



Hybrid super-aligned carbon nanotube/carbon black conductive networks: A strategy to improve both electrical conductivity and capacity for lithium ion batteries

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HIGHLIGHTS

- ▶ A hybrid conductive network consists of super-aligned CNT films and carbon black.
- ▶ Super-aligned CNT films play an important role for long-range conductive pathways.
- ▶ Carbon black is an essential component for short-range conductive pathways.
- ▶ Highly uniform distribution of CNT and carbon black is realized.
- ▶ Conductivity and cell performance are improved with extraordinary low amount of CNT.

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ABSTRACT

Super-aligned carbon nanotube (SACNT) films drawn from SACNT arrays are uniformly introduced into LiCoO₂-Super P composite cathodes by a cold-rolling method, and a hybrid conductive network consisting of SACNTs and carbon black powders is obtained. This attempt results in reduced percolation threshold and increased conductivity of the LiCoO₂-Super P cathodes with addition of less than 0.01 wt% of SACNTs. The strength and flexibility of the LiCoO₂-Super P-SACNT composites can be improved significantly due to the excellent mechanical properties of SACNTs. The continuous SACNT films play an important role for the formation of a homogeneous network for long-range conductive pathways. Super P is also an essential component to form short-range conductive pathways. By comparing with control samples that only contain Super P or SACNT films, we demonstrate that the LiCoO₂-Super P-SACNT composites possess the best cycling stability (150 mA h g⁻¹ at 0.1 C with a capacity retention of 99.7% after 50 cycles) and rate capability (87 mA h g⁻¹ at 5 C). Combining both short-range and long-range conduction, the hybrid Super P-SACNT conductive network manifests itself as a promising strategy to improve the battery performances with a minimum amount of conductive fillers.

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1. Introduction

Rechargeable lithium ion batteries (LIBs) are widely used in various portable electronic devices, such as mobile phones, digital cameras, and notebook computers, due to their high energy density, long cycle lifetime, and excellent rate performance. Currently, the most commonly used cathode active materials in commercial LIBs are LiCoO₂ with layered structure, LiMn₂O₄ with spinel structure, and LiFePO₄ with olivine structure [1–5]. However, the electrical conductivities of LiCoO₂, LiMn₂O₄, and LiFePO₄ are as low as 10⁻³ S cm⁻¹, 10⁻⁴ S cm⁻¹, and 10⁻⁹ S cm⁻¹ respectively [4,6–8],

which make it difficult to achieve their full theoretical capacities at practical charge and discharge rates. A variety of methods were used to increase the electrical conductivities of the active materials, such as lattice doping and surface conductive coating, which require additional material processing [9–14]. Alternatively, a certain amount of conducting agent such as carbon black and graphite powders is commonly introduced to the active materials to increase the electrical conductivities of the composite cathodes [15–18]. The role of the conducting agent is to form conduction bridges among active material particles and thus enhance the electrical conductivity via a percolation mechanism. Typically, the content of the conducting additive in the cathode is up to 10–20 wt%, which inevitably results in a sacrifice in specific capacity of the LIBs due to the extra weight and volume of the electrochemically inert additive.

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It has been established that conductive fillers with a high aspect ratio, such as carbon fibers and carbon nanotubes (CNTs), are more effective to form conductive pathways throughout the composite and to gain a much lower percolation threshold compared with the traditional conductive agents such as carbon black [19–21]. However, challenges still remain. Tubular-shaped CNTs provide a poor surface coverage on active particles and only the electron transfer along the CNT axis is favored, which make it difficult for electron transfer across the surface of individual active particles. In comparison, it is easier for traditional carbon black powders (such as Super P) to provide a conductive layer covering individual active particles. Accordingly, it is a promising strategy to fabricate a type of hybrid conductive agent consisting of fillers with a wide range of aspect ratios. It was reported that LiFePO_4 cathodes with a mixture of carbon fibers and carbon black powders exhibited better power performance than the electrode containing a single type of conductive agent [22]. It is also worth to note that, a homogeneous dispersion of such fillers in the active material matrix is crucial regardless of what type of conductive agents is added [15]. Additives with large aspect ratios always suffer heavy agglomeration. For instance, heavy agglomeration was observed in CNTs because of the strong inter-tube attraction (typical attractive interaction potential among nanotubes is 0.5–2 eV [23,24]). Non-uniform spatial distribution of the conductive fillers will result in heavy polarization as well as severe capacity fading of the composite electrodes. Extensive research has been focused on the dispersion of CNTs, including ball milling [25], ultrasonication [26,27], and physical and chemical modification [28]. Nevertheless, these methods generally require complicated processing, and might break CNTs into shorter segments [29].

In this work, we take advantage of the prominent properties of super-aligned CNTs (SACNTs) to demonstrate a homogeneous and hybrid conductive network consisting of SACNTs and Super P powders made by a simple and fast cold-rolling procedure. Continuous SACNT films, which can avoid agglomeration of CNTs, were directly drawn from SACNT arrays with an end-to-end joining mechanism [30–33], and then cold rolled into the LiCoO_2 –Super P composites. There are several advantages of using such a hybrid SACNT–Super P conductive network. (1) The hybrid conductive network containing tubular SACNTs and spherical Super P powders can afford versatile charge transportation not only across the surface of individual LiCoO_2 particles in the short range but also among multiple LiCoO_2 particles in the long range. Thus outstanding conductivity and excellent rate behavior of the composite cathodes are achieved. (2) Drawing SACNT films from SACNT arrays can overcome the problem of heavy agglomeration and thus full utilization of the conductive agents can be achieved. As a result, high capacities of the composite electrodes are obtained with addition of SACNTs at extraordinary low weight ratio and cost. (3) Due to the high strength and resilience of SACNTs, contacts between the active particles and the conductive agents can be better maintained when any volumetric change occurs during cycling, and excellent cycling performance is attained. (4) Fabrication of this kind of LiCoO_2 –Super P–SACNT composite is quite simple, and holds great potential in large scale production.

2. Experimental

The active cathode materials are LiCoO_2 powders (10 μm in diameter, Reshine, China). Polytetrafluoroethylene (PTFE) suspension in water was used as binder. Carbon black powders (Super P, Timcal Ltd., Switzerland) were used as purchased. The first type of cathodes contained LiCoO_2 and PTFE at a weight ratio of 8: 1, together with Super P in the range from 1 to 10 wt%. LiCoO_2 and Super P powders were first dry-mixed in a mortar. The PTFE

suspension was then added and the resulting paste was stirred continuously and cold rolled to form thin strips. The second type of cathodes consisted of hybrid SACNT–Super P conductive additives. The preparation details of SACNT arrays can be referred to early publications [30,31,34]. 20 layers of SACNT films drawn from the SACNT array with an areal density of 0.04 mg cm^{-2} were cross-stacked onto the above-mentioned cathode strips (Fig. 1a), then curled and cold rolled together (Fig. 1b–d). During the curling and rolling process, SACNTs were squeezed and their orientations were randomized. After repeated curling and rolling (Fig. 1e–f), SACNTs were homogeneously distributed in the composite cathode strips (Fig. 1g). In the third type of cathode, only SACNT films were mixed with LiCoO_2 particles and PTFE by the same cold rolling process, without the presence of any Super P. Each cathode strip was punched into several circular discs with a diameter of 7 mm and dried at 120 $^\circ\text{C}$ for 24 h in a vacuum oven.

Microstructures of the conductive agents and the composite cathodes were analyzed using a scanning electron microscope (SEM, Sirion 200, FEI, USA) and a transmission electron microscope (TEM, Tecnai 20 G2 STWIN, FEI, USA). Electrical conductivities of the cathodes were characterized by a four-point probe method. Tensile tests of the composite cathodes were performed using an Instron 5848 microtester with a strain rate of $1\% \text{ min}^{-1}$ and a gauge length of 1 cm.

Coin-type (CR 2016) half-cells were assembled in an argon-filled glove box (M. Braun inert gas systems Co. Ltd., Germany) with both moisture and oxygen levels below 0.1 ppm. The LiCoO_2 composite discs were used as the cathodes. A porous polymer film (Celgard 2400, USA) was used as the separator. A Li-metal foil with a thickness of 400 μm was used as the counter electrode. The electrolyte was a 1 M LiPF_6 solution in ethylene carbonate (EC) and diethyl carbonate (DEC) mixed at a weight ratio of 1:1. The charge–discharge cycles were performed using a Land battery test system (Wuhan Land Electronic Co., China) with cut-off voltages of 3.0–4.3 V. Electrochemical impedance spectroscopy (EIS) results were collected using a PARSTAT 2273 Potentiostat/Galvanostat (Advanced Measurement Technology Inc., USA) with a small perturbation voltage of 5 mV in the frequency range from 100 mHz to 100 kHz. All the electrochemical tests were performed at room temperature.

3. Results and discussion

Fig. 2a and b show TEM images of Super P powders and a SACNT. Spherical Super P powders with a diameter of about 50 nm cannot form conductive networks until they aggregated together. The diameter and length of SACNTs used in this study are around 10–20 nm and 300 μm respectively. Thus the aspect ratio of SACNTs is about 15,000 times that of Super P. Typically, a SACNT yarn showed a conductivity of $9.2 \times 10^2 \text{ S cm}^{-1}$ [32], whereas carbon black compacts only displayed a conductivity of $1.4 \times 10^1 \text{ S cm}^{-1}$ [35]. Therefore, continuous SACNT films composed of SACNT bundles can serve as a type of long-range conductive additive. Fig. 2c shows an SEM image of the top surface of a pre-rolled LiCoO_2 cathode strip covered with 20 layers of SACNT films. LiCoO_2 particles underneath the continuous and aligned SACNT films can be clearly seen. The areal density of one layer of SACNT film is as low as 0.002 mg cm^{-2} , and the thickness and density of the LiCoO_2 cathode strip are around 300 μm and 1.3 g cm^{-3} respectively, from which it can be calculated that the mass fraction of SACNTs in the cathode is less than 0.01%. Fig. 2d shows a cross-sectional SEM image of a LiCoO_2 –Super P–SACNT composite cathode after the cold-rolling process. Most SACNTs connected with multiple LiCoO_2 particles and uniformly extended throughout the composite cathode. No obvious entanglement of SACNTs was observed. Such

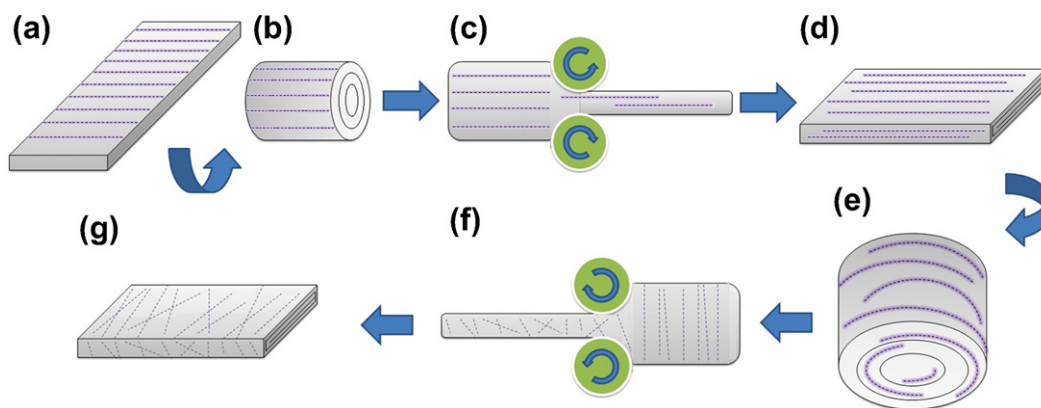


Fig. 1. Schematic of the cold-rolling procedure for the fabrication of the LiCoO₂-Super P-SACNT composites. The dashed lines represent SACNTs.

homogeneous distribution ensures high utilization of SACNTs and efficient long-range conductive pathways, as well as sufficient contact between active materials and SACNTs. In addition, Super P powders covered the surface of individual LiCoO₂ particles to form a conductive layer, which facilitated electron transfer across the surface of LiCoO₂ particles in the short range. Accordingly, it is promising to achieve high conductivity of the composite cathodes with such uniformly dispersed and hybrid conductive additives.

To get a deep understanding of how the hybrid conductive network performs, it is necessary to discuss the charge transfer process in such composite cathodes. As schematically shown in

Fig. 3, the charge transfer pathways in the cathode can be divided into two categories, short-range pathways crossing the surface of individual LiCoO₂ particles (purple arrows) and long-range pathways linking multiple LiCoO₂ particles (green arrows). With a large aspect ratio, SACNTs have the advantage in forming long-range charge transfer paths, which then evolve into a conductive network in the active matrix with a lower percolation threshold. Hence a smaller amount of conductive fillers with high aspect ratios is required to reach the same level of conductivity compared to those with low aspect ratios. Such phenomena were also reported in CNT-polymer nanocomposites by several groups [36,37]. Nevertheless,

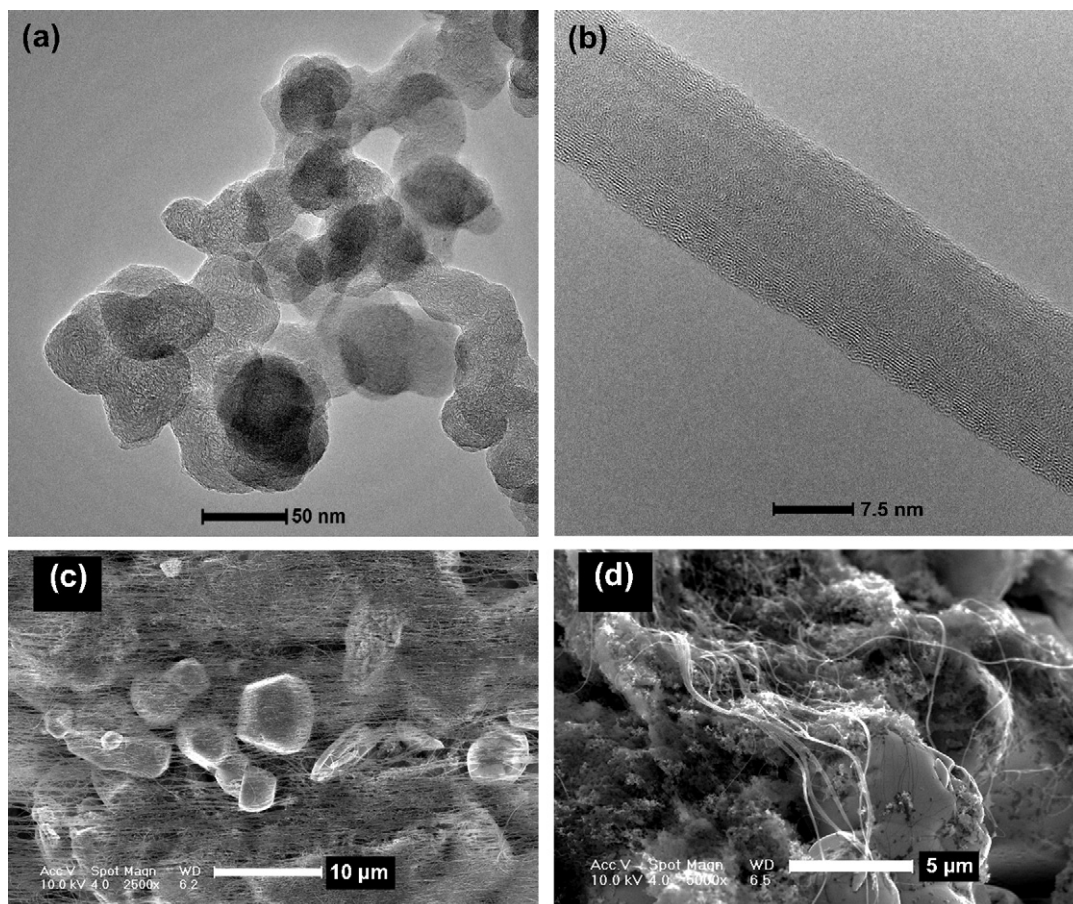


Fig. 2. TEM images of (a) carbon black powders and (b) a SACNT. (c) SEM image of the top surface of a pre-rolled cathode strip containing LiCoO₂, Super P, and PTFE covered with 20 layers of SACNT films. (d) Cross-sectional SEM image of a LiCoO₂-Super P-SACNT composite cathode after the cold-rolling process.

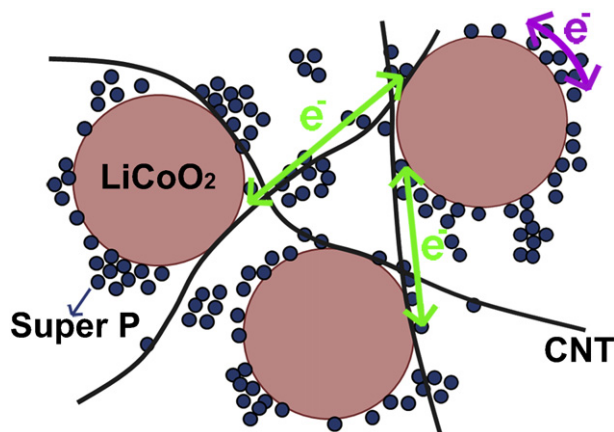


Fig. 3. Schematic of a hybrid Super P-SACNT conductive network providing both short-range and long-range conductive pathways in the LiCoO₂ matrix.

SACNTs also have drawbacks in electron transfer across surface of individual particles, since a single SACNT can only provide limited contact area with LiCoO₂ particles and directional electron transfer along its axis. Super P, on the other hand, is an effective alternative to deal with such problem. With a spherical shape and a small size, it will be quite convenient for Super P powders to make up a surface conductive layer around each LiCoO₂ particle. However, it requires a number of Super P particles for long-range conductive paths, since Super P particles tend to form localized conductive path rather than a chain-like one running through the composite electrodes. Thus, continuous conductive path for electron transfer among multiple LiCoO₂ particles has to be fulfilled by the long SACNTs. By mixing SACNTs and Super P powders together, a hybrid conductive network that meets both short-range and long-range conduction requirements can be constructed with comparably lower amounts of inert fillers.

Electrical conductivities of the LiCoO₂ cathodes with 1–10 wt% Super P are shown in Fig. 4. As discussed above, SACNTs only account for a negligible weight ratio in the LiCoO₂-Super P-SACNT composite. Therefore, it can be approximated that both LiCoO₂-Super P and LiCoO₂-Super P-SACNT cathodes possess the same amount of carbon conductive agents at any given content of Super P. Accompanied with the content of Super P increasing from 1 wt% to

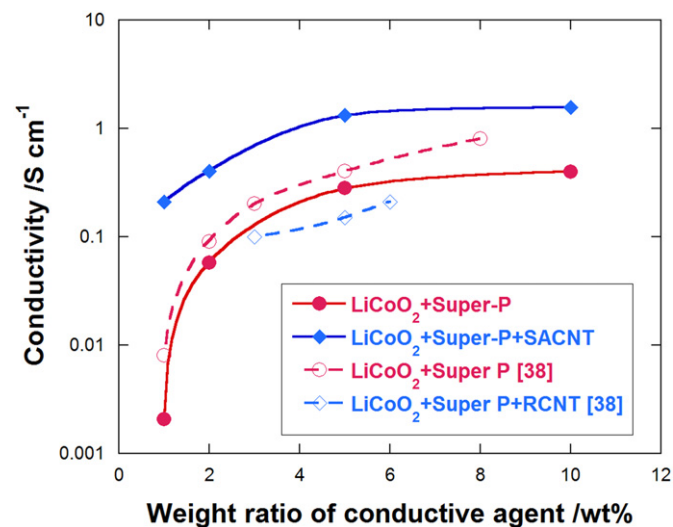


Fig. 4. Electrical conductivities of the LiCoO₂-Super P and LiCoO₂-Super P-SACNT cathodes in comparison with literature data.

10 wt%, electrical conductivity of the LiCoO₂ cathode is boosted from 2.06×10^{-3} to 2.72×10^{-1} S cm⁻¹. The sharp increase in conductivity, corresponding to the percolation threshold, does not occur until the weight ratio of Super P reaches 2%. In contrast, LiCoO₂-1 wt% Super P cathode with the addition of SACNT films attains an electrical conductivity as high as 2.10×10^{-1} S cm⁻¹, which is almost same with that of the LiCoO₂-10 wt% Super P cathode. These results clearly show that, in the LiCoO₂-Super P-SACNT cathodes, the percolation threshold is greatly reduced to less than 1 wt% by introducing SACNT films into the LiCoO₂-Super P composite. Considering such significant improvement is achieved with an extraordinary low amount of SACNTs (less than 0.01 wt%), it is demonstrated that the SACNTs must be efficiently utilized, due to the uniform dispersion of CNTs. Besides, for the LiCoO₂-10 wt% Super P cathode, the conductivity can also be further increased by one order of magnitude with the addition of SACNT films. The conductivities of LiCoO₂-Super P-SACNT composites are also compared with other works. Park et al. [38] introduced randomly oriented CNTs (RCNT) and Super P into LiCoO₂ by an ultrasonic method. As shown in Fig. 4, both kinds of LiCoO₂-Super P cathodes display similar conductivities, while the LiCoO₂-Super P-RCNT composites exhibit much lower conductivities than those of the LiCoO₂-Super P-SACNT composites. When part of the Super P content was replaced by RCNT, a decrease in conductivity was observed [38]. This result strongly indicates that the conducting network in the LiCoO₂-Super P-RCNT composites is still mainly provided by Super P, and further verifies the necessity of introducing CNTs into the composite in the film format to minimize aggregation.

To demonstrate the effect of high strength and resilience of SACNTs on the mechanical performance of the cathode composites, tensile tests were carried out for the LiCoO₂-5 wt% Super P composites with and without SACNT films, and their stress-strain curves are shown in Fig. 5a. The Young's modulus of the LiCoO₂-5 wt% Super P-SACNT composite is 5.81 MPa, which is more than 4 times greater than the cathode without SACNTs (1.08 MPa). Their tensile strength results follow the same trend. The tensile strength of the LiCoO₂-5 wt% Super P-SACNT composite sample is 0.36 MPa while that of the LiCoO₂-5 wt% Super P composite is as low as 0.04 MPa. Both Young's modulus and tensile strength results demonstrate an outstanding strengthening effect of SACNTs, due to the high intrinsic modulus and strength of SACNTs. The high Young's modulus and strength of the LiCoO₂-Super P-SACNT composite also indicate close contact and efficient load transfer between SACNTs and LiCoO₂ particles. Moreover, the LiCoO₂-Super P-SACNT composites also display better flexibility than the LiCoO₂-Super P composites, due to the high resilience of SACNTs. The strain at fracture for the LiCoO₂-5 wt% Super P-SACNT composite is 15.6%, which is much larger than that without SACNTs (4.6%). Photographs of both LiCoO₂-Super P and LiCoO₂-Super P-SACNT composite cathodes after tensile testing are shown in the inset of Fig. 5a, demonstrating more roughened fracture surface of the cathode containing SACNTs. SEM image of the fracture surface of a LiCoO₂-5 wt% Super P-SACNT composite further shows both fracture of SACNTs and pull-out of SACNTs from the composite matrix (Fig. 5b), contributing to the increased strength and flexibility of the composites. Such high strength and high flexibility of the LiCoO₂-Super P-SACNT composites are beneficial to endure any volumetric change and maintain electrical contact for efficient charge transfer on cycling. Taking the high conductivity, high strength, and high flexibility of the LiCoO₂-Super P-SACNT composites into account, both outstanding charge transfer ability and structural durability can be achieved for the cathodes containing the hybrid Super P-SACNT conductive network. Thus better cycling stability and rate behavior of such LiCoO₂-Super P-SACNT composites can be expected.

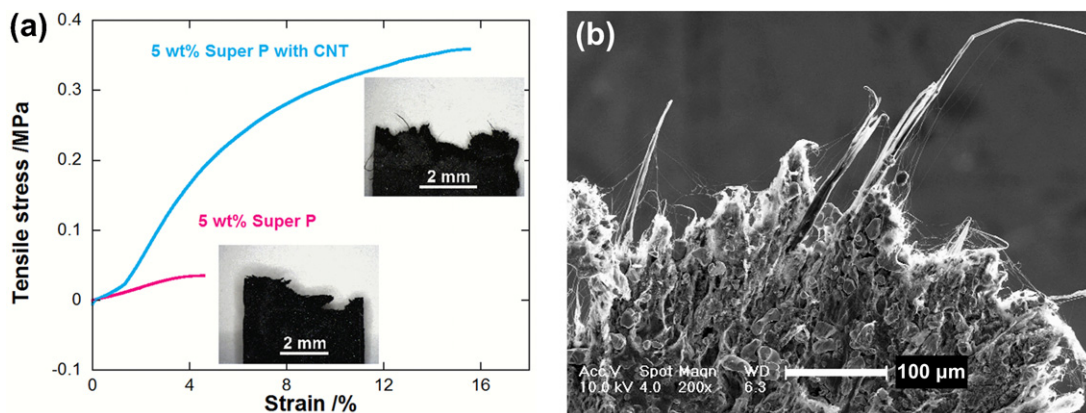


Fig. 5. (a) Tensile stress–strain curves of the LiCo₂–Super P and LiCo₂–Super P–SACNT composite cathodes with inset photos of the fractured cathode sheets. (b) SEM image of the fracture surface of a LiCo₂–Super P–SACNT composite.

By charging and discharging the cells at 0.1 C, cycling performances of the LiCo₂–Super P and LiCo₂–Super P–SACNT cathodes were compared. All the composite cathodes exhibit similar initial capacities at about 150 mA h g⁻¹, and the cycling stability of these cathodes is improved as the weight ratio of Super P increases, as shown in Fig. 6. With same content of Super P, the capacity retention of the LiCo₂–Super P–SACNT cathodes is clearly superior to that of the LiCo₂–Super P cathodes. The LiCo₂–5 wt% Super P–SACNT cathode displays a capacity retention of 96.1% after 50 cycles, which is even higher than that of the LiCo₂–10 wt% Super P cathode (93.9% after 50 cycles). The LiCo₂–10 wt% Super P–SACNT cathode exhibits the best cycling performance, with a capacity retention as high as 99.7% after 50 cycles. The improvement in capacity retention for the LiCo₂–Super P–SACNT composites is consistent with the results of tensile tests and conductivity tests. The LiCo₂–Super P–SACNT composites with high strength and flexibility can effectively accommodate any volumetric change of active materials during charge/discharge processes and thus lead to excellent cycling stability. As polarization is also responsible for capacity degradation, the excellent cycling stability of the LiCo₂–Super P–SACNT composites is also attributed to the homogeneous distribution of the hybrid Super P–SACNT conductive fillers and the resulting high conductivity of the composite cathodes.

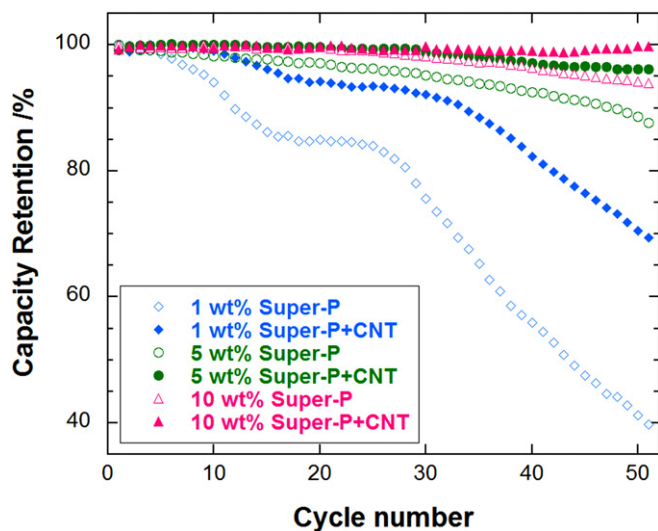


Fig. 6. Cycling performance of the LiCo₂–Super P and LiCo₂–Super P–SACNT composite cathodes.

In addition to the cycling performances, rate capabilities of the LiCo₂–Super P and LiCo₂–Super P–SACNT composites were also studied by measuring the discharge capacities at various rates, as shown in Fig. 7. Compared to the LiCo₂–2 wt% Super P composite, the LiCo₂–2 wt% Super P–SACNT composite obtains capacities at 137 mA h g⁻¹ (0.5 C), 99 mA h g⁻¹ (1 C), and 25 mA h g⁻¹ (2 C), corresponding to remarkable improvements of 38.0%, 159%, and 199%, respectively. As the weight ratio of Super P reaches 10 wt%, the advantage of the hybrid conductive network is more pronounced at the discharge rate of 5 C. The LiCo₂–10 wt% Super P–SACNT cathode attains a capacity of 87.0 mA h g⁻¹, while the cathode without SACNTs shows a capacity of only 63.9 mA h g⁻¹. At large discharge currents, a sufficient number of conductive paths are required to prevent polarization, where local charge accumulation interferes with further charge transportation and leads to capacity loss. The overall uniform charge distribution throughout the cathodes can be realized by the tubular SACNTs, while the local uniform charge distribution across the surface of individual LiCo₂ particles can be achieved by the Super P powders. As a consequence, the hybrid conductive network can help to prevent charge accumulation both in the long and short ranges, and thus better performance at high rates can be achieved. The excellent cycling stability and rate capability of the LiCo₂–Super P–SACNT cathodes are ascribed to their high conductivity and excellent

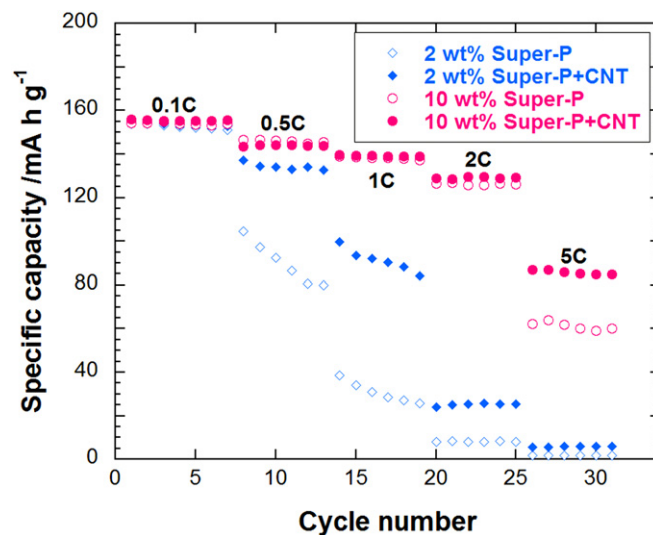


Fig. 7. Rate performance of the LiCo₂–Super P and LiCo₂–Super P–SACNT composite cathodes.

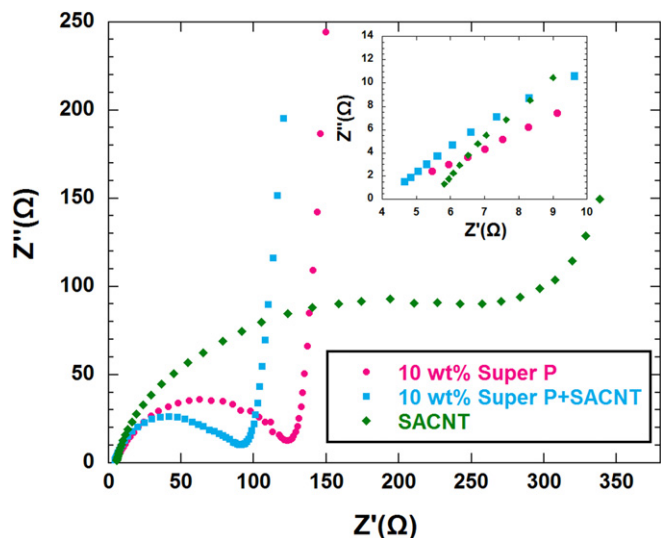


Fig. 8. Electrochemical impedance spectra of the LiCoO₂–10 wt% Super P, LiCoO₂–10 wt% Super P–SACNT, and LiCoO₂–SACNT cathodes. High frequency region is zoomed.

mechanical properties, and strengthen the viewpoint about the superiority of the hybrid Super P–SACNT conductive network.

In order to evaluate the cell performance of the LiCoO₂–Super P–SACNT cathodes more objectively, batteries based on hybrid or pure CNT conductive additives described in other literatures are also compared. For instance, a LiCoO₂–5 wt% Super P–5 wt% KS6 cathode only delivered a specific capacity of 138 mA h g^{−1} at 0.5 C [16]. This value is inferior to our LiCoO₂–10 wt% Super P–SACNT cathodes and this difference is attributable to the greater aspect ratio of SACNTs than that of KS6. In comparison to other batteries that only used CNTs as conductive additives, the LiCoO₂–Super P–CNT cathodes were demonstrated to have comparable cell performance with the same content of carbon additives [27,39]. Currently, the price of CNTs is still much higher than that of Super P. From the viewpoint of cost-effective, it is obvious that the LiCoO₂–Super P–SACNT cathodes reported in this work present the highest capacity (energy)/cost ratio. For rate performance, a LiCoO₂–2 wt% Super P–4 wt% RCNT cathode delivered a specific capacity of 115 mA h g^{−1} at 5 C [38], even though it displayed a relatively low conductivity as shown in Fig. 4. The difference in rate capability in our work may be ascribed to the quality of LiCoO₂ powder, which contributes more greatly in electrochemical processes than in the conductivity. Considering the prominent effect of the hybrid Super P–SACNT additive on increasing conductivity, it is reasonable to suggest that comparable or even better cell performance may have been achieved if the same LiCoO₂ material was employed.

The electrochemical processes involved in the LiCoO₂–Super P and LiCoO₂–Super P–SACNT composites were further characterized by EIS. As shown in Fig. 8, the EIS spectra consist of a depressed semicircle in the high frequency range and a straight line in the low frequency range. The intersection with the real axis at high frequency corresponds to ohmic resistance R_{ohm} as shown in the inset of Fig. 8, which reflects the electronic and ionic resistance of the two

electrodes and electrolyte/separator. Considering the resistance of electrolyte/separator can be assumed to be the same, the smaller R_{ohm} (4.7 Ω) in the LiCoO₂–10 wt% Super P–SACNT cathode than that in the LiCoO₂–10 wt% Super P cathode (5.5 Ω) reflects the higher conductivity of the former electrode. The diameter of the depressed semicircle refers to the charge transfer resistance (R_{ct}). According to the EIS spectra, R_{ct} in the LiCoO₂–10 wt% Super P–SACNT cathode is 85.7 Ω, which is much smaller than that of the LiCoO₂–10 wt% Super P cathode (117.0 Ω). This improvement in charge transfer also reflects the fact that the hybrid Super P–SACNT conductive network can promote more sufficient ion and electron transfers among LiCoO₂ particles and the electrolyte, leading to superior cell performances of the LiCoO₂–Super P–SACNT cathodes.

It is demonstrated that the hybrid Super P–SACNT conductive network has benefits in both long and short range charge transportation. The necessity of using Super P for short-range charge transfer is manifested by the third type of cathode, LiCoO₂–SACNT cathode, in which only a 20-layer- SACNT film was employed as conductive agent. As listed in Table 1, the conductivity of the LiCoO₂–SACNT cathode ($1.8 \times 10^{-2} \text{ S cm}^{-1}$) is higher than that of the LiCoO₂–1 wt%–Super P cathode ($4.2 \times 10^{-3} \text{ S cm}^{-1}$). Note the large standard deviations in Table 1 indicate the scattered feature of conductivities for samples with carbon contents as low as 1 wt%. The improvement in conductivity can be interpreted as a result of the introduction of SACNTs, however, surface charge transfer on each individual LiCoO₂ particles is still restricted due to the absence of Super P. As shown in EIS measurements (Fig. 8), the LiCoO₂–SACNT cathode showed an ohmic resistance of 5.8 Ω at the high frequency region but the largest diameter of the semicircle, corresponding to a significant charge transfer resistance of 251.5 Ω. Therefore, a large portion of LiCoO₂ particles cannot be fully utilized and polarization will take place. As the charge transfer step was critical in electrochemical processes, a very limited average initial specific capacity of only 113.4 mA h g^{−1} was observed. Even though our results suggested that SACNTs would improve capacity retention (95.7% after 20 cycles), it clearly turned out that spherical Super P particles were also important for both high specific capacity and high capacity retention. The LiCoO₂–SACNT cathode delivered the lowest specific capacity out of three types of cathodes because of the highest charge transfer resistance resulting from the low coverage of conducting additives on individual LiCoO₂ particles (Table 1). Please note that the content of the SACNT films is less than 0.01 wt%. Theoretically, the content of the carbon additive can be increased by introducing more layers of SACNT films into the LiCoO₂ cathodes. However, as the number of SACNT layers increases to 50, the composite cathodes become too hard to be cold-rolled due to the extensive strengthening effect of SACNTs. Thus, from a feasibility point of view, it is necessary to use the optimal amount of Super P powders and SACNT films to form a hybrid conductive network that can provide both short-range and long-range conductive pathways without deteriorating the flexibility of the composite cathodes too significantly. Among the LiCoO₂–Super P, LiCoO₂–Super P–SACNT, and LiCoO₂–SACNT cathodes listed in Table 1, the LiCoO₂–Super P–SACNT cathode displays the highest conductivity ($1.3 \times 10^{-1} \text{ S cm}^{-1}$) and best cycling stability (94.4% after 20 cycles), further verifying the superiority of the hybrid Super P–SACNT conductive network.

Table 1
Conductivities and cell performances of the LiCoO₂–Super P, LiCoO₂–Super P–SACNT, and LiCoO₂–SACNT cathodes.

Sample description	Conductivity/S cm ^{−1}	Initial capacity at 0.1 C/mA h g ^{−1}	Capacity after 20 cycles/mA h g ^{−1}
LiCoO ₂ –1 wt% Super P–SACNT	$1.3 \times 10^{-1} \pm 0.8 \times 10^{-1}$	149.7 ± 2.7	141.3 ± 5.4
LiCoO ₂ –1 wt% Super P	$4.2 \times 10^{-3} \pm 2.0 \times 10^{-3}$	145.7 ± 3.5	119.2 ± 6.9
LiCoO ₂ –SACNT	$1.8 \times 10^{-2} \pm 0.8 \times 10^{-2}$	113.4 ± 7.6	108.5 ± 8.9

4. Conclusions

SACNT films were uniformly introduced into the LiCoO₂–Super P composites to form a hybrid Super P–SACNT conductive network. By drawing SACNT arrays into films, the problem of agglomeration is avoided and alleviation of polarization is realized. The hybrid Super P–SACNT conductive network can supply charge transfer pathways by both linking multiple LiCoO₂ particles in the long range and crossing the surface of individual LiCoO₂ particles in the short range. Experimental results demonstrate that the hybrid conductive network has a significant effect on decreasing the percolation threshold and increasing the conductivity of the composite electrodes. Furthermore, the Young's modulus, strength, and flexibility of the LiCoO₂–Super P–SACNT composite cathodes are also greatly improved due to the excellent mechanical properties of SACNTs, which are beneficial to tolerate any volumetric change during cycling. Therefore, the LiCoO₂–Super P–SACNT cathodes exhibit much better cycling and rate performances compared with the LiCoO₂–Super P cathodes. In addition, by comparing with samples that only contain Super P or SACNT films as sole conductive agent, it can be concluded that the strategy of using hybrid conductive agents and the introduction of SACNTs into the LiCoO₂ cathodes in the form of continuous films are key factors to increasing the conductivity of the composite cathodes and improving the cell performances. The fabrication of LiCoO₂–Super P–SACNT composite could be implemented with a roll-to-roll process and hold great promises toward the large-scale production. The strategy to introduce hybrid super-aligned carbon nanotube/carbon black conductive network is also promising to be applied to other composite systems that demand high conductivities.

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