

# Development of high capacity, high rate lithium ion batteries utilizing metal fiber conductive additives

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## Abstract

As lithium ion cells dominate the battery market, the performance improvement is an utmost concern among developers and researchers. Conductive additives are routinely employed to enhance electrode conductivity and capacity. Carbon particulates—graphite or carbon black powders—are conventional and popular choices as conductive fillers. However, percolation requirements of particles demand significant volumetric content of impalpable, and thereby high area conductive fillers. As might be expected, the electrode active surface area escalates unnecessarily, resulting in overall increase in reaction with electrolytes and organic solvents. The increased reactions usually manifest as an irreversible loss of anode capacity, gradual oxidation and consumption of electrolyte on the cathode—which causes capacity decline during cycling—and an increased threat to battery safety by gas evolution and exothermic solvent oxidation. In this work we have utilized high aspect ratio, flexible, micronic metal fibers as low active area and high conductivity additives. The metal fibers appear well dispersed within the electrode and to satisfy percolation requirements very efficiently at very low volumetric content compared to conventional carbon-based conductive additives. Results from 18650-type cells indicate significant enhancements in electrode capacity and high rate capability while the irreversible capacity loss is negligible. © 1999 Elsevier Science S.A. All rights reserved.

*Keywords:* Battery; Lithium-ion; Conductive additive; Metal fiber

## 1. Introduction

In lithium-ion battery electrodes conductive fillers are routinely added to construct conductive percolation network. The conductive network is essential to compensate for the low electronic conductivity of electrode active materials such as  $\text{LiCoO}_2$ ,  $\text{LiMn}_2\text{O}_4$ ,  $\text{LiNiO}_2$ , and MCMBs and to achieve full electrode utilization [1–3]. The conduction network also increases battery power, enabling faster charge and discharge [3,4]. Battery cycle life is also significantly augmented by the presence of conductive additives. Fig. 1 demonstrates how electrode capacity maintains with cycles upon the addition of conductive additive.

However, conductive additives are not innocent material and adverse side effects may result. Since commonly employed additives are carbon black powders with relatively large surface area, their reactivity with electrolyte and organic solvents are high. Furthermore, complete per-

colation of particles require significant amount of materials, causing overall increase in parasitic reaction. This increased reaction shows as an increased irreversible loss of anode capacity, gradual oxidation and consumption of electrolyte on the cathode, which in turn causes capacity decline during cycling, and threatens battery safety by gas evolution and exothermic solvent oxidation.

The percolation requirement is explained by the fact that the conduction network is formed by the carbon powders residing in the void of active powder beds and interconnected by particle to particle point contacts. The interconnection must fully percolate from one side, usually a current collector surface, to the other, the outer-most active particle layer. The conductive particles must be fine enough to fit in the opening of active particle layer. Fig. 2 shows a model of electrode film composed of active particulates and finer conductive powders, which are represented by identical spheres for simplicity. The minimum amount of conductive fillers required to render the electrode pervious to electrons can be calculated using the model. Since the conductive filler resides in the void of

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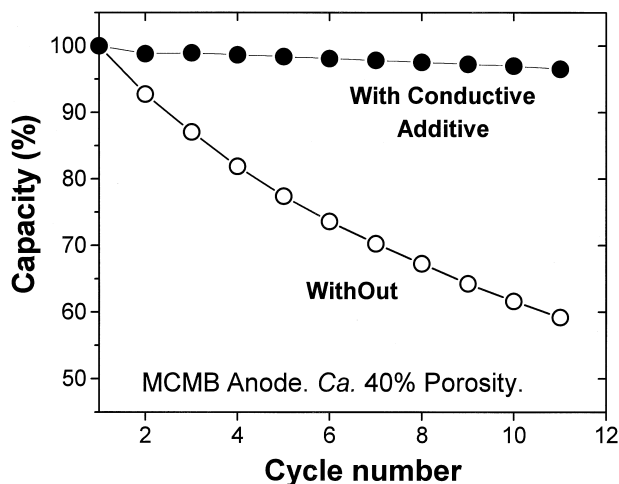


Fig. 1. Influence of conductive additive on electrode cycle behavior. The electrode active material is MCMB and the electrode porosity is approximately 40%. About 4 wt.% of carbon black was used as a conductive additive. The electrodes were cycled at 0.1 C rate between 0.01 and 1.5 V (vs. Li/Li<sup>+</sup>). Electrode capacities are ca. 3 mA h/cm<sup>2</sup>.

active particle beds, the volume fraction of the filler is  $\varepsilon(1 - \varepsilon_f)$ , where  $\varepsilon$  and  $\varepsilon_f$  are void fractions of active particle bed and conductive filler packing. The minimum amount is then obtained after eliminating redundant portion of the filler. This concept is evolved from applying critical probability for percolation of three dimensional fractals [5]. Thus, the minimal requirement for conductive filler is now,

$$\nu_f = \varepsilon(1 - \varepsilon_f)P_c$$

where  $P_c$  is the critical probability for three-dimensional percolation, which can be calculated to be 0.395. The permissible diameter of filler is also calculated from the opening of the close-packed active spheres, [6]

$$d_f \leq 0.1547d$$

where  $d$  is diameter of active particle. Approximate calculations from the above volume fraction equation and com-

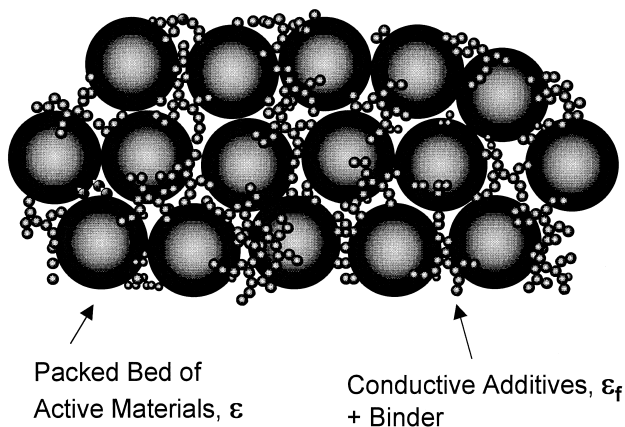


Fig. 2. Electrode model representing packing of active particles and finer conductive filler powders. Identical spheres were adopted for simplicity.

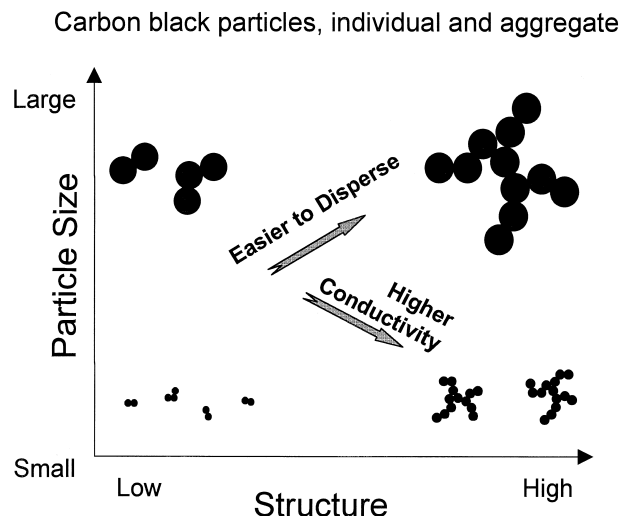


Fig. 3. Effects of particle size and structure of conductive filler materials on dispersion and electrical conductivity.

mon practice in Li-ion battery industry indicate the volume fraction of conductive filler should range somewhere between 6 to 15 volume percent of the total electrode volume [1,2,7].

With this amount of carbon black powders added into viscous slurry, uniform dispersion is not effortlessly achieved. Fig. 3 is a brief summary of relationship between dispersion and conductivity of carbon blacks commonly used as conductive filler materials. Though higher conductivity is obtained, fine, high structure carbon blacks are notably arduous to distribute within electrode. Poorly-dispersed electrodes sacrifice not only battery performance but also production speed, yield, and battery safety.

Our approach in this work is to utilize high aspect ratio, flexible, micronic metal fibers [8,9] as low active area and high conductivity additives to replace trains of point-contacted particulate carbon blacks. Compared to a train of particulates, a strand of fiber possesses lower surface area to volume ratio and superior electrical conductivity due to the lack of contact resistance. We observed the metal fibers are well dispersed within the electrode and to satisfy percolation requirements very efficiently at very low volumetric content compared to conventional carbon-based conductive additives.

## 2. Experimental

The active materials employed during electrode preparation were MCMBs (Osaka Gas) for anodes and LiCoO<sub>2</sub> (Seimi) for cathodes. As a fibrous conductive additive, 316L stainless steel fibers (Ribtec) has been employed based on the ready availability. The stainless steel fibers were nominally 1.5  $\mu\text{m}$  in diameter and ca. 0.1–2 mm in length. The 316L fibers were chopped using a lab blender

prior to addition into electrode slurry. As particulate conductive fillers, powders of artificial graphite (KS6, TIMCAL), or carbon black (Ketjen Black International) were utilized. Poly(vinylidene fluoride) (PVDF, Kureha) was used as a polymeric binder of electrode coat. Current collectors were either foil-Cu and Al for anode and cathode, respectively, or nickel mesh.

Electrode active materials and conducting agents, carbon particulates or metal fibers, were dispersed in NMP (*n*-methyl-2-pyrrolidone) solution of PVDF. And the viscous slurry was coated onto current collectors, followed by drying at 130°C. Dried electrodes were pressure-compacted to a predetermined packing fraction to enhance particulate contacts and adhesion onto foils. Typical active mass loading of the electrodes corresponded to electrode capacity of about 3.0 mA h/cm<sup>2</sup>.

Electrode charge/discharge profiles were recorded from a battery tester (Toyo) using 2016-type coin cells or

three-electrode, beaker-type test cells. All the experiments were conducted at room temperature and in ambient conditions. Electrolyte was 1 M LiPF<sub>6</sub> in EC/DEC (1:1 volume ratio) throughout the experiments. For tests using prototype batteries cylindrical 18650-size cells were selected and assembled using LG Chemical's battery pilot plant facility.

### 3. Results and discussion

Fig. 4 attests that the individual metal fibers can be dispersed remarkably well within the electrodes. Though the fiber dispersion remained uniform up to 10 wt.%, there seems to exist a range for optimal fiber load where the facility of slurry mixing and the electrode uniformity are not sacrificed. This optimal content appears, in this experiment, less than 4.5%. Beyond this limit the electrode

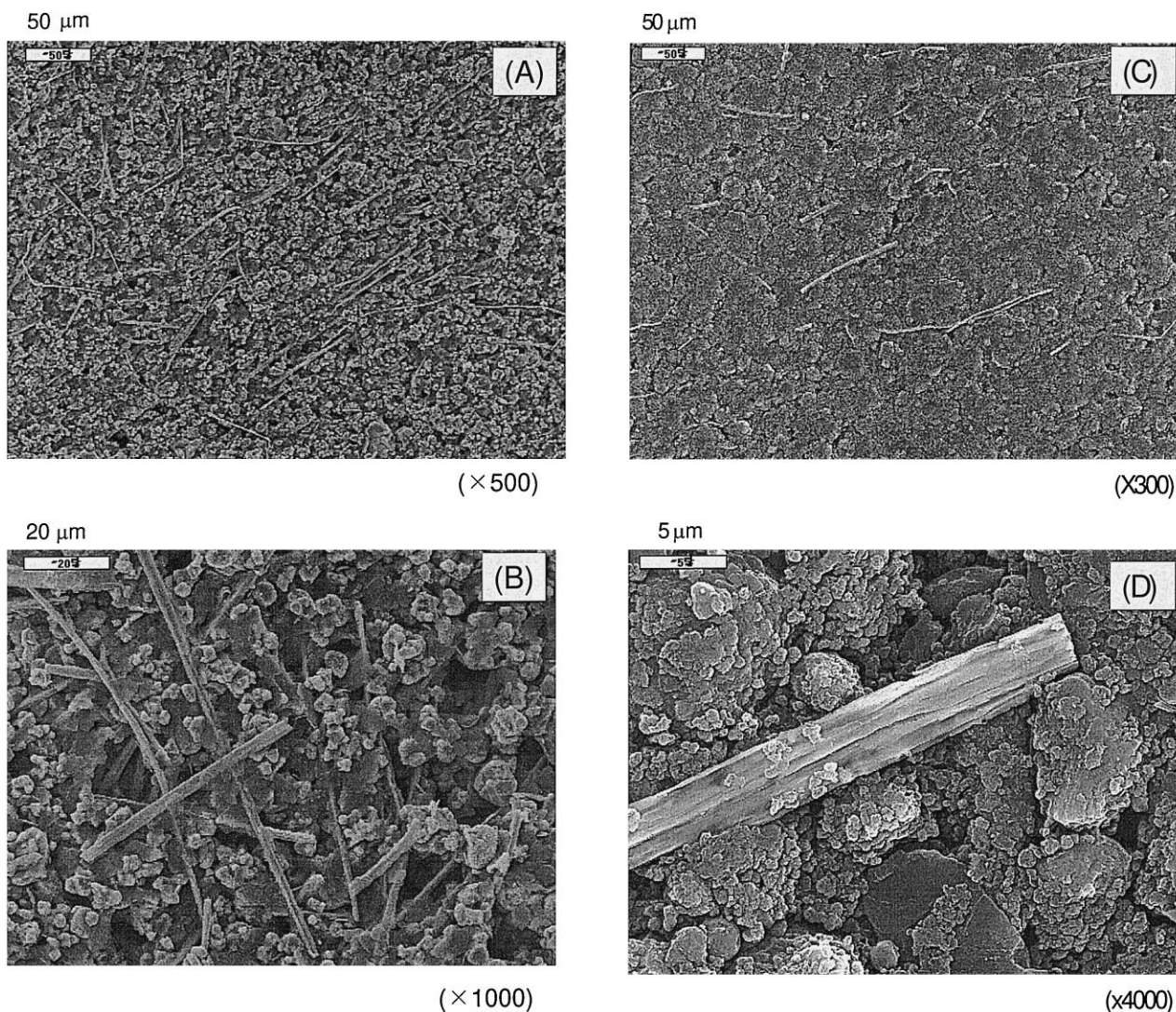


Fig. 4. Scanning electron micrographs of metal fiber-containing electrodes. (A) LiCo<sub>2</sub> cathode with 4 wt.% of stainless steel 316L fiber, (B) LiCo<sub>2</sub> cathode with 7 wt.% of fiber, (C) and (D) MCMB anode with 0.5% of 316L fiber. The metal fibers are 1.5 μm in diameter.

surface began to look rough and the particle adhesion became poor probably due to the increased electrode porosity resulting from the presence of fiber.

The fiber-added electrodes were tested with lithium metal anode in a half cell configuration for discharge capacity. Fig. 5 shows cathode discharge curves indicating electrode capacity increasing to a maximum, followed by a quick drop with further increase in metal fiber content. One can attribute the capacity increase to enhancement in electrode utilization as physically isolated  $\text{LiCoO}_2$  particles gain access to electron channels upon the addition of fibers. This enhancement, however, was nullified after a certain critical metal content, being between 4 and 7% in this experiment, which coincides with the fiber load that starts to perturb electrode uniformity as discussed earlier. We have noticed that the presence of fibers impedes close packing of active powders, decreasing packing fraction and further losing particle to particle contacts. And net result is a capacity decline. It was also noted that this higher porosity seemed to persist even after compaction by a roll press.

While effective in enhancing electrode capacity, the metal fiber's electrochemical stability becomes an issue for the positive electrode. As we can see in Fig. 6 where cathode cycle behavior is compared with a control electrode, the cathode containing stainless steel 316L fibers exhibited slightly lower current efficiency, around 98% vs. control cathode's over 99%, which may indicate dissolution of stainless steel at cathode potentials. This corrosion problem, if any, is, however, expected to be overcome by adopting other corrosion-resistant fibers such as those from aluminum, which is a common material for positive current collector for lithium ion batteries.

The irreversible lithium ion uptake as well as reversible capacity from anodes have been examined and displayed

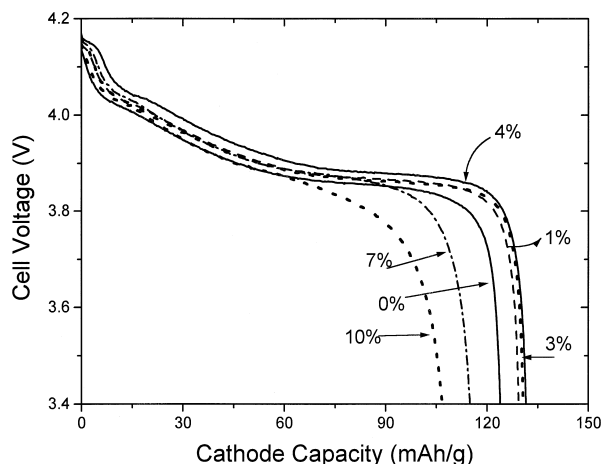


Fig. 5. Influence of metal fiber addition on cathode discharge profile. The cathodes are composed of  $\text{LiCoO}_2$  particles, PVDF binder, graphite conductive additive, and indicated weight percentage of metal fiber. Electrodes were discharged at  $1/40$  C rate. Voltage limit: 3.0 to 4.2 V vs.  $\text{Li}/\text{Li}^+$ .

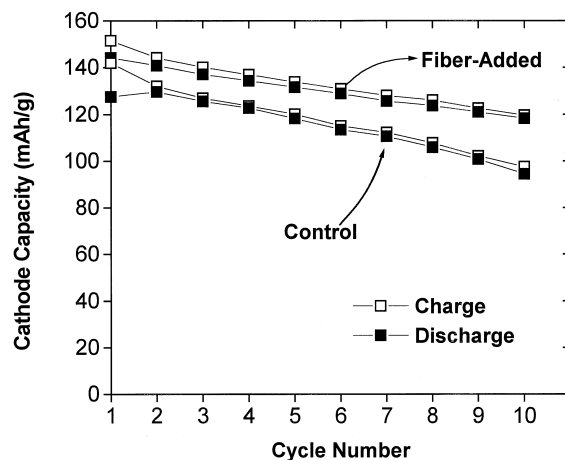


Fig. 6. Comparison of cathode cycle behavior. Fiber content is 2 wt.%. Note the metal fiber-added cathode retains higher capacity as cycle proceeds.

in Fig. 7. Compared to a control that contains no conductive additives, the fiber-containing electrode exhibited about 14% increase in reversible capacity while the increase in irreversible reaction is only by 2 mA h/g. Carbon black-added anode with comparable volumetric quantity to fibers also exhibits similar level of reversible capacity, however, only at the expense of almost twofold increase in irreversible capacity toll.

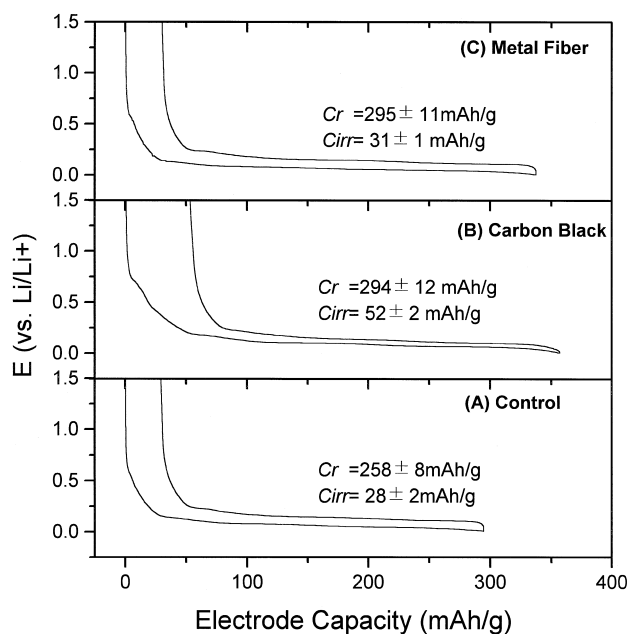


Fig. 7. Impact of conductive additives on anode reactions with lithium ion. The volume fraction of conductive additives were maintained at approximately 0.8%. The electrodes were cycled at 0.1 C rate between 0.01 and 1.5 V (vs.  $\text{Li}/\text{Li}^+$ ). At least three electrode specimens were tested and the reversible and irreversible capacities calculated.  $C_r$  and  $C_{irr}$  are defined as reversible and irreversible lithium ion uptake, respectively.

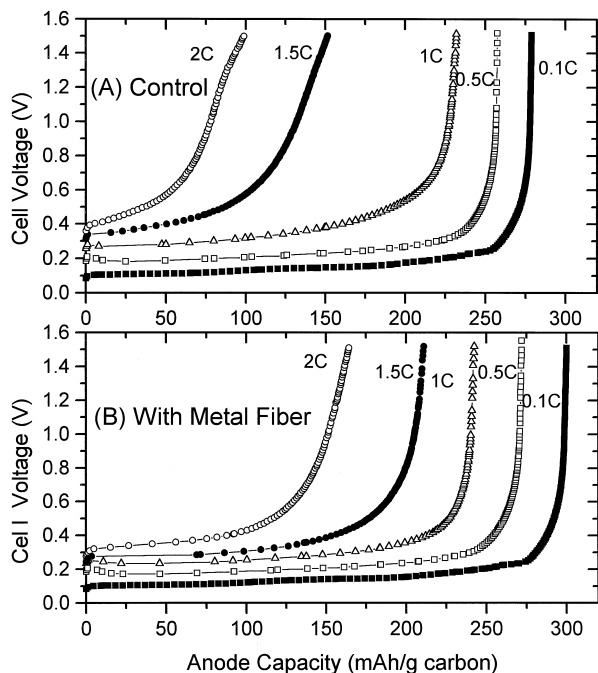


Fig. 8. Anode discharge profiles as a function of C rate. Charge rate is 0.1 C with 0.01 V cutoff.

The above results indicate that there is almost no contribution of metal fiber to the increase in the irreversible lithium uptake. The contribution from fiber to the electrode active area has been calculated and found negligible while the carbon black at the comparable volume content almost quadruples the electrode area. The increase in the reversible capacity is, again as in the case of cathodes, attributed to improved utilization of MCMB particles and lower ohmic drop that prevents the electrode from reaching to the cutoff potential prematurely. The reduction of internal resistance in the fiber-added electrode is more vividly seen from the discharge profiles at various C rates in Fig. 8.

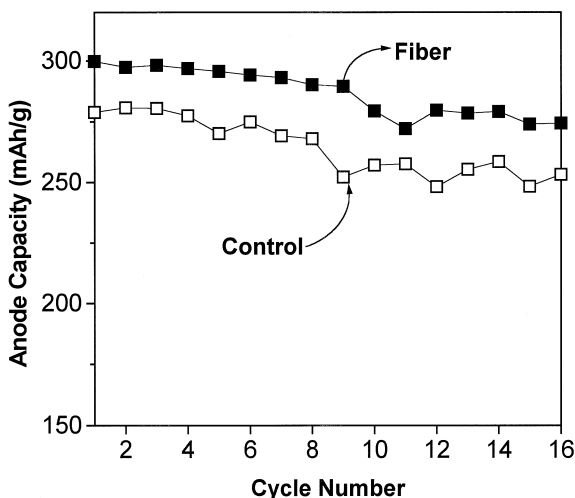


Fig. 9. Effect of added metal fiber on anode cycle characteristics.

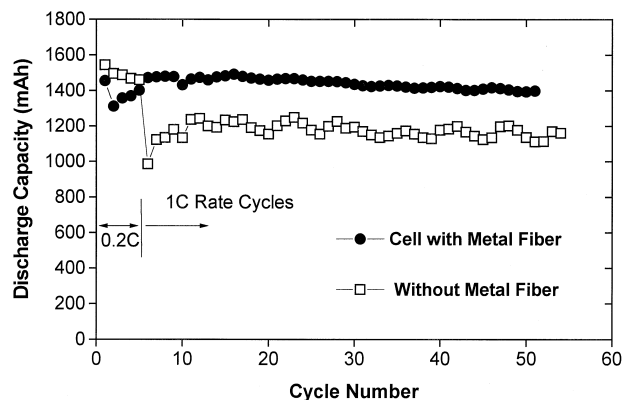


Fig. 10. Battery capacity behavior with cycling. The particular cell with metal fiber, shown here, was fabricated using 316L fiber-containing anode (2% w/w) and regular cathode devoid of metal fiber.

The anode cycle characteristics are depicted in Fig. 9. Similar to the cathodes' behavior (Fig. 6), higher capacity persists and is less fluctuating for fiber-contained anode.

In order to verify the efficacy of fibrous conductive additives in real Li-ion battery applications, commercial-size cylindrical cells were manufactured using 316L fiber-added electrodes. The 18650 cells were compared at a nominal capacity of ca. 1400 mA h with all the electrode process variables and physical characteristics adjusted accordingly.

The assembled batteries were subjected to cycle tests in the following order; (i) preconditioning at a 1/10 C rate for the first charge and discharge sequence, (ii) followed by four 1/5 C rate cycles, and (iii) subsequent 1 C rate cycles with a restriction on the total charge time, which was 2.5 h in the experiments shown in Fig. 10. During the 1 C rate charge constant current mode with voltage limit of 4.1 V was applied.

For the first five cycles, where the charge/discharge current is low, the capacities for the two cells are similar. But when the current was raised to a 1 C rate, it was evident that the capacity of the control cell sharply drops by more than 200 mA h and do not keep up with the metal fiber-added counterpart.

#### 4. Conclusions

Conductive additives are essential for good-performing lithium ion batteries but traditional carbon blacks pose undesired impact on electrode reaction and battery fabrication. We have demonstrated in this study that micron-sized metal fiber is an excellent, low signature candidate for low active area, highly effective conducting agents for use in lithium ion batteries. Tests from half-cells and prototype cylindrical batteries affirm that parasitic reactions are minimal, while electrode capacity and cycle life enhance, and the higher capacity sustains at higher discharge rates. No

adverse impact from adopting fibrous materials on the electrode fabrication and battery assembly seems to exist.

## References

- [1] G.M. Ehrlich, C.M. Orndorf, R.M. Hellen, 1997 ECS and ISE Joint International Meeting Abstracts, Vol. 97-2, Abst. No. 217, 1997.
- [2] S. Hossain, in: D. Linden (Ed.), Handbook of Batteries, 2nd (edn.), Chap. 36.37, McGraw-Hill, New York, 1995.
- [3] D. Guyomard, J.M. Tarascon, Solid State Ionics 69 (1994) 222.
- [4] Z.X. Shu, R.S. McMillan, J.J. Murray, J. Electrochem. Soc. 140 (1993) 922.
- [5] A.-L. Barabasi, H.E. Stanley, Fractal Concepts in Surface Growth, Cambridge Univ. Press, New York, 1995.
- [6] P.W. Atkins, Physical Chemistry, 5th (edn.) Oxford Univ. Press, Oxford, 1994.
- [7] T. Takei, A. Kozawa, R.V. Mostev, ITE Battery Newsletter 4 (1997) 55.
- [8] C. Marrion, D. Cahela, S. Ahn, B. Tatarchuk, J. Power Sources 47 (1994) 297.
- [9] S. Ahn, B. Tatarchuk, J. App. Electrochem. 27 (1997) 9.