



Constructing multidimensional conducting networks on LiCoO₂ cathode for enhanced rate performance and cycle stability

Jiangpei Xue^a, Chunhai Jiang^{a,*}, Bingxuan Pan^b, Zhimin Zou^{a,*}

^a Fujian Provincial Key Laboratory of Functional Materials and Applications, Institute of Advanced Energy Materials, School of Materials Science and Engineering, Xiamen University of Technology, 600 Ligong Road, Jimei District, Xiamen 361024, China

^b Xiamen 3-Circles Battery Co. Ltd, 519 Jimei North Street, Xiamen 361023, China

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ABSTRACT

The effects of different assemblies of Super P, carbon nanotubes (CNTs) and graphene as hybrid conductive additives on the rate performance and cyclic stability of LiCoO₂ (LCO) cathode material were systematically investigated. The results indicated that adding graphene, CNTs or mixture of them into the conventional Super P conductive agent was effective to reduce the overall mass ratio of the carbonaceous conductive additive in the LCO electrode while significantly improving the rate performance and cycle stability. The best electrochemical performance was achieved on the electrode with 1 wt% (G + SP) and 1 wt% CNTs. Microstructural investigations indicated that a multidimensional conducting network had been constructed within this cathode, which provided efficient electronic and ionic transportation pathways, as evidenced by the reduced transport resistance and improved Li-ion diffusion dynamics. With this composition, a high discharge capacity of 118 mA h g⁻¹ was obtained at a current density of 10 C (1400 mA g⁻¹), and a high capacity retention of 92.3% was maintained after 100 cycles at 1 C.

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1. Introduction

The rapid development of electric vehicles (EVs) calls for large improvement of energy and power densities of lithium ion batteries (LIBs) [1–3]. As it is commonly accepted, the low energy densities of the currently available LIBs are majorly determined by the low specific capacities of cathode materials, such as LiCoO₂, LiFePO₄, and LiMn₂O₄ [4–6]. Therefore, exploring novel cathode materials with high specific capacity, like Li-rich manganese oxide and ternary cathode materials with high nickel content, has been the intensive research focus in recent years [7–10]. However, although many progresses have been achieved on these investigations, commercialization of such novel cathode materials has encountered big challenges, for example, the low initial coulombic efficiency, rapid voltage fade, and poor cycle stability of the Li-rich manganese oxide [11,12].

Instead of exploring alternative high specific capacity cathode materials, optimizing other factors based on the currently available cathode materials has been another effective way to improve the energy density of LIBs. Among the various strategies employed, reducing the mass percentage of the inactive conductive additives as well as increasing the mass loading of active cathode materials through utilizing novel carbon additives has been recognized as a very effective and practical way

[13,14]. The roles of conductive carbon additives in the electrode include building up electronic connection between granulates of the active materials and also between them with the current collector. At present, the most widely used carbonaceous conductive additives in commercial LIBs are Super P (SP) and acetylene carbon black (ACB), which are nanosized carbon particles with low packing density and high degree of aggregation [15]. On the one hand, a high mass ratio of the nanosized carbon additives (normally not less than 3 wt% of the whole electrode mixture) is required to ensure good electrical contact considering their severe aggregation and poor dispersion. Such a high mass ratio of inactive and loosely packed carbon additives will inversely lower the loading density of active materials, resulting in low volumetric density. On the other hand, the nanosized carbon particles will predominantly exist in the gaps between the micrometer-sized granulates of active materials [15]. That means that there is still lack of a good conducting network covering all over the active granulates, resulting in low electronic conductivity and poor rate capability.

Thanks to the rapid technical progress for scalable fabrication of carbon nanotubes (CNTs) and graphene, these highly electronic conductive one-dimensional and two-dimensional carbon materials have enriched the choice of carbon additives in LIBs. CNTs are one dimensional tubular nanomaterials rolled from monolayer or multilayer graphene, which can form long range conductive contact within the electrode when used as conductive additives [13]. V. Alberto et al. [16] found that adding 1 wt% multi-walled carbon nanotubes (MWCNTs) into the

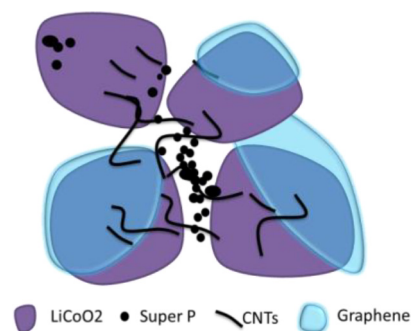
* Corresponding authors.

E-mail addresses: chjiang@xmut.edu.cn (C. Jiang), zmzou@xmut.edu.cn (Z. Zou).

$\text{LiNi}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.33}\text{O}_2$ cathode could significantly enhance the rate capability at all investigated current rates. The specific capacity at 5 C increased from 58 mA h g^{-1} in the MWCNTs-free cathode to 87 mA h g^{-1} in the MWCNTs-loaded cathode. However, the strong Van der Waals' force between CNTs will lead to their poor dispersion among the active material, which may hinder the construction of effective conducting network. Since the verification of graphene, this novel two-dimensional carbon material has attracted great attention as conductive additive in LIBs because of its super high theoretical specific surface area ($2630 \text{ m}^2 \text{ g}^{-1}$), excellent electrical conductivity and thermal conductivity. Due to its ultrathin and two-dimensional flexible feature, graphene is expected to wrap on all the active particles and form a three dimensional continuous conductive network. Su et al. [17] proposed a "plane-to-point" contact model between graphene and the active substance. They supposed that the soft and ultrathin graphene had high contact efficiency with LiFePO_4 , and the added graphene all involved in the formation of conductive network. With a much lower fraction of graphene, the LiFePO_4 half-cell showed much better charge/discharge performance than the one made using commercial carbon black. However, it was found that the effect of graphene additive was strongly correlated to the structure of the cathode materials. For example, when it was used in a commercial 10 A h soft-packaged battery assembled by LiFePO_4 nanoparticles, the transportation of Li^+ ions was hindered at high charge/discharge rate because of the low Li^+ diffusion coefficient of graphene [18]. Wei et al. [19] found that when LiFePO_4 nanoparticles were semi-coated with graphene, the electronic conductivity and ionic conductivity of the electrode were improved simultaneously. However, when LiFePO_4 nanoparticles were completely covered by graphene, the rate capability of LIBs was greatly reduced because of the blocked Li^+ diffusion into/from the active materials. This is consistent to the recent report of Shi et al., in which the authors demonstrated that graphene with low disorder degree and large size was not suitable for LiCoO_2 cathodes as conductive additive [14].

Based on the above mentioned problems related to graphene additive, Tang et al. [20] proposed a binary conductive additive consisting of a small portion of graphene balanced with the conventional Super P carbon black, taking micron-sized LiCoO_2 cathode as the example. Because of the small amount of graphene added in the conductive additive, there was no obvious steric effect that hindered the Li^+ diffusion in the micron-sized LiCoO_2 cathode. Meanwhile, the binary conductive additives constructed both short-range and long-range electrical contact, forming an effective conducting network within the electrode. As reported by the authors, a binary carbon additive consisting of only 0.2 wt% graphene nanosheets and 1 wt% Super P carbon was adequate to guarantee good electrochemical property of the cathode material.

It should be pointed out that, graphene nanosheets have large area and are usually highly aggregated because of their high surface energy, which will inevitably reduce their electrical linkage to all active particles when a low mass ratio is used. Under this circumstance, the active particles that do not contact with graphene nanosheets can only rely on their connection with Super P carbon. This brings out a contradiction between the amount of graphene used and the negative impact of high content graphene in limiting Li^+ diffusion. To overcome this problem, herein we propose a ternary hybrid carbon additive composed of the zero dimensional Super P nanoparticles, one-dimensional carbon nanotubes and two-dimensional graphene nanosheets, to construct a multidimensional conducting network in the electrode. For references, binary conductive additives, SP + CNTs and G + SP (the mostly studied ones in previous works), were also systematically studied, based on a recipe of commercial LCO Li-ion batteries. As schematically illustrated in Scheme 1, the micron-sized LiCoO_2 granulates are partially covered by graphene nanosheets, and the Super P nanoparticles majorly fill in the gap between different LiCoO_2 granulates, acting as electrolyte reservoir. The CNTs link the graphene nanosheets, Super P nanoparticles, and the LiCoO_2 granulates, forming a multidimensional conducting network. By the proposed ternary hybrid carbon additive, the amount of carbon



Scheme 1. Schematic illustration of the ternary hybrid carbon additive consisting of graphene nanosheets, CNTs and Super P nanoparticles for constructing a multidimensional conducting network on granulate LiCoO_2 cathode.

additive can be reduced while good electronic and ionic conducting paths can be guaranteed. As it will be reported, the rate performance and cycle stability of the half-cells made from granulate LiCoO_2 cathode material using the ternary hybrid carbon additive has been greatly improved.

2. Experimental

2.1. Preparation and characterization of LCO electrodes

Commercially available micron-sized LiCoO_2 (LCO) granulates produced by Battery Corporation (Shenzhen, China) were used as the cathode material. Commercial carbon nanotubes (CNTs) slurry (5 wt% of CNTs balanced with *N,N*-dimethyl pyrrolidone (NMP) solvent and other dispersion agent) was purchased from Sanshunzhongke New Materials Ltd (Shenzhen, China). The graphene (G) slurry balanced with some Super P in NMP solvent and some amount of dispersion agent, hereafter refereed as G + SP, was obtained from Global Graphene Group (USA). The Super P (SP) carbon black was produced by Timical (Switzerland). To prepare the electrode, the CNTs and G + SP slurries were homogeneously mixed by ultrasonication for 1 h at first. Polyvinylidene fluoride (PVDF) with an concentration of 3 wt% was dissolved in NMP as the binder. The LCO granulates and Super P were ball-milled for 1 h at 200 rpm, which was then mixed with the CNTs or graphene slurries and PVDF binder by further ball milling for another 1 h at 250 rpm. The working electrodes with mass ratios of 96.3:2:1.7 or 97.3:1:1.7 (w/w/w, LCO cathode material: conductive agent: PVDF binder) were casted on aluminum foil and dried at 110°C overnight in a vacuum oven. The electrodes with different fractions of conductive agents were named and listed in Table 1. Disk-type electrodes of 12 mm in diameter were punctured out from the coated foil and pressed at 6 MPa for 10 s. The loading amounts of LCO active materials in each electrode were about $3\text{--}3.2 \text{ mg cm}^{-2}$. To make a comparison, an electrode with 3 wt% Super P (the mass ratio of carbon additive in commercial LIBs) as the sole conductive agent, 95.3 wt% LCO, and 1.7 wt% PVDF was also prepared. The conducting network built up on LiCoO_2 cathode

Table 1
Different mass fractions of the conductive agents.

Sample name	G + SP wt%	CNTs wt%	SP wt%	Sample name	G + SP wt%	CNTs wt%	SP wt%
3SP	0	0	3	1(G + SP)	1	0	0
1CNTs	0	1	0	2(G + SP)	2	0	0
1CNTs-1SP	0	1	1	1(G + SP)-1CNTs	1	1	0
2CNTs	0	2	0				

was examined using scanning electron microscopy (SEM, Zeiss Sigma 500, Germany).

2.2. Electrochemical tests

The 2025-type coin cells were assembled in an Ar-filled glove box. The electrolyte was a 1 mol/L solution of LiPF_6 dissolved in ethylene carbonate and dimethyl carbonate ($v/v = 1/1$). Lithium metal foil of

14 mm in diameter and 0.45 mm in thickness was used as the counter electrode. A polypropylene membrane (Celgard 2400) was used as the separator. Galvanostatic charge/discharge measurement were carried out on LAND CT2001A battery cyler (Wuhan Kingnuo Electronic Co., China) in the voltage range of 3–4.2 V (vs. Li/Li^+). Cyclic voltammetry was recorded at scan rates of 0.1 to 1 mV s^{-1} using a CHI660e electrochemical workstation (Chenhua, Shanghai). Electrochemical impedance spectroscopy (EIS) was measured on an electrochemical

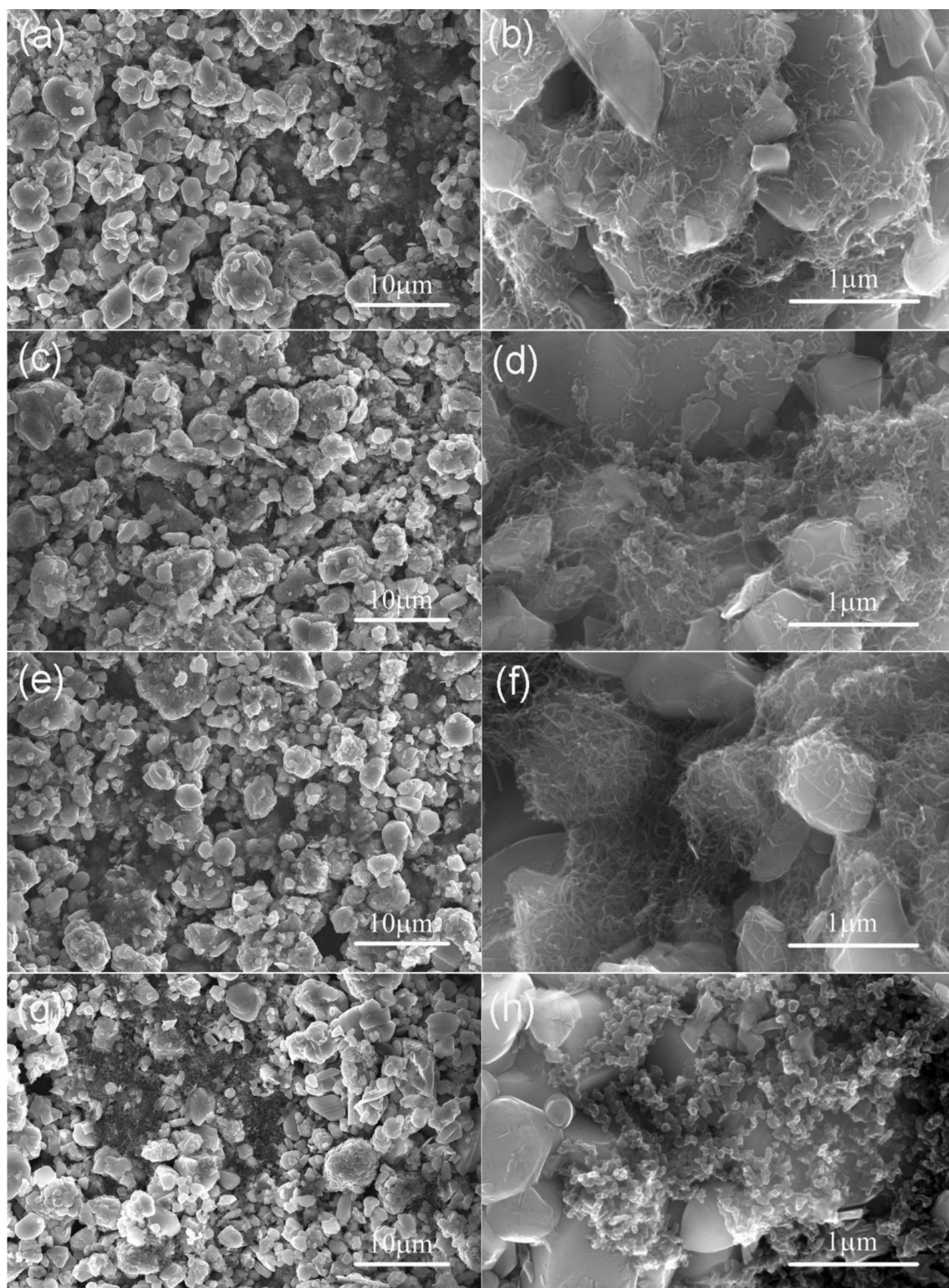


Fig. 1. SEM images of the LCO electrodes prepared with 1CNTs (a, b), 1CNTs-1SP (c, d), 2CNTs (e, f) and 3SP (g, h).

workstation (PARSTAT™ MC, AMETEK, USA) in the frequency range from 100 kHz to 0.01 Hz with an alternative amplitude of 5 mV.

3. Results and discussion

3.1. CNTs-based conductive additives

Fig. 1 shows the SEM images of the electrodes prepared using CNTs-based carbon additives, as named by 1CNTs (a and b), 1CNTs-1SP (c and d), and 2CNTs (e and f), respectively, see detail in Table 1. The reference electrode named as 3SP is also compared in Fig. 1g and h. The LiCoO₂ cathode materials are micron-sized granulates with typical diameters of about 4–6 μm. As shown in Fig. 1a and b, when 1 wt% CNTs is added as the sole conductive additive, some of the LiCoO₂ granulates are still not contacted to CNTs although some others are well covered by the one-dimensional tubular carbon additive. This can be caused by both the severe agglomeration and small mass ratio of CNTs used in this electrode. By adding one weight percent of SP into this electrode, as shown in Fig. 2c and d, although the SP nanoparticles mostly rest in the gaps between different LiCoO₂ granulates, they are effectively linked by the one-dimensional CNTs, resulting in much improved coverage of conductive agents on the active material. Instead, if one more weight percent of CNTs are added, most of the LiCoO₂ granulate are covered by CNTs, but a few number of naked active granulates can be still observed, see Fig. 1e and f. When 3 wt% SP is used as the sole conductive additive (Fig. 1g and h), the aggregated Super P nanoparticles fill in the voids of LCO granulates and also cover on some of them, but a large portion of the LCO granulates still show naked surface, suggesting that there is still lack of an effective conducting network.

Fig. 2a presents the rate performance and the associated coulombic efficiencies of LCO cathodes prepared with different fractions of CNTs and SP. At a low current density, namely 0.2 C (1 C = 140 mA g⁻¹), the cell with 3SP displays the highest specific capacity. This can be

attributed to the reduced current density in this electrode induced by the high carbon content and also the sufficient Li-ion diffusion time. However, with the increase of current density, the rate performance of the LCO electrodes varied obviously. For example, the specific discharge capacities of 1CNTs, 1CNTs-1SP, 2CNTs and 3SP at 10 C are 100.0, 104.3, 109.0 and 102.5 mA h g⁻¹, with the capacity retentions of 71.4%, 74.7%, 76.5% and 71.2%, respectively, as compared to that at 0.2 C. Except in the initial few cycles at 0.2 C, the coulombic efficiencies of the LCO cathodes prepared with different CNTs-based conductive additives are all near to 100%, do not show much difference even at 10 C. This clearly indicates that adding some CNTs into the carbon additive has effectively improved the rate capability of LCO, even reducing the total carbon content from 3 wt% in 3SP to 2 wt% in 1CNTs-1SP and 2CNTs. Adding 1 wt% CNTs as the sole conductive agent is not enough to ensure good conductivity.

The cycling performances of the above studied LCO cathodes at 1 C rate are shown in Fig. 2b. The capacity retentions after 100 cycles are 88.6%, 90.3%, 91.4% and 82.5% for 1CNTs, 1CNTs-1SP, 2CNTs and 3SP, respectively. It is clear to see that the LCO cathodes with 2CNTs and 1CNTs-1SP show much better cycle stability than 3SP, which displays the worst cycling stability among all of these cells. It is very interesting to note that even replacing 3SP by 1CNTs, the LCO cathode can still preserve higher discharge capacity at 1 C, indicating that CNTs are more efficient than SP in building up high conductive networks.

3.2. Graphene-based conductive additives

It is known that CNTs are not good electrolyte reservoir, but Super P carbon black is. Therefore, although the cell named as 2CNTs showed the best electrochemical performance among the above test cells, such an electrode composition is not accepted by Li-ion battery industries. However, if further adding Super P to this electrode, for example to yield a composition of 2CNTs-1SP, it will discount the merit of using CNTs in reducing the use of inactive conductive additives. As seen in Fig. 2, the LCO cathode with 1CNTs-1SP also shows good electrochemical performance. To take the advantages of CNTs in good conductivity and SP in good electrolyte reservation, some of the SP is to be replaced by graphene to further improve the electrochemical performance. To examine the effect of graphene additive, the binary conductive additive consisting of graphene and Super P (the exact composition is not provided by the producer) is evaluated at first. As shown in Fig. 3a and b, with the composition of 1(G + SP), the thin graphene mostly covers on the LCO particles, and the Super P nanoparticles rest mostly in the gaps of LCO particles. The graphene links well to the Super P nanoparticles in some area, forming a good conducting network. However, because of the small mass ratio of the total carbon additive, some naked LCO particles can be easily observed. By increasing the total carbon additive to 2(G + SP), as shown in Fig. 3c and d, a good conducting network with higher carbon coverage on LCO particles is obtained. The thin and soft graphene nanosheets wrap on the surface of LCO particles, together with the Super P nanoparticles filling in the gaps between them, forms both long-range and short-range conductive pathways.

The electrochemical performances of the LCO cathodes prepared with different graphene-based conductive additives are displayed in Fig. 4. As can be seen, the rate performance (Fig. 4a) of 1(G + SP) is much lower than that of 3SP, indicating that the binary carbon additive with a total carbon content of 1 wt% is not enough to guarantee good electrical contact. The agglomeration of graphene nanosheets and SP nanoparticles, especially at such a low carbon content, as shown in Fig. 3a and b, may be able to account for the poor conductivity of this electrode. As compared to 1(G + SP) and 3SP, the specific capacity of 2(G + SP) is improved within the current density range of 0.5 C to 10 C, although 3SP shows higher specific capacity at 0.2 C. The specific capacity of 2(G + SP) at 10 C is 105 mA h g⁻¹, which is 73.6% of that at 0.2 C. This improvement over 3SP is not so obvious, possibly due to the steric effect of graphene at high current rates. However, as seen from Fig. 4b, at a moderate current rate of 1 C, the cycle stability of 2

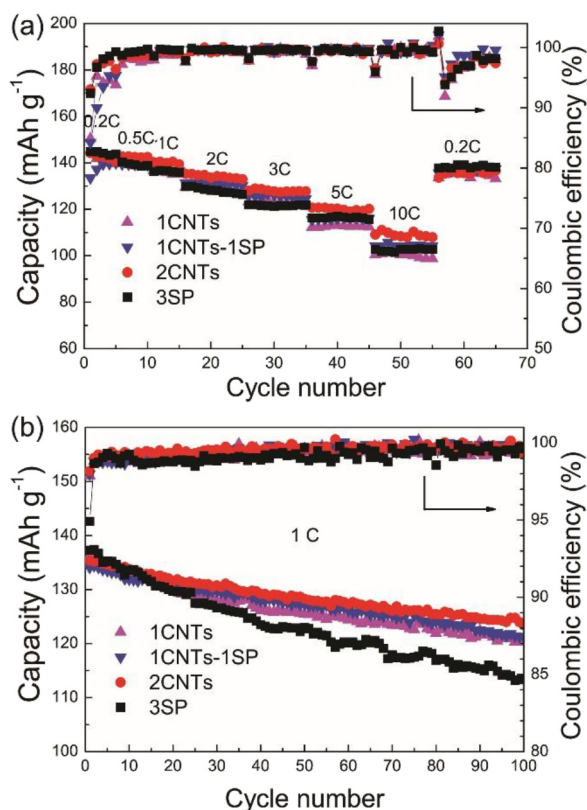


Fig. 2. Rate (a) and cycle performances (b) of the LCO cathodes prepared with different conductive additives (1CNTs, 1CNTs-1SP, 2CNTs and 3SP).

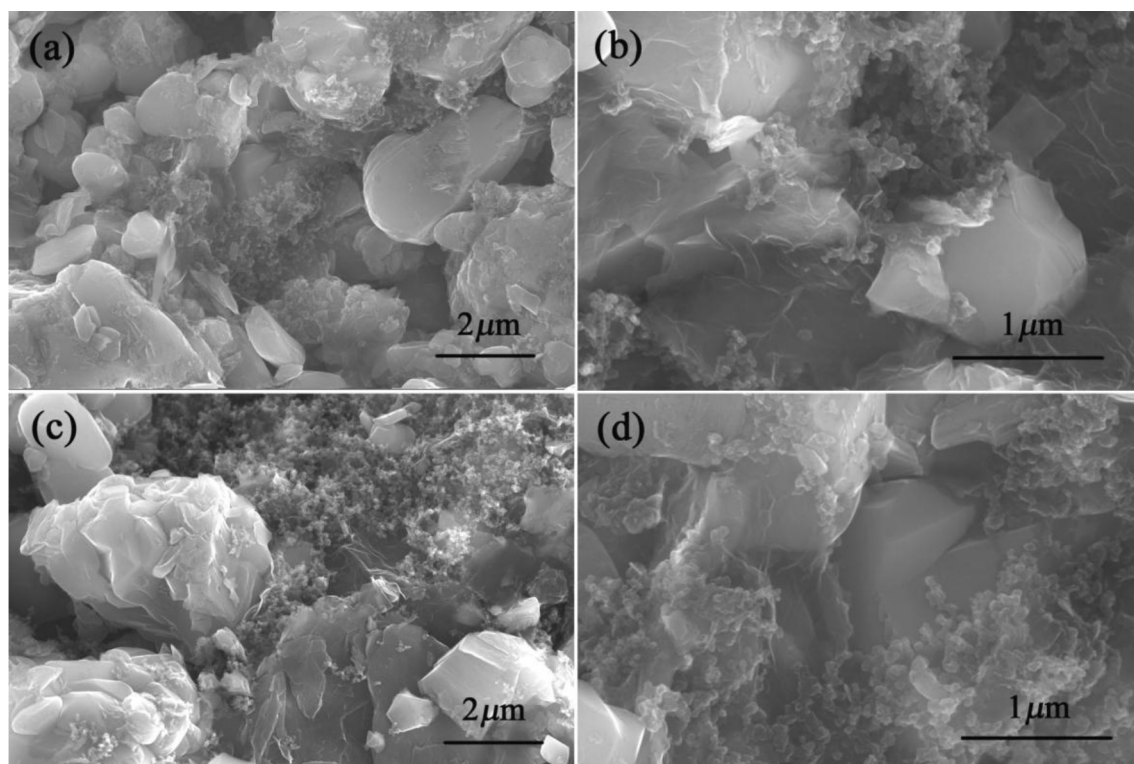


Fig. 3. SEM images of the LCO cathodes prepared with 1(G + SP) (a, b) and 2(G + SP) (c, d) as conductive additives.

(G + SP) is much better than that of 3SP and 1(G + SP). In fact, seeing more closely to Fig. 4b, one can find that even the LCO cathode with 1(G + SP) also shows slightly better cycle stability than 3SP. This means that

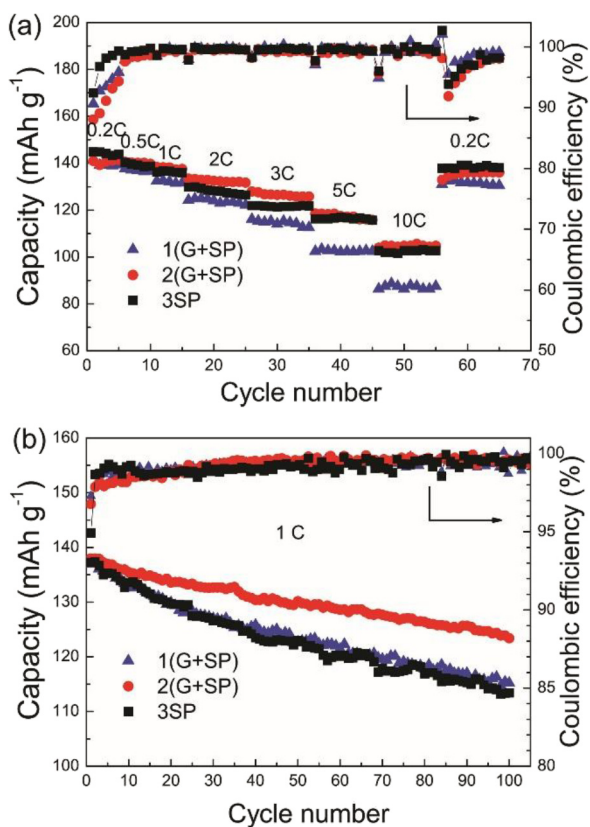


Fig. 4. Rate performance (a) and cycle stability (b) of the LCO cathodes prepared with different graphene-based conductive additives.

adding proper amount of graphene in SP can stabilize the cycle performance of LCO cathode. However, it should be also pointed out that, although the cell 2(G + SP) shows the highest capacity and best cycle stability, its coulombic efficiencies shown in both Fig. 4a and b all undergoes a steady increasing stage at 0.2 C in the initial few cycles. This indicates that it may need an activation process for the graphene loaded LCO cathode to reach the full charge/discharge equilibrium. Such an activation process may also be caused by the steric effect of large area graphene nanosheets on Li^+ ion diffusion.

3.3. Ternary hybrid conductive additives

Based on the electrochemical performances of the LCO cathodes prepared with CNTs and graphene-based binary carbon additives, it is clear that a total conductive carbon content of 1 wt% is not enough to form an effective conducting network. Increasing the weight percentage of CNTs or graphene in the hybrid conductive additive up to 3 wt% in total may be able to improve the electrochemical property of the batteries, but this will be at the expense of higher cost. It also does not fulfill the motivation of replacing some of the non-active carbon additive by active material. Therefore, in the following experiments, the total carbon content is kept at 2 wt%, while composing 1 wt% CNTs and 1 wt% (G + SP), forming a ternary conductive additive. Fig. 5 shows the typical SEM images of the LCO cathode prepared with 1(G + SP)-1CNTs taken at different magnifications. It is clear to see that the graphene, CNTs and SP are well dispersed among the LCO granulates. As shown in Fig. 5b, the graphene nanosheets partly cover on the surface of LCO particles and also link the Super P nanoparticles locating at the gaps of LCO particles. The CNTs attach to the graphene nanosheets and also to the surface of other LCO particles, forming a multidimensional conducting network. Such a conductive mode possesses both long- and short-range conductive pathways, providing more efficient electronic and ionic transportation pathways.

The rate capability and cycle performance of the LCO cathode prepared with 1(G + SP)-1CNTs are compared with those of 2(G + SP) and 2CNTs in Fig. 6a and b, respectively. As expected, the rate and

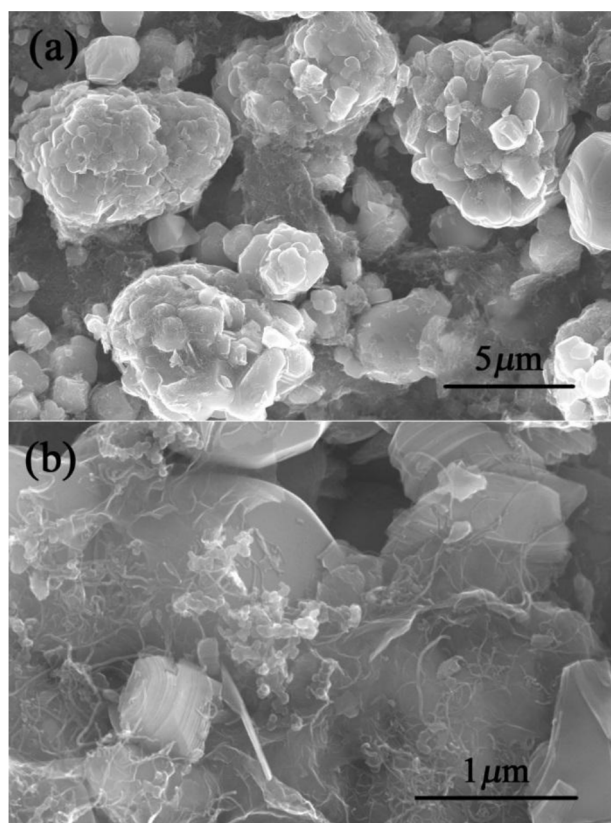


Fig. 5. SEM images of the LCO cathodes prepared with 1(G + SP)-1CNTs at different magnifications.

cycle performances of the LCO cathode with 1(G + SP)-1CNTs are significantly improved in comparison to the other two samples. For example, its specific capacity at 10 C is as high as 118 mA h g^{-1} , which is

81.2% of that measured at 0.2 C. After cycling at 1 C for 100 cycles, the cell can still deliver a capacity of 125 mA h g^{-1} , with a very low capacity decay rate of only 0.077% per cycle. In addition, as compared to the LCO cathode with 2(G + SP), its coulombic efficiency does not show the climbing stage at 0.2 C, indicating the less steric effect of the hybrid conductive additive on Li ion diffusion. These results clearly demonstrate the advantage of the ternary hybrid carbon additive in building up a more efficient conducting network within the LCO electrode while keeping the same weight percentage of the total carbon content at 2 wt% as that of 2CNTs and 2(G + SP). It is believed that the synergistic effect of the interconnected graphene, CNTs and SP nanoparticles have helped to construct a multidimensional conducting network as illustrated in Scheme 1, which has not only provided both long and short-range conductive routes, but reduced the steric effect of graphene in blocking Li ion transmission.

To explore the mechanism of capacity decay in different cathodes, the charge and discharge curves of the first and 100th cycles at 1 C are displayed in Fig. 6c. In the first cycle, all the cathodes show almost overlapped charge and discharge curves, except that of 1(G + SP)-1CNTs, which shows slightly longer voltage plateau. This is reasonable because all the cathodes possess fresh LCO particles at the early cycling stage, and the cathode 1(G + SP)-1CNTs owns better conducting network. However, after 100 cycles, besides a higher capacity loss associated to the cathode with 2(G + SP), this cathode also exhibits a slight voltage decay, indicating that more severe polarization might have occurred due to the steric effect of the higher mass ratio of graphene. By contrast, the discharge curves of the cathodes with 1(G + SP)-1CNTs and 2CNTs well maintain the voltage plateau although small capacity losses are also observed. This means that by building up an effective conducting network, good electronic and ionic conduction have been preserved after long term cycling test, which maintains stable electrochemical performance of the LCO cathodes.

As discussed above, different assemblies of carbon additive have resulted in different conducting networks, which are directly correlated to the rate capability and cycle stability of the LCO cathodes. To further identify the effect of different carbon additives, electrochemical

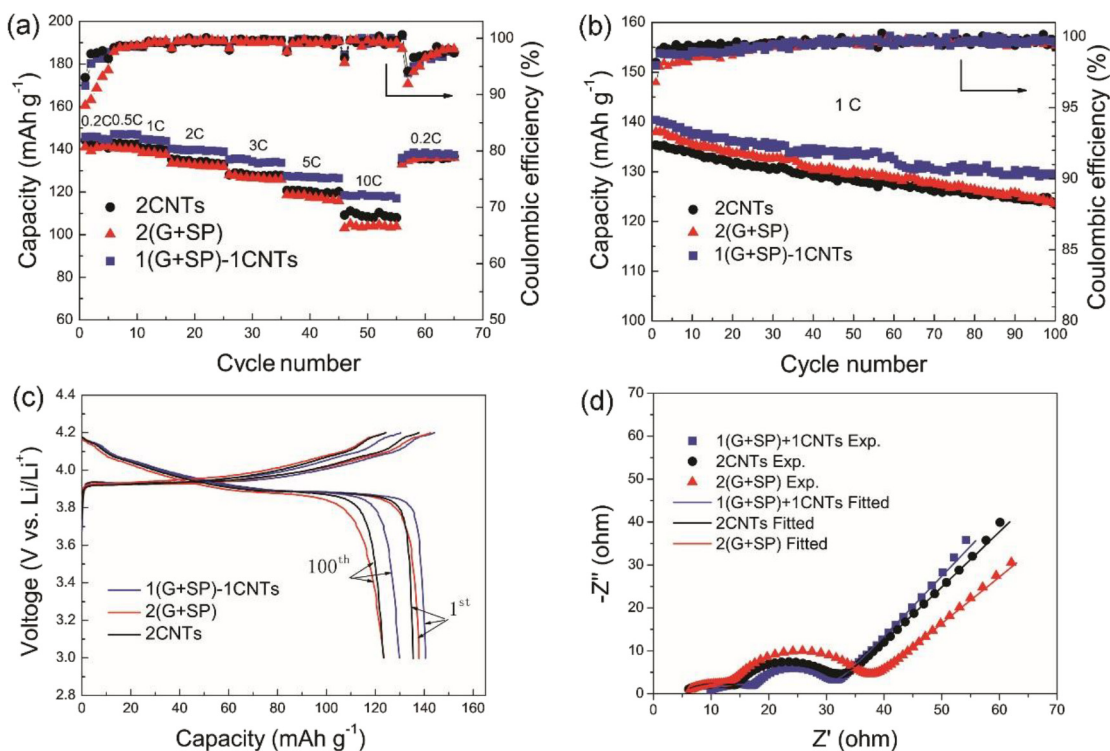


Fig. 6. Rate capability (a), cycle performance at 1 C (b), charge and discharge curves of the first and 100th cycle at 1 C (c), and the electrochemical impedance spectra (d) of the LCO cathodes prepared with different conductive additives, 2CNTs, 2(G + SP), and 1(G + SP)-1CNTs.

impedance spectra (EIS) of the cycled coin cells were measured at the charged state, as shown in Fig. 6d. The Nyquist plots of all the EIS spectra are composed of two depressed semicircles in the high and middle-frequency regions and a sloped straight line in the low frequency, respectively. The first and second semicircles are known to correspond to the resistance of Li^+ ions penetration through the solid electrolyte interface (R_{eis}) and the charge transfer resistance (R_{ct}) between the electrolyte and electrode, respectively. The oblique line of the low frequency region interprets the diffusion impedance of Li^+ ions in the electrode bulk. As estimated by Zview fitting, the R_{ct} values for 1(G + SP)-1CNTs and 2CNTs are 11.9 and 15.3 Ω , respectively, which are much smaller than that of 2(G + SP), 21.1 Ω . This evidently implies that by constructing a multidimensional conducting network, the resistance of Li^+ ions transportation through the electrolyte/electrode interface has been greatly reduced. From above electrochemical performance, CNTs can be the sole carbon additive to bring out high conductivity in LCO cathode, but as we have mentioned, they are not good electrolyte reservoir and also more expensive than Super P. The higher R_{ct} value in 2(G + SP) again indicates that high mass ratio of graphene nanosheets in the cathode is harmful for Li^+ ions diffusion because of the steric effect, which is consistent to the results of previous reports [14].

The effect of different conductive additives on the lithiation/delithiation kinetic in LCO cathode were further investigated by CV measurements at scan rates varying from 0.1 to 1 mV s^{-1} within the voltage range of 3–4.2 V (vs. Li/Li^+), as shown in Fig. 7a for 2CNTs, Fig. 7b for 2(G + SP) and Fig. 7c for 1(G + SP)-1CNTs, respectively. The relationship between the square roots of the scan rates ($v^{1/2}$) and the anodic peak currents (I_p) is presented in Fig. 7d. As seen from Fig. 7a–c, all CV curves present typical oxidation and reduction peaks of LCO phase associated to the delithiation and lithiation reactions. With the increase of scanning rate, the shifts of the oxidization peak to higher potential and the reduction peak to lower potential become more severe in 2(G + SP) than those in 1(G + SP)-1CNTs and 2CNTs. This indicates that more pronounced polarization has occurred in the former sample. As displayed in Fig. 7d, the peak current, I_p , and square

root of the scan rate, $v^{1/2}$, exhibit good linear relation for all three samples, suggesting the Li^+ diffusion controlled electrochemical reaction processes [21]. The higher slope of the straight line, $I_p-v^{1/2}$, of the LCO cathode prepared with 1(G + SP)-1CNT demonstrates that the Li ion diffusion in this cathode is more efficient than in other two samples. This means that the ternary hybrid carbon additive has constructed a more effective conducting network and facilitated the electronic and ionic transportation. The cathode 2(G + SP) displays the lowest Li ion diffusion rate among these three samples, which is consistent to its lower rate capability and worse cycle stability, attributing to the blocking effect of graphene nanosheets on Li ion diffusion.

4. Conclusions

The effects of different assemblies of Super P nanoparticles, CNTs and graphene conductive additive on the electrochemical properties of LiCoO_2 cathode in terms of rate capability and cycle stability have been systematically investigated in this work. As compared to the conventionally used 3 wt% Super P in commercial LiCoO_2 -based Li-ion batteries, the total carbon content can be reduced to 2 wt% when an appropriate amount of CNTs and graphene nanosheets were added. Further decreasing the total carbon content to 1 wt% led to degraded electrochemical performance. A ternary hybrid conductive additive consisting of 1 wt% (G + SP) and 1 wt% CNTs was able to construct a multidimensional conducting network in the LiCoO_2 cathode. Both long and short-range electronic transportation pathways can be built up in this assembly, which greatly enhanced the rate capability and cycle stability of the test cells. Loading high mass fraction of graphene in the mixed conductive additive with Super P resulted in higher transportation resistance between the electrode and electrolyte, and finally poor rate and cycle performance of the LCO cathodes, possibly because of the steric effect of graphene on Li ion diffusion. From a practical application point of view, it is suggested that utilizing a hybrid conductive additive composing of 0 D Super P nanoparticles, 1 D carbon nanotubes and 2 D graphene nanosheets in an appropriate mass ratio but keeping

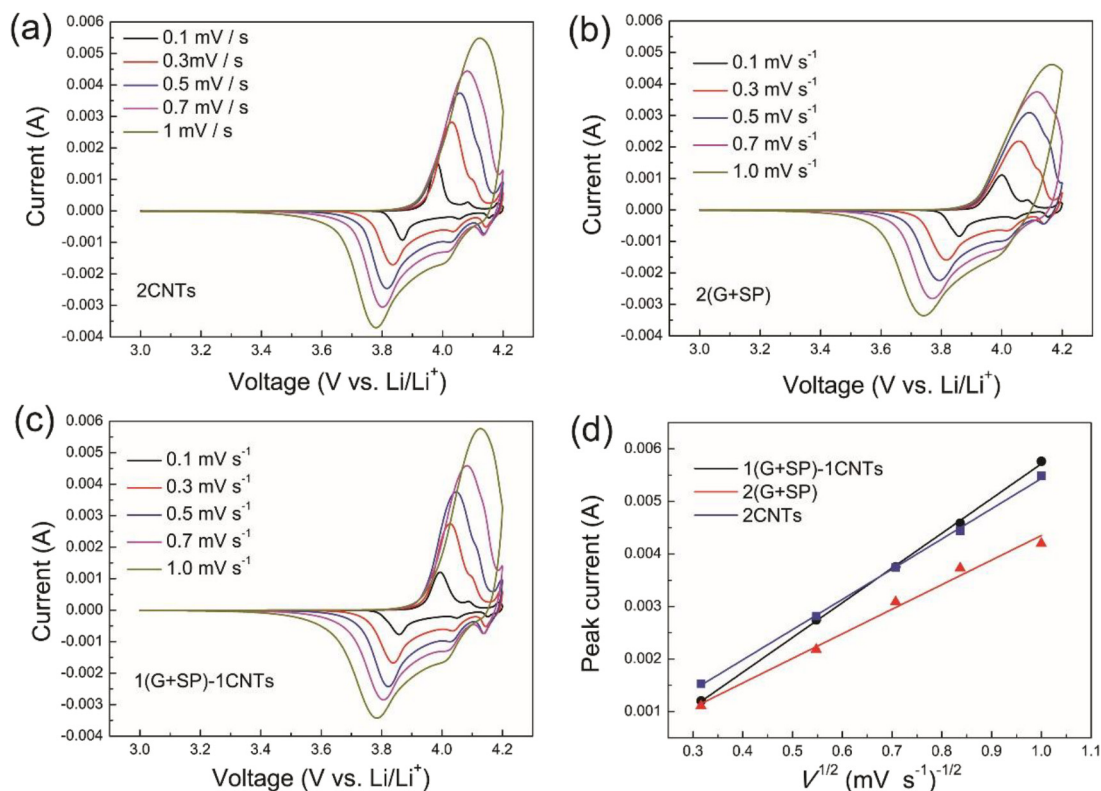


Fig. 7. CV curves of 2CNTs (a), 2(G + SP) (b) and 1(G + SP)-1CNTs (c) at different scan rates, a, and the relationship between the oxidation peak currents and the square root of scan rate (d).

the total carbon content less than the conventionally used value is more plausible to improve the energy density of Li-ion batteries while preserving or even increasing the electrochemical property of the current available cathode materials.

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