Short Communication

Improved Electrochemical Performance of LiNi$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$ Cathode with Different Carbon Additives for Lithium-ion Batteries

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Four types of commercial carbon additives (Super P, 350G, carbon nanotubes (CNTs) and graphene) are adopted to form effective conducting network in LiNi$_{0.5}$Co$_{0.2}$Mn$_{0.3}$O$_2$ (NCM523) cathode for lithium-ion battery. The results suggested that cathode with multi-carbon additives exhibited great improvement in capacity and rate capability. Morphology difference of carbon additives is found to have significant influence on the improvement of electrochemical performance. The use of CNTs and graphene makes up the shortage of commercial carbon black (Super P and 350G). When all the carbon additives worked together, NCM523 particles were well wrapped by paper-like graphene, with Super P and 350G particles coating onto the surface, and the whole sheet was connected by the network of CNTs, providing electrons both "short range" and "long range" highway to transport, contributing to the improvement of electrochemical performance of NCM523 for lithium ion battery.

Keywords: lithium ion battery, cathode, carbon additives, electrochemical performance

1. INTRODUCTION

The rapid growing demand for electric vehicles (EVs) requires high performance rechargeable batteries [1–4]. So far, lithium-ion battery is regarded as the most promising power source and is widely applied for EVs, due to its high specific energy and other advantages compared to other energy storage devices. The performance of lithium-ion battery is largely determined by the cathode material. In the past decades, many efforts have been made to obtain cathode materials with high voltage and capacity, thus offering high energy [5-13].

Since LiNi$_{0.33}$Co$_{0.33}$Mn$_{0.33}$O$_2$ (NCM111) was firstly reported in 2001 by Ohzuku's group, ternary transition metal oxide systems of LiNi$_x$Co$_y$MnzO$_2$ (with x+y+z=1) has been recognized as the

potential replacement of traditional $LiCoO_2$ cathode material of lithium-ion battery for its higher specific energy, lower toxicity, higher safety performance, and lower cost [5-7, 14-19]. In this group of cathode material, capacity is mainly generated from the valence change of Ni, while Mn remains almost unchanged during cycling. Therefore, high Ni content is helpful to specific capacity and one typical representative, $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ (NCM523), has already attracted great interests due to its high energy density and relative low cost contributed by high Ni content and reduction of Co [20-25]. However, NCMs still suffer from poor cycling performance and rate capability especially at high current densities due to their low electronic conductivities and limited point contacts between their micro particles [23-25].

In order to minimize the problem of the poor electrical conductivity of NCM cathode, conductive additives are required to be added to the cathode. So far, nano-carbon materials, such as carbon black, carbon fibers, carbon nanotubes (CNTs), and graphene (including reduced graphene oxide (rGO)), have been widely applied. [26-36]. Among them CNTs and graphene with their unique 1D tubular and 2D planar structure, high electrical conductivity and large surface area, attracted many attentions [22-36]. They were considered to function as conductive bridges to form 3D conducting networks and thus reduce the inner resistance between the active material particles. Nevertheless, so far, either CNTs or graphene was only separately adopted with carbon black to form NCM cathode. The legitimate improvement is expected if they are employed together.

In this work, four types of different carbon additives were introduced in cathode fabrication. NCM523 electrodes were prepared with different carbon additives combination and their electrochemical performance was investigated. Multi-carbon additives including CNTs and graphene were together applied in NCM523 cathode for the first time and significant improvement on electrochemical performance was achieved.

2. EXPERIMENTAL

2.1 Electrode and cell making

Four types of carbon materials, Super P carbon black (Scmchem, Shanghai), 350G carbon black (Scmchem, Shanghai), CNTs (Scmchem, Shanghai), and Graphene (Sinopharm Chemical Reagent), were used as conducting agents. Three types of carbon combination consisted of Super P/350G (mass ratio, 1:1), Super P/350G/CNTs (mass ratio, 3:3:4) and Super P/350G/CNTs/Graphene (mass ratio, 2:3:3:2), were adopted and denoted as C1, C2 and C3, respectively. NCM electrodes with different carbon additive combination were prepared as follow. NCM523 powder (Shanshan Tech) and carbon additives was firstly mixed by ball milling under the speed of 350 r min^{-1} for 12 hours. Then the mixed powder was continuously mixed with polyvinyldifluoride (PVDF) (Shanshan Tech) in N-methyl-2-pyrrolidone (NMP) (Sigma–Aldrich) anhydrous solvent to make the slurry. At last the slurries were coated onto aluminum (Al) foils by using doctor blade and dried at 100 ^{o}C for 12 h to remove residual solvent. The weight ratio in all cathode electrodes was fixed at 85:10:5 (NCM523:carbon additive:PVDF). The electrode sheets prepared with C1, C2 and C3 carbon additives

were labeled as E1, E2 and E3 respectively. Electrode weight and thickness was measured by electrobalance (MS105DU, MettlerToledo) and thickness gauge (Mitutoyo).

2.2 Characterization and electrochemical test

The morphologies of electrodes were observed by a scanning electron microscope (SEM, FEI, Quanta 250 FEG, USA). The electrochemical properties of all samples were tested with CR2032 coin cells assembled in an argon-filled glove box (M-Braun). The electrolyte was 1 M $LiPF_6$ in ethylene carbonate (EC)/dimethyl carbonate (DMC)/ethyl methyl carbonate (EMC) (1:1:1, v/v/v) (Tinci, Guangzhou) and a lithium sheet was used as counter electrode. The cells were charged and discharged at different current densities (1 C = 160 mA g^{-1}) in the voltage ranges of 2.4–4.2 V on a battery test system (CT2001A, LAND). The electrochemical impedance spectroscopy (EIS) was conducted on an electrochemical workstation (CHI660E, Chenhua, Shanghai), when the cell was charged to 4.2 V at 0.1 C, in the frequency range of 100 kHz– 0.01 Hz. The amplitude of the AC signal was 5 mV.

3. RESULT AND DISCUSSION

After drying, all three electrodes exhibit a black dense surface. No apparent large particle is viewed by naked eyes.
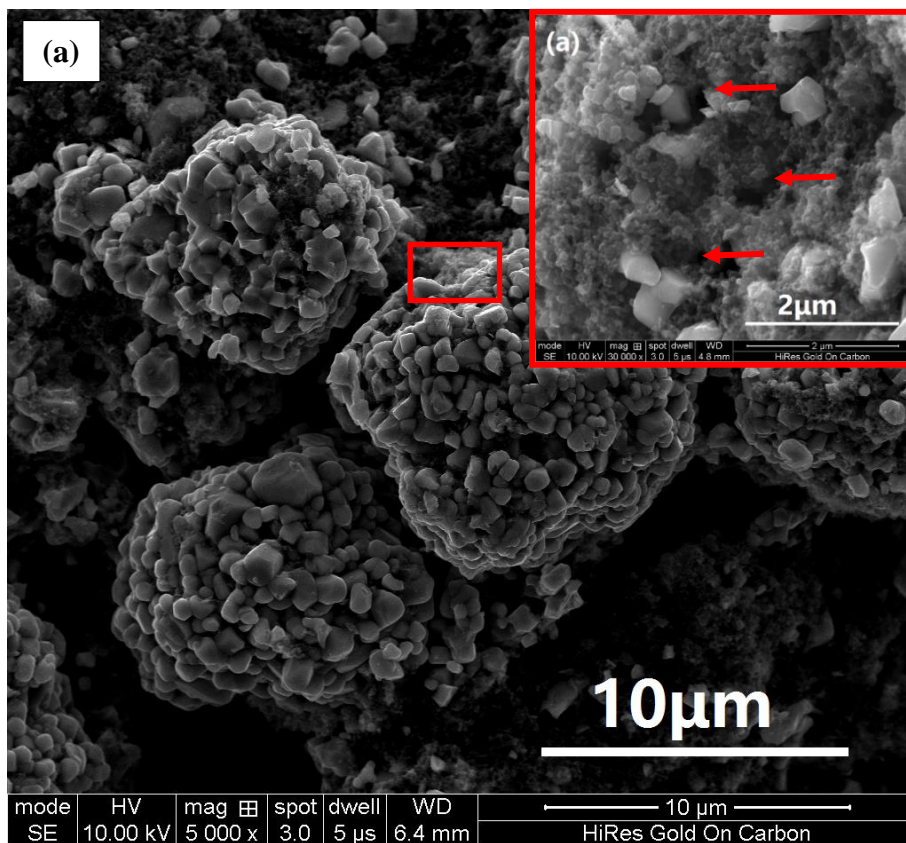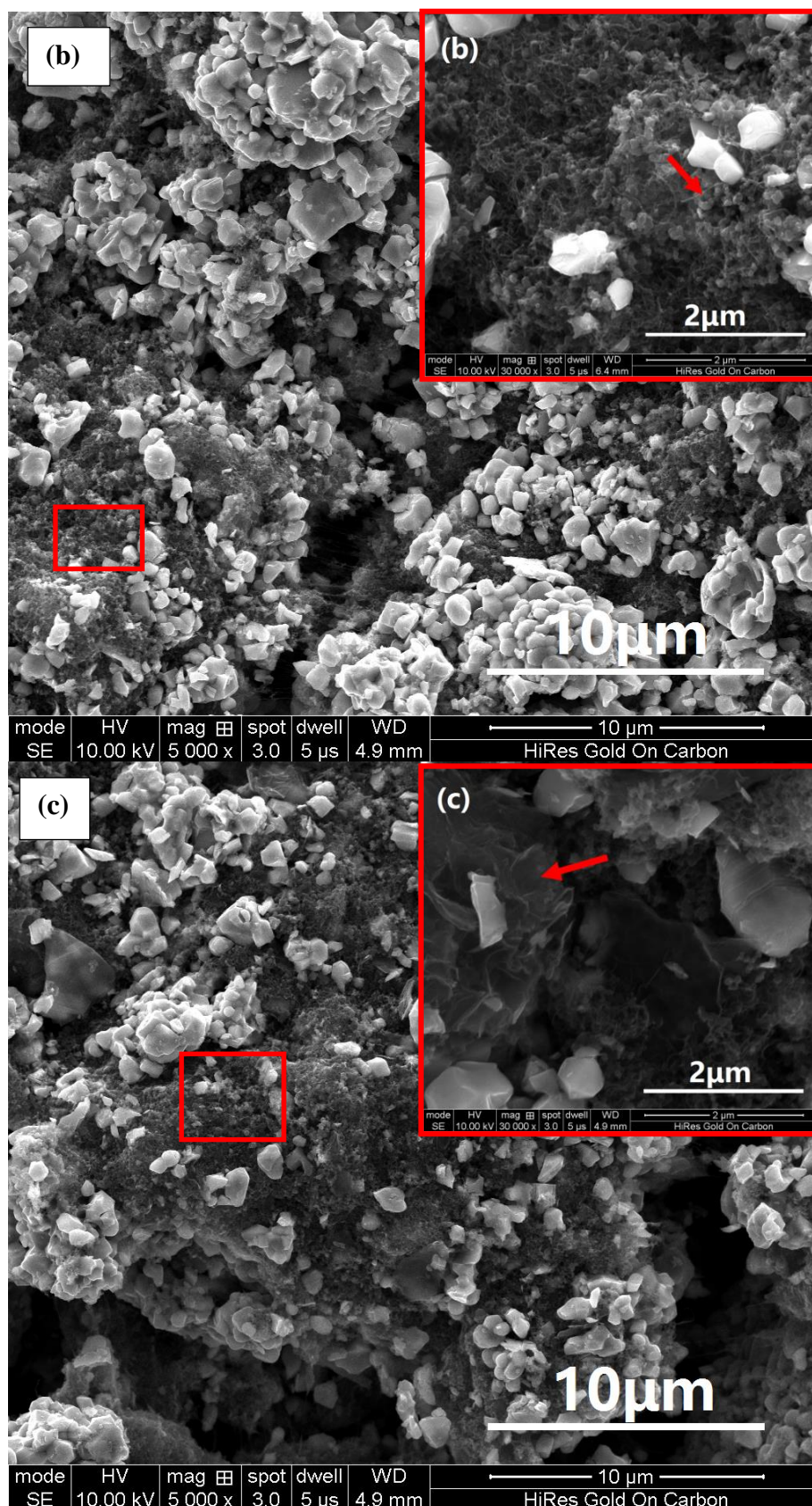
Figure1. SEM images of electrode (a) E1, (b) E2, and (c) E3.

The thickness of E1, E2 and E3 is measured, which shows 40μm, 39μm and 39μm respectively, exhibiting high consistency of electrode thickness. Nevertheless, their microstructure is different under the observation of SEM (Fig. 1 (a-c)) Partial enlarged figures are highlighted by red box. Although all images indicate that NCM523 particles with high consistent size of 500 nm are well separated by carbon additives, significant difference in the connecting structure of the additives are clearly observed. In electrode only containing carbon black particles (Super P and 350G) (E1, Fig. 1a), many small holes are randomly dispersed on the surface of electrode (see red arrows, Fig. 1a insert), which means that carbon additives are not fully connected in the whole sheet. However, with the introduction of CNTs (see red arrow, Fig. 1b insert), the amount of empty holes largely decreases (E2, Fig. 1b). A well-defined carbon network is clearly viewed, in accord with the one dimensional feature of carbon nanotube. When Graphene (see red arrow, Fig. 1c insert) is further imported, it is observed that the surface of electrode is partially covered by lamellar Graphene, further reducing the empty holes (E3, Fig. 1c). Moreover, some NCM523 particles are well wrapped by Graphene as well. Morphology is a key character of electrode and is highly related to electrochemical performance.

The electrochemical performances of all three types of electrode is shown in Fig.2. E3 electrode delivers a high initial specific discharge capacity of 143 mAh g^{-1} at 0.1 C, obviously higher than the corresponding value of E1 and E2, which is only 116.2 mAh g^{-1} and 116.6 mAh g^{-1}, respectively (Fig. 2a). Rate capability test was also conducted (Fig. 2b). Discharge capacity under different C-rate (0.1C, 0.2C, 0.5C, 1C, 2C) were tested. It is observed that E3 electrode shows highest discharge capacity under all C-rate. A stable discharge capacity of around 114 mAh g^{-1} (79.7% of the discharge capacity under 0.1C) is still kept under 2C, while the other two electrodes deliver almost no discharge capacity under the same rate. Moreover, although E1 and E2 show almost same discharge capacity under 0.1C, rate performance under higher C-rate are different. Apparently, E2 delivers higher discharge capacity under 0.2C, 0.5C and 1C, indicating a better rate capability.

The rate performance of electrode are considered to be determined by several factors, which are ionic/electronic conductivity of electrode, size of active material particles, thickness of electrode, and ionic conductivity of electrolyte [37]. Conduction is considered as one of the main barriers [38]. However, in this work factors including active material, binder, electrode formulation and thickness and electrode fabrication process can be excluded because of high consistency. The only variable here is the different composition of conductive carbon additives which plays the key role in enhancing the electronic conductivity of electrode.

To correlate the electrochemical performance, especially rate capability of NCM523 electrode owning different conductive carbon formula with electrode morphology, it is legitimate to deduce that electrode exhibiting dense conductive carbon network feature is possible to own high electronic conductivity and is prone to deliver high discharge capacity, especially under high C-rate. Carbon network plays an important role on the electrochemical performance of NCM523 electrode.

To further investigate the influence of conductive carbon addition on electrode, EIS measurements were carried out to determine the cathode resistance of NCM523/Li cells. Fig. 3 shows the Nyquist plots for all three types of cell, in which each plot displays a single semicircle at high-to-medium frequency range and an inclined line at low frequency range, related to the charge transfer resistance and the mass transfer process, respectively. Nevertheless, the diameter of semicircle differs.

Cell with E3 exhibits a semicircle with smallest diameter, suggesting a lowest charge transfer resistance. On the other hand, although the charge transfer resistance of cell with E2 is larger than the cell with E3, it is significantly smaller than the cell with E1. The charge transfer resistance is highly related to electrode conductivity. Apparently, a dense conductive carbon network feature reduces the charge transfer resistance of electrode and thus is helpful to make electrode deliver more discharge capacity especially under high C-rate. Similar results were also reported in literature when comparing the charge transfer resistance of NCM electrode with carbon black solely and electrode with composite carbon networks [34, 35]. Huang et al. [34] reported that electrical networks formed by carbon black alone is rather incomplete and discontinuous, leading to occasionally high contact resistance, while the import of CNTs compensates the discontinuous carbon black chains, resulting the decrease in charge transfer resistance. Besides, the charge transfer resistance is also sharply decreased by the design of reduced graphene oxide (RGO) conducting networks with carbon black inlaid [35].
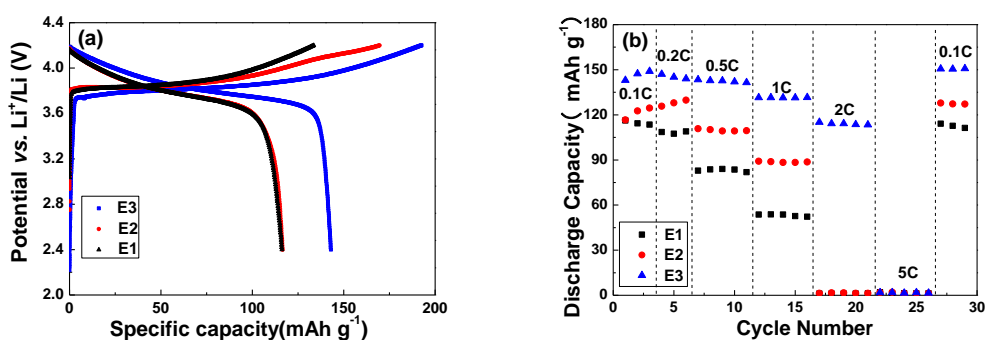

Figure 2. Electrochemical performances of three types of electrode: (a) the initial charge/discharge profile at 0.1C; (b) rate capabilities.
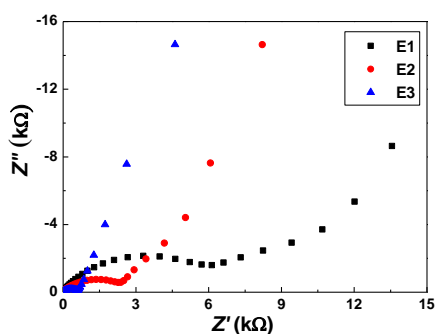

Figure 3. Impedance spectroscopy of NCM523/Li cells containing electrode E1, E2 and E3.

Considering all the results above, it is reasonable to infer that multi-carbon additives are helpful to improve the electrochemical property of NCM523. The improvement is not only depended on its intrinsic electric conductivity of carbon additives but also the connecting structures for additives and active materials. After mixing, carbon black particles like Super P and 350G can be coated on the

particles of NCM523 and distributed on its surface. Therefore, electrons can be effectively transported to the whole surface of all NCM523 particles. However, Super P and 350G can just provide the electrons the "short range" highway; they have no advantages when it comes to the electron transport in the whole electrode. On the contrary, Graphene and carbon nanotubes can provide a big conducting framework in the whole electrode, even they can only partially contact with active particles. When all carbons come to work together, the advantages of each carbon are mutually complemented. The unique structure in E3 provides electrons both "short range" and "long range" highway to transport, contributing to the improvement of electrochemical performance of NCM523 for lithium ion battery, as shown in Fig.4.
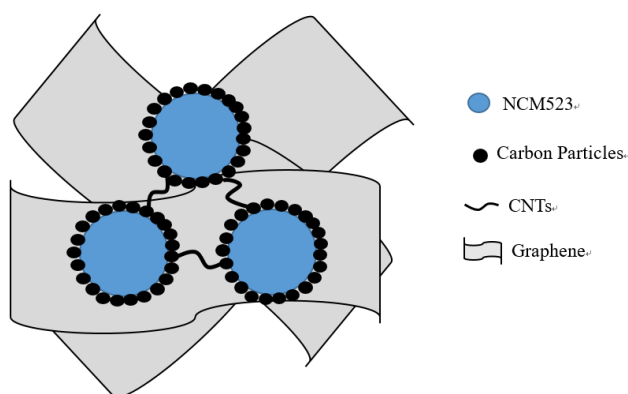

Figure 4. Schematic diagram of effective conducting network in E3

4. CONCLUSIONS

Four types of commercial carbon additives (Super P, 350G, carbon nanotubes (CNTs) and graphene) were adopted as conductive agents of $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ (NCM523) cathode for lithium-ion battery. NCM523 cathode with multi-carbon additives of Super P/350G/CNTs/Graphene (2:3:3:2, m/m) exhibits superior discharge capacity and rate capability. Morphology difference of carbon additives was found to have significant influence on the improvement of rate performance. The use of CNTs and graphene is able to make up the shortage of commercial carbon black (Super P and 350G). When all the carbon additives work together, NCM523 particles were well wrapped by paper-like graphene, with Super P and 350G particles coating onto the surface, and the whole sheet was connected by the network of CNTs, providing electrons both "short range" and "long range" highway to transport, contributing to the improvement of electrochemical performance of NCM523 for lithium ion battery.

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