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Electrochemical Performances of Carbon-Coated $Li[Li_{0.29}Mn_{0.57}Co_{0.14}]O_2$ Cathode Materials for Lithium-ion Batteries

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Carbon coated Mn-based Li-rich $Li[Li_{0.29}Mn_{0.57}Co_{0.14}]O_2$ materials have been successfully prepared by glucose pyrolysis in air. X-ray diffraction (XRD) analyses inferred that the phase structure of layered oxide $Li[Li_{0.29}Mn_{0.57}Co_{0.14}]O_2$ was not damaged during coating processing. Transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS) revealed that the surface of $Li[Li_{0.29}Mn_{0.57}Co_{0.14}]O_2$ particles was coated by carbon. Electrochemical tests presented the discharge capacities and the rate performances of $Li[Li_{0.29}Mn_{0.57}Co_{0.14}]O_2$ were improved by carbon coating. At the current densities of 50 mA/g and 100 mA/g, the initial capacities of the sample modified by 10 wt% glucose increased by 85.7% and 241.5% than that of the sample without carbon coating. The electrochemical impedance spectroscopy (EIS) manifested the enhanced electrochemical performances for carbon coated samples could contribute to the reduction of the charge transfer resistance and solid electrolyte interphase resistance.

Keywords: Lithium-ion battery, carbon coating, electrochemical performance, lithium-rich materials

1. INTRODUCTION

Nowadays, the researchers are pursing cathode materials of lithium-ion batteries with higher specific capacities for the application in electric vehicles or energy storage devices. Mn-based Li-rich Li_2MnO_3-$LiMO_2$ (M=Mn, Ni, and Co, …) solid solution materials are of promising cathode materials because of their high reversible capacities[1-7]. However, this kind of Li-rich cathode materials showed poor rate capability due to their low electrical conductivity, which limited their further application [8-11].

Surface modification has been tried to enhance the electrochemical performances of Li-rich materials. An extra improved rate capability could be achieved by coating various kinds of materials, such as MnO_x[12], Nb_2O_5[13], SnO_2[14], TiO_2[15], $LiCoPO_4$[16], Li_2SiO_3[17] and YF_3[18] with an enhancement in the cyclability of Li-rich materials. Compared with above-mentioned compounds, carbon is expected to be more impactful in improving the rate capability of electrode materials due to its high electronic conductivity, which has been successfully used in modifying $LiFePO_4$. However, the routine used in coating $LiFePO_4$ will involve high temperature and inert atmosphere, which easily results in the reduction of Mn^{4+} and Co^{3+}, and finally degrades the structure of Mn-based Li-rich cathode materials. Therefore, it is difficult to surface modify Li-rich cathode materials by a common carbon coating process. Recently, there was a report to modify Li-rich materials using conductive acetylene black by physical grinding [19]. However, the contact between carbon and parent cathode materials could be limited.

In this study, the carbon coating process was performed through glucose pyrolysis in air. The variations of the structure and electrochemical performances of $Li[Li_{0.29}Mn_{0.57}Co_{0.14}]O_2$ derived by carbon coating were investigated. It can be found that carbon-coated $Li[Li_{0.29}Mn_{0.57}Co_{0.14}]O_2$ materials could be successfully prepared. The carbon coating in air showed to be effective for achieving an improvement on electrochemical performances of $Li[Li_{0.29}Mn_{0.57}Co_{0.14}]O_2$ cathode materials.

2. EXPERIEMTAL

2.1 Materials preparation

$Li[Li_{0.29}Mn_{0.57}Co_{0.14}]O_2$ was prepared by a self-propagating combustion method. Firstly, $LiNO_3$, $Mn(NO_3)_2$ and $Co(CH_3COO)_2$ were dissolved in distilled water at the required stoichiometry. Then, citric acid was added to the solution and the pH was kept at around 8 by $NH_3 \bullet H_2O$. The mixture was stirred at 80°C until a viscous liquid formed, and then dried at 80 °C to become dry gel. After that, the dry gel undergone self-propagating combustion at 500 °C for several minutes to obtained the precursors. Subsequently, the precursors were calcined at 700 °C for 12 h to produce final $Li[Li_{0.29}Mn_{0.57}Co_{0.14}]O_2$ powders.

Carbon coating was performed through the following approach. Glucose was used as carbon source and mixed with obtained $Li[Li_{0.29}Mn_{0.57}Co_{0.14}]O_2$ at the ratios of 5wt%, 10wt%, 15wt% and 20wt% by planetary ball-milling for 6 hours at 1000 rpm. The mixtures were heated at 400 °C for 1 hour under air. The produced samples were marked as LMC1, LMC2, LMC3 and LMC4, respectively.

2.2 Materials Characterization

The crystal structures of all samples were measured by X-ray diffraction (XRD, X'Pert, PANalytical) with Cu Kα radiation (λ= 1.5406˚A) with 2θ range of 10–70° and a step size 0.02°. The morphologies of the bare and coated samples were investigated with scanning electron microscopy (FESEM, S-4800) and transmission electron microscopy (TEM, JEM-2100F). The surface properties of the bare and carbon-coated samples were detected by X-ray photoelectron spectroscopy (XPS) on a ESCALAB250Xi.

2.3 Electrochemical measurements

The CR2025 coin cells were used to evaluate electrochemical performances, in which the Lithium metal, Celgard 2400 and the mixture of Li[$Li_{0.29}Mn_{0.57}Co_{0.14}$]$O_2$, carbon black and polyvinylidene fluoride (weight ratio: 8:1:1) were used as anode, separator and cathode, respectively. The electrolyte solution was 1 mol/L $LiPF_6$ in ethylene carbonate and dimethyl carbonate (50%: 50% by volume). CHI660B electrochemical workstation was used to measure electrochemical impedance spectra (EIS) between 10^5 Hz to 10^{-2} Hz. Charge–discharge experiments were carried out on a LANDE-CT2001A system between 2.0~4.8 V at 30 ^oC.

3. RESULTS AND DISCUSSION

To confirm the effects of glucose on the surface morphology of Li-rich materials, TEM characterizations were carried out for the bare, LMC2 and LMC4 samples. As shown in Fig. 1b, a coating with 3-5 nm thickness covers the Li[$Li_{0.29}Mn_{0.57}Co_{0.14}$]$O_2$ particle for 10wt% glucose modified sample. With the amount of glucose further added to 20wt%, the thickness of out-layer increases to 10-20 nm (see Fig. 1c). In addition, it can be found that the inner materials display clear lattice fringes, suggesting the good crystallinity of Li[$Li_{0.29}Mn_{0.57}Co_{0.14}$]$O_2$. However, no obvious lattice fringes for out-layer can be seen, which should account for the amorphous state of carbon originated from glucose at 400^{o}C under air.

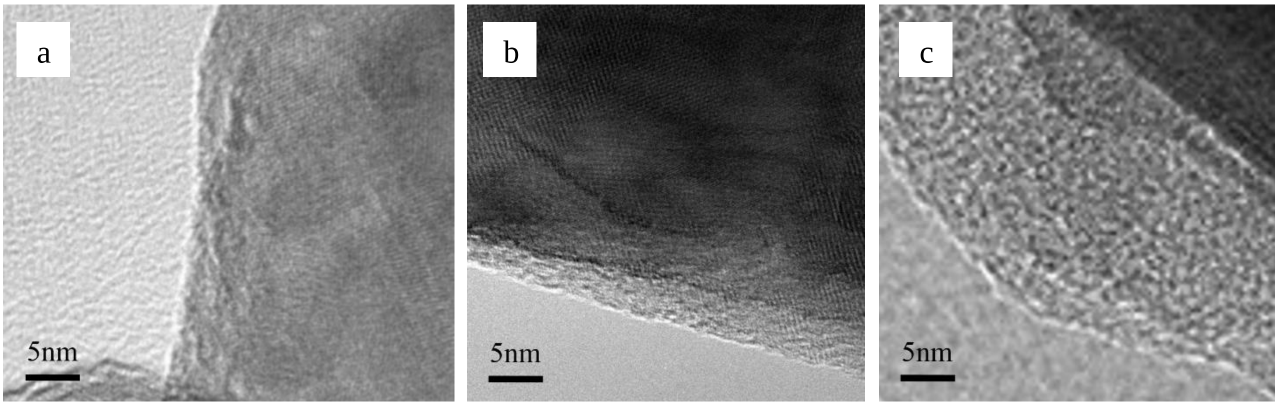

Figure 1. TEM images of the (a) bare, (b) LMC2 and (c) LMC4 samples

XPS spectra of C_{1s} of bare and LMC2 samples are illustrated in Fig. 2. It can be found that the XPS spectra of C_{1s} for the two samples are different. The peak at around 284.4 in C_{1s} spectrum for bare sample is relevant to amorphous carbon with sp^2 C−C bonds, while the peak at around 286.6 eV is related to C-O bond, which can contribute to the adventitious carbon [20, 21]. An additional peak at around 288.9 eV could be assigned to the C=O bond for the modified sample[21], which can contribute to the carbon coating layer on the Li[$Li_{0.29}Mn_{0.57}Co_{0.14}$]$O_2$ particle produced during calcining the sample at 400 ^{o}C in air. Compared with the bare one, the stronger C-C and C-O peaks and the appearance of C=O peak infer that carbon phase indeed exists in the coated samples and the carbon obtained in this work is amorphous. Combined with the results of TEM, we can conclude that the pyrolysis process in air can obtain carbon layer on the particle surface.

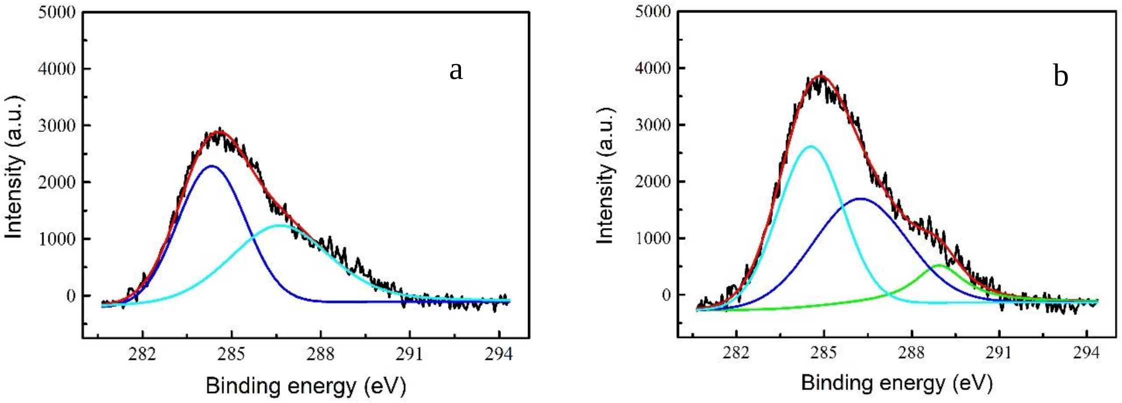

Figure 2. XPS spectra of the (a) bare and (b) LMC2 samples

XRD patterns of the bare and modified samples are exhibited in Fig. 3. All peaks of the bare sample can be indexed to the α-$NaFeO_2$ structure, except for the super-lattice peaks observed between 20 and 25°. The clear splitting of 006/012 around 38° and 108/110 around 65° reflections correspond the well-developed layered structure. Compared with the bare sample, no apparent impurity peaks are presented for the carbon-coated samples. The above observation suggests that the phase structure of $Li[Li_{0.29}Mn_{0.57}Co_{0.14}]O_2$ is not destroyed owing to carbon surface modification in air. Moreover, we also cannot find any diffraction peaks related to carbon, which could account for the amorphous state of carbon.

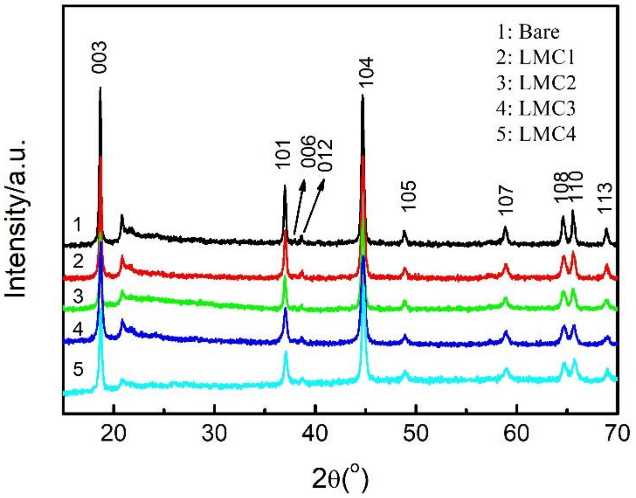

Figure 3. XRD patterns of the bare and LMC1, LMC2, LMC3 and LMC4 samples

Fig. 4 shows the SEM images of the bare and modified samples. The bare $Li[Li_{0.29}Mn_{0.57}Co_{0.14}]O_2$ materials consist of uniformly distributed particles with size range of 60~200 nm (Fig. 4a). When the addition amount of glucose is low, no noticeable changes on the particle size and morphology can be observed (see Fig. 4b). While the glucose amounts add to 15wt% and 20wt%, obvious decrease on the primary particle size and rise on the degree of the particles aggregation (see Fig. 4d and Fig. 4e) happen. Similar trends on the particle size and morphology were also reported in previous literature[22].

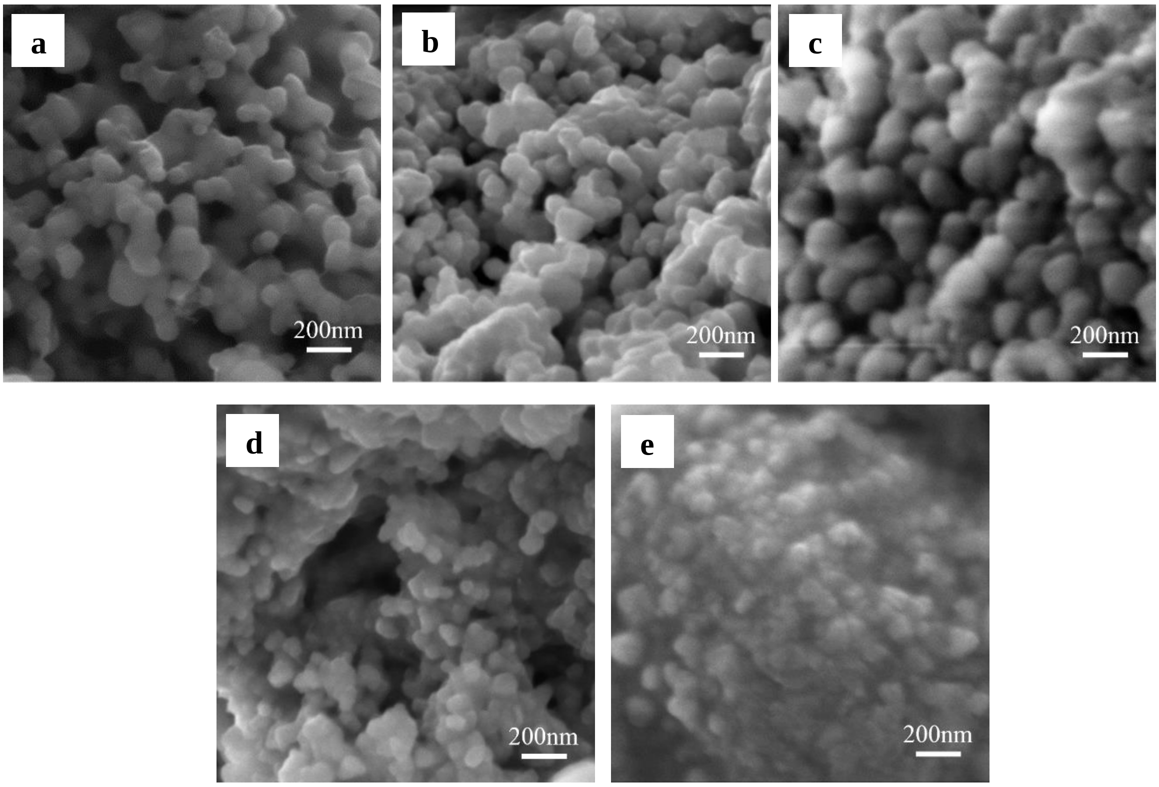

Figure 4. SEM images of the (a) bare, (b)LMC1, (c)LMC2, (d)LMC3 and (e) LMC4 samples

The charge/discharge curves of all samples during 1st cycle are displayed in Fig.5. It should be mentioned that a moderate amount of carbon coating will enhance the discharge capacities of $Li[Li_{0.29}Mn_{0.57}Co_{0.14}]O_2$. As shown, the $Li[Li_{0.29}Mn_{0.57}Co_{0.14}]O_2$ materials modified by 5wt% and 10wt% glucose show higher first discharge capacities than the bare one. However, the samples with more glucose present a little decreases in discharge capacities. Considering the same composition of parent cathode materials, the above variations in the capacities could be attributed to the effects of carbon coating. Therefore, a proper amount of carbon will be important for determining the discharge capacities of the samples.

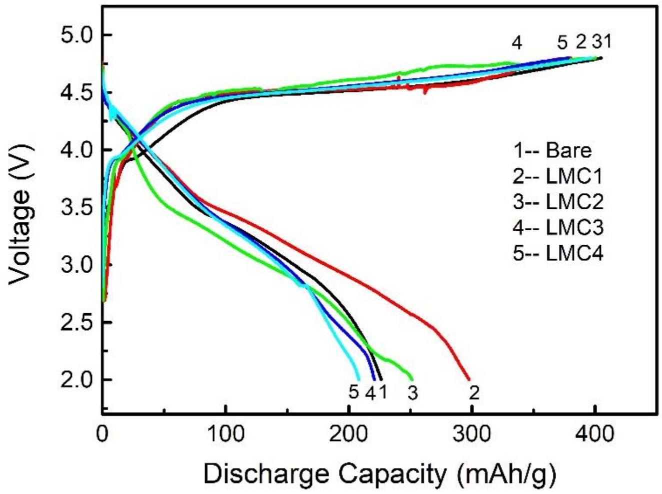

Figure 5. Initial charge and discharge curves of the bare, LMC1, LMC2, LMC3 and LMC4 samples at 5 mA/g

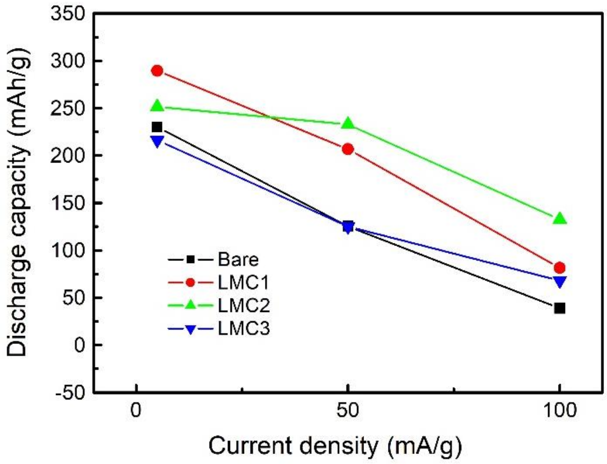

Figure 6. Initial discharge capacities of the bare, LMC1, LMC2 and LMC3 samples at different current densities

Fig.6 compares the initial discharge capacities of the bare and coated $Li[Li_{0.29}Mn_{0.57}Co_{0.14}]O_2$ materials at different current densities between 2.0–4.8 V. As shown, an increase in current density will result in a deterioration of the discharge capacities for all samples. However, at a given current density, the samples with an appropriate amount of carbon show superior discharge capacities compared to the bare sample. The bare one exhibits the discharge capacities of 125.4 mAh/g under 50 mA/g and 38.7 mAh/g at 100 mA/g in 1st cycle, which are only 54.5% and 16.9% of the first discharge capacity under 5 mA/g, respectively. Nevertheless, the initial discharge capacities of LMC1, LMC2 and LMC3 are 206.7, 232.9 and 125 mAh/g at 50 mA/g, respectively, the capacity decay corresponding to 28.6%, 7.3% and 42.2% of the individual first discharge capacity at 5 mA/g. In addition, the initial discharge capacities of LMC1, LMC2 and LMC3 at 100 mA/g are 81.5, 132.5 and 68.1 mAh/g, respectively, which are 28.1%, 52.7% and 31.4% of the individual first discharge capacity at 5 mA/g. Especially, the sample modified by 10 wt% glucose exhibits the best rate performance, which can bring about the increase of first discharge capacities by 85.7% and 241.5% than the sample without carbon coating at the current densities of 50 mA/g and 100 mA/g, respectively. Compared with the reported Mn-based Li-rich materials in some previous work, the carbon coated sample in this work shows higher initial discharge capacity at 50 mA/g (shown in Table 1), suggesting carbon coating in air is a promising way to improve the electrochemical performances of Mn-based Li-rich materials.

Table 1. The discharge capacities of the sample in this work and some reported Mn-based Li-rich materials

Cathode materials	Discharge capacity (mAh/g)	Voltage (V)	Current Density (mA/g)	Ref.
$LiMnO_2/Li_2MnO_3$	134.4	2.0-4.5	50	23
Li_2MnO_3-$LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$	215	2.0-4.8	50	24
Li_2MnO_3-$LiMn_{0.42}Ni_{0.42}Co_{0.16}O_2$	184	2.0-4.6	50	25
Li_2MnO_3/TiO_2	185.13	2.0-4.8	50	26
Li_2MnO_3-$LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$	210	2.0-4.6	50	27
$Li_{1.2}Ni_{0.12}Co_{0.12}Mn_{0.56}O_2$	187.2	2.0-4.8	50	28
$Li[Li_{0.29}Mn_{0.57}Co_{0.14}]O_2/C$ (LCM2)	232.9	2.0-4.8	50	This work

Fig. 7 shows the cycle performances of the bare and LMC2 samples at 5mA/g between 2.0-4.8 V. All samples show discharge capacity reductions with cycling, which might result from the structural variation of this kind of materials and serious parasitic reactions between cathode and electrolyte at 4.8 V[29-34]. Only 67.9% discharge capacity is remained at 30th cycle for the bare sample. However, for modified sample, the capacity retention can maintain at 74.5% after 30 cycles. The results show that enhanced capacity fading could be achieved by carbon coating.

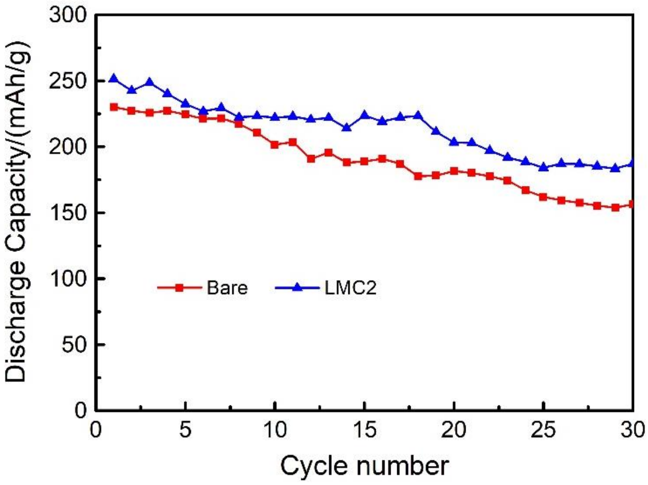

Figure 7. Cycle performances of the bare and LMC2 samples at 5mA/g

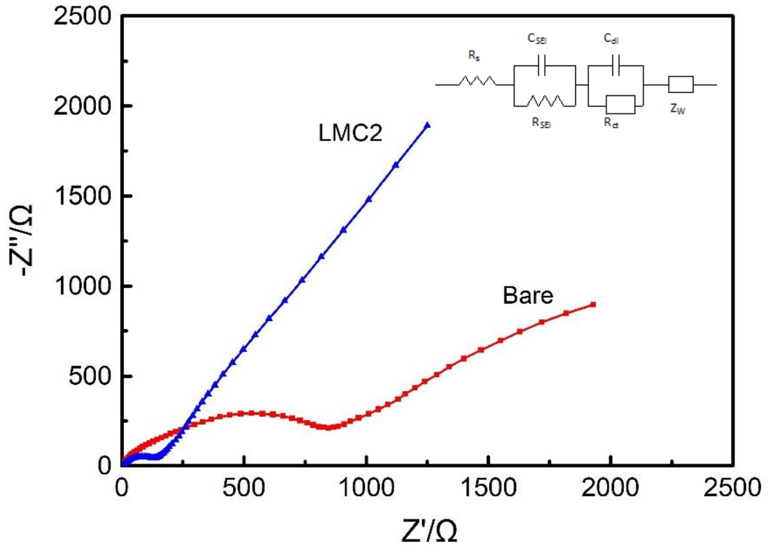

Figure 8. EIS of the bare and LMC2 samples. Inset: the equivalent circuit

Fig. 8 presents the EIS patterns of the bare and LMC2 samples after 30 cycles. The equivalent circuit (see the inset of Fig. 8) was used to simulate the EIS curves, in which R_s , R_{SEI} and R_{ct} stand for the ohmic resistance, solid electrolyte interphase resistance and charge transfer resistance, respectively. The fitted values of these parameters are listed in Table 2. As shown in Table 2, R_s values are almost same and negligible for bare and carbon coated samples. Compared with the bare sample, carbon coated sample exhibits a significant reduction in R_{SEI} and R_{ct}. The drop of R_{ct} and R_{SEI} signifies that a proper amount of carbon coating will be advantageous to overcome kinetic limit and extract/insert more Li^+ of cathode materials upon cycling, thus benefit for the rate capability and the specific capacity. Therefore, carbon coating will be favorable for electrochemical performance of $Li[Li_{0.29}Mn_{0.57}Co_{0.14}]O_2$ materials during cycling at higher rate.

Table 2. Calculated impedance parameters based on Figure 8

Samples	R_S(Ω)	R_{SEI}(Ω)	R_{ct}(Ω)
Bare	5.5	234.8	1146
LMC2	4.3	16.9	168.8

4. CONCLUSIONS

Carbon-coated $Li[Li_{0.29}Mn_{0.57}Co_{0.14}]O_2$ materials were obtained via glucose pyrolysis at 400°C in air. The carbon coating did not degrade the phase structure of $Li[Li_{0.29}Mn_{0.57}Co_{0.14}]O_2$. Electrochemical tests verified that the improved discharge capacities, rate capability and cyclability of $Li[Li_{0.29}Mn_{0.57}Co_{0.14}]O_2$ can be achieved by carbon coating. The enhanced electrochemical performances can put down to the decline of the charge transfer resistance and solid electrolyte interphase resistance.

Carbon coating by glucose pyrolysis under air hence could be taken as a potential strategy to promote the electrochemical performances of Mn-based Li-rich cathode materials.

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