe method pioneered by Wenner in 1916, see Ref. [47]. The test fixture is shown in Fig. 4. The design incorporates a bar-shaped cavity into which the carbon was placed and compacted using a piston at a controlled pressure. Secured to the ends of the mold are probes used to pass current. Attached to the fixture insert bar are two more probes placed a known distance apart, $l$. The potential developed across these two probes was measured as current was passed through the end probes of the cavity. The compact's volume electrical resistivity ($\rho$) was determined as a function of the applied pressure from $l$, the cross-sectional area of the sample, $A$, and the potential drop, $\Delta V$, between the inner probes for a known current flow, $I$, through the bar, using the equation:

$$\rho = (\Delta V/I)(A/l) \tag{2}$$

Carbon electrode catholyte absorption capability and rate of catholyte absorption were measured by immersing an electrode assembly in the catholyte and recording weight gain as a function of time. The electrodes were fabricated by pressing cut carbon electrode disks (diameter: 11.70 mm) at 21 MPa onto one side of an expanded nickel screen (diameter: 12.45 mm) with an attached nickel lead. The lead was resistance spotwelded to the top of the circular screen and served two purposes. First, the lead, like a handle, facilitated entry and exit from the catholyte. Second, the end of the lead, bent in the shape of a hook, suspended the cathode assembly in the catholyte during testing. After pressing, the electrode assemblies were dried at 140 °C for a minimum of 6 h prior to immersion. The assemblies were then weighed and immersed in the catholyte for 15, 30 s, 1, 2, and 5 min. At each of these intervals, the wetted assembly was removed from the catholyte (no evidence of drip was prevalent indicating an unsaturated condition) and reweighed. The 5 min end time was based on pre-studies to determine when saturation occurred. No significant change in weight occurred between 5 min and 10 min on four electrodes (two made using carbon black with Teflon™ and two using ADNH filaments with Teflon™), and saturation was indicated by development of catholyte beads on the cathode surface after 5 min. After the weight uptake measurements, the carbon was removed from the screen/lead assembly. The screen/lead assembly was sonicated in acetone, air-dried for 5 min and then weighed. The carbon weight was determined by difference, i.e., the electrode assembly weight minus the screen/lead assembly weight.

Carbon electrode mechanical properties were determined using a Sintech/2D screw action mechanical test system. Carbon sheets were prepared as described above. The test sample was cut into test strips 30.50 mm × 7.10 mm × 0.60

mm. The carbon strips were gripped at their ends by the testing system jaws and evaluated at a displacement rate of 1.0 mm/min. Tensile strength and carbon electrode modulus of elasticity were determined. Four samples for carbon black, two samples for ADNH filaments with Teflon™ and two samples for ADNH filaments without Teflon™ were tested.

## 3. Results

Two types of carbon filaments, H79 and ADNH, were obtained from Applied Sciences Inc. The ADNH filaments, as shown in Fig. 5(b), are relatively straight, substantially larger in diameter ( ~ 1500 Å) and less crystalline in nature in comparison with the H79 filaments of Fig. 5(a), which are more curved, twisted and smaller in diameter ( ~ 500 Å) [41]. Carbon black, with which the filaments are being compared, is 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.

In general, porous electrodes made with ADNH carbon filaments yielded higher specific capacities per g of carbon, per unit density of carbon, and per unit volume of carbon than did those from carbon black (Table 1). The specific capacity per unit area, however, was comparable when electrode thickness was similar (45 mAh/cm$^2$), and lower when electrode thickness decreased (38 mAh/cm$^2$) due to the corresponding decrease in active surface area. The H79 carbon filament porous electrode, on the other hand, yielded less specific capacities per g of carbon and per unit volume of carbon than both the ADNH filament and carbon black porous electrodes, higher specific capacity per unit density than carbon black but lower than ADNH filament porous electrodes, and higher specific capacity per unit area than both ADNH filament and carbon black porous electrodes (Table 1). The primary reason for the performance difference was attributed to pore size and structure. As shown in Table 1, the as-filtered ADNH filament (diameter: 1500 Å) electrode packing densities were substantially less than that of either as-filtered H79 filament (diameter: 500 Å) or as-rolled carbon black (spherical and of mean diameter: 500 Å) electrodes, suggesting higher electrode porosity. After pressing the ADNH electrode at 21 MPa (the pressure applied while rolling the carbon black electrodes was 1 MPa) to achieve a higher density (and therefore a lower thickness and porosity), the capacity, the specific capacity per g of carbon, the specific capacity per unit area and the specific capacity per unit density all decreased from the values for the as-filtered ADNH filament electrodes. Only the specific capacity per unit volume increased. The effect of pressing on the alignment of the filaments and the pore structure are shown in Fig. 6. Pressing (Fig. 6(b)) resulted in partial collapse of the pores, filament breakage and preferential, two-dimensional filament alignment. In contrast, the unpressed ADNH filament electrode (Fig. 6(a)) displayed a more evenly distributed and three-dimensional filament arrangement. Carbon black electrodes (Fig. 6(c)) displayed pores which were less open than the carbon filament electrodes.

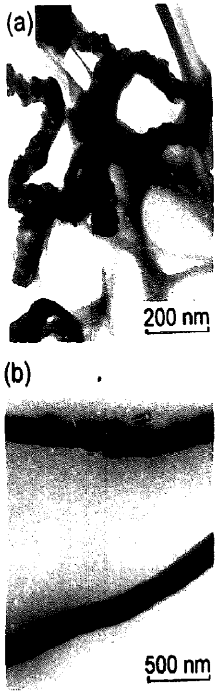

Fig. 5. Transmission electron microscope photographs of carbon filaments: (a) H79, and (b) ADNH.

The effect of electrode packing density on performance of the porous electrode is more clearly shown by comparing electrodes of similar thickness. As shown in Table 1, the as-filtered (unpressed) ADNH electrode (0.56 mm thick) achieved about 20% more specific capacity per g of carbon than did the carbon black electrode (0.48 mm thick) and about 60% more specific capacity per g of carbon than the H79 electrode (0.43 mm thick). The packing density of the unpressed ADNH electrode was about 1.5 times less than the carbon black electrode and 2.5 times less than the H79 electrode. Pressing the ADNH electrode to decrease the thickness by 50% and increase the packing density by a factor of 2 resulted in a decrease in specific capacity per g of carbon of 48%. The effect of pore structure, then, is significant relative to the efficiency of the carbon (the capacity achieved per g of carbon). The use of the smaller diameter H79 filaments, which, in turn, produced smaller channel-like pores than the ADNH filaments, yielded less carbon efficiency than the carbon black porous electrodes, which had a large variation in pore size due to the variation in size of the agglomerated carbon black and Teflon™ particles (Fig. 6(c)). The larger channel-like pores produced using ADNH filaments (Fig. 6(a)) resulted in a substantial increase in carbon efficiency. The collapse of the pore structure of ADNH filament porous

Table 1
Discharge results and electrode characteristics

| Carbon type | Carbon treatment | OCV (V) | CCV (V) | Electrode | | | Capacity to 2.0 V (mAh) | Capacity to 2.0 V (mAh/g C) | Capacity to 2.0 V (mAh/cm$^2$ C) | Capacity to 2.0 V (mAh/cm$^3$ C) | Capacity to 2.0 V (mAh/g/cm$^3$ C) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Thickness (mm) | Weight (g) | Packing density (g/cm$^3$) | | | | | |
| | | ±0.002 | ±0.002 | ±0.05 | ±0.0005 | ±0.06 | ±5 | ±25 | ±5 | ±25 | ±5 |
| 1. ADNH [a,b] | As filtered | 3.938 | 3.743 | 0.18 | 0.0022 | 0.23 | 17 | 8730 | 38 | 2030 | 75 |
| 2. ADNH [a,b] | Pressed | 3.894 | 3.705 | 0.08 | 0.0024 | 0.65 | 10 | 4880 | 23 | 3180 | 15 |
| 3. ADNH [a,b] | As filtered | 3.921 | 3.826 | 0.56 | 0.0069 | 0.22 | 23 | 3340 | 45 | 730 | 108 |
| 4. ADNH [a,b] | Pressed | 3.877 | 3.713 | 0.25 | 0.0082 | 0.61 | 17 | 2070 | 33 | 1260 | 27 |
| 5. ADNH [a,b] | Methylene chloride cleansed, as filtered | 3.896 | 3.789 | 0.59 | 0.0092 | 0.31 | 17 | 1830 | 33 | 560 | 55 |
| 6. ADNH [a,b] | Acetone cleansed, as filtered | 3.921 | 3.828 | 0.83 | 0.0026 | 0.62 | 26 | 1010 | 52 | 620 | 43 |
| 7. H79 [a,b] | As filtered | 3.882 | 3.777 | 0.43 | 0.0180 | 0.81 | 28 | 1580 | 56 | 1250 | 35 |
| 8. Carbon black [b,c] | As rolled | 3.938 | 3.762 | 0.48 | 0.0127 | 0.47 | 23 | 1810 | 45 | 1400 | 30 |
| 9. ADNH [c,d] | As filtered and rolled | 3.933 | 3.906 | 1.55 | 0.0538 | 0.06 | 470 | 8660 | 85 | 550 | 7420 |
| 10. Carbon black [c,d] | As rolled | 3.938 | 3.909 | 1.27 | 0.1566 | 0.23 | 360 | 2850 | 81 | 640 | 1610 |

[a] Fabricated without Teflon$^{TM}$ binder.
[b] Plate electrode.
[c] Fabricated with Teflon*TM* binder.
[d] Jellyroll electrode.

electrodes by pressing (Fig. 6(b)) reduced the efficiency of the carbon.

Fig. 7 compares typical discharge curves per g of carbon for carbon black and ADNH filament electrodes of similar thickness and weight. The efficiency of the carbon filament electrode is superior to that of the carbon black electrode. The impact of carbon filament electrode thickness on carbon efficiency is shown in Fig. 8 for electrodes that are filtered, i.e., not pressed. A 67% decrease in thickness resulted in a 62% increase in carbon efficiency. Pressing of the filament electrode resulted in a 38% decrease in carbon efficiency (Fig. 9) due to the increase in packing density (Table 1).

A low packing density was not the only factor resulting in capacity improvements observed for ADNH electrodes. Electrode catholyte absorption capability and rate of absorption also played a role. As shown in Table 2, ADNH electrodes with and without Teflon$^{TM}$ absorbed more catholyte per g of carbon and faster (2 and 3 times that of carbon black, respectively) than did the carbon black electrodes with Teflon$^{TM}$. The large aspect ratio of the carbon filaments compared with carbon black is the cause of this difference in absorption properties. In the case of the filaments, the pores were more channel-like, thus producing a wicking action of the catholyte rather than a sponge-like absorption displayed by carbon black. The presence of Teflon$^{TM}$ inhibited the wicking capability of the filaments, but not enough to produce absorption properties inferior to carbon black. These results are important in that ADNH filament electrodes for wound cells require a Teflon$^{TM}$ binder to provide added strength to the filament electrode so that cracking of the electrode during winding was inhibited. (Teflon$^{TM}$ binder was not needed for plate electrodes.) Minimum required Teflon$^{TM}$ content is expected to be less for carbon filament jellyrolls than carbon black jellyroll, though the same Teflon$^{TM}$ content was used for both for the sake of comparison. As shown in Table 1 and Fig. 10, about 3 times more specific capacity per g of carbon was achieved using Teflon$^{TM}$ bound ADNH in place of Teflon$^{TM}$ bound carbon black.

The carbon efficiency of the ADNH filament porous electrodes compared with carbon black was most notable for electrodes of carbon weights less than 0.01 g (Fig. 11) and thicknesses less than 0.64 mm (Fig. 12). The useability of the carbon filament electrodes at such low weights and thicknesses was due to the electrode mechanical properties. Table 3 compares the mechanical properties of the carbon black/Teflon$^{TM}$ porous electrode with ADNH filament/Teflon$^{TM}$ and ADNH filament/no Teflon$^{TM}$ porous electrodes. The strength of the ADNH filament electrode without Teflon$^{TM}$ was less than half that of the carbon black with Teflon$^{TM}$, but the variability in strengths achieved was higher for carbon black than ADNH. Addition of Teflon$^{TM}$ to the ADNH filaments more than doubled the strength compared with that without Teflon$^{TM}$, and increased the strength by about one-fifth over the carbon black electrode with

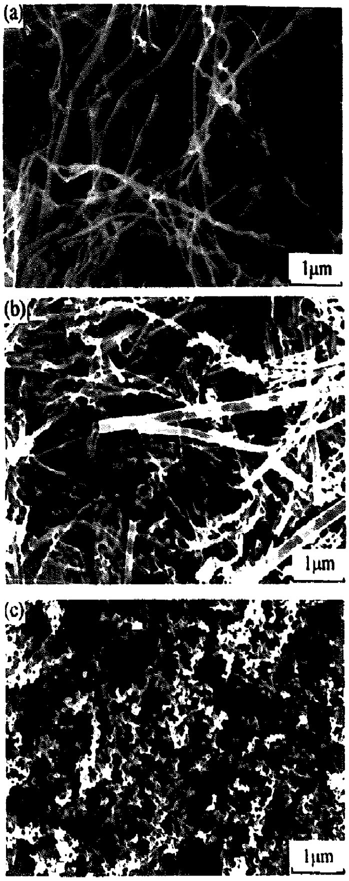

Fig. 6. Scanning electron microscope photographs through the thicknesses of porous electrodes: (a) ADNH, as-filtered (unpressed); (b) ADNH, pressed, and (c) carbon black, rolled, with Teflon binder.

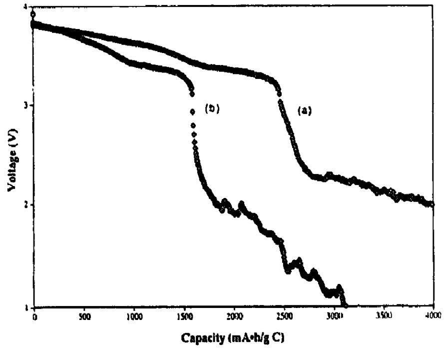

Fig. 7. Discharge results comparing specific capacities per g carbon (carbon efficiency) for plate porous electrodes of similar thickness and weight using (a) ADNH carbon filaments without Teflon™ binder and (b) carbon black with Teflon™ binder.

Teflon™. The addition of Teflon™ to the ADNH also increased the variability of the strengths achieved compared with that without Teflon™, but less than that observed for carbon black with Teflon™. In the case of carbon black, the Teflon™ alone provided bindability and strength to the electrode, whereas, for ADNH, both the Teflon™ and the filaments provided bindability and strength. The stiffness of the ADNH electrodes was higher than for the carbon black electrode (the ADNH with Teflon™ twice that of carbon black with Teflon™, and the ADNH without Teflon™ only 3 MPa higher than carbon black with Teflon™). In the case of the ADNH filament electrodes, the ease of winding is dependent on the thickness of the electrode as well as the modulus of the material being wound. The fact that thin ADNH electrodes with and without Teflon™ were possible (shown in Table 1 as low as 0.18 mm without Teflon™; during this investigation, as low as 0.25 mm with Teflon™), and that thick ADNH filament electrodes with Teflon™ were successfully wound and discharged, indicated that the higher modulus of the ADNH electrodes compared with carbon black electrodes was not of significant consequence.

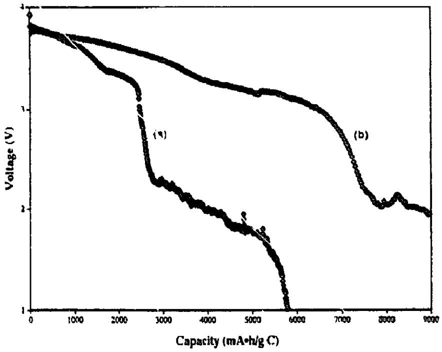

Fig. 8. Discharge results to a cutoff voltage of 2 V comparing specific capacities per g carbon (carbon efficiency) for as-filtered ADNH carbon filament plate porous electrodes without Teflon™ binder and of two thicknesses: (a) 0.56 mm, and (b) 0.18 mm.

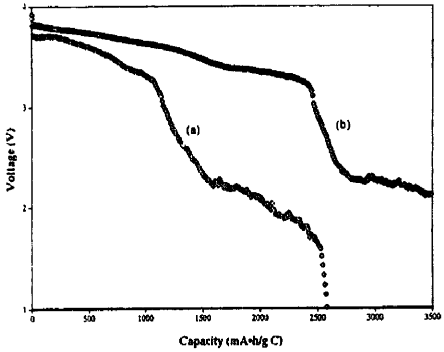

Fig. 9. Discharge results to a cutoff voltage of 2 V comparing specific capacities per g carbon (carbon efficiency) for ADNH carbon filament plate porous electrodes without Teflon™ binder: (a) pressed, and (b) as-filtered.

Table 2
Carbon electrode catholyte absorption capability and rate of catholyte absorption

| Carbon type | Condition | Catholyte absorption (g catholyte/g carbon) ±0.5 | Rate of absorption (g catholyte/g carbon in 15 s) ±0.5 |
|---|---|---|---|
| ADNH | Without Teflon™ | 99.5 | 340 |
| ADNH | With Teflon™ | 61.6 | 217 |
| Carbon black | With Teflon™ | 35.7 | 121 |

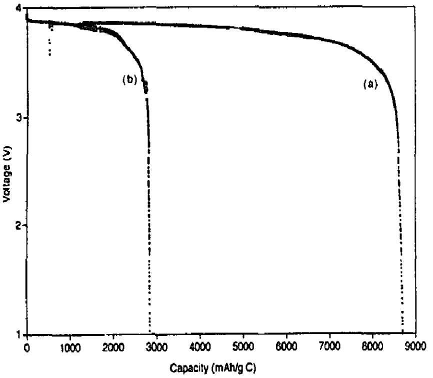

Fig. 10. Discharge results to a cutoff voltage of 2 V comparing specific capacities per g carbon (carbon efficiency) for jellyroll porous electrodes using: (a) ADNH carbon filaments with Teflon™ binder, and (b) carbon black with Teflon™ binder.

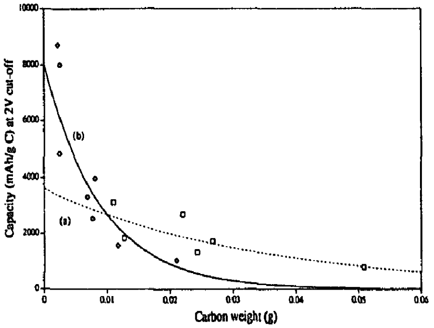

Fig. 11. Plot of specific capacity (at 2 V cutoff voltage) per g carbon vs. carbon weight. ADNH data are designated by the symbol (◇) and the solid curve. Carbon black data are designated by the symbol (□) and the dashed curve.

The open (OCV) and closed (CCV) circuit voltages obtained for the ADNH filament electrodes were, in general, equivalent to those obtained with carbon black. Pressing of the ADNH electrodes resulted in depressed OCV and CCV. The effects of pressing on OCV and CCV may be related to the collapse of the pore structure, since the OCV of as-received H79 (which has a very small pore structure) was similar to that of pressed ADNH.

The electrical resistivity of the ADNH filament compact was lower than that obtained for the carbon black compact (Table 4). The amount of heat generated during discharge as a result of resistance to current flow within the ADNH carbon filament electrode should therefore be less, which is attractive for preserving the operational safety of this system. In the case of the H79 carbon filament electrode, the electrical resistivity of the compact is higher than both the ADNH and the carbon black compacts.

Finally, the discharge performance of the carbon types (labeled 1–10) in Table 1 is shown in Table 5 in terms of specific energy density. As shown by comparing 1 to 2 and 2 to 3 in Table 5, the pressing of the ADNH carbon filament plate electrodes lowered the specific energy per g of carbon.

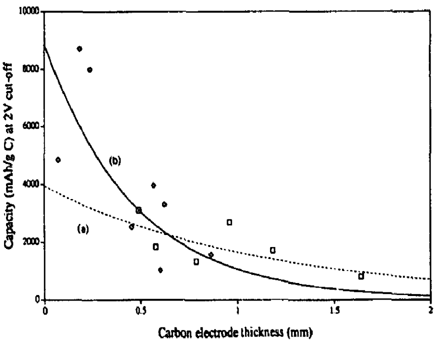

Fig. 12. Plot of specific capacity (at 2 V cutoff voltage) per g carbon vs. electrode thickness. ADNH data are designated by the symbol (◇) and the solid curve. Carbon black data are designated by the symbol (□) and the dashed curve.

Table 3
Mechanical properties of carbon sheets

| Carbon type | Strength (kPa) | Modulus (MPa) |
|---|---|---|
| Carbon black with Teflon™ | 60.1 ± 32.5 | 9.2 ± 1.2 |
| ADNH with Teflon™ | 74.8 ± 8.9 | 18.3 ± 0.1 |
| ADNH without Teflon™ | 36.2 ± 1.7 | 11.0 ± 2.3 |

Table 4
Electrical resistivity of carbons (as-received) at 7 MPa pressure. (From Ref. [42])

| Carbon type | Density (g/cm$^3$) | Resistivity (Ω cm) |
|---|---|---|
| ADNH | 0.562 | 0.041 |
| H79 | 0.795 | 0.106 |
| Carbon black | 0.618 | 0.069 |

Table 5
Specific energy densities

| Carbon type | Carbon treatment | Capacity to 2.0 V (mAh/g C) ±25 | Specific gravimetric energy density (Wh/g C) ±0.02 | Capacity to 2.0 V (mAh/cm$^2$ C) ±5 | Specific volumetric energy density (Wh/cm$^3$ C) ±0.02 |
|---|---|---|---|---|---|
| 1. ADNH [a,b] | As filtered | 8730 | 27.44 | 38 | 6.40 |
| 2. ADNH [a,b] | Pressed | 4880 | 16.23 | 23 | 10.57 |
| 3. ADNH [a,b] | As filtered | 3340 | 12.26 | 45 | 3.43 |
| 4. ADNH [a,b] | Pressed | 2070 | 6.22 | 33 | 3.79 |
| 5. ADNH [a,b] | Methylene chloride cleansed, as filtered | 1830 | 5.88 | 33 | 2.70 |
| 6. ADNH [a,b] | Acetone cleansed, as filtered | 1010 | 3.46 | 33 | 3.19 |
| 7. H79 [a,b] | As filtered | 1580 | 5.13 | 56 | 4.13 |
| 8. Carbon black [b,c] | As rolled | 1810 | 6.31 | 45 | 4.88 |
| 9. ADNH [c,d] | As filtered and rolled | 8660 | 31.43 | 85 | 4.38 |
| 10. Carbon black [c,d] | As rolled | 2850 | 10.25 | 81 | 3.12 |

[a] Fabricated without Teflon™ binder.
[b] Plate electrode.
[c] Fabricated with Teflon™ binder.
[d] Jellyroll electrode.

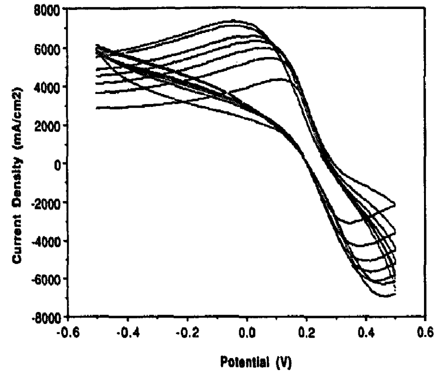

Fig. 13

Fig. 13. Cyclic voltammetry results for as-received ADNH filaments.

By either not pressing or using an electrode thickness <0.2 mm, the ADNH carbon filament plate electrode exhibited higher specific energy per g of carbon than the carbon black plate electrode. In the case of the jellyroll carbon filament electrode (labeled 9 in Table 5), specific energy per g of carbon was higher than for carbon black for a similar electrode thickness. (In this case, the carbon filament weight used to fabricate the similar thickness electrode was about 1/3 that of the carbon black weight, as shown in Table 1.) For energy densities per cm$^3$ of carbon, the carbon filament plate electrodes were slightly less efficient than the carbon black, except for the plate electrodes of thickness <0.20 mm. Nevertheless, the jellyroll carbon filament electrode displayed a higher specific volumetric energy density than did the carbon black counterpart. H79 carbon filament plate electrodes fell short of carbon black in both specific gravimetric and volumetric energy densities.

The carbon filaments produced by Applied Sciences Inc. are covered with a tarry contaminant (mostly polyaromatic hydrocarbons) which affected their performance when used as a conductive additive in the Li/MnO$_2$ system [42]. Solvent cleansing of the tarry residue offered no benefit in the Li/BCX system, however, as shown by the specific capacities of Table 1 and specific energy densities of Table 5. In fact, the specific capacities and energy densities were lower after cleansing than when the filaments were utilized to fabricate electrodes as-received, regardless of the solvent used. In the case of acetone cleansing, the results are in contrast to that shown for solvent treatment of carbon black [13]. The data indicate that for the Li/BCX system, pore size and pore distribution are the critical factors in the electrochemical performance of the carbon filament electrodes. This is clearly seen when reviewing electrode packing density data. The cleansed filaments resulted in higher packing densities, as filtered, than that achieved using the as-received filaments (e.g. ~40% increase in similarly thick filament plate electrodes after cleansing with methylene chloride; compare the sample labeled 3 with that labeled 5). The increase in packing density is consistent with the detailed study of packing density and CV conducted [41].

To have any influence on electrochemical performance, then, cleansing of the filaments without negative impact on electrode porosity would have to be achieved. One scenario for achieving cleansing without impact on electrode porosity would be for the filaments in the formed electrode to be cleansed by the catholyte in which discharge testing was conducted. By comparing the CV response of the as-received filaments (Fig. 13) and the CV response of the filaments that had been cleansed with either acetone or methylene chloride [41] with the CV responses of the filaments that had been treated by various catholyte constituents, evidence as to the

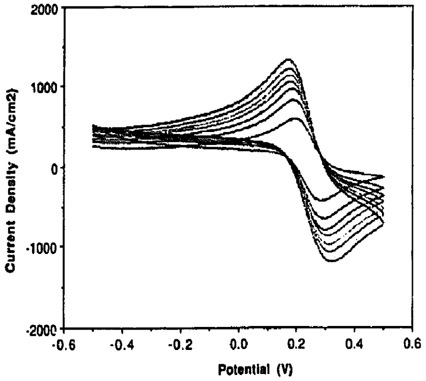

Fig. 14. Cyclic voltammetry results for thionyl chloride treated ADNH filaments.

cleansing action of the catholyte could be obtained. Of the catholyte constituents investigated, treatment of the filaments with neat thionyl chloride (Fig. 14) strongly suggested it to act as the filament cleansing agent. These results further support the notion that the negative effect of solvent cleansing is associated with the increase in the filament packing density after cleansing, and that the as-received filaments used to fabricate the electrodes are cleansed by immersion in the catholyte while maintaining the pore structure which results in better electrode performance compared to the electrodes made with the solvent cleansed filaments.

## 4. Discussion

Porous electrodes made with as-received carbon filaments (Grade ADNH rather than Grade H79, from Applied Sciences Inc.) typically yielded higher specific capacities than did those from carbon black, due to their low packing density and channel-like pore structure. The channel-like pores created using ADNH, which encouraged catholyte flow (likened to capillary action) into the electrode, made the soluble cathode readily available for reduction at the carbon filament electrode. The higher absorptivity also allowed for more efficient replenishment of catholyte within the carbon filament electrode. Finally, the elongated larger pore structure of the ADNH carbon filament electrode, and their random three-dimensional arrangement throughout the electrode, allowed more efficient packing of the discharge product.

The effect of pore structure on performance was more evident when results obtained with the H79 filaments were similar to or less favorable than those obtained with carbon black. The H79 filaments (500 Å in diameter and more curved and twisted than ADNH) simulate the structure of the carbon black agglomerates. Therefore, the pore structure created using H79 was less like ADNH (channel-like) and more like carbon black (smaller and less open). In fact, the as-filtered H79 filament (diameter: 500 Å) electrode packing density was higher than that of the as-rolled carbon black, suggesting even smaller pore size than that obtained using carbon black. Further supporting this argument are the results obtained using ADNH electrodes that were pressed. After pressing the ADNH filament electrode, which resulted in a higher density (and therefore a lower thickness and porosity), the specific capacities per g of carbon, per $cm^3$ carbon and per unit density of carbon decreased due to the partial collapse of the pores, filament breakage and preferential, two-dimensional filament alignment. The variations of the specific energy densities can be similarly explained.

The importance of pore structure was also indicated by the negative effect of solvent cleansing of the filaments on the specific discharge capacity per g of carbon and the increase in packing density of the as-filtered electrode when the solvent cleansed filaments were used in place of the as-received filaments.

Solvent cleansing serves to remove the tarry residue from the as-received filaments. This cleansing greatly improves the electron transfer kinetics, as shown by cyclic voltammetry [41]. In this work, similar improvement of the electron transfer kinetics was obtained by BCX catholyte treatment, as the thionyl chloride in the catholyte apparently acted as a cleanser. Therefore, even though as-received filaments gave electrodes with high Li/BCX specific discharge capacity per g of carbon, the electrodes made from as-received filaments were effectively cleansed while being immersed in the BCX catholyte in the discharge testing. Yet to be determined, however, are the effects of these impurities on cell storage and voltage delay.

The ADNH carbon filament jellyroll electrode superseded the carbon black jellyroll electrode in both specific gravimetric and volumetric energy densities. (The higher capacities achieved for the same carbon material with the jellyroll configuration compared with the plate configuration are due to the lower current density, and, therefore, lesser loading demand, of the jellyroll configuration.) In this case, the specific energy densities achieved is attributed to the fact that a functional ADNH electrode of ~ 1/3 the weight and density of the carbon black electrode was manufacturable. The ADNH electrode absorptivity was sufficiently better than the carbon black electrode, even though Teflon™ was used to improve its strength. The addition of the Teflon™ for strength left the pore structure of the ADNH electrode uncompromised and the absorptivity sufficient for soluble cathode reduction and catholyte replenishment. For this study, the same wt.% of Teflon™ binder was used to compare the performance of the jellyroll carbon materials alone. The required amount of Teflon™ binder for jellyroll carbon filament electrodes, however, is expected to be less than that required for carbon black because of the binding nature of the filaments which is not inherent using carbon black. A decrease in the amount of Teflon™ is expected to further improve the carbon efficiency. The Teflon™ binder provided the added strength to the filament electrode, inhibiting cracking of the electrode during winding. Filament plate electrodes did not require the use of Teflon$^{TM}$ binder.

## 5. Conclusions

Substitution of carbon filaments (ADNH) for carbon black in the current collector (i.e. porous reduction electrode) in plate and jellyroll configurations of the Li/BCX cell resulted in higher capacity (up to 30%) and higher specific capacities per g of carbon (up to 380%), per unit volume (up to 130%) and per unit density (up to 360%). The highest specific capacities were obtained when the filament current collector was not pressed after forming by slurry filtration. The higher specific capacities of the carbon filament porous electrodes demonstrate superior carbon efficiency compared with carbon black porous electrodes. The carbon filament current collector of plate configuration did not require any Teflon$^{TM}$ binder for handleability, whereas the carbon black current collector did. Nevertheless, the binder increased the tensile strength and modulus of the filament current collector. Carbon filament porous electrodes as thin as 0.18 mm could be economically fabricated (use of the binder being optional and dependent on electrode application, i.e. plate or jellyroll type), in contrast to the conventionally prepared carbon black porous electrodes. The carbon filament current collector had up to 179% higher BCX absorptivity and up to 181% higher rate of BCX absorption than the carbon black current collector, due to the low packing density and channel-like pores in the former. This contributed to the former's higher specific capacities. The addition of the Teflon$^{TM}$ binder to the carbon filament current collector, however, decreased the BCX absorptivity by 40% and the rate of absorption by 35%. The carbon filament current collector exhibited 50 to 75% lower packing density than the carbon black counterpart. This contributes to improved discharge performance by precluding premature blockage of the electrode pores by the discharge product. By using solvent (acetone or methylene chloride) cleansed filaments instead of as-received filaments, the packing density was increased, thus decreasing the specific capacity per g of carbon. Cyclic voltammetry using the $Fe^{2+}/Fe^{3+}$ couple shows the change from irreversible to reversible response after BCX treatment of the filaments, suggesting that the thionyl chloride in the catholyte acted as a cleanser. The carbon filament current collector exhibited 40% lower resistivity than the carbon black counterpart. This should result in less heat generation (and therefore preserving cell safety) within the cathode during cell discharge.

## Acknowledgements

The authors would like to thank New York State Energy Research and Development Authority for funding a part of this work.

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