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Short Communication

Synthesis of $0.4Li_2MnO_3$•$0.6LiNi_{2/3}Mn_{1/3}O_2$/graphene Nano-Composite Materials with Cross-Linked Structure and Enhanced Rate Performance for Lithium-Ion Batteries

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Nano $0.4Li_2MnO_3$•$0.6LiNi_{2/3}Mn_{1/3}O_2$/graphene composites have been synthesized by a facile sol-gel method and temperature programmed calcination route. The as-obtained products exhibited a nice morphology which was nano-sized cross-linked structure. And it showed an excellent rate performance when it was used as cathode materials for lithium ion batteries. When it was at the current density of 2 C, the discharge capacity could reach to 205 mAh g^{-1} for the first cycle and the capacity retention stayed over 97 % after 100 cycles. The superior electrochemical behavior of $0.4Li_2MnO_3$•$0.6LiNi_{2/3}Mn_{1/3}O_2$/graphene nanocomposite materials could be ascribed to the unique nano-sized cross-linked structure, the maintaining of electrode integrity, the short diffusion distance, and continuously and rapidly electron conducting.

Keywords: $0.4Li_2MnO_3$•$0.6LiNi_{2/3}Mn_{1/3}O_2$/grapheme; microstructure; cross-linked structure; nanocomposite; cathode; lithium ion batteries.

1. INTRODUCTION

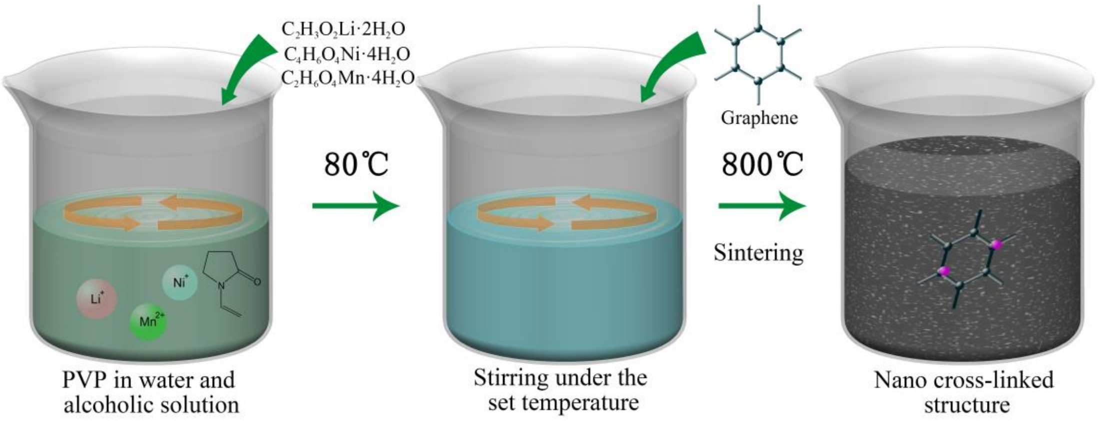
Lithium-rich manganese layered oxides with excellent structural stability not only pay a low cost but also possessed a great capacity performance of lithium ion at high voltages[1-6]. For instance, the xLi_2MnO_3•$(1-x)LiMn_{0.5}Ni_{0.5}O_2$ delivered a capacity of 287 mAh g^{-1} at 1/24 C between 2.0 and 5.0 V which was higher than that of commercial Li_2MnO_3[7]. However, the lithium-rich manganese layered oxides usually has a poor cycle performance at higher rates. As reported, nano-structure reduced the diffusion distance for both the lithium ions and the electrons within the bulk of the electrode materials and increased the surface area available for interfacial charge transfer to improve the electrode performance. For instance, nanochain of $LiMn_2O_4$ was prepared by the sol–gel method using an aqueous solution of metal salts containing starch. It showed a reversible capacity of 100 mAh

g^{-1} at 100 mA g^{-1} (about 1 C) and 58 mAh g^{-1} even at a charge rate of 20 C. In addition, when the cathode was charged at 1 C, 70 mAh g^{-1} (70 % capacity at 1 C) could be achieved even at a discharge rate of 50 C[8].

However the high specific surface area of nano-structure could lead to agglomeration that finally results in fading of capacity. For instance, it was reported that xLi_2MnO_3•(1-x)$LiMn_{1/3}Ni_{1/3}Co_{1/3}O_2$ (x=0.3, 0.5, 0.7) nano-particles could reach 313 mAh g^{-1} at 20 mA g^{-1} when x=0.5. But the capacity faded seriously with the increase of cycle numbers[9]. Compared with the simple nano structure, it is found that nano cross-linked structure could overcome the shortages above. In addition, this structure improved electrode materials comprehensive performance which contained capacity density and high-rate discharge ability. For instance, the as-obtained porous $0.4Li_2MnO_3$•$0.6LiNi_{2/3}Mn_{1/3}O_2$ nano cross-linked structure could reach 291 mAh g^{-1} in the first cycle and maintained 92.3 % after 100 cycles at 15 mAh g^{-1}. Even at 200 mA g^{-1}, capacity could remain 208 mAh g^{-1}[10-13].

Herein, we reported a $0.4Li_2MnO_3 \cdot 0.6LiNi_{2/3}Mn_{1/3}O_2$/graphene nanocomposite materials with cross-linked structure. The nano cross-linked structure offered short diffusion distance while conducting electrons continuously and rapidly. As a cathode active material, the composite material could deliver a discharge capacity of 205 mAh g^{-1} at 2 C and after 100 cycles, about 97% of the capacity was maintained.

2. EXPERIMENTAL



Scheme 1 Schematic representation for preparation of $0.4Li_2MnO_3$•$0.6LiNi_{2/3}Mn_{1/3}O_2$/graphene nano composite materials.

The $0.4Li_2MnO_3$•$0.6LiNi_{2/3}Mn_{1/3}O_2$/graphene nanocomposite was prepared by a polyvinylpyrrolidone (PVP) assisted method. Firstly, 3.57 g $C_2H_3O_2Li$•$2H_2O$, 2.48 g $C_4H_6O_4Ni$•$4H_2O$ and 3.67 g $C_2H_6O_4Mn$•$4H_2O$ were added to a beaker. Then, the graphene was added with a 1:0.1 molar ratio of $0.4Li_2MnO_3$•$0.6LiNi_{2/3}Mn_{1/3}O_2$. Secondly, 3.6 g PVP was added as a modifier. Finally, solids were dissolved in water and ethanol with the volume ratio of 5:1. A dark green gel was formed under stirring. Then the gel was evaporated at 85 °C until deionized water and ethanol were disappeared and the as-obtained mixture was heated from room temperature to 800 °C with an increasing speed of 4 °C min^{-1} then stay at 800 °C under nitrogen atmosphere for 8 h, finally it was cooled to 25 °C with the rate of 4 °C min^{-1} to get gray ashes as the product. The schematic representation is introduced by Scheme 1.

The sample was characterized by X-ray diffraction (XRD; Bruker, Germany) using Cu-Kα radiation. The transmission electron microscopy (TEM, H7650) and scanning electron microscopy (SEM, JEOL-JSM-6700F) were used to analyze the ingredient and the structure of the sample.

Charge/discharge performances were tested on button cells (size: 2016), assembled in a glovebox (Mikrouna, Super1220/750/900, China) filled with argon. The electrode slice was manufactured from a mixture of $0.4Li_2MnO_3•0.6LiNi_{2/3}Mn_{1/3}O_2$, carbon black and polyvinylidene Fluoride (PVDF) with the mass ratio of 75: 20: 5 with N-methyl pyrrolidone (NMP). Then, the mixture on the aluminum foil became a film. We dried the film at 100 °C in a vacuum oven. Land battery Test System (Wuhan, China) was used to cycle the coin-type cells and the CHI 760E electrochemical workstation was used to perform the characteristic of electrochemical impedance spectroscopy (EIS).

3. RESULTS AND DISCUSSION

The XRD spectrum of $0.4Li_2MnO_3•0.6LiNi_{2/3}Mn_{1/3}O_2$ is shown in Figure 1 which possesses sharp peaks indicating fine crystallinity and can be well indexed into a spinel phase (PDF card NO. 52-0457). The parameter of a=2.878, b=2.878, c=14.222 revealed that crystal is rhombohedral. A minor peak 20-25° is evident of the presence of an unavoidable impurity phase (Li_2MnO_3) [14].

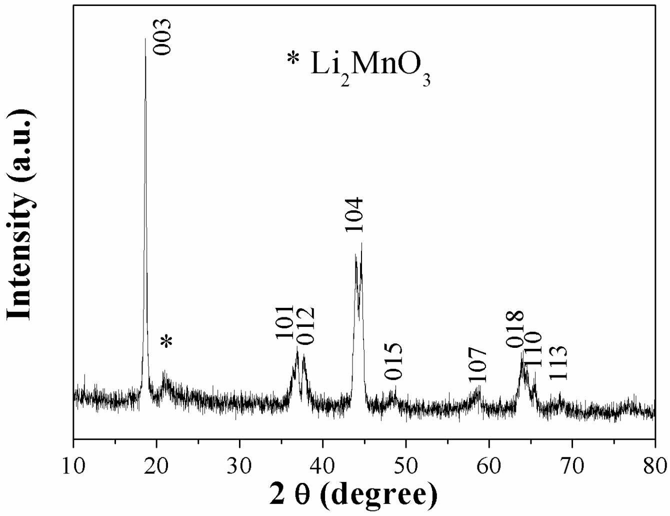


Figure 1. XRD pattern of $0.4Li_2MnO_3•0.6LiNi_{2/3}Mn_{1/3}O_2$ sample in the 2θ range of 10-80°.

Figure 2a and 2b show the typical SEM images of the nano cross-linked $0.4Li_2MnO_3•0.6LiNi_{2/3}Mn_{1/3}O_2$/graphene composite, in which high proportion of $0.4Li_2MnO_3•0.6LiNi_{2/3}Mn_{1/3}O_2$/graphene composite particles is observed (Figure 2a). From Fig. 2b, it can be seen that the average diameter of the $0.4Li_2MnO_3•0.6LiNi_{2/3}Mn_{1/3}O_2$/graphene composite particles are between 100 and 200 nm. Figure 2c and d show the typical TEM image of the $0.4Li_2MnO_3{\bullet}0.6LiNi_{2/3}Mn_{1/3}O_2$/graphene composite in which nano colloidal particles can be observed. In Figure 2d, the nano cross-linked structure can be seen. The $0.4Li_2MnO_3{\bullet}0.6LiNi_{2/3}Mn_{1/3}O_2$ particles were distributed in the carbon three-dimensional net structure evenly and randomly.

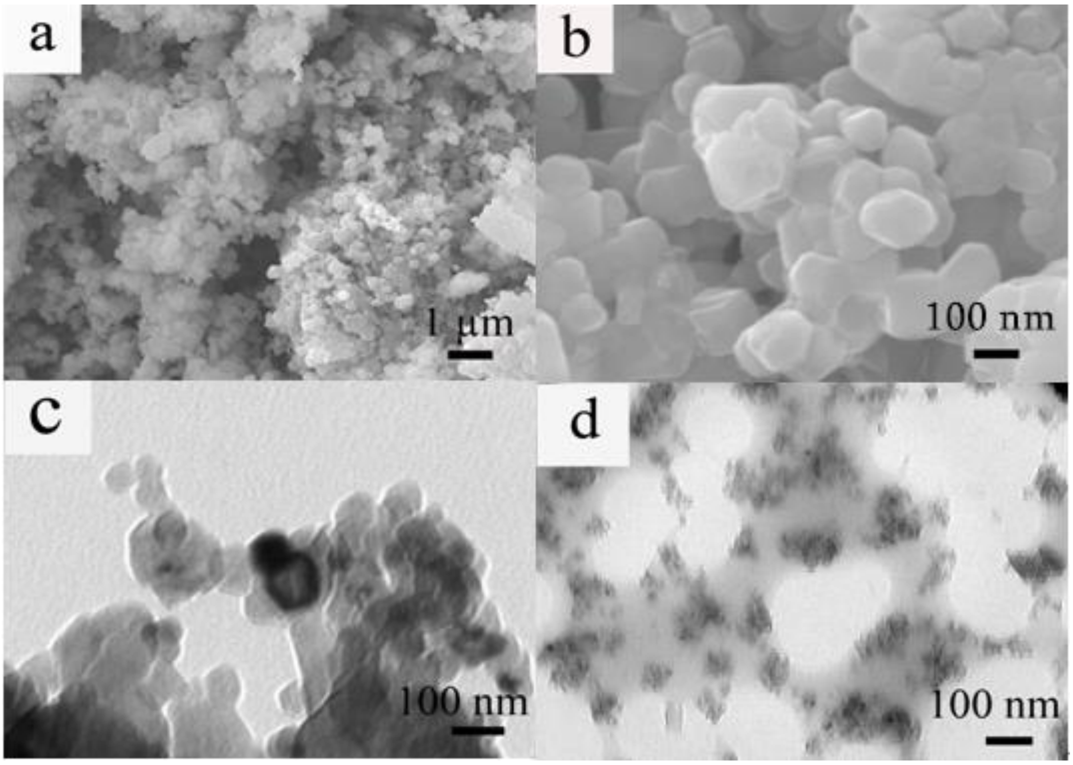


Figure 2. (a, b) SEM of nano cross-linked $0.4Li_2MnO_3{\bullet}0.6LiNi_{2/3}Mn_{1/3}O_2$/graphene composite, (c, d) TEM of nano cross-linked $0.4Li_2MnO_3{\bullet}0.6LiNi_{2/3}Mn_{1/3}O_2$ /graphene composite.

The electrochemical performances of $0.4Li_2MnO_3{\bullet}0.6LiNi_{2/3}Mn_{1/3}O_2$/graphene composite are depicted by Figure 3. Charge-discharge between 2 and 4.8 V for the $0.4Li_2MnO_3{\bullet}0.6LiNi_{2/3}Mn_{1/3}O_2$/ graphene cathode at a rate of 2 C is showed in Figure 3a. The high-voltage plateaus 4.0 V is visible. At the rate of 2 C, the cell delivered an initial reversible discharge capacity of 205 mAh g^{-1}, together with a coulomb efficiency of 97 %. Figure 3b showed the cycle life performance of $0.4Li_2MnO_3{\bullet}0.6LiNi_{2/3}Mn_{1/3}O_2$/graphene composite. At the first cycle, the capacity reaches to 205 mAh g^{-1} with coulombic efficiency of 94.5 % while the highest capacity of second cycle is 204 mAh g^{-1} with coulomb efficiency of 95.5 %. With the increase of cycle number the coulomb efficiency is improved. To explore the stability of the $0.4Li_2MnO_3{\bullet}0.6LiNi_{2/3}Mn_{1/3}O_2$/ graphene composite cathode, the battery is cycled at alternant rates of 1 and 2 C. Figure 3c depicted that the capacity of the battery is 273 mAh g^{-1} at first cycle 1 C. It can stay at 223 mAh g^{-1} after 70 cycles and remain steadily. EIS of the sample is carried out, as shown in Figure 3d, the impedance changes not too much after the fifth cycle. It is proved that the nano cross-linked structure is stable.

Researchers have made similar materials recently. For example, Jaephil Cho's group synthesis the $Li[Ni_{0.25}Li_{0.15}Mn_{0.6}]O_2$ nanowires which achieved a high capacity of 294 mAh g^{-1}[15].The

Li_2MnO_3 nanowires were performed by Mei's group. A good capacity of 159.8 mAh g^{-1} was maintained after 40 cycles at a current rate of 0.04 C [16]. Similar research has been included in the table 1:

Table 1. Similar materials have been made by other researchers recently.

Compound and morphology	Synthetic method	Cycling stability	Rate capability	Ref
$Li[Ni_{0.25}Li_{0.15}Mn_{0.6}]O_2$ nanowires	Template-free synthesis	294 /80/0.3 C	295/4 C	[15]
Li_2MnO_3 nanowires	molten-salt method	159.8/40/0.04 C	70/0.44 C	[16]
$LiNi_{2/3}Mn_{1/3}O_2$ submicron particles	polymer-assisted solid-state reaction	120/70/0.1 C	111/1 C	[17]
uniform structural morphological $LiNi_{0.5}Mn_{0.5}O_2$	solid reaction	190/100/0.25 C	117.5/6 C	[18]
spherical $Li_{1.2}Mn_{0.56}Ni_{0.16}Co_{0.08}O_2$	microwave hydrothermal method	185.4/100/200 mA g^{-1},	131.2/2000 mA g^{-1},	[19]
$0.4Li_2MnO_3$•$0.6LiNi_{2/3}Mn_{1/3}O_2$/ graphene Nano-Composite	facile sol-gel method	223/70/2 C	205/2 C	this work

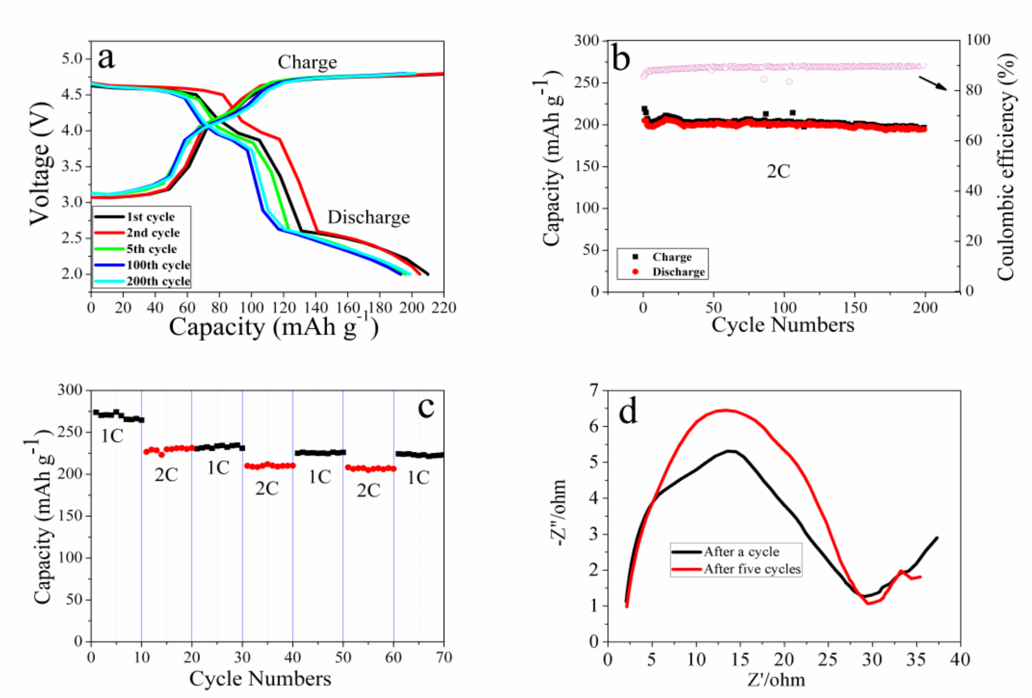


Figure 3. (a) Typical galvanostatic charge and discharge curves of nano cross-linked $0.4Li_2MnO_3$•$0.6LiNi_{2/3}Mn_{1/3}O_2$/graphene composite, (b) the cycle life performances of nano cross-linked $0.4Li_2MnO_3$•$0.6LiNi_{2/3}Mn_{1/3}O_2$/graphene composite 2 C, (c) the rate performances of nano cross-linked $0.4Li_2MnO_3$•$0.6LiNi_{2/3}Mn_{1/3}O_2$/graphene composite at alternant rates of 1 and 2 C, (d) SIM of nano cross-linked $0.4Li_2MnO_3$•$0.6LiNi_{2/3}Mn_{1/3}O_2$/graphene composite.

The excellent performance of $0.4Li_2MnO_3•0.6LiNi_{2/3}Mn_{1/3}O_2$/graphene composite could be ascribed to the nano cross-linked structure which offered advantages as following: (a) nano link-crossed particle attached to graphene net structure overcame the aggregation effect, maintained the electrode integrity and offered short diffusion distance; (b) the cross-linked structure conducted electron continuously and rapidly; (c) benefited from the linked structure, the materials buffered the volume change while cycling; (d) the cross-linked structure not only expanded the area that contact Li^+ ions between the electrode and electrolyte but also expedited the diffusion of Li^+ ions.

4. CONCLUSIONS

The $0.4Li_2MnO_3•0.6LiNi_{2/3}Mn_{1/3}O_2$/graphene nano composite was synthesized by the sol-gel method and temperature programmed calcinations route. Because of the nano-sized cross-linked structure, the composite showed a great rate performance. The discharge capacity could reach to 205 mAh g^{-1} at the first cycle under 2 C and the capacity stayed over 97 % after 100 cycles. Therefore, we could conclude that the nano-sized cross-linked structure could maintain the electrode integrity, conduct electron continuously and rapidly, and offer short diffusion distances.

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