Short communication

High-density positive electrodes containing carbon nanotubes for use in Li-ion cells

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Abstract

Multi-walled carbon nanotubes (MWNT) are evaluated as a conducting agent in a high-density cathode for a Li-ion cell. Cathodes of $LiCoO_2$ with a density of up to $4.0\,g\,cm^{-3}$ are fabricated using alternate conducting agents of MWNT and conventional carbon black (Super P). An electrode containing MWNT (MWNT-cathode) is superior to one containing Super P (Super P-cathode) in terms of both high-rate (1 C) performance and cycle-life. Results from ac impedance and scanning electron microscopy (SEM) studies indicate that the improved performance of the former electrode is due largely to the resilience of the MWNT aggregates that form conductive bridges between particles of the active material. These resilient bridges maintain intimate contacts between the particles even when the composite expands on cycling. By contrast, similar but rigid bridges of carbon black in the Super P-cathode are broken on cycling. Overall, it is found that MWNT is a good candidate conducting agent to replace Super P and other carbon blacks and hence develop a high-energy Li-ion cell.
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1. Introduction

Rechargeable Li-ion batteries are considered to be promising power sources for many applications in which high energy and high power are needed. For instance, ever-increasing specific is being demanded by many portable electronic devices such as cellular phones and notebook computers, while an extremely high power capability is requested by electric vehicles and hand-held power tools [1]. Development of a high-density positive electrode (cathode) is one of the most important factors for achieving a Li-ion cell with a high specific energy, while a cathode with high conductivity is critical for high power [2]. Although there are several candidate cathode materials, e.g., $LiCoO_2$, $LiMn_2O_4$ [3,4], $LiFePO_4$ [5], $LiCoO_2$ is used almost exclusively in commercially-available Li-ion cells. The cathodes in these cells have an active-material density (cathode density) that ranges from 3.15 to $3.84\,g\,cm^{-3}$ [6]. One way to improve the specific energy of the cell is to increase the cathode density since this cell component has the largest volume and the heaviest weight [7]. Unfortunately, however, deterioration of the electrode with cycling should accelerate as the density increases and would thus render the electrode less conductive and thereby accentuate the role of the conducting agent in ensuring adequate service life from the cell.

The commonly used conducting agents are carbon black and graphite powder, e.g., "Super P" [8]. Carbon black particulates

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form conduction bridges between particles of the active material and thus enhance the electrical conductivity via a percolation mechanism [9]. Compression of the electrode to increase the composite density generally enhances the electrical conductivity [10,11]. When the composite swells with cycling, however, the conduction bridges formed by the carbon particles are easily broken and this increases cell resistivity that becomes more pronounced as the cathode density increases. Therefore, it is highly desirable to find new conducting additive that may retain conduction bridges even when the composite swells with cycling. Carbon nonotubes (CNT) are known to have electrical resistances as low as metals (i.e., 2×10^{-4} to $3 \times 10^{-4} \, \Omega \, cm$) [12]. Moreover, their large aspect ratio may be helpful in retaining the conduction bridges when the composite swells. Indeed, a recent study of the use of single-wall nanotubes (SWNT) as the conducting additive in a low-density cathode gave a better performance than that obtained with carbon black. The SWNT have a long aspect ratio and thus makes electrode compression unnecessary for good particle-to-particle contacts. On the other hand, the specific energy of the resulting electrode is rather poor. It was found that uncompressed cathodes with an excessive amount (12 wt.%) of SWNT delivered optimum performance [2].

The present work involves a study of high-density, high-capacity MWNT-cathodes that show a much improved capacity over those with a conventional additive (Super P) as a conducting agent. A possible mechanism by which the MWNT offer performance improvements, especially with respect to cycle-life, is presented.

2. Experimental

Multi-walled carbon nanotubes (MWNT) were prepared by means of a catalytic chemical vapour deposition process developed by Iljin Nanotech in Korea. The average diameters and lengths of MWNT were 10–15 nm and 10–20 μm, respectively. The pristine sample contained about 5 wt.% of iron particles. Positive active-material (LiCoO$_2$) with an average particle size of about 10 μm was purchased from Umicore Corp., Belgium. A 5% suspension of MWNT in N-methyl-2-pyrrolidone (NMP) was prepared by ball-milling for 48 h. The positive electrode slurry was prepared by manually mixing appropriate amounts of LiCoO$_2$, polyvinylidene fluoride (PVDF) as binder and the MWNT suspension. For the purposes of comparison, conventional Super P was also used for the conductive agent. The weight ratio of LiCoO$_2$, PVDF and the conductive agent in the slurry was 94:3:3. The resulting slurry was coated on one side of an aluminium foil substrate followed by drying in a convection oven for 20 min at 120 °C. The green electrode samples had rather low densities that ranged from 1.5 to 1.8 g cm^{-3}. These electrodes were compressed under a rolling press to increase the density of the composite active mass to 4.0 g cm^{-3} since the low-density electrodes are not suitable for a high-capacity Li-ion cell. The MWNT-cathodes required several compressions before the required density was attained. This was because the thickness of the electrode sprang back substantially after each compression due to the resilience of the composite. By contrast, only a single compression was necessary with Super P-cathodes.

Test electrodes were prepared with two discrete composite density values of 3.3 and 4.0 g cm^{-3} (± 0.05) for the two different conducting additives. The density of all test electrodes throughout the paper without further identification was 4.0 g cm^{-3}. Each electrode was cut into a circular disc of 2 cm^2 in area. Coin-type half-cells were assembled in an argon-filled glove-box. A porous polypropylene film was used as the separator. A Li-metal foil of 700 μm in thickness was used as the counter electrode. The electrolyte was a 1M LiPF$_6$ solution of 1:1 (v/v) of ethylene carbonate (EC) and diethyl carbonate (DEC). Test cells were sealed at ambient atmosphere after evacuation for 5 min to allow the electrolyte to penetrate homogeneously into the pores of the electrode. Electrical tests were carried out with a Toyo Cycle Tester after ageing the cells for 10 h. The initial charge–discharge cycle was performed at a low rate of 0.2 C and the following 40 cycles at the 1 C rate (140 mAh g^{-1}).

Measurements of ac impedance before and after cycling tests for 40 cycles were carried out in an electrolyte-flooded, three-electrode, beaker cell using an EG&G Impedance Analyzer (Model 273A). Electrodes after the initial cycle and one after the cycling test (40 cycles) were cut into discs of 1 cm^2. A beaker-cell stack assembly was made with the electrode disc as the working electrode with its coated side facing an oversized Li counter electrode. A small Li-foil reference electrode was located at the uncoated side of the working electrode. The whole beaker cell was sealed air-tight. The impedance measurements were undertaken in the frequency range from 100 kHz to 10 mHz.

3. Results and discussion

The surface morphologies of the Super P- and MWNT-cathodes before compression are shown in Fig. 1. These conducting agents have discretely different morphologies. Super P-cathode has the usual powdery morphology while the MWNT-cathode has a fiber-like (or long rod-like) morphology with a large aspect ratio of approximately 1000. Super P appears to be relatively well dispersed throughout the composite but forms some aggregate clusters in the pores between powder grains, as shown in Fig. 1(a). The formation of such clusters is more pronounced in the MWNT-cathode than in the Super P-cathode, as shown in Fig. 1(b). Even though individual fibers of MWNT are not visible due to insufficient resolution of the micrograph, some portion of the MWNT must be spread over the surface of the particles of active material to give the observed high conductivity of the electrode.

Charge and discharge curves at the 1 C rate are shown in Fig. 2 for the high-density cathodes containing the two conducting agents, respectively, for the 1st, 20th and 40th cycles. The charge and the discharge curves of the two electrodes are not significantly different from each other in voltage and capacity at the initial cycle. As cycling progresses, however, deterioration in both voltage and capacity is readily noticeable. Charge voltage curves are raised, discharge voltages are depressed and capacity is reduced with cycling. These changes are more pronounced on the discharge half-cycle, especially for the Super P-cathode which shows rather severe distortion of the curve
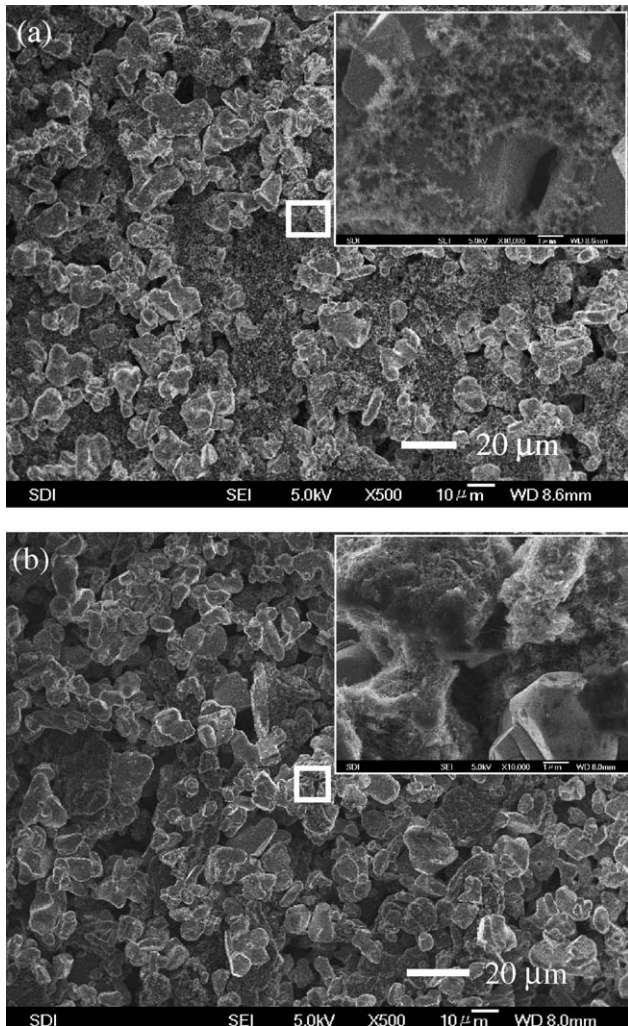
Fig. 1. Scanning electron micrographs of freshly-prepared electrodes before compression: (a) Super P-cathode; (b) MWNT-cathode.
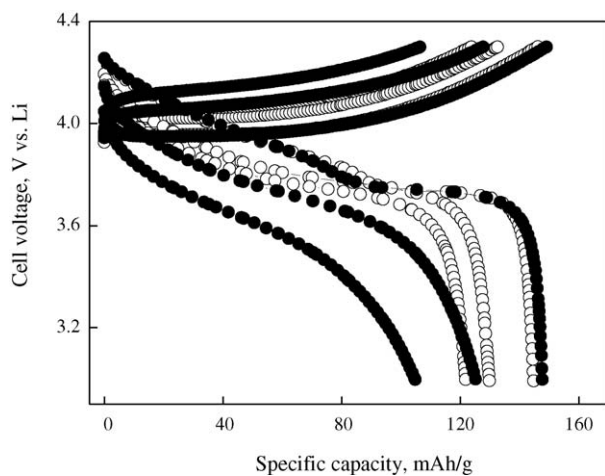

Fig. 2. Charge and discharge curves for electrodes after 1, 20 and 40 cycles from right to left at 1 C rate; filled symbols for Super P-cathode; open circles for MWNT-cathode.
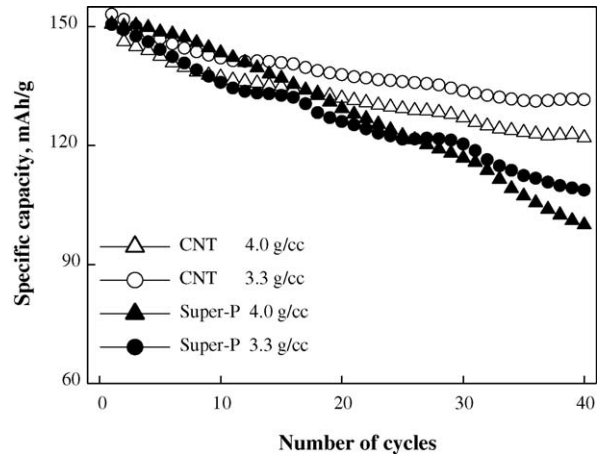

Fig. 3. Comparison of cycle performance at 1 C rate of MWNT-cathode vs. Super P-cathode having two different composite densities of 3.3 and 4.0 g cm^{-3}.

after a relatively short period of 20 cycles. By contrast, the MWNT-cathode retains the shape of the initial curve even after 40 cycles. These changes appear to indicate that the conductivity of the latter electrode is sufficiently high to support the 1 C discharge rate, even after the cycling. The cycling performance of these electrodes, as well as similar pair of electrodes at lower density (3.3 g cm^{-3}) is shown in Fig. 3. The capacity retention with cycling of the MWNT-cathode at both densities (3.3 and 4.0 g cm^{-3}) is clearly superior to that of Super P-cathodes. The high-density MWNT-cathode retains over 120 mAh (an average value from five coin cells) as compared with less than 100 mAh for the corresponding Super P-cathode. For a given conductive additive, cathodes with a lower density display superior cycle-life. The present results agree well with those of Qian and Horb [2] in that a SWNT-containing electrode exhibited superior performance in terms of voltage and capacity retention compared with that of an electrode with carbon black. The present findings for electrodes that are compressed to a high density indicate that MWNT is a pro conductive additive for a high-capacity cathode.

Since one of possible electrode deterioration mechanisms is electrochemical isolation of active material particles due to electrode swelling with cycling [16], a study has been made of the swelling behaviour of a pair of electrodes of each type, as follows. One out of each pair was cycled while the other was kept soaked in the electrolyte at open-circuit for control. The results of thickness measurements are shown in Fig. 4. All electrodes expanded severely after the first cycle, especially the MWNT-cathode that showed a reduction in composite density from 4.0 to 2.85 g cm^{-3} (71%). By contrast, the Super P-cathode reduced to 3.4 g cm^{-3} (85%) after the initial cycle. Such severe swelling is due mostly to introduction of the electrolyte rather than to the cycling itself, as shown by the large swelling of the control samples. This swelling should in large part result from the absence of stack pressure in the test cell. The MWNT-cathode expanded much more after the first cycle and after the electrolyte loading but the rate of expansion with cycling was approximately equal to, or a little less, than that of the Super P-cathode, as shown in Fig. 4. The overall expansion of the MWNT-cathode from the initial density is much higher than that of the other. This
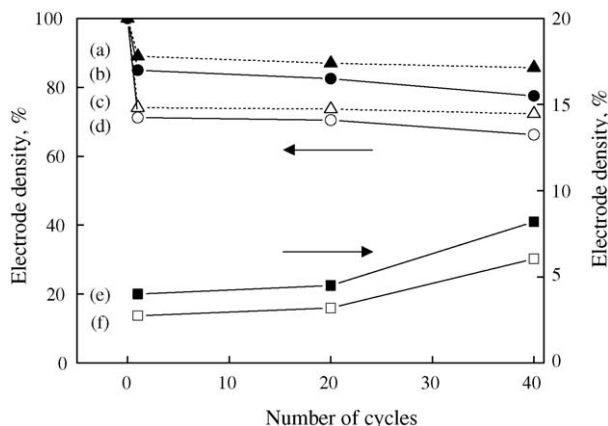
Fig. 4. Plots of electrode density and change with cycling in percentages of initial value (4.0 g cm^{-3}): (a) Super P-cathode soaked in electrolyte while sister electrode was cycled as the control; (b) Super P-cathode at various number of cycles; (c) MWNT-cathode that was kept soak; (d) MWNT-cathode at various number of cycles; (e) changes due to cycling only for the Super P-cathode (equals to a–b); (f) changes due to cycling only for MWNT-cathode (equals to c–d).

observation is somewhat unexpected in view of the rather drastic improvement in performance of the MWNT-cathode over that of the Super P-cathode.

The ac impedance of the two different types of electrode were measured in a three-electrode beaker-type cell at 3.69 ± 0.02 V versus Li after the first cycle and at 3.81 ± 0.02 V after 40 cycles, as shown in Fig. 5. Two rather distorted semicircles, each of which might be composed of two overlapping ones, were observed for both cathodes after the first cycle. The high-frequency semicircles in Fig. 5(b) are similar in size (approximately 7 Ω for the Super P-cathode and 8 Ω for Super P-cathode) but the low-frequency semicircle for the Super P-cathode is substantially larger than that of the MWNT-cathode, as seen in Fig. 5(a). The high-frequency semicircles are probably associated with the impedance that arises from particle-to-particle contacts in the electrode composite, whereas the low-frequency semicircles are associated with the charge-transfer impedance [13].

Transformation of each distorted high-frequency semicircle into two semicircles became apparent after 40 cycles, as shown in Fig. 5(b). Similar semicircle pairs to these have been reported [14] to be associated with the impedance of the particle-to-particle contacts and the formation of a LiCO$_3$ layer at the surface of the active material. The size of the high-frequency semicircle pair for the Super P-cathode grew approximately three times (from 7 to 20 Ω) during 40 cycles, while that for the MWNT-cathode increased by only 25% (from 8 to 10 Ω). This indicates that the combined resistance of the particle-to-particle contacts in the Super P-cathode increased greatly while that in the MWNT-cathode increased only slightly. The sizes of the low-frequency semicircles for both cathodes grew substantially during 40 cycles, which suggests that the charge-transfer impedance increases rapidly with cycling, as shown in Fig. 5(a). Quantitative comparison of these changes is not available from the present data because of the unfortunate variation of the electrode potential in the present measurements before and after the cycle test. It has been reported that the charge-transfer impedance
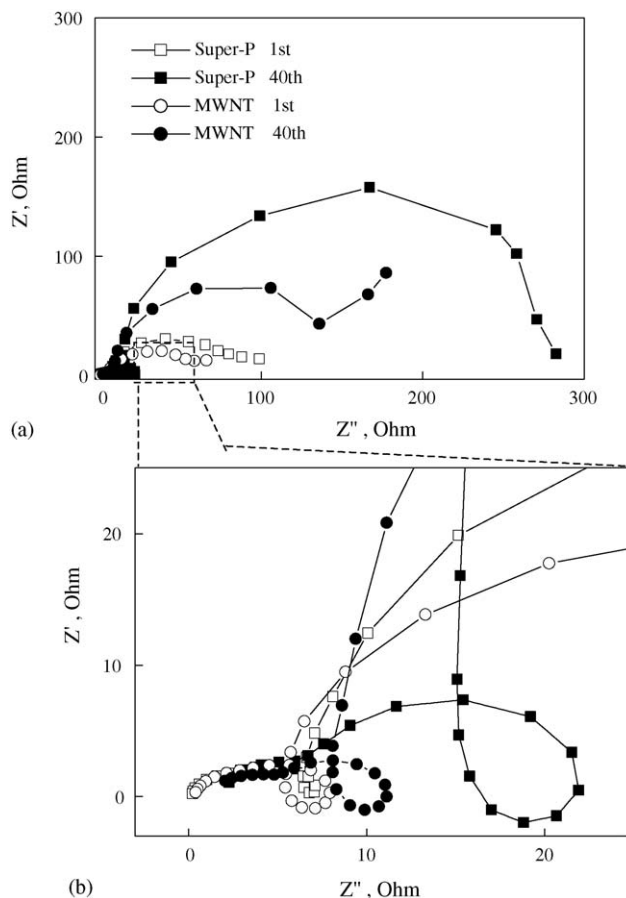

Fig. 5. Plots of ac impedance of MWNT- and Super P-cathodes at 3.69 ± 0.02 V vs. Li after first cycle and 3.81 ± 0.02 V after 40 cycles: (a) full plots; (b) expanded view of high-frequency part of plots.

is rather sensitive to potential [15]. The overall impedance of the Super P-cathode after the cycle test is approximately twice that of the MWNT-cathode, as seen in Fig. 5(a). This difference in impedance appears to explain the large differences in polarization of the two different electrodes as seen in Fig. 2. The large increase in the overall impedance of the Super P-cathode with cycling Fig. 5(a) might originate, at least partially, from the loss of the particle-to-particle contacts as indicated by the data in Fig. 6 and also suggested earlier by Rubino et al. [16].

Changes in electrode structure with cycling were studied carefully by inspection of scanning electron micrographs of the electrode surface in order to obtain additional clues as to why the MWNT-cathode displays better cycling performance than the Super P-cathode despite the fact that overall electrode expansion behaviour of the former is worse than that of the latter electrode. Micrographs of the electrode after the first and 40 cycles are presented in Fig. 6. Discrete cracks that are not observed in the electrode after the first cycle (Fig. 6(a)) are present in the Super P-cathodes after the 40-cycle test, as indicated by the arrows in Fig. 6(c). The MWNT-cathodes, however, do not exhibit such cracks after the cycle tests, as seen in Fig. 6(b and d). This is probably due to the resilience of the MWNT aggregates. Schematic representations of the observation are given in Fig. 6(e and f).
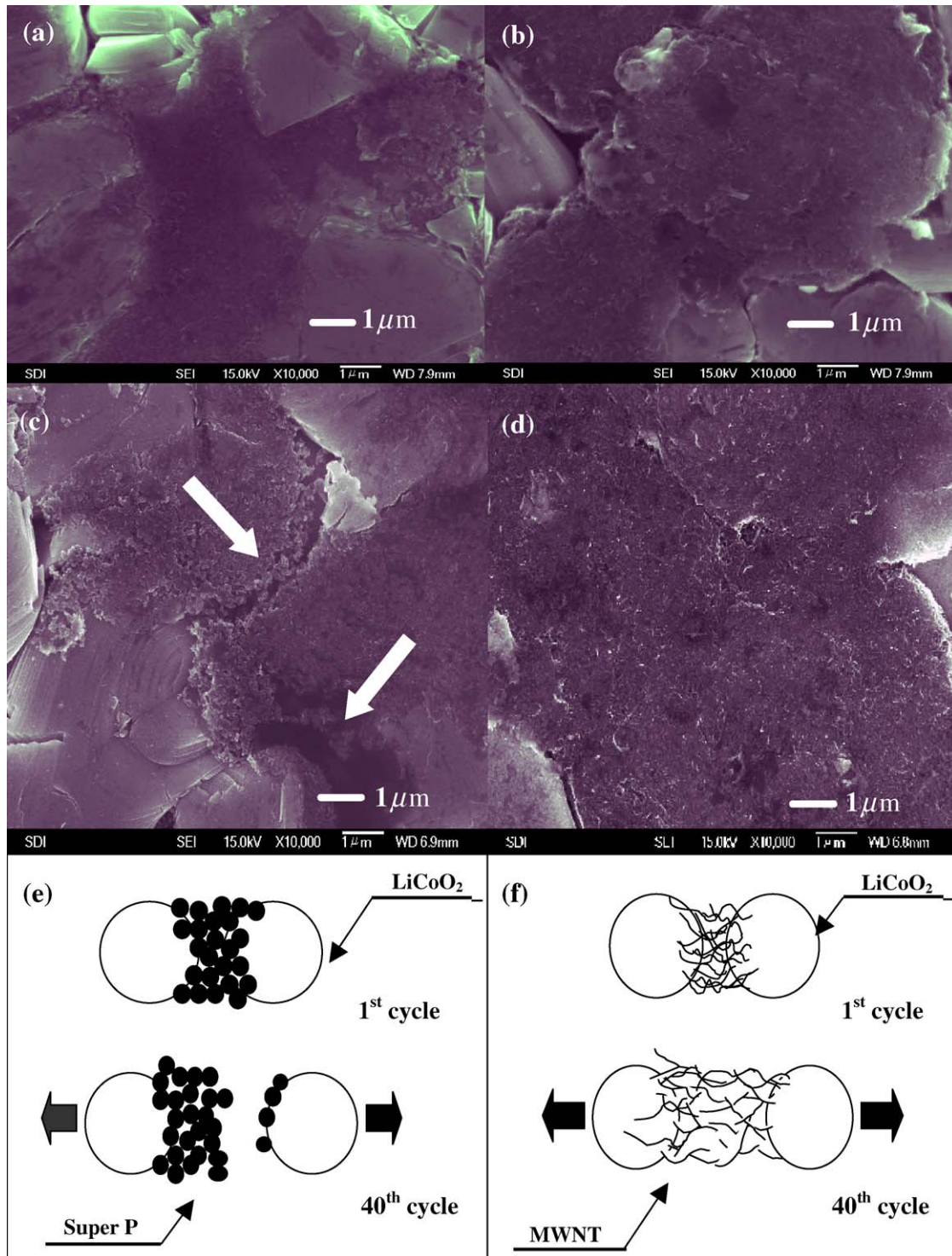
Fig. 6. Scanning electron micrographs of electrodes after 1 and 40 cycles and schematic representation of observed changes: (a) Super P-cathode after 1 cycle; (b) MWNT-cathode after 1 cycle; (c) Super P-cathode after 40 cycles; (d) MWNT-cathode after 40 cycles; (e) schematic representation of changes in Super P-cathode; (f) schematic representation of changes in MWNT-cathode.

Such cracks in the Super P-cathode should promote electrical isolation of active material particles and be responsible for the rapid performance degradation in impedance (Fig. 5), voltage (Fig. 2) and capacity (Fig. 3). Conversely, the improved performance of the MWNT-cathode is due to the lack or reduced tendency of such crack formation with cycling.

4. Conclusions

The present results show that carbon nanotubes (MWNT) are a much better conductive additive in a high-density cathode for Li-ion cells than Super P carbon black. The improved performance of the former appears to be largely due to the

resilience of the MWNT aggregates that form conductive bridges between particles of the active material. When the composite expands during cycling, the conductive bridges in the MWNT-cathode are kept relatively intact, whereas similar but rigid bridges in the Super P-cathode are broken and result in rapid increase in the particle-to-particle contact resistance.

Although the overall expansion of the MWNT-cathode after 40 cycles is rather excessive in the loosely-constrained cell used in the present test, electrode expansion may be controllable by application of high stack compression in a commercial Li-ion cell. For example, the cell stack expansion in an 18650-type cell should be largely limited by the can dimension. With this consideration, the present findings show that the MWNT is a good candidate conducting agent that can replace currently used carbon blacks for a high-energy Li-ion cell.

Acknowledgments

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