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# Bifunctional effects of carbon coating on high-capacity $\text{Li}_{1.2}\text{Ni}_{0.13}\text{Co}_{0.13}\text{Mn}_{0.54}\text{O}_2$ cathode for lithium-ion batteries

J. J. Chen · Z. D. Li · H. F. Xiang · W. W. Wu · X. Guo · Y. C. Wu

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**Abstract** Coating the Li-rich layered oxide cathode  $\text{Li}_{1.2}\text{Ni}_{0.13}\text{Co}_{0.13}\text{Mn}_{0.54}\text{O}_2$  with small amount of conductive carbon is realized by low-temperature sucrose carbonization in air. Carbon coating gives rise to a small amount of  $\text{Mn}^{3+}$  on the surface of the  $\text{Li}_{1.2}\text{Ni}_{0.13}\text{Co}_{0.13}\text{Mn}_{0.54}\text{O}_2$ . The 1.2 wt% carbon-coated  $\text{Li}_{1.2}\text{Ni}_{0.13}\text{Co}_{0.13}\text{Mn}_{0.54}\text{O}_2$  shows obviously enhanced electrochemical performances, especially in improving rate capability and suppressing the voltage fading during long-term and high-rate cycling. According to the analysis from cyclic voltammetry (CV) and electrochemical impedance spectra (EIS), the improvements on the electrochemical performances are mainly because the coated carbon layer can function by not only increasing the electronic conductivity at the interface with electrolyte but also improving bulk electronic and ionic conductivity by small amounts of  $\text{Mn}^{3+}$ . Therefore, carbon coating is a promising approach to improve the cyclic stability of the Li-rich layered oxides.

**Keywords** Lithium-rich layered oxide · Carbon coating · Lithium-ion batteries

## Introduction

Further development of electric vehicles (EVs) and smart grids have stimulated the demand for advanced rechargeable batteries, among which lithium-ion battery (LIB) is the most promising candidates owing to its high energy density and successful commercialization in the portable electronic devices [1–3]. However, the presently available cathodes have a limited capacity ( $<200 \text{ mAh g}^{-1}$ ) [4–6]. Solid solutions between  $\text{Li}_2\text{MnO}_3$  and  $\text{LiMO}_2$  (denoted as  $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ ,  $M=\text{Ni, Co, Mn, or combinations}$ ), with a reversible capacity of  $\sim 250 \text{ mAh g}^{-1}$ , is quite attractive to high-energy LIBs for EVs and smart grid applications [7–9]. However, their drawbacks of large irreversible capacity loss during the initial cycle and poor rate capability limit their commercial utilization. The large irreversible capacity in the initial cycle is attributed to the extraction of  $\text{Li}_2\text{O}$  followed by elimination of oxygen ion vacancies from the lattice for activation of  $\text{Li}_2\text{MnO}_3$  component and formation of the thick cathode-electrolyte interface (CEI) layer [10–12]. The poor rate capability is possible resulting from the high-impedance CEI layer and the low electronic conductivity at the electrode/electrolyte interface [13–15]. It is obvious that the interfacial property significantly affects the electrochemical performance of the Li-rich layered oxides.

In our previous paper [12], CEI layer was optimized by introduction of trimethyl phosphite (TMP) as high-voltage electrolyte additive and the electrochemical performance and thermal stability of Li-rich layered oxide cathode were obviously improved. Besides the reformulation of the electrolytes, surface coating on the cathode material is an effective alternative to modify the CEI film between the Li-rich layered oxide and the electrolyte [16–18]. Surface coating by  $\text{Al}_2\text{O}_3$  [16],  $\text{CeO}_2$  [17] and  $\text{AlF}_3$  [18] was proved to effectively reduce irreversible capacity loss in the first cycle and improve the cycle stability, but

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depressed the electronic conductivity at the interface. Carbon is an ideal conductive coating agent because on one hand it can serve as protective layer to cover the active sites and reduce the contact between the active material and the electrolyte and on the other hand it can enhance surface electronic conductivity [19–22]. Carbon coating is widely used to enhance the electrochemical properties of phosphate-based cathode [23]. But for the metal oxide cathode containing high valance metal ions such as  $\text{Mn}^{4+}$ , when the carbon coating was conducted in a high-temperature condition, the high valance metal ions is easily to be reduced. At the same time, carbon coating has been found efficient to enhance cycling and rate performance of metal oxide cathode such as  $\text{LiMn}_2\text{O}_4$  [24, 25],  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  [26], and  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  [27]. Recently, Manthiram et al. [19] reported that surface modification of the  $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$  with carbon film enhanced the surface electronic conductivity by 40 % and thus improved the rate capability and cycling performance of the Li-rich cathode material. Tu et al. [20] claimed that the discharge capacity and cycling performance of carbon-coated  $\text{Li}_{1.048}\text{Mn}_{0.381}\text{Ni}_{0.286}\text{Co}_{0.286}\text{O}_2$  were improved because carbon coating can protect the Li-rich cathode material from reacting with the electrolyte and retard the incrustation of the CEI film on the surface of oxide particles. In order to avoid carbon reducing  $\text{Mn}^{4+}$  at high temperature, both Manthiram and Tu coated the carbon film on Li-rich cathode material via a physical route. The former used thermal evaporation in a JEOL thermal evaporator with a vacuum of  $\sim 10^{-7}$  Torr and the latter chose direct-current magnetron sputtering. However, Deng et al. [21] fabricated carbon-coated  $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$  cathode by polymer pyrolysis in air, and that carbon-coated cathode exhibited the enhanced specific capacity and rate performance because of suppressing the formation of the thick solid electrolyte interfacial layer and partly reducing  $\text{Li}_2\text{CO}_3$  impurity on the  $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$  particle surface.

Basically, either physical or chemical carbon coating is effective to improve the performance of the Li-rich cathode materials, and especially the organics pyrolysis is the more facile and economic route for commercial production. However, the surface chemistry of the Li-rich cathode materials should be carefully investigated after the chemically carbon coating. Herein, we performed the carbon coating on the  $0.5\text{Li}_2\text{MnO}_3\cdot 0.5\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  cathode (denoted as  $\text{Li}_{1.2}\text{Ni}_{0.13}\text{Co}_{0.13}\text{Mn}_{0.54}\text{O}_2$ , and abbreviated as LNCMO hereafter) by sucrose pyrolysis in air. It was found that chemical carbon coating has the bifunctional effects on the LNCMO cathode. On the one hand, it can increase the electronic conductivity at the interface with electrolyte because of the conductive nature of carbon. On the other hand, the introduction of  $\text{Mn}^{3+}$  from the carbon thermal reduction of small

amount of  $\text{Mn}^{4+}$  can improve bulk electronic conductivity and ionic conductivity of LNCMO. So, the optimal carbon-coated LNCMO (abbreviated as C-LNCMO hereafter) exhibits not only obviously reduced initial irreversible capacity loss and improved rate capability but also suppressed the voltage fading during long-term and high-rate cycling.

## Experimental

### Materials preparation

The pristine LNCMO was synthesized by a coprecipitation method combined with a solid-state reaction. The coprecipitation of the carbonate precursor was carried out as follows: 2 M  $\text{Na}_2\text{CO}_3$  solution and 0.2 M ammonium hydroxide were simultaneously added dropwise into a solution containing manganese, nickel, and cobalt sulfates with a total concentration of 2 M and stirred for 12 h under 60 °C. The carbonate precursor was washed with deionized water and vacuum dried at 100 °C for 24 h. The carbonate precursor was then mixed with lithium carbonate and decomposed at 500 °C for 5 h in air. The decomposed powder was then calcined at 900 °C for 12 h in air to obtain the pristine LNCMO. Surface coating of the LNCMO with carbon were carried out as follows: the pristine LNCMO was mixed with 1, 3, and 5 wt% sucrose, then heat up to 200 °C at a rate of  $1\text{ }^\circ\text{C min}^{-1}$  and then to 350 °C at a rate of  $3\text{ }^\circ\text{C min}^{-1}$  in air.

### Characterization and electrochemical measurements

The crystalline structures of the pristine LNCMO and C-LNCMO were identified by X-ray diffraction (XRD) using a diffractometer (D/MAX2500 V, Cu K $\alpha$  radiation). The diffraction patterns were recorded in the 2 theta range from 10° to 80°. The amount of carbon coated on the LNCMO was examined by a thermogravimetric analyzer (TGA, Q5000). The particle size and morphology of the pristine LNCMO and C-LNCMO were observed by scanning electron microscopy (SEM, Hitachi, SU8020) and transmission electron microscopy (TEM, Hitachi, H800). X-ray photoelectron spectroscopy (XPS, ESCALAB250 with monochromatic Al K $\alpha$  radiation) was performed to characterize the surface state of the obtained products.

The electrochemical properties of the cathode materials were evaluated in CR-2032 type cells assembled in the glove box (MBraun). In order to make the electrode laminate, a slurry containing 84 wt% active material, 8 wt% acetylene black, and 8 wt% polyvinylidene fluoride (PVDF) dispersed in N-methyl-2-pyrrolidinone (NMP) was cast onto an aluminum current collector. After vacuum drying at 70 °C, the laminate was punched into discs ( $\Phi$  14 mm) for assembling the coin cells. The mass loading in the electrode was

controlled at about  $1.5 \text{ mg cm}^{-2}$ . Celgard 2400 microporous polypropylene membrane was used as separator. Highly pure lithium foil was used as the counter electrode and reference electrode for the cell assembly. The electrolyte was 1 M  $\text{LiPF}_6$ /ethylene carbonate (EC) + dimethyl carbonate (DMC) (1:1 w/w). The cell performance of pristine LNCMO and C-LNCMO were evaluated on a multichannel battery cycler (Neware BTS2300). For activation, all the cells were initially cycled twice between 2.0 and 4.8 V at a current rate of 0.1 C ( $1 \text{ C}=250 \text{ mA g}^{-1}$ ). Then the cycling tests were performed at a current rate of 0.5 C in the constant current–constant voltage (CC-CV) charge mode and constant current (CC) discharge mode between 2.0 and 4.6 V. Cyclic voltammograms (CV) were performed over the potential range of 2.0–4.8 V at a scanning rate of 0.2 to  $0.8 \text{ mV s}^{-1}$  on a CHI 604D electrochemical workstation (Shanghai Chenhua Instruments Co. Ltd.). The electrochemical impedance spectra of the cells were also measured on the CHI 604D electrochemical workstation with the frequency range of 1 MHz to 0.01 Hz and potential perturbation of 10 mV at the SOC (state of charge) of 50 %.

## Results and discussion

Since the sucrose is selected as carbon source to modify the surface of the LNCMO, the amount of residual carbon with different sucrose dosage should be initially investigated. Figure 1 shows TG curves of the pristine LNCMO and the carbon-coated LNCMO prepared from 3 wt% sucrose coated LNCMO from room temperature to  $750^\circ\text{C}$  in air. A small weight loss ( $<0.2\%$ ) occurs at  $80\text{--}180^\circ\text{C}$  for the pristine LNCMO due to the trace moisture in the material. However, the carbon-coated sample has two weight loss steps at  $90\text{--}180^\circ\text{C}$  and  $300\text{--}450^\circ\text{C}$ , respectively, with the total mass loss of

1.4 %. Both the samples have the comparative moisture, so the 1.2 wt% ( $1.4\text{--}0.2$ ) more weight loss attributed to carbon oxidization in air [26]. It means 1.2 wt% carbon is coated on LNCMO from 3 wt% sucrose (this sample was denoted as 1.2 % C-LNCMO hereafter). Analogously, 1 and 5 wt% sucrose coating results in 0.4 and 2.0 wt% carbon residual (samples were denoted as 0.4 % C-LNCMO and 2.0 % C-LNCMO hereafter), respectively.

The X-ray diffraction patterns of the pristine LNCMO and 1.2 % C-LNCMO are shown in Fig. 2. All the major diffraction peaks can be indexed as a layered oxide lattice based on a hexagonal  $\alpha\text{-NaFeO}_2$ -type structure with a space group R-3m [28]. Both (006)/(102) and (108)/(110) doublets are clearly split, suggesting that the material crystallized in the layered structure without formation of any spinel structure [29]. The weak peaks between  $20$  and  $25^\circ$  (marked by asterisk) are reflected by a monoclinic unit cell with a C2/m symmetry, due to a  $\text{LiMn}_6$  cation arrangement that occurs in the transition metal layers of  $\text{Li}_2\text{MnO}_3$  region. No peak of carbon is observed due to its low quantity and/or its amorphous nature, illustrating that the coating processes do not destroy the structure of the Li-rich layered oxides and no impurity appears in the XRD patterns.

The morphologies of the pristine LNCMO and 1.2 % C-LNCMO were investigated by SEM, as shown in Fig. 3. From Fig. 3a, b, the pristine LNCMO are block-like particles of  $200\text{--}500 \text{ nm}$  in size. As shown in Fig. 3c, d, some stuff can be found on the surface of the 1.2 % C-LMNCO. Moreover, the color change in our experiment from red-brown of pristine LNCMO to black of 1.2 % C-LNCMO also indicates that sucrose was carbonized and carbon is coated on the LNCMO particles. Figure 4 shows the TEM images of the pristine LNCMO and 1.2 % C-LNCMO particles. Compared with the smooth surface of the pristine LNCMO (Fig. 4a), amorphous carbon layer is coated on the surface of the 1.2 % C-LNCMO with a thickness of  $10\text{--}30 \text{ nm}$  (Fig. 4b). From the

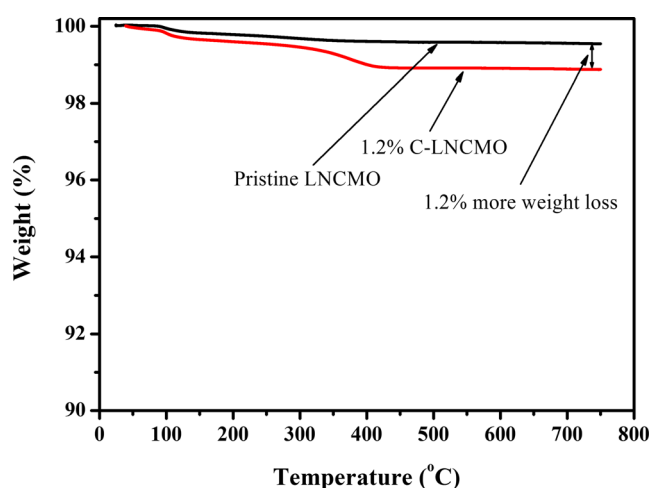


Fig. 1 TG curves of the pristine LNCMO and 1.2 % C-LNCMO

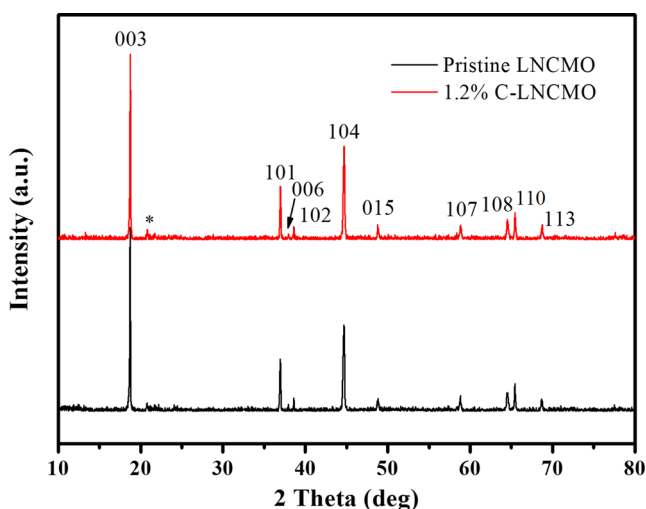
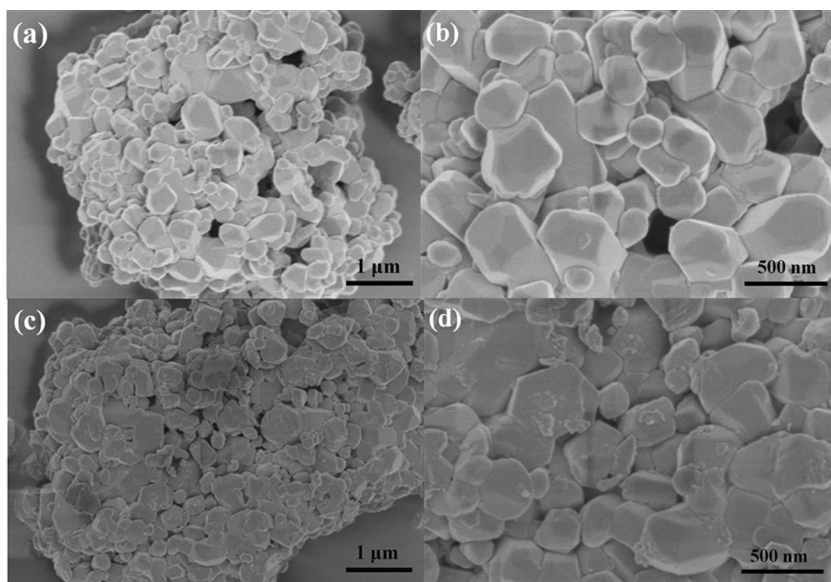


Fig. 2 XRD patterns of the pristine LNCMO and 1.2 % C-LNCMO

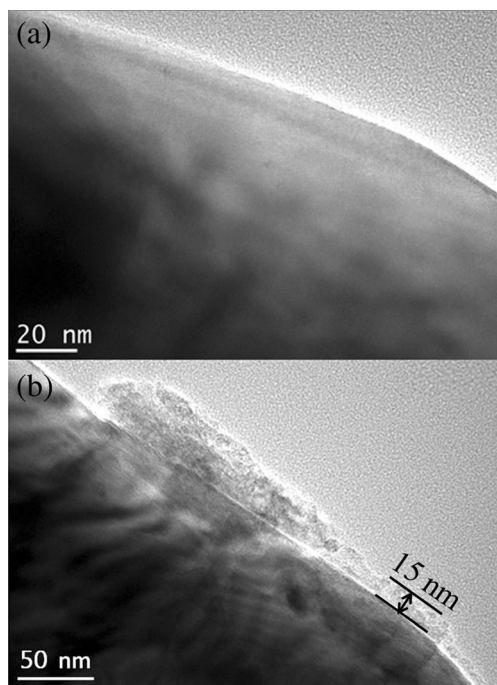
**Fig. 3** SEM images of the pristine LNCMO (a) and 1.2 % C-LNCMO (c) at low magnification ( $\times 2.0k$ ), the pristine LNCMO (b) and 1.2 % C-LNCMO (d) at high magnification ( $\times 5.0k$ )



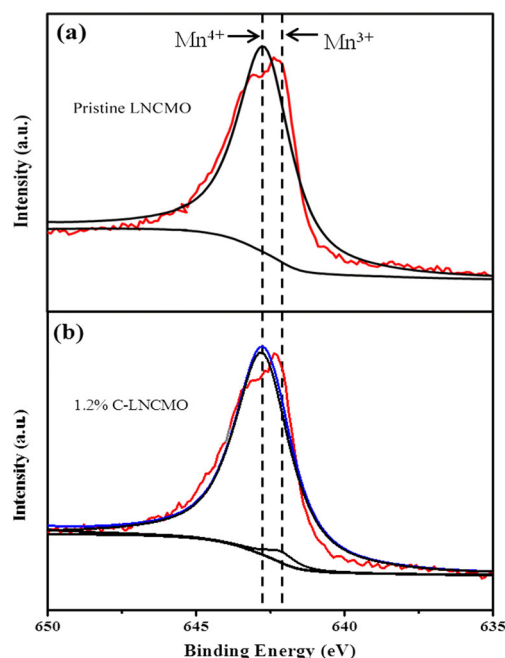
SEM and TEM results, we expected that carbon layer could effectively decrease the direct contact area between the high-voltage cathode material and electrolyte.

It has been proved that the  $Mn^{4+}$  in LNCMO has the possibility to be reduced to  $Mn^{3+}$  by carbon in the process of sucrose carbonization, especially at the particle surface [26]. The oxidation state of Mn before and after carbon coating was investigated and the XPS spectra of the pristine LNCMO and 1.2 % C-LNCMO are shown in Fig. 5. These XPS spectra have been calibrated according to the binding energy of the C1s peak at 284.8 eV. As can be seen from

Fig. 5a, the major binding energy peak of 642.7 eV corresponds to  $Mn^{4+}$  (assigned to Mn 2p<sub>3/2</sub>) in pristine LNCMO. According to the results showed in Fig. 5b, for the 1.2 % C-LNCMO, the existence of  $Mn^{3+}$  at energy peak of 642.0 eV (assigned to Mn 2p<sub>3/2</sub>) could be observed by peak separation and the amount of  $Mn^{3+}$  is 3.17 % determined from its corresponding peak areas [30]. This result confirms that carbon coating process gave rise to a small amount of  $Mn^{3+}$  on the surface of the 1.2 % C-LNCMO, which will contribute to higher bulk electronic conductivity and ionic conductivity owing to stronger conductivity and larger ionic radius of



**Fig. 4** TEM images of the pristine LNCMO (a) and 1.2 % C-LNCMO (b)



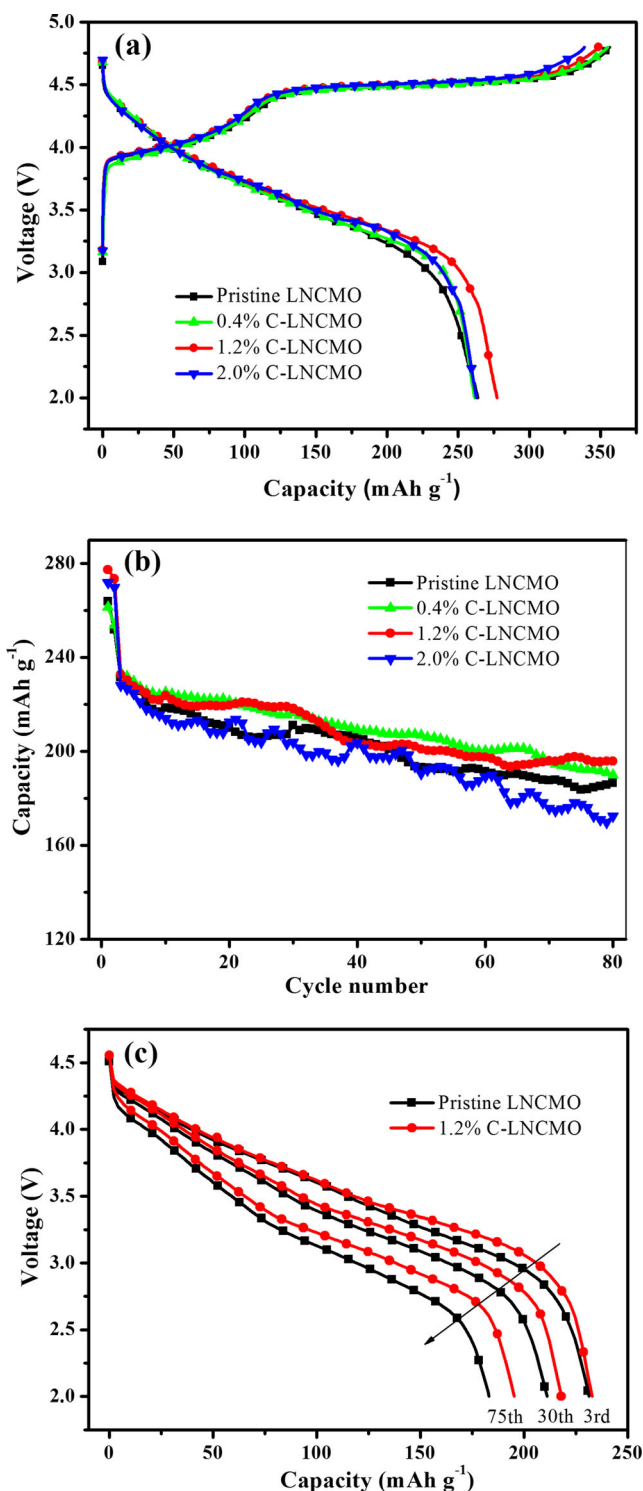
**Fig. 5** XPS spectra of the pristine LNCMO (a) and 1.2 % C-LNCMO (b)



$\text{Mn}^{3+}$  than those of  $\text{Mn}^{4+}$  [31]. During the reduction of  $\text{Mn}^{4+}$  into  $\text{Mn}^{3+}$ , the main reaction is possibly as  $\text{Mn(IV)O}_x + y/2 \text{C} = \text{Mn(III)O}_{x-y} + y/2 \text{CO}_2$ .

The initial charge and discharge curves and the cycling performances of the LNCMO with various amounts of carbon coating are shown in Fig. 6. As shown in Fig. 6a, all the samples show similar charge/discharge profiles. Table 1 compares the initial charge and discharge capacities and the irreversible capacity loss. The initial discharge capacity of the pristine LNCMO is  $263.7 \text{ mAh g}^{-1}$  with the irreversible capacity of  $101.6 \text{ mAh g}^{-1}$  and coulombic efficiency of 74.0 %. The 1.2 % C-LNCMO shows the highest discharge capacity ( $277.3 \text{ mAh g}^{-1}$ ) with the lowest irreversible capacity of  $71.3 \text{ mAh g}^{-1}$  and the highest coulombic efficiency of 79.5 %. It seems that coated carbon layer can suppress the loss of oxygen in the initial charge process so as to retain more oxygen vacancies in the bulk lattice to provide sufficient active sites for lithium ion insertion in the subsequent discharge process. Figure 6b shows the cycling performance of LNCMO with various carbon coating. After two formation cycles at 0.1 C, the discharge capacities of the different cells are quite close to  $230 \text{ mAh g}^{-1}$  at the third cycle. However, at the 80th cycle, the residual discharge capacities are 186.4, 189.9, 195.8, and  $172.2 \text{ mAh g}^{-1}$  for the pristine LNCMO, 0.4 % C-LNCMO, 1.2 % C-LNCMO, and 2.0 % C-LNCMO, respectively. It is obvious that appropriate amount of carbon coating improves the electrochemical performance of the LNCMO cathode materials by suppressing the side reactions between the active cathode materials and the electrolyte. The relatively low capacity of the 2.0 % C-LNCMO could be the result of structural instability induced by more  $\text{Mn}^{3+}$  introduced into the LNCMO lattice [17]. The discharge curves of the pristine LNCMO and 1.2 % C-LNCMO in the 3rd, 30th, and 75th cycles at 0.5 C are compared in Fig. 6c. It can be observed that voltage fading of the 1.2 % C-LNCMO is less serious compared with those of the pristine LNCMO during long-term cycling.

Figure 7 shows rate capability of the LNCMO with various amounts of carbon coating. After two formation cycles at 0.1 C, all the cells were charged at a rate of 0.5 C and discharged at incremental rates from 0.5 to 5 C then recovering back to 0.5 C. In the case of the pristine LNCMO, its discharge capacity decrease to 199.5, 176.4, and  $137.1 \text{ mAh g}^{-1}$  at 1, 2, and 5 C, respectively. However, the discharge capacities of the 1.2 % C-LNCMO are 203.9, 180.3, and  $154.7 \text{ mAh g}^{-1}$  at 1, 2, and 5 C, respectively. That is, appropriate carbon coating could improve the rate capability of the LNCMO. In addition, the discharge curves of the pristine LNCMO and 1.2 % C-LNCMO at 0.5, 2, and 5 C are compared in Fig. 7b. It is observed that for the pristine LNCMO besides the obvious capacity reducing, the discharge voltage fading is more and more serious with discharge rate increasing due to the  $\text{Li}^+$  diffusion impedance in the bulk



**Fig. 6** Initial voltage profiles at 0.1 C (a), cycling performance at 0.5 C (b) of LNCMO with various amounts of carbon coating, and discharge curves of the pristine LNCMO and 1.2 % C-LNCMO electrodes (c)

LNCMO [32]. 1.2 % carbon coating can suppress not only the capacity reducing but also the voltage fading. According to the previous literature [33, 34], the voltage fading has been attributed to the formation of a spinel-like phase. Surface coating oxides/phosphates and electrolyte additives have been

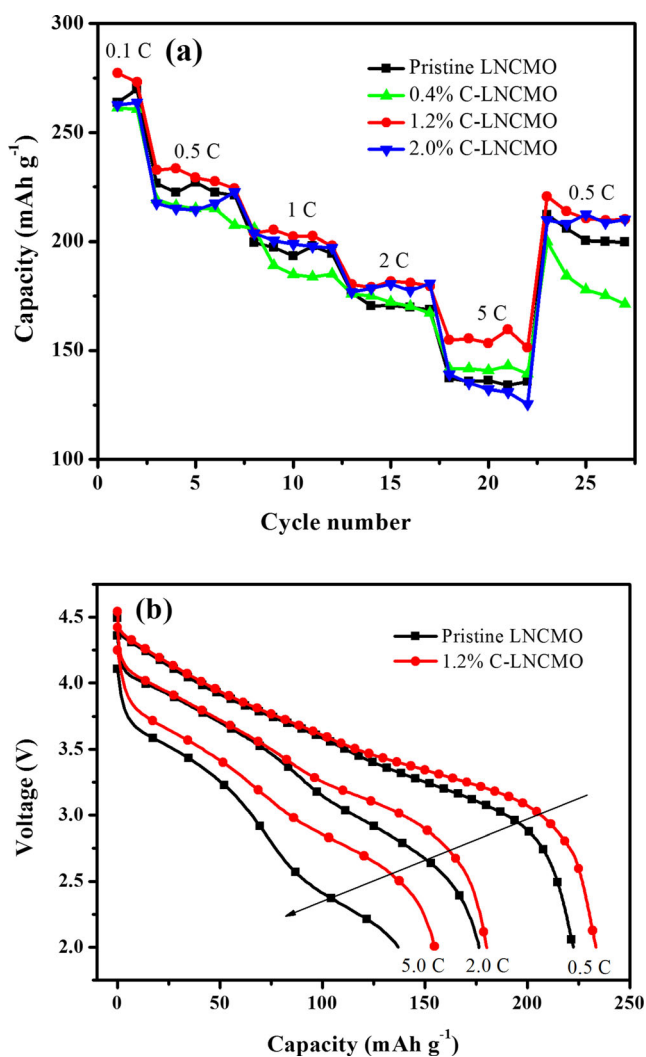
**Table 1** Information of the initial charge and discharge performances of LNCMO with various amounts of carbon coating

Samples	First charge capacity (mAh g <sup>-1</sup> )	First discharge capacity (mAh g <sup>-1</sup> )	Irreversible capacity loss (mAh g <sup>-1</sup> )
Pristine LNCMO	356.3	263.7	101.6
0.4 % C-LNCMO	355.0	261.4	93.6
1.2 % C-LNCMO	348.6	277.3	71.3
2.0 % C-LNCMO	338.7	262.7	76.0

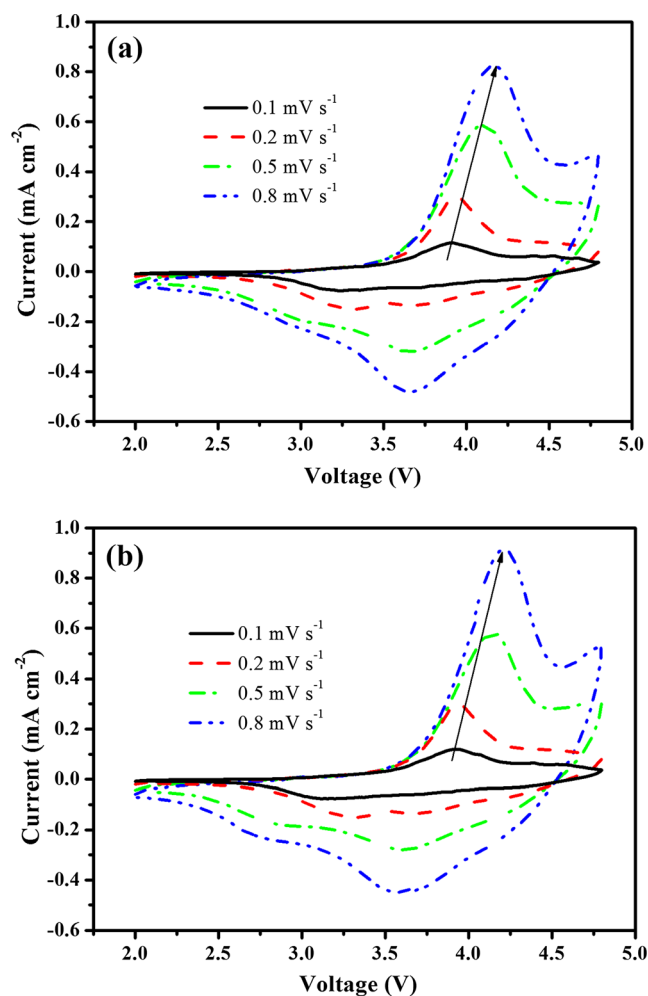
used to stabilize the capacity of cathode materials and enhance cycling ability, but have little-to-no effect on voltage fading [34]. Herein, introduction of Mn<sup>3+</sup> is apt to stabilize the structure during cycling, which could mitigate the layered oxide transformation into the spinel phase.

CV is a useful tool to study the oxidation/reduction and/or phase transformation processes in electrode reactions and to

estimate the chemical diffusion coefficient of lithium ion. Figure 8 shows the initial CV curves of the pristine LNCMO and 1.2 % C-LNCMO measured at the sweep rates of 0.1, 0.2, 0.5, and 0.8 mV s<sup>-1</sup>, respectively. The anodic peaks of both samples around 4.1 V are due to the oxidation process of Ni<sup>2+</sup> and Co<sup>3+</sup> to higher oxidation states, while the second anodic peaks above 4.5 V are normally associated with the Li<sub>2</sub>O removal from the layered lattice. During cathodic reactions, the broad peaks between 4.3 and 3.2 V are regarded as the reduction processes of Ni<sup>4+</sup> and Co<sup>4+</sup>, while another peak



**Fig. 7** Rate capability of LNCMO with various amounts of carbon coating (a), and discharge curves at various C rates of the pristine LNCMO and 1.2 % C-LNCMO electrodes (b)



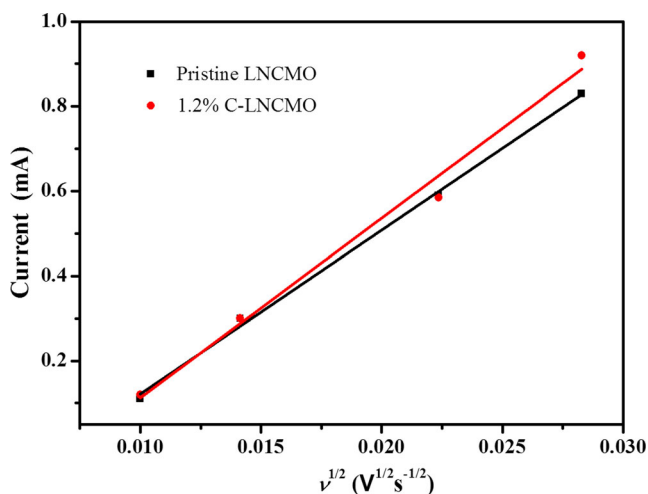
**Fig. 8** Cyclic voltammetry of the pristine LNCMO and 1.2 % C-LNCMO electrodes at a series of sweep rates

around 2.7 V is believed to be due to insertion of  $\text{Li}^+$  accompanied with  $\text{Mn}^{4+}$  reduction in surface spinel component [14, 30]. As the sweep rate increases, the anodic peaks shifted to higher potential and the corresponding cathodic peaks to lower potential, indicating that the irreversible behaviors become more manifest at higher sweep rates, in agreement with the voltage fading. The irreversibility is caused by the polarization that originates from either the incomplete extraction/insertion from/into the electrode of  $\text{Li}^+$  during the time interval of a higher rate sweep or the slow electronic transfer [30]. It is interesting to point out that more apparent cathodic peaks around 2.7 V of 1.2 % C-LNCMO is associated with the  $\text{Mn}^{4+}/\text{Mn}^{3+}$  redox reaction, which is beneficial to mitigate voltage fading during cycling [35, 36]. Thackeray proposed the possible existence of a “layered-spinel-rocksalt” composite structure to minimize transition metal ion diffusion between the close packed layers of the oxygen sublattice during cycling [36].

Figure 9 presents the relationship between the anodic peak current and the sweep rate. As can be seen, the peak current shows a square root dependence on the sweep rate. This behavior is expected for a diffusion-controlled process in electrode [26], therefore the relationship of the peak current ( $I_p$ ) and the sweep rate can be expressed as Eq. 1 [37]:

$$I_p = 2.69 \times 10^5 n^{3/2} A D_{\text{Li}^+}^{1/2} C_{\text{Li}} \nu^{1/2} \quad (1)$$

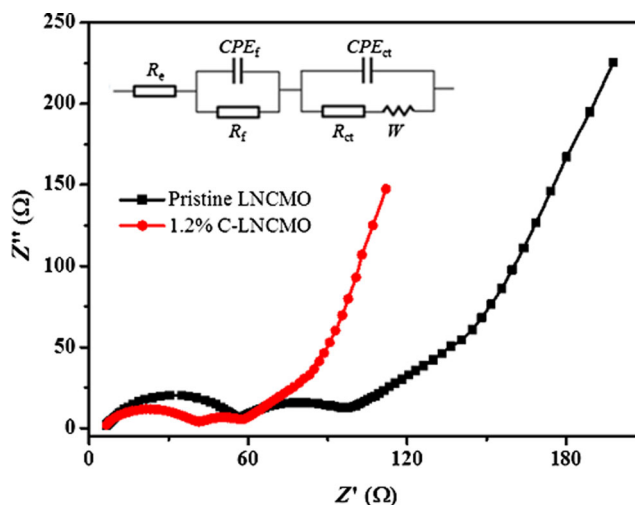
where  $I_p$  is the peak current (A, directly obtained from CV curves),  $n$  is the charge-transfer number,  $A$  is the surface area of the electrode ( $1.54 \text{ cm}^2$ ),  $C_{\text{Li}}$  is the concentration of lithium ions in the electrode ( $2.98 \times 10^{-3} \text{ mol cm}^{-3}$ , calculated from the volume of LNCMO ( $401.6 \text{ \AA}^3$ )), and  $\nu$  is the potential scan



**Fig. 9** Relationship between the peak current and the square root of sweep rate of the pristine LNCMO and 1.2 % C-LNCMO electrodes

rate ( $\text{V s}^{-1}$ ).  $D_{\text{Li}^+}$  is the diffusion coefficient and that of the pristine LNCMO and 1.2 % C-LNCMO could be calculated to be  $5.6 \times 10^{-10}$  and  $6.8 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$ , respectively. It is apparent that the kinetics of  $\text{Li}^+$  diffusion can be improved by 1.2 % carbon coating. It is reasonable that small amount of  $\text{Mn}^{3+}$  in the 1.2 % C-LNCMO contributes to higher bulk electronic conductivity and ionic conductivity and eventually improves the rate capacity.

EIS test was carried out to further understand the effect of carbon coating on the LNCMO electrodes. Before the EIS measurement, the cells were subjected to three galvanostatic charge–discharge cycles for activating and stabilizing the electrodes. Figure 10 shows the Nyquist plots of the pristine LNCMO and 1.2 % C-LMNCO electrodes at the SOC of 50 %. As shown in Fig. 10, Nyquist plots for both samples have two semicircles in the mid- and high-frequency regions and a straight line in the low-frequency. EIS results were fitted by using an equivalent circuit, in which  $R_e$ ,  $R_f$ ,  $R_{ct}$ , and  $W$  stand for internal resistance of the cell, the impedance of  $\text{Li}^+$  diffusion in the interface (herein CEI) film, the impedance of charge transfer and Warburg impedance, respectively [38, 39]. The fitted impedance parameters of the equivalent circuit are listed in Table 2. The value of  $R_e$  of the 1.2 % C-LNCMO is relatively smaller than that of the pristine LNCMO, which suggests that the 1.2 wt% carbon coating can suppresses the growth of CEI film on the LNCMO surface. The value of  $R_f$  of the 1.2 % C-LNCMO ( $34.650 \text{ }\Omega$ ) much lower than that of the pristine LNCMO ( $51.010 \text{ }\Omega$ ) due to conductive carbon enhancing the surface electronic conductivity and introduction of  $\text{Mn}^{3+}$  improving bulk electronic conductivity. The value of  $R_{ct}$  drastically decreases from 31.030 to  $12.480 \text{ }\Omega$  after 1.2 wt% carbon coating (consistent with the  $\text{Li}^+$  diffusion coefficient calculated previously) [40]. The Warburg impedance coefficient ( $\sigma_W$ ) decreases from 18.335 to  $11.177 \text{ }\Omega \text{ cm}^2$



**Fig. 10** Nyquist impedance spectra of the pristine LNCMO and 1.2 % C-LNCMO electrodes, the inset shows equivalent circuit for Nyquist plots



**Table 2** Fitted impedance parameters of the pristine LNCMO and 1.2 % C-LNCMO

Sample	$R_e$ ( $\Omega$ )	$R_f$ ( $\Omega$ )	$R_{ct}$ ( $\Omega$ )	$\sigma_W$ ( $\Omega \text{ cm}^2 \text{ s}^{-1/2}$ )
Pristine LNCMO	6.377	51.010	31.030	18.335
1.2 % C-LNCMO	5.684	34.650	12.480	11.177

$s^{-1/2}$  after 1.2 % carbon coating due to the improved ionic conductivity.

## Conclusions

Coating the Li-rich layered oxide cathode material with small amounts of conductive carbon has realized by the sucrose carbonization. Appropriate coated carbon layer cannot only increase the electronic conductivity at the interface with electrolyte but also improve bulk electronic conductivity and ionic conductivity by reducing small amounts of  $\text{Mn}^{4+}$  to  $\text{Mn}^{3+}$ . As a result, not only the initial coulombic efficiency and rate capability of the LNCMO have been significantly improved but also the discharge voltage fading has been mitigated by carbon coating. The carbon coating is experimentally proved as a very effective way for improving the electrochemical performance of  $\text{Li}_{1.2}\text{Ni}_{0.13}\text{Co}_{0.13}\text{Mn}_{0.54}\text{O}_2$ , and the appropriate carbon-coated  $\text{Li}_{1.2}\text{Ni}_{0.13}\text{Co}_{0.13}\text{Mn}_{0.54}\text{O}_2$  is a promising cathode candidate for advanced lithium ion batteries.

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