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Carbon-nanofiber composite electrodes for thin and flexible lithium-ion batteries

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Abstract Addition of vapor-grown carbon nanofiber (VGCF) into a $LiCoO_2$ composite electrode increases electrode's conductivity and adhesion strength significantly. These increases are attributed to the uniform distribution of network-like VGCF of high conductivity; VGCF not only connects the surface of the active materials, its network penetrates into and connects each active material particle. VGCF composite electrode also improves the electrochemical performance of thin and flexible lithium-ion batteries such as discharge capacity at high current densities, cycle-life stability, and low-temperature (at –20 °C) discharge capacity. These improved electrochemical properties are attributed to the well-distributed network-like carbon nanofibers, VGCF, within the cathode. The addition of VGCF reduces the electron conducting resistance and decreases the diffusion path for lithium ions, hence increases the utilization of active materials during high-current discharge and low-temperature discharge. In addition, network-like VGCF forms a more uniform cathode structure so as to have a lower deterioration rate and correspondingly better life cycle stability.

Introduction

Demand on rechargeable batteries for portable electronics has become pressing. While these electronics tend to decrease in size and become thin and flexible, batteries of high flexibility and variable sizes and shapes must consequently evolve to compensate these new requirements. Among many rechargeable batteries, lithium-ion battery is most attractive because of its high energy density, high working voltage, and low self-discharge rate.

A flexible lithium-ion battery is composed of electrodes, electrolyte, and a plastic laminated aluminum foil case [1]. Electrolyte and laminated aluminum foil are the more flexible elements than electrodes. Thus, the electrode characteristics, such as conductivity and adhesion strength, constrain the flexibility of the battery. A composite electrode consists of active materials, conducting additives, and polymer binder. Generally, conductivity of the active materials, especially for cathode, is insufficient for high-rate charge/discharge; it may be improved by the addition of conducting additives such as graphite and carbon black [2–7]. Conducting additives improve the uptake/absorption of liquid electrolyte by the composite electrodes, hence a good contact between lithium ions and the particles of active materials results and leading to a better utilization of active materials [2, 3]. Good absorption of electrolyte improves greatly the performance of cathode; for wetting in $LiCoO_2$ (lithium cobalt oxide) cathodes is generally more difficult than in mesocarbon microbeads (MCMB) anodes of the same electrolyte composition, and thereby limits much of the cathodes' performance [8]. The role of polymer binder in an electrode is to bind active materials with

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the conducting additive to the substrate. Increasing the amount of polymer binder increases the adhesion strength of the electrode, but at a disadvantage of decreasing the electrode conductivity (thereby impairs its electrochemical performance). When energy density and volumetric density are valued, minimizing the binder amount becomes essential [7].

VGCF has a relatively high mechanical strength and electrical conductivity [9]. VGCFs are graphitized carbon fibers and have high length/diameter ration, so they have high conductivity and tend to form special network-like morphology by nature [9]. VGCFs have been characterized in terms of the highly preferred orientation of their graphitic basal planes parallel to the fiber axis, with an annular ring texture in the cross section. This structure gives rise to excellent mechanical properties, very high electrical and thermal conductivity, and a high graphitizability [9–11]. In order to improve the conductivity and adhesion of the composite cathode during bending, VGCF was added to form a network-like composite electrode as shown in Fig. 1. The interconnected structure not only provides high conductivity but also binds all other compositions together. Electrochemical performances of the thin and flexible batteries with carbon-nanofiber composite cathodes were investigated in terms of life-cycle stability, high-current discharge behavior, and low-temperature discharge performance.

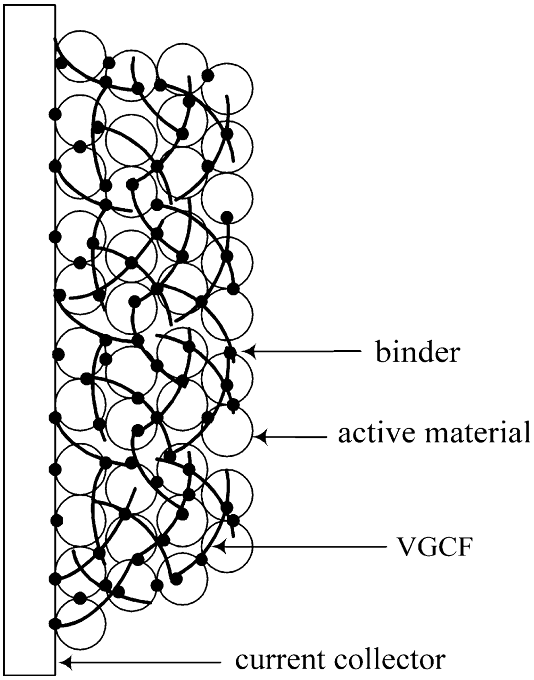

Fig. 1 Schematic diagram of the network-like VGCF distribution in cathode

Experimental

Thin and flexible test batteries had soft aluminum-plastic laminated film exterior (Showa Denko, Japan) with dimensions of 2.5 mm × 2.5 mm × 0.45 mm. An average capacity was 12 mAh and weighed 0.45 g. The lithium cobalt oxide electrode (cathode) contained 89 wt.% $LiCoO_2$ (LICO, Taiwan), 4 wt.% polyvinylidene fluoride (PVDF, Kuraha Chemical, Japan) binder, and 7 wt.% conducting additives. The conducting additives were synthetic graphite (Timrex KS6, Timcal, Switzerland) and vapor-grown carbon nanofibers (VGCFs). Carbon nanofibers were commercially available (Showa Denko, Japan). VGCFs were typically 100–200 nm in diameter and 10–20 μm in length. Four different sets of conducting additives proportions were 7 wt.% KS6 + 0 wt.% VGCF, 6 wt.% KS6 + 1 wt.% VGCF, 5 wt.% KS6 + 2 wt.% VGCF, and 4 wt.% KS6 + 3 wt.% VGCF. All powder constituents were mixed with the solvent N-methyl-2-pyrrolidone (NMP, Mitsubishi Chemical, Japan) to form slurry. The slurry was coated onto aluminum foil (20 μm in thickness) then dried at 140 °C. The electrode was pressed to a resultant thickness of 87 μm. The MCMB electrode (anode), 93 wt.% MCMB (25 μm in diameter, Osaka Gas, Japan), 7 wt.% PVDF binder and NMP, was coated on copper foil (15 μm in thickness) and went through the same manufacturing steps as the cathode. The resultant thickness of MCMB electrode was 75 μm.

Conductivity of the composite electrodes was measured by means of the four-point probe method [12]. The adhesion strength was determined by a balanced beam scrape adhesion tester. Scanning electron microscopy (SEM) was taken with a FE-SEM (LEO-1530) at an accelerating voltage of 5 keV.

All test batteries were assembled in a well-controlled dry room (temperature 25 °C, relative humidity 0.22%). Manufacturing process was as follows: both electrodes were dried at 120 °C for 3 h at a reduced pressure of 60 mmHg, then the electrodes were cut into appropriate sizes, separator (20 μm in thickness, Celgard 2320, USA) was carefully inserted in between the electrodes, and finally the battery case was thermally sealed off at a reduced pressure of 60 mmHg. Electrolyte was 1 M lithium hexafluorophosphate ($LiPF_6$, Tomiyama Pure Chemical, Japan) with ethylene carbonate/propylene carbonate/diethylene carbonate (EC/PC/DEC = 1/1/2, by volume, Ferro, USA). Detailed electrode and battery manufacturing procedures were stated in a previous publication [13, 14].

Test batteries were cycled between 4.2 and 2.75 V by means of a charge/discharge unit (Arbin, model BT2042, USA). The procedure was composed of a constant-current of 2 mA followed by constant-voltage at 4.2 V until the current tapered down to 0.2 mA. Batteries were discharged at a constant-current of 2 mA. In C-rate tests, test batteries were charged as above but discharge at different current densities. Low-temperature tests were conducted by stabilizing the test batteries to a desired specific temperature in a temperature-controlled chamber for 2 h before discharge.

Results and discussion

Electrode characteristics

Figure 2 shows the SEM images of the composite cathodes. In Fig. 2a shows the cathode of 7 wt.% KS6 and no VGCF. Surface of the electrode is partially covered with flake-like KS6. Flaky KS6 generally covers and connects only the surface of the electrode and not in between. Covered areas may exhibit high conductivity; but uncovered areas do not. When conductive additive is functional in only partial areas, the electrode's properties are not consistent throughout the entire electrode. In Fig. 2b shows the cathode of 4 wt.% KS6 + 3 wt.% VGCF. Total amount of conductive additive is the same in Fig. 2a and b, but the images are very different. The surface of the electrode is covered with both the flake-like KS6 and the network-like VGCF. Similarly with Fig. 2a, some areas are covered with KS6 and some are not. But the additional networking VGCF connects those uncovered areas, and complements the uneven distribution of KS6 and the inconsistency of the electrode's surface. In addition, VGCF not only connects the active material surface, the network actually distributes into and connects each particles. An electrode contains both KS6 and VGCF has a well-connected conducting network and therefore provides high conductivity and adhesion strength.

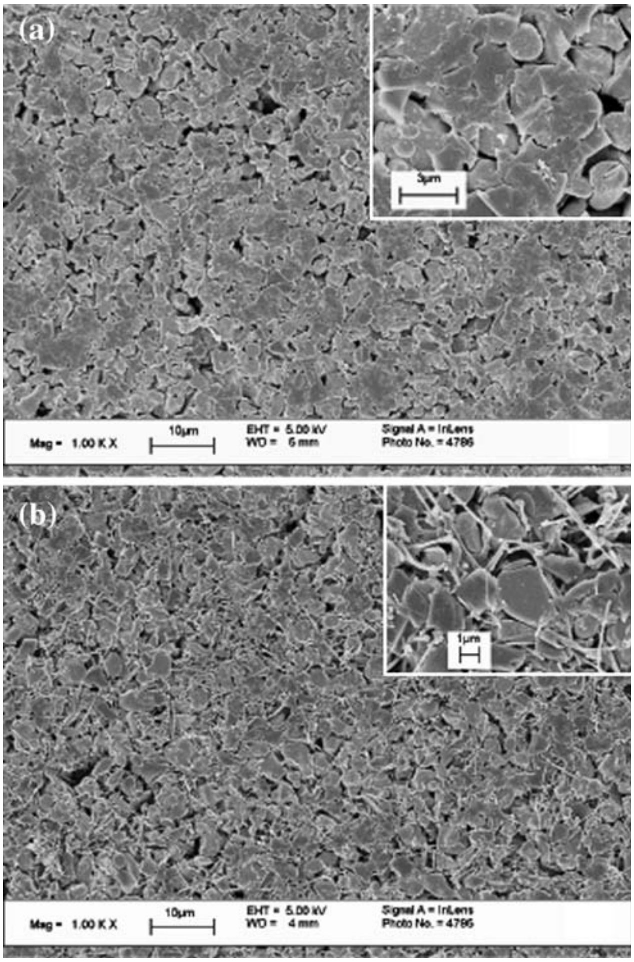

Fig. 2 SEM images of the composite cathodes: (**a**) 7 wt.% KS6 addition and (**b**) 4 wt.% KS6 + 3 wt.% VGCF addition

Figure 3 shows the conductivity of the composite cathodes with different amount of VGCF addition. By increasing the VGCF amount, conductivity of the electrode is increased. Conductivity increases from 0.018 S cm^{-1} of 0 wt.% addition to 0.7 S cm^{-1} of 3 wt.% addition. The increase is most significant when the addition amount is less than 2 wt.%. The increase levels off when the addition is more than 2 wt.%, therefore a maximum of 3 wt.% is assumed to be enough. When a cathode contains only the flake-like KS6, its conductivity is low (0.018 S cm^{-1}); but with the addition of the network-like VGCF, conductivity increases. VGCF has a high conductivity in nature

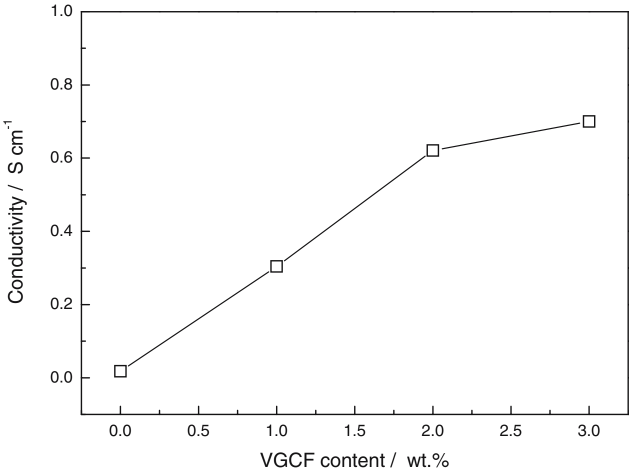

Fig. 3 Conductivity of the composite cathodes with different amount of VGCF addition

and a good network distribution in the composite electrode. Connection on both the surface and in between particles by VGCF clearly shows an elevation in conductivity by providing more paths for electrons to take.

Figure 4 shows the adhesion strength of the composite cathodes with different amount of VGCF addition. Similar to conductivity, adhesion strength increases with the amount of VGCF. Adhesion strength of the cathode of 3 wt.% addition, 0.60 kg cm^{-1}, is higher than that of only the KS6 addition, 0.12 kg cm^{-1}. Clearly, with only KS6 as the conducting additive is not enough; for a network-connection within particles by VGCF increases further the adhesion strength. Increase of adhesion strength levels off slowly and an addition of more than 3 wt.% is thereby assumed to be needless. Adhesion strength of a cathode is a combination from between the substrate-active material and between the particles, in which both the polymer binder and VGCF may help to increase. Increasing the amount of polymer binder, both the substrate-active material adhesion and the inter-particle adhesion may be increased; but conversely, conductivity decreases as the polymer binder isolates electronic conductance resulting in a poor electrochemical performance of the battery. Increasing the amount of VGCF, on the other hand, increases both the inter-particle adhesion and the conductivity by connecting particles in a network. The substrate-active material adhesion may also be increased with VGCF binding the particles to substrate. KS6 addition has a limited effect on increasing the electrode's adhesion, specifically on the inter-particle adhesion, because flake-shape is incapable in squeezing in between the particles.

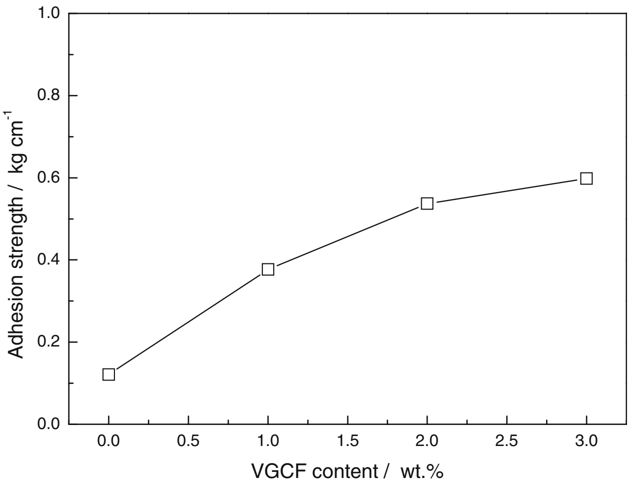

Fig. 4 Adhesion strength of the composite cathodes with different amount of VGCF addition

Mizuno et al. [15] studied the effects of conductive additives in composite positive electrodes on charge-discharge behaviors of all-solid-state lithium secondary batteries. They compared the effects of different conducting additive such as acetylene black (AB), Ni, VGCF, and TiN on the positive electrode. Their purpose was to reduce the resistance of positive electrode, as well as to reduce the interfacial resistance between the glass-ceramic electrolyte and the positive electrode. They found that among the conducting additives tested, VGCF has the greatest effects in reducing the total cell resistance. The presence of VGCF helps $LiCoO_2$ grains to obtain good contact with both grains of glass-ceramic electrolyte and the conductive additive. And good contact enhances reversible electrochemical reactions in the solid–solid interfaces between the grains [15].

Charge/discharge performance of thin and flexible batteries

Resultant test batteries have copper foil tab and aluminum foil tab as the negative and the positive current collectors respectively. Electrodes are flexible, so is the soft aluminum-plastic laminated film exterior case. Figure 5 shows the resultant thin and flexible lithium-ion battery. The shape of such batteries may be various: flat, curve, and bend. No electrolyte leaks when the battery shape changes, because electrolyte has been absorbed within the porous structure of the electrodes and separator.

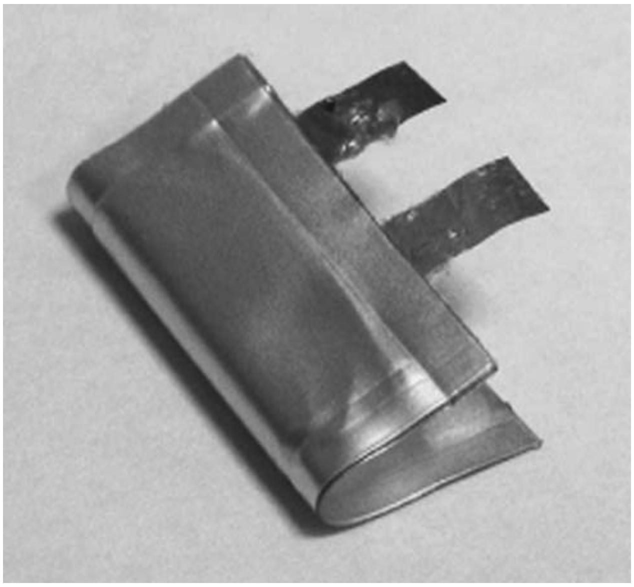

Fig. 5 A resultant thin and flexible lithium-ion battery

A lithium-ion battery after manufacture is tested in several ways to investigate its electrochemical properties. Figure 6 shows the charge and discharge curves of the 5th cycle of a test battery of 3 wt.% VGCF in cathode. In a battery, the charge and discharge capacities are normally equivalent, except for the first cycle due to the solid electrolyte interphase (SEI) formation. Both charge and discharge curves of the bend test battery are similar to that of a flat battery, demonstrating bending has no effect on the battery's charge/discharge performance. A change in shape does not result in detachment of active materials from the substrate or disconnection between particles; 3 wt.% VGCF addition provides good adhesion and high conductivity.

C-rate performance of thin and flexible batteries

High-current discharge behavior (C-rate test) is very important in high-power electronics applications. When a battery or batteries cannot perform satisfactorily in terms of high C-rate, the applied power tool may not even be able to start. Lithium-ion batteries generally used in power tools are large and heavy. A large battery contains more active materials, and while a characteristic of lithium-ion battery is that its temperature rises at discharge, especially pronounced in high C-rate [16], the created heat in a large battery for power tools is significant. Temperature increase has both positive and negative effects on the battery's performance. High temperature accelerates reaction rates and increases the electrolyte conductivity, thereby enhances the discharge behavior. Higher temperature, on the other hand, increases also the danger of fire and explosion. With the large area of electrodes and the massive volume of a large battery, a less uniform distribution of the dissipated heat may cause a local melting of the separator which leads to short-circuit and possibly fire or explosion [13]. A thin and flexible battery, in contrast, is small and thin; such a small volume provides more uniform heat dissipation, and the thin layer of active materials generates less heat.

C-rate behavior of an advanced lithium-ion battery is mainly controlled by lithium ion diffusion in $LiCoO_2$ cathode [14], but the cathode's conductivity also plays a part. Figure 7 shows the discharge curves of two test batteries (cathodes with and without VGCF addition) under different discharge rates of 0.2 and 3.0 C current densities. In 0.2 C discharge, the two discharge curves almost overlap each other with a capacity value of 12 mAh, demonstrating a small effect of the VGCF amount. But at a discharge current as high as 3 C, the two capacity values differ. The battery without VGCF has a much lower capacity of 9.12 mAh, which is only 76% of its 0.2 C-discharge capacity. On the other hand, the battery in which composite cathode contains 3 wt.% VGCF has a discharge capacity of 11.28 mAh, equals to 94% of its 0.2 C-discharge capacity. Since the compositions in both batteries are the same (same weight percent of $LiCoO_2$, binder, and conducting additive), diffusion behaviors in both cathodes are expected to be similar. For C-rate performance is controlled by the cathode's diffusion behavior and its conductivity, as the diffusion behaviors being similar, the only obtainable difference lies in the conductivity. The composite cathode with VGCF addition has a higher discharge

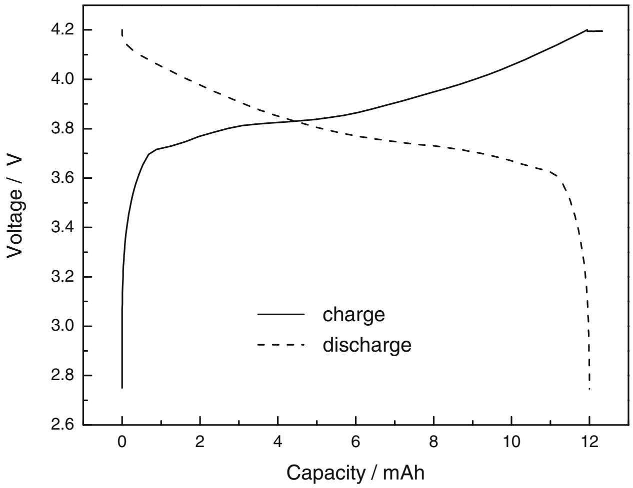

Fig. 6 Charge and discharge curves of a test battery of 3 wt.% VGCF in cathode after five charge/discharge cycles

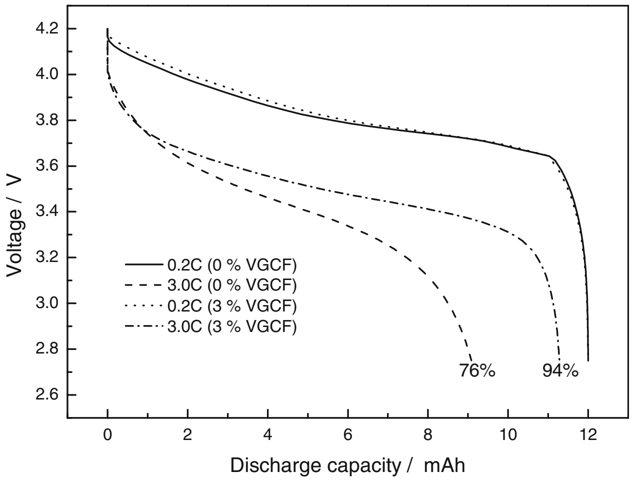

Fig. 7 Discharge curves of two test batteries (cathodes with and without VGCF addition) under different discharge rates of 0.2 and 3.0 C current densities

capacity because of its high conductivity, assures an efficient electronic transport through the electrode. High conductivity reflects a well-distributed carbon nanofiber conducting network exists within the cathode to reduce the electron conducting resistance and consequently, decreases the diffusion path for lithium ions and increases the utilization of active materials during high-current discharge.

Low-temperature performance of thin and flexible batteries

Figure 8 shows the 0.2 C-discharge curves of the two test batteries under different temperatures. At room temperature, both discharge capacities are similar and at –20 °C both values dropped. 93.8% of the original capacity of 12 mAh was obtained for the battery with 3 wt.% VGCF in cathode at –20 °C, and 81.2% for battery with no VGCF. Electrolyte composition determines the low temperature performance of lithium-ion cells, both in terms of its ionic mobility and of the formation of suitable SEI films over carbon anode and transition metal oxide cathode [17, 18]. $LiCoO_2$ material behaves like semi-conductors in which the conductivity increases as the operating temperature increases [19]. While both batteries have exactly the same compositions and the same amount of electrolyte, the only possibility to the difference in low-temperature performance is the VGCF amount. Discharge curves show an instantaneous voltage drop at the beginning of discharge increases with decreasing temperature; a result of an increased overall battery resistance raised by the ohmic resistance. Addition of VGCF helps to increase the cathode conductivity, and conversely decreases the ohmic resistance during low-temperature discharge.

Cycle-life performance of thin and flexible batteries

Cycle-life performance is referred to as a battery's performance after been charged and discharged repeatedly for a period of time. Each complete cycle consists of one charge and one discharge step. Figure 9 shows the relationships between 0.2 C-discharge capacity and cycle number of test batteries with 0 and 3 wt.% VGCF in cathodes. After 30 cycles, capacity of the battery with no VGCF decays to 91% of its original capacity, whereas the capacity of 3 wt.% VGCF decays only to 97%. Previous studies have showed that $LiCoO_2$ cathode is the major factor in capacity decay of an advanced lithium-ion battery [14, 20]. The difference between the two batteries is the amount of VGCF addition. As VGCF connects the particles and the surface of the electrode in a network, the cathode with VGCF addition is more homogeneous and uniform than the cathode without. As lithium ions intercalate into and de-intercalate out of the cathode during cycling, a more uniform cathode structure (both internally and superficially) corresponds a lower deterioration rate and thereby a better life cycle performance. In a less uniform cathode structure, certain compositions react in the cycling process, and partial reactions collapse easily the $LiCoO_2$ structure and lead to a shorter life.

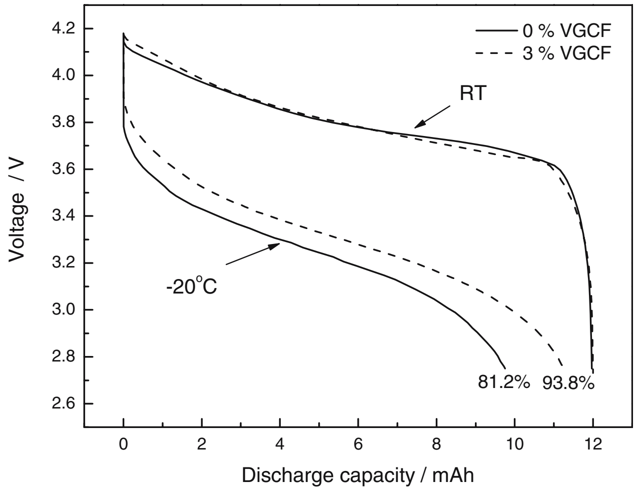

Fig. 8 0.2 C-discharge curves of two test batteries (cathodes with and without VGCF addition) under different temperatures

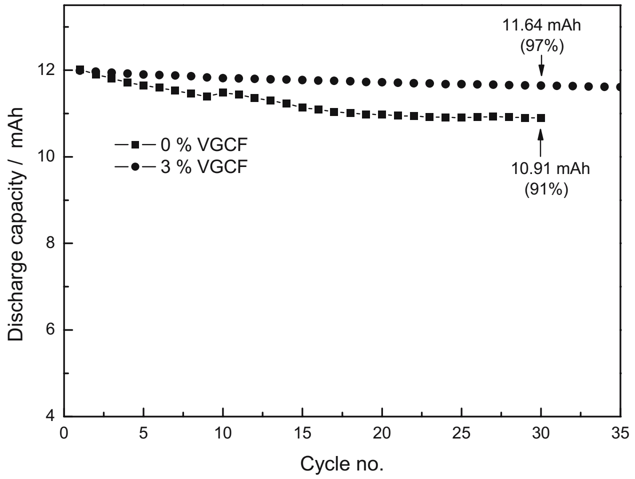

Fig. 9 Relationships between 0.2 C-discharge capacity and cycle number of thin and flexible batteries with 0 and 3 wt.% VGCF in cathodes

Conclusion

Thin and flexible lithium-ion batteries evolve to fit the growing demand by the flexible portable electronics. In this work, a type of carbon nanofiber, VGCF, as a conducting additive, is added to enhance the conductivity and adhesion strength of the composite cathode. By increasing the VGCF amount in cathode, conductivity and adhesion strength of the electrode are increased. Conductivity increases from 0.018 S cm^{-1} of 0 wt.% addition to 0.7 S cm^{-1} of 3 wt.% addition. Adhesion strength of 3 wt.% VGCF addition, 0.60 kg cm^{-1}, is higher than of 0 wt.% addition, 0.12 kg cm^{-1}. At bending state, test batteries still retain a high percentage of reversible lithium ions to their original capacities. Battery without VGCF in cathode has a much lower capacity during high-current discharge: 3 C-discharge capacity of 9.12 mAh, which is only 76% of its 0.2 C-discharge capacity. On the other hand, the battery with 3 wt.% VGCF has a 3.0 C-discharge capacity of 11.28 mAh, 94% of its 0.2 C-discharge capacity. This improved C-rate behavior is attributed to the high conductivity of cathode by the conducting network shortening the diffusion paths for lithium ions and hence increases the diffusion rate. At room temperature, discharge capacities of batteries with 0 and 3 wt.% VGCF are similar, while at –20 °C, both capacities dropped: 93.8% of the room-temperature capacity was obtained for the battery with 3 wt.% addition, 81.2% was obtained for 0 wt.% addition. Low-temperature behavior has been improved as the poor conductivity of $LiCoO_2$ electrode has bee improved, and utilization of $LiCoO_2$ been increased. After 30 cycles of charge/discharge, capacity of the battery with no VGCF decays to 91%, and capacity of battery with 3 wt.% VGCF decays only to 97%. Cycle-life improvement is attributed to the networking of VGCF in creating a more uniform cathode structure both internally and superficially, hence results in a lower deterioration rate of $LiCoO_2$ and correspondingly a better life cycle performance.

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