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1. Introduction

To meet the increasing demanding requirements for the storage and utilization of clean energy, Li-ion batteries have been proposed for their lower cost, higher capacity, faster charging/ discharging rate, longer cycling life, and better environmental benignancy.¹⁻⁵ However, the presently dominant cathode material LiCoO₂ has a reversible capacity of 140 mA h g⁻¹, only 50% of the theoretical capacity, as limited by its structural stability.⁶⁻⁸ This low capacity cannot meet the high energy requirements for practical applications. Another demerit is the use of cobalt, an expensive and toxic element. Therefore, there is immense interest in developing alternative cathode materials. In this regard, layered structure LiNi_xCo_yMn_zO₂ (x + y + z =1),⁹⁻¹³ olivine LiFePO₄,¹⁴⁻¹⁷ and spinel LiMn₂O₄^{18,19} are the alternatives with the dual advantages of lower cost and toxicity.

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Gel-combustion synthesis of Li_{1.2}Mn_{0.4}Co_{0.4}O₂ composites with a high capacity and superior rate capability for lithium-ion batteries

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Owing to the merits of high capacity and low cost, Li-rich layered composite cathode materials have received extensive attention. Nevertheless, such materials always suffer from a poor rate capability, which seriously hinders their widespread practical applications. In this work, Li12Mn0.4Co0.4O2 composites were fabricated by a gel-combustion method, in which lithium carbonates formed by an in situ burning reaction were homogeneously mixed with metal oxides, leading to excellent electrochemical properties. The sintering temperature and time were optimized to 900 °C and 15 h. The samples prepared at optimum conditions exhibited a high discharge capacity and excellent rate capability. At a current density of 20 mA q^{-1} , the specific discharge capacity was 310.5 mA h q^{-1} for the first cycle and the capacity retention was 75.8% after 30 cycles. When the current densities increase by 10 times to reach 200 mA q^{-1} , the initial discharge capacity is still as high as 241.4 mA h q^{-1} , superior to that of 203 mA h g^{-1} at the same current density reported previously by the oxalate-precursor method. Even when the current densities increase by 20 times, the capacity remained as high as 203.7 mA h g^{-1} , and the capacity retention was 79.4% over 30 cycles. The high discharge capacity and improved rate capability of the optimized sample were beneficial with a perfect layered structure with c/a > 5.0, appropriate particle size of about 450 nm, high lithium ion diffusion coefficient around 1.42×10^{-13} cm² s^{-1} , and the presence of a maximum content of Mn³⁺ (11.6%), as determined by XPS. The preparation method reported herein may provide hints for obtaining various advanced Li-rich layered composite materials for use in high-performance energy storage and conversion devices.

Nevertheless, these materials have to face the challenge of greatly increasing their capacities.

Structurally integrated Li_2MnO_3 -LiMO₂ (M = Mn, Ni, Co) composites could provide high reversible capacities > 250 mA h g^{-1} and a relatively lower cost than LiCoO₂, and therefore have been regarded as very promising cathode materials.²⁰ However, the introduction of an insulating Li₂MnO₃ component in the composites with low electronic conductivity always causes inferior rate capability,^{21,22} which hinders their practical applications. To enhance the rate capability, great efforts have been carried over the past years, which include: (i) the partial substitution of foreign atoms, such as Cr, Mo, Mg, Al, Ga or Ti,²³⁻²⁶ which improves the structure stability and cycle and rate performance. However, introducing guest atoms into the crystal lattices of the Li-rich layered composite materials may also cause a lowering of capacity, because dopants are usually electrochemically inactive; (ii) surface coating with metal oxides (Al₂O₃),²⁷ phosphates (AlPO₄),²⁸ or carbon materials²⁹ which could improve the stability of electrodes and prevent dissolution of Mn and side reactions at the electrode/electrolyte interface, thus improving the rate capability. However, to achieve perfect surface coatings is often extremely difficult. Owing to the significant relationship between the electrochemical

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performance and synthetic method, an optimized synthetic method perhaps is a better and more direct route to promote rate performance.

Current preparation methods to prepare the composites are usually based on mixed hydroxide or carbonate co-precipitation with lithium sources, which can result in micron-sized large spherical aggregates, and thus impede Li-ion transport.³⁰ On the other hand, when using these conventional methods, raw materials cannot mix uniformly at a molecular level. Particularly, some unwanted metal-ions (*e.g.* Na⁺) are inevitably introduced.^{31,32} All these may give rise to disadvantages in enhancing the rate performance.

In this work, we employed a novel gel-combustion method and prepared Li-rich $\text{Li}_{1.2}\text{Mn}_{0.4}\text{Co}_{0.4}\text{O}_2$ composites. During the synthesis, precursors of lithium, manganese and cobalt were mixed uniformly. The resulting $\text{Li}_{1.2}\text{Mn}_{0.4}\text{Co}_{0.4}\text{O}_2$ composites showed a high capacity and superior rate capability. The methodology reported here may provide hints to obtain various advanced Li-rich composites for use in high-performance energy storage and conversion devices.

2. Experimental section

2.1. Sample syntheses

Li_{1.2}Mn_{0.4}Co_{0.4}O₂ composites were synthesized using a mannitol assisted gel-combustion method. The preparation procedure can be briefly described as follows: firstly, 27.6 mmol CH₃COOLi · 2H₂O (15%) excess lithium), 8 mmol Mn(CH₃COO)₂·4H₂O, and 8 mmol Co(CH₃COO)₂·4H₂O were dissolved in 100 mL water. Secondly, 100 mL of 0.2 M mannitol solution was dropped into the above mentioned metal acetate solution under stirring. Thirdly, the pH of the mixed solution was adjusted to 2 using concentrated nitric acid to form a red transparent sol. Then, the obtained sol was evaporated overnight to dryness at 80 °C and was heated up to burn spontaneously with a flame to form a brown ash. Finally, the brown ash was sintered at 700, 800, 900, and 1000 °C for 15 h, respectively, and then guenched to room temperature. The final products were named as T700, T800, T900, and T1000, respectively. The calcinations for different periods of time, such as 5, 10, and 20 h (named as H5, H10, and H20) at 900 °C were also conducted to optimize the electrochemical performance. The synthesis process is depicted in Fig. 1. In addition, for convenience of the discussion, T900 was also named as H15.

2.2. Sample characterization

The phase structure and purity of the samples were characterized by powder X-ray diffraction (XRD) on a Rigaku Miniflex apparatus (Cu K α , $\lambda = 1.5418$ Å). Lattice parameters of the samples were calculated by Rietveld refinement using GSAS software.³³ KCl powder serves as an internal standard for peak positions calibration. The particle sizes and morphologies of the samples were observed by field-emission scanning electron microscopy (SEM) (JEOL, model JSM-6700). Chemical compositions of the samples were quantitatively determined using inductively coupled plasma atomic emission spectrometry (ICP-AES). Thermo-gravimetric (TG) analysis and differential thermal analysis (DTA) were carried out on a Netzsch Model STA449F3 thermal analyzer at a heating rate of 10 °C min⁻¹ in flowing air from room temperature to 1200 °C. The valence states of transition metal ions in the samples were determined by X-ray photoelectron spectroscopy (XPS) on an ESCA-LAB MKII apparatus performed with a monochromatic Al Ka X-ray source. During XPS measurements, the base pressure of the sample chamber was kept below 3.0×10^{-10} Mbar. Emission lines were calibrated with the C1s signal at 284.6 eV.

2.3. Electrochemical measurements

The electrochemical behaviour of the samples was examined using a CR-2025-type coin cell. The cells were composed of a cathode and a lithium foil anode separated by a polymer separator (Celgard 2320). The cathode film was fabricated from a mixture of the synthesized samples, carbon black (Super P Li, Timcal) and binder (polyvinylidene fluoride (PVDF), Alfa Aesar) in a weight ratio of 8:1:1 using N-methyl pyrrolidinone (NMP, Alfa Aesar) as the solution. The resulting slurry was coated on Al foil by a doctor blade technique and dried at 100 °C for 10 h. The cells were assembled in an argon-filled glove box (H_2O and $O_2 <$ 1 ppm) using 1 M LiPF₆ in EC : EMC : DMC (1:1:1 in volume)as the electrolyte. The cells were charged and discharged galvanostatically at different current densities using a battery cycler (Neware Test System) in the voltage range of 2.0 and 4.6 V at room temperature. The electrochemical impedance spectroscopy (EIS) was measured using an electrochemical workstation (CHI660C) and the applied frequency was from 100 kHz to 10 mHz.

3. Results and discussion

3.1. Gel-combustion synthesis of the $Li_{1.2}Mn_{0.4}Co_{0.4}O_2$ composites

Until now, layered Li-rich composites have been mainly prepared by a conventional co-precipitation method, in which hydroxides or carbonates precursors are not easily homogeneously mixed with lithium sources. As a result, micron-sized spherical aggregates are always obtained, which would impede Li-ion transport. In this work, we designed a novel mannitol assisted gel-combustion method with an aim to overcome the drawbacks of the conventional preparation methods.

Fig. 1 illustrates the synthetic process we have newly designed for Li_{1.2}Mn_{0.4}Co_{0.4}O₂ composites. During the synthesis process, mannitol plays dual important roles: (i) as a complexing agent. The metal ions coordinated with the hydroxyl of mannitol may make the solution form a sol and ensure the uniform mixing of the metal ions at a molecular level. (ii) As a combustion agent. Heat from the redox reaction of mannitol and nitrate may make the gel flame. As shown in Fig. 2a, the brown ash precursors obtained after combustion at 200 °C are composed of lithium carbonate (Li₂CO₃) and oxides of manganese and cobalt. Thus, Li₂CO₃ obtained during the in situ burning reactions could be uniformly mixed with metal oxides. which is beneficial for achieving excellent



Fig. 1 Illustration of the preparation process of the $Li_{1,2}Mn_{0,4}Co_{0,4}O_2$ cathode material by the gel-combustion method



Fig. 2 (a) XRD pattern and (b) TG and DTA curves of the brown ash precursor obtained from burning the gel.

electrochemical properties. Our previous work³⁴ has reported that gas CO₂ would be released when Li₂CO₃ reacts with transition metal oxides to form the layered materials. The released gas (CO₂) reduces the oxygen partial pressure near the reactants and results in the presence of Mn^{3+} in Li₂MnO_{3- δ}. The presence of Mn^{3+} ions in the lithium-rich composites could improve the electronic conductivity and furthermore the electrochemical

performance.^{30,34-36} Therefore, using the synthetic process designed in this work it is possible to achieve optimized materials with superior electrochemical performance.

3.2. Optimized preparation conditions: impact of sintering temperature

To optimize the sintering temperature, the TG and DTA of the brown ash precursor were examined, as indicated in Fig. 2b. The TG data showed that the mass loss process underwent three steps. In the first one, a continuous mass loss occurred below 200 °C, which could be assigned to the evaporation of water. The second one involved a rapid weight loss from 230 to 500 °C, accompanied by an exothermic peak on the DTA curve, indicating the formation of a layered phase above 500 °C. The third one is characterized by a continuous slow mass loss from 500 to 1200 °C, which could be ascribed to the decomposition of Li₂CO₃ in the layered-phase formation process and a small amount of evaporation of lithium. Therefore, we sintered the precursors at 700, 800, 900, and 1000 °C, respectively, to optimize the synthetic conditions.

In order to make clear the components of the obtained samples at different temperatures, ICP-AES measurements were conducted, as listed in Table 1. One can see that the molar ratios of Li : Mn : Co were closer to the initial molar ratios.

The impacts of the sintering temperature on the structures of the samples were monitored by XRD, as shown in Fig. 3. The strong diffraction peaks were all indexed well in a hexagonal α -NaFeO₂ structure with the *R*-3*m* space group of layered LiCoO₂, while weak peaks attached onto the strong (003) peak at $2\theta = 20-25^{\circ}$ are indicative of the existence of the monoclinic Li₂MnO₃ phase (*C*2/*m*) with a cation ordering between Li and

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Table 1 E	Experimentally	determined of	compositions o	f the samples and	lattice parameters	of the layered LiCoC	₂ component in t	he samples
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Samples	Experimental metal-ion molar ratios			Lattice parameters			
	Li	Mn	Со	a (Å)	<i>c</i> (Å)	c/a	$V(Å^3)$
T700	1.167	0.411	0.421	2.8376(1)	14.159(1)	4.9897	98.73(1)
T800	1.173	0.416	0.411	2.8361(1)	14.1658(8)	4.9948	98.676(6)
T900	1.141	0.420	0.440	2.83081(7)	14.1663(7)	5.0043	98.312(7)
T1000	1.143	0.421	0.436	2.82869(6)	14.1656(5)	5.0078	98.161(5)



Fig. 3 XRD patterns of the samples synthesized at different sintering temperatures. Black asterisks (*) denote the internal standard KCl.

the transition metal layer.^{37–40} For sample T700, weak peaks around the two theta of 32° are assigned to the residual Li₂CO₃. With increasing the sintering temperature, the splitting of the pair reflections (006)/(012) and (018)/(110) became more obvious, indicating the improvement of the layered structure.^{41,42}

Lattice parameters of the layered LiCoO_2 for the samples were determined using GSAS software,³³ as exhibited in Table 1. It is well documented that the axis ratio of c/a is an indicator of the hexagonal ordering.⁴³ That is, the larger c/a, the better the hexagonal ordering. In this regard, the axis ratio c/a was taken as an important structural parameter to examine the impacts of the sintering temperature on the lithium de-intercalation in the lattice of the samples. As shown in Table 1, as the temperature increased from 700 to 1000 °C, the axis ratio of c/a gradually increased from 4.9897 to 5.0078, which also indicates that the layered structure was improved by elevating the temperature. Meanwhile, the intensities of the diffraction peaks increased, and their full width at half-maximum (FWHM) of the reflection peaks decreased, demonstrating the better crystallinity and the larger particle sizes. Therefore, the as-prepared samples have high crystallinity, good hexagonal ordering, and improved layered characteristics. In short, $\rm Li_{1.2}Mn_{0.4}Co_{0.4}O_2$ with an improved layered structure was successfully synthesized by the current gel-combustion method.

Fig. 4 displays the typical morphologies and particle size distributions taken by SEM for the samples sintered at 700–1000 $^{\circ}$ C. It is seen that the particle sizes and particle size distributions exhibited huge differences for all of the samples. Samples T700 and T800 showed nearly the same particle size, mainly distributed around 250 nm. Sample T900 synthesized at



Fig. 4 SEM images and particle size distributions of the samples prepared at different temperatures: (a and b) T700, (c and d) T800, (e and f) T900, and (g and h) T1000.

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900 °C had a slightly bigger particle size, and the mean particle size was about 450 nm. Moreover, it has a smooth surface, which indicates good crystallization. When the sintering temperature increased to 1000 °C, the particles grew into blocks with a size distribution in the range of 1–3.5 μ m, as shown in Fig. 4h. These results are compatible with the XRD analyses. It is thus concluded that the sintering temperature has a great influence on particle size, and that a high sintering temperature is beneficial for the formation of bigger particle sizes.

The electrochemical performances for the samples sintered at different temperatures are compared in Fig. 5. Fig. 5a depicts the initial charge and discharge curves between 2.0 and 4.6 V for the $Li_{1,2}Mn_{0,4}Co_{0,4}O_2$ at a current density of 20 mA g⁻¹. One can see two charging regions corresponding to different electrochemical reactions. The first region is ascribed to the oxidation of cobalt ions from Co^{3+} to Co^{4+} in the voltage region of 3.8 to 4.4 V, while the subsequent plateau region is assigned to the irreversible removal of Li₂O from the electrode.⁴⁴⁻⁴⁶ The capacity of the sloping region for the samples prepared at different temperatures is almost the same. However, there is a big difference for the plateau region that comes from the activation of Li₂MnO₃. With increasing the sintering temperature from 700 to 900 °C, the length of the plateau region gradually increased, and the sample T900 exhibited the longest length, which reached up to about 300 mA h g^{-1} . Meanwhile, the discharge capacities gradually increased from 151.3, 208.6, to 310.5 mA h g^{-1} , and the coulomb efficiency also gradually increased from 54.7, 58.3, to 75.8%. These results indicate that



Fig. 5 (a) Initial charge–discharge curves and (b) cycle performance at a current of 20 mA g^{-1} between 2.0 and 4.6 V for the samples synthesized at 700, 800, 900, and 1000 °C.

the elevated sintering temperature is beneficial for activating the Li_2MnO_3 component and achieving a higher discharge capacity. The reasons for this observation may be attributed to the improved crystallinity, better layer structure, and increased particle size. However, when the sintering temperature further increased to 1000 °C, the electrochemical performance began to decrease. The length of the plateau region, the discharge capacity, and coulomb efficiency were only about 180 mA h g⁻¹, 155.4 mA h g⁻¹, and 55.2%, respectively. These results may be due to the oversized particles (about 2 μ m), which result in longer lithium intercalation and de-intercalation paths.

The cycle performance of the samples sintered at different temperatures was further compared, as indicated in Fig. 5b. For samples T700 and T800, the discharge capacities quickly decreased with an increase in the cycle number. After 30 galvanostatic charge-discharge cycles, the discharge capacities were only 57.6 and 106.2 mA h g^{-1} , respectively. For sample T900, the discharge capacity was still up to 234.1 mA h g^{-1} , and maintained 75.4% of its initial capacity. The sample T1000 exhibited a relatively high cycle capability, but with a lower discharge capacity. It is thus obvious that the sample T900 displayed the most excellent electrochemical performance among all of the samples. Apparently, the sintering temperature dependence of the electrochemical performance observed in this work is totally different from that previously reported for Li_{1.2}Mn_{0.54}Co_{0.13}Ni_{0.13}O₂ composites by Croguennec et al.⁴⁷ For the latter case, the sintering temperatures are announced to have less impact on the electrochemical performance of the composites Li_{1.2}Mn_{0.54}Co_{0.13}Ni_{0.13}O₂. Therefore, the chemical compositions and choice of chelating agent (like organic acid or alcohol) could alter the burning temperatures of the precursors and also the microstructure and properties of the desired samples (e.g., particle size, valence state of the transition metals, lattice parameters, and electrochemical performance).

The results mentioned above reveal that the sintering temperature could be used to greatly tune the crystallinity, structure, particle size of the composites, and the length of the plateau region in the first charging process. A low sintering temperature gives rise to smaller particle sizes, but lower crystallinity and poor layered structures, leading to a poor cycle performance and lower discharge capacity. Higher sintering temperatures result in higher crystallinity, a better layered structure, but larger particle size, also leading to poor electrochemical performance. Apparently, 900 °C is the optimal sintering temperature. Therefore, in the following, all of the samples were prepared at 900 °C with different periods of time to obtain the optimum electrochemical performance.

3.3. Optimized preparation conditions: impact of sintering time

3.3.1. Electrochemical performance of the samples prepared with different sintering times. Fig. 6a shows the initial charge–discharge curves of the samples prepared at 900 °C for 5, 10, 15, and 20 h at a current density of 20 mA g^{-1} in a voltage window of 2.0–4.6 V at room temperature. Upon the first charge to 4.6 V, the electrochemical reaction of lithium with the



Fig. 6 (a) Initial charge–discharge curves and (b) cycling performance at a current density of 20 mA g^{-1} in a voltage range from 2.0 to 4.6 V for the samples synthesized at different sintering times at 900 °C.

Li_{1.2}Mn_{0.4}Co_{0.4}O₂ electrode occurs in two distinct steps as follows: the first step occurs at a voltage of <4.4 V vs. Li/Li⁺, which corresponds to the lithium extraction from LiCoO₂ component with the concomitant oxidation of Co³⁺ to Co⁴⁺. The second step corresponds to the removal of lithium from the Li₂MnO₃ component accompanied by oxygen evolution when charged above 4.4 V vs. Li/Li⁺. During the oxygen loss plateau, the Li₂MnO₃ component was activated to form the MnO₂-like component⁴⁴⁻⁴⁶ and thus the material could deliver a high discharge capacity during the subsequent discharge process.

As indicated in Fig. 6a, the obtained samples H5, H10, H15, and H20 cathodes delivered discharge capacities of 230.1, 271.9, 310.5, and 199.6 mA h g⁻¹, respectively, with an initial coulombic efficiency of 64.9%, 69.7%, 75.8%, and 51.6%, calculated from the first charge–discharge capacity values at a specific current density of 20 mA g⁻¹. The discharge capacity of the sample H15 is higher than the previous reports.^{31,48,49} It is clear that, when compared to the samples H5 and H10, the sample H15 sintered at 900 °C for 15 h had a larger charge plateau above 4.4 V and further exhibited a relatively high discharge capacity. This observation indicates that a longer sintering time is beneficial for activation of the Li₂MnO₃ component. But when the sintering time increased to 20 h, the length of charge plateau above 4.4 V began to decline, and the coulombic efficiency was the lowest among all of the samples.

Fig. 6b compares the cycling performance of all of the samples between 2.0 and 4.6 V at a current density of 20 mA g^{-1} . It is clear that the discharge capacities of the 30 cycles gradually increased with the sintering time from 5 to 15 h. When the

sintering time increased to 20 h, the discharge capacities were the lowest among all of the samples. That is to say that the sample H15 has the best capacity performance. After 30 cycles, the discharge capacities and capacity retention ratio of the sample H5 were 143.6 mA h g^{-1} and 60.7%, while those of the sample H10 were 211.9 mA h g^{-1} and 77.9%. For sample H15, after 20 cycles, the discharge capacity of the Li_{1.2}Mn_{0.4}Co_{0.4}O₂ electrode reached up to 250.4 mA h g^{-1} , larger than the retained capacity of 195 and 235 mA h g^{-1} , respectively, reported previously.^{31,48} Moreover, after 30 cycles, the discharge capacity still remained at 234.1 mA h g^{-1} , and the capacity retention ratio was 75.4%. In addition, the discharge capacities and capacity retention ratio of sample H20 was 109.8 mA h g^{-1} and 55%. It is obvious that the sintering time has a huge influence on the cycling and capacity performance.

In order to investigate the electrochemical performance of the samples H5, H10, H15, and H20 at high current densities, the charge and discharge profiles were conducted at room temperature in a voltage range between 2.0 and 4.6 V. The first charge–discharge curves of all the samples at different current densities are exhibited in Fig. 7. As mentioned above, all the charge curves consisted of a sloping region and a plateau region at approximately 3.8–4.4 V and 4.4–4.6 V, respectively. Both voltage plateaus shifted towards higher potentials with an increase in the current densities for all of the samples, This indicates that the polarization in the electrodes increased with the increasing current densities, which may be associated with the poor conductivity of the lithium-rich composites.^{21,22}

In addition, with increasing the current density from 60 to 400 mA g^{-1} , the discharge capacities of all of the samples decreased. As seen from Fig. 7a, the discharge capacity for sample H5 decreased from 229.7 to 140.7 mA h g^{-1} . The discharge capacities of the sample H10 were 227.4, 218.3, 189.4, and 194.7 mA h g^{-1} , respectively, at current densities of 60, 100, 200, and 400 mA g^{-1} , (Fig. 7b). These discharge capacities are the second largest. Sample H15 exhibited the largest discharge capacity among all four of the samples. The first discharge capacities were 258.1, 245.7, 241.4, and 203.7 mA h g^{-1} at current densities of 60, 100, 200, and 400 mA g⁻¹, respectively. In our previous work,³¹ the Li_{1.2}Mn_{0.4}Co_{0.4}O₂ composite prepared by an oxalate-precursor method exhibited a first discharge capacity of 203 mA h g^{-1} at a current density of 200 mA g^{-1} . By the current gel-combustion method, the first discharge capacity was increased to 241.4 mA g^{-1} at the same current density. Both values are higher than the reference reports.48 However, with the sintering time increased to 20 h, the discharge capacities of the sample H20 shown in Fig. 7d were only 159.1, 142.6, 130.8, and 109.7 mA h g^{-1} , respectively. The results indicate that sample H15 had a fairly high discharge capacity at high current densities and superior rate performance.

The cycle and rate performance of the samples H5, H10, H15, and H20 at high current densities were also investigated, as shown in Fig. 8. At the same current density of 60 mA g^{-1} , the discharge capacities were 167.3, 202.3, 190.6, and 138.3 mA h g^{-1} after 30 cycles, for sample H5, H10, H15 and H20, and their corresponding capacity retention ratios relative to the highest



Fig. 7 Initial charge-discharge curves at different currents between 2.0 and 4.6 V for the samples: (a) H5, (b) H10, (c) H15, and (d) H20 synthesized using different times at 900 $^{\circ}$ C.

capacity among 30 cycles were 83.4%, 85.4%, 73.8%, and 80.6%, respectively. When the current densities increased to 200 mA g^{-1} , the discharge capacities of all of the samples were 140.0, 177.6, 204.1, and 125.3 mA h g^{-1} with the capacity retention

ratio of 84.7%, 87.4%, 82.7%, and 85.6%, respectively. Furthermore, when the current densities increased to 400 mA g^{-1} , the discharge capacities of all of the samples still remained as 123.0, 168.1, 173.0, and 100.8 mA h g^{-1} , with the



Fig. 8 Cycle performance of the samples: (a) H5, (b) H10, (c) H15, and (d) H20 at current densities of 60, 100, 200, and 400 mA g⁻¹.

capacity retention ratios of 83.7%, 83.8%, 79.4%, and 83.4%, respectively. It can be seen from these results that sample H10 has the best cycling performance among all of the samples. Compared to the samples H5, H10, and H20, the sample H15 has a superior rate capability, as evidenced by an almost overlapping of the curves of the discharge capacity *vs.* the cycle number curves. All of this demonstrates that sample H15 exhibited an optimum electrochemical performance, as represented by having the largest capacity, best rate capability and relatively high cycling performance.

In short, with prolonging the sintering time, the electrochemical performances of the composites started to show an optimum. When the sintering time was prolonged from 5 to 15 h, the electrochemical performance of the composites exhibited a huge difference. Sample H5 had a low discharge capacity at different current densities, and sample H10 showed the best cycle performance, while sample H15 had the highest discharge capacity, the best rate performance, and relatively high cycle performance. When the sintering time was extended to 20 h, the electrochemical performances began to decrease to show the lowest among all of the samples.

Then, an important question appears: what are the primary reasons for the variations of electrochemical performance with sintering time? To answer this question, several factors that may contribute to the electrochemical performance, such as chemical composition and structure, particle size, electrochemical redox reactions, reaction kinetics and diffusion coefficient of the lithium ion have to be taken into account.

3.3.2. Reasons for the differences in the electrochemical **performance.** In order to understand the differences of the electrochemical performance among the samples H5, H10, H15, and H20, the phase structure analyzed by XRD refinement using GSAS software, particle size estimated by SEM, electrochemical redox potential determined from differential capacity *vs.* voltage (dQ/dV) curves, as well as the diffusion coefficient of lithium ion based on electrochemical impedance spectroscopy (EIS) were systematically examined.

Due to the importance of the relationship between the structure and electrochemical performance of the electrode materials for lithium batteries, it is necessary to firstly understand the structure of the Li_{1,2}Mn_{0,4}Co_{0,4}O₂ composites. Fig. 9 shows XRD patterns of the samples sintered at 900 °C for 5, 10, 15, and 20 h. These patterns showed similar characteristics to those at different temperatures in Fig. 3, which indicates the formation of Li₂MnO₃ and LiCoO₂ composites. Through XRD refinement using GSAS software,33 lattice parameters for the layered R-3m structures were obtained, as shown in Table 2. The data showed that the values of *a* and *c* decreased, while the axis ratio of c/a was not obviously changed with increasing the sintering-time. Moreover, the values of c/a for all of the samples are greater than 5.0,^{31,43} indicating that all of the samples had a good layered structure. Therefore, the structure factor can be dismissed. The chemical compositions for all of the samples were detected by the ICP-AES technique. As shown in Table 2, the molar ratios of Li and Mn to Co were closer to each other within an error range, approaching the designed ratios. Hence, the influence of the chemical compositions were also neglected.



Fig. 9 XRD patterns of the samples synthesized using different times (5, 10, 15, and 20 h) at 900 $^{\circ}$ C. Black asterisk symbol (*) denotes the internal standard of KCl.

The particle size of the cathode materials may impact on the electrochemical performance. As the particle size decreases, the transport path of the lithium ion becomes shorter, which can improve the kinetic properties of the electrodes to some extent, leading to a higher rate capability.¹¹ Fig. 10 shows the morphologies and particle size distributions obtained by SEM observations on samples prepared at 900 °C for 5, 10, 15, and 20 h. It is seen that the constituent particles for all of the samples were approximately round and obviously aggregated. As the sintering time increased, the particle sizes and particle size distributions for the samples H5, H10, and H15 was closer, and their mean particle sizes were 390, 430, and 450 nm, respectively. However, when the sintering time increased to 20 h, the sample H20 had a bigger particle size, and its mean particle size was increased up to 830 nm. These observations suggest that the particle size effect on the electrochemical performance for samples H5, H10, and H15 could be ignored, while the biggest particle size for sample H20 among all the samples should be the primary reason for its worse electrochemical performance.

To recognize the electrochemical redox reactions which might occur during the charge and discharge processes, differential capacity curves (dQ/dV vs. V) of different cycles for all of the samples sintered at different times were plotted, as shown in Fig. 11. In the first cycle, the oxidation peaks at 3.9–4.0 V are attributed to the oxidation from Co³⁺ to Co^{3.6+}, and that at about 4.36 V is assigned to the oxidation process of Co^{3.6+}/Co⁴⁺, which is consistent with the sloping region in the

Samples	Experimental metal-ion molar ratios			Lattice parameters			
	Li	Mn	Со	<i>a</i> (Å)	<i>c</i> (Å)	c/a	$V\left(\mathring{A}^{3} ight)$
H5	1.152	0.424	0.425	2.83802(6)	14.2078(5)	5.0062	99.103(5)
H10	1.159	0.419	0.421	2.83525(7)	14.1849(7)	5.0031	98.751(6)
H15	1.141	0.420	0.440	2.83081(7)	14.1663(7)	5.0043	98.312(7)
H20	1.163	0.414	0.423	2.83021(7)	14.1629(6)	5.0042	98.247(5)

Table 2Experimentally determined compositions for the samples H5, H10, H15, and H20, and lattice parameters of the layered $LiCoO_2$ component in the $Li_{1.2}Mn_{0.4}Co_{0.4}O_2$ composites for samples H5, H10, H15, and H20



Fig. 10 SEM images and particle size distributions of the samples: (a and b) H5, (c and d) H10, (e and f) H15, (g and h) H20 prepared using different times at 900 $^{\circ}$ C.

first charge curve.^{31,44,45,50,51} The corresponding reduction peak of Co^{4+} to Co^{3+} is also observed at 3.9 V in the discharge process. The whole redox couple shows that the reaction of $\text{Co}^{3+}/\text{Co}^{4+}$ is reversible. Among the four samples, the peaks derived from the redox couple of $\text{Co}^{3+}/\text{Co}^{4+}$ for sample H5 is sharper than those of the other samples, which indicates that the contribution to the total capacity from LiCoO₂ component for sample H5 is greater than others. The very strong peak observed at 4.45– 4.47 V for all of the four samples matched with the voltage

plateau above 4.4 V which predominantly corresponds to the highly irreversible activation process of stripping Li₂O off the Li₂MnO₃ component and forming an active MnO₂-like component.44-46 Because of the irreversibility of the activation reaction, no corresponding reduction peak was observed in the initial discharge process, but it induces a new peak at 3.43-3.47 V, which stems from the reduction reaction of Mn⁴⁺ to Mn³⁺.^{31,49} In the second cycle, peaks at about 4.6 V were observed for samples H5 and H10, which stem from the further activation process of the residual Li₂MnO₃ component. With the cycles increasing, two new conspicuous oxidation peaks were observed around 3.02/3.04 and 3.29/3.28 V in the charging process for samples H10 and H15. Both two oxidation peaks can be ascribed to the Li⁺ de-intercalation from the spinel-like structure (in 3.02/3.04 V region) and layered LiMnO₂ structure (in 3.29/3.28 V region), respectively.31 Their corresponding reduction peaks appeared at around 2.86 and 3.0 V. Furthermore, when compared to the sample H10, these two redox couples are more obvious for the sample H15. Comparing to sample H5 that only showed one new conspicuous oxidation peaks around 3.05 V, there are not any new conspicuous oxidation peak appearing for sample H20. These results demonstrate the existence of trivalent manganese ions in sample H5, H10, H15, and H20, and the content of trivalent manganese ions among these four samples increases in the sequence: H20 < H5 < H10 < H15 after some cycles. According to the reports in literature,^{30,34-36} some Mn³⁺ ions in the lithium-rich composites could improve the electronic conductivity and furthermore the electrochemical performance. Therefore, the content of Mn³⁺ could be one primary reason for the variation of the discharge capacities.

The different particle size and content of Mn^{3+} for the samples H5, H10, H15 and H20 should be associated with the sintering time. It is well known that 900 °C is the decomposition temperature of Li₂CO₃, which is higher than its melting point.³⁴ Therefore, in the initial stage of Li₂CO₃ decomposition, with the short sintering time of 5 h, the generated CO₂ gradually removes the air from the surfaces of the reactant particles and reduces the oxygen partial pressure, resulting in the slight content of Mn^{3+} . In the second stage, as the sintering time increases (*i.e.* 10 and 15 h), air near the surface of the reactant particles was further eliminated by the released CO₂ gas, resulting in a bigger content of Mn^{3+} . Finally, when the sintering time increased to 20 h, since Li₂CO₃ is almost decomposed completely, the released CO₂ gas gradually decreased and the oxygen partial pressure increased. Therefore, the amounts of



Fig. 11 Differential capacity vs. voltage (dQ/dV) curves corresponding to the charge–discharge curves of different cycles at a current density of 20 mA g⁻¹ for the samples: (a) H5, (b) H10, (c) H15, (d) H20.

 Mn^{3+} would be re-oxidized to Mn^{4+} . In the first two stages, some amounts of Li_2CO_3 were melted and the reaction between the liquid and solid occurred, leading to mean particle sizes that were almost the same for the samples H5, H10, and H15. However, when the sintering time increased to 20 h, all the reactions mainly preceded in solid–solid forms, which gave rise to the apparent particle growth.

In order to prove the above hypothesis, XPS spectra of the samples were measured to examine the valence states of Mn and Co ions. As shown in Fig. 12(a–d), four signals that include two spin–orbit splitting peaks and two corresponding satellite peaks were detected for the Co 2p core level. Co $2p_{3/2}$ binding energies for samples H5, H10, H15, and H20 were around 780 eV, and their spin–orbit splitting values were all about 15 eV. Moreover, all the Co 2p core levels exhibited a sharp $2p_{3/2}$ peak: the full-width at half-maximum (FWHM) is only about 1.9 eV, and the binding energy difference between $2p_{3/2}$ and its satellite is about 9.6 eV. All of this indicates that the cobalt ions for all the samples are in an oxidation state of +3 with a low-spin state.^{52–54}

Fig. 12(e–h) shows the XPS data for Mn 2p, in which two broad peaks with FWHM > 3 eV were observed. Both peaks are assigned to Mn $2p_{3/2}$ and $2p_{1/2}$. The binding energy difference between $2p_{3/2}$ and $2p_{1/2}$ was about 11.5 eV, which indicates that most of the Mn ions are present in +4. The broadened FWHM observed also means the occurrence of mixed valence Mn³⁺ and Mn^{4+,55-57} To determine the relative content of Mn³⁺, Mn 3s spectra were studied, which is based on the following considerations: (i) Mn 3s electrons belong to the outer level ones, which are sensitive to the chemical environment, especially upon valence change; and (ii) the splitting of the double peaks in Mn 3s is 4.5–4.7 eV for Mn⁴⁺ ions, and the value increases obviously to 5.2–5.5 eV when the valence state of Mn ions decreases to +3.⁵⁶ The Mn 3s spectra are illustrated in Fig. 12(i– l). The main broad peak at 84.4 eV is asymmetric at the lower binding energy side, which could be well fitted in two peaks using mixed Gaussian–Lorentzian profiles. Similarly, its multiple splitting peak at a higher binding energy is also decomposed into two peaks. During the data fit, two constraints have to be imposed: (i) the splitting of two doublets were set at about 4.6 eV for Mn⁴⁺ and 5.5 eV for Mn³⁺, respectively, and (ii) FWHM values of photoelectron peaks were smaller than 2.6 eV. From the fitting results, one can see that the relative content of Mn³⁺ varied in a range from 5.0 to 11.6% in the sequence: H20 < H5 < H10 < H15, as indicated in Fig. 12(i–l).

Electrochemical impedance spectroscopy (EIS) represents an important technique for evaluating the interfacial electrochemistry, and reaction kinetics and diffusion coefficient of the lithium ion in Li-ion battery materials.^{31,58} Impedance spectra for the samples prepared at 900 °C with different sintering periods of time were measured on the Li_{1.2}Mn_{0.4}Co_{0.4}O₂/Li cells which were charged to 4.6 V in initial charge. Fig. 13 shows the Nyquist plots of Li_{1.2}Mn_{0.4}Co_{0.4}O₂ electrode test from 100 KHz to 10 mHz, in which Z_i and Z_r denote the imaginary and real part of impedances, respectively. Corresponding profiles of Zr vs. $\omega^{-1/2}$ in the frequency region of 0.1–0.01 Hz are used to calculate the Warburg factor. The impedance spectra were analyzed by Zswinpwin software and the data fitted to the equivalent electrical circuit is shown in the insert of Fig. 13a. Here, R_e represents the internal resistance of the cell, R_{sf} and C_{sl} are the



Fig. 12 XPS data of (a–d) Co 2p, (e–h) Mn 2p, and (i–l) Mn 3s for sample H5, H10, H15, and H20, respectively. Symbol "S" represents the satellite peaks for the Co 2p levels.

resistance and capacitance of the SEI film, the formation of which involves a series of spontaneous reactions between the cathode active materials and the electrolyte solvents. $R_{\rm ct}$ and $C_{\rm dl}$ (in Fig. 13a) are the charge transfer resistance due to the lithium intercalation/de-intercalation process and double layer capacitance, and W describes the Warburg impedance which is directly related to the solid state diffusion of lithium ion inside the active particles, signified by the straight sloping line at the low frequency region.

The diffusion coefficient of lithium ion (D_{Li}^{+}) is calculated from the straight sloping line at low frequency region according to the following equation,^{31,34}

$$D_{\rm Li}^{\ +} = 0.5R^2T^2/n^4A^2F^4C^2\sigma^2 \tag{1}$$

where *R* is the ideal gas content, *T* is the absolute temperature, *n* is the number of electron(s) per molecule oxidized, *A* is the surface area of the electrode, *F* is the Faraday constant, *C* is the concentration of Li^+ in the cathode, and σ is the Warburg factor which has the relationship with Z_r as in the following equation,

$$Z_{\rm r} = R_{\rm e} + R_{\rm sf} + R_{\rm ct} + \sigma \omega^{-1/2} \tag{2}$$

From eqn (2), the Warburg factor (σ) can be obtained from the linear fitting of $Z_r \nu s. \omega^{-1/2}$, as shown in Fig. 13b. The calculated results of lithium diffusion coefficient for sample H5, H10, H15, and H20 were exhibited in Table 3.

As indicated in Fig. 13a, all the Nyquist plots exhibited two semicircles in the high and middle frequency region and a slope in the low frequency region. The values of $R_{\rm e}$, $R_{\rm sf}$, $R_{\rm ct}$, and $R_{\rm total}$ (total resistances) for samples H5, H10, H15, and H20 are given in Table 3. It can be seen that sample H5 had the highest $R_{\rm total}$ and $R_{\rm ct}$, while sample H10 had the lowest $R_{\rm total}$ and $R_{\rm ct}$, which indicates that the sample H10 had the maximum electronic conductivity, accounting for it having the best cycling performance and relatively high rate performance. Sample H15 had the maximum lithium diffusion coefficient and second smallest $R_{\rm ct}$ value, leading to the best electrochemical performance when comparing among all of the samples. In addition, sample H20 had a relatively low lithium diffusion coefficient and high $R_{\rm total}$ and $R_{\rm ct}$, explaining its inferior electrochemical performance.

In addition, all four samples exhibited a capacity fading with an increase of the cycle number, which might be due to the following reasons: (1) dissolution of the cobalt⁵⁹ and manganese, in which dissolution of the Mn happens in



Fig. 13 (a) Electrochemical impedance spectroscopy (EIS) of different cells measured when charged to 4.6 V, and (b) profiles of the real parts of impedance (Zr) vs. $\omega^{-1/2}$ from 0.1 to 0.01 Hz and corresponding linear fitting curves for samples H5, H10, H15, and H20.

 Table 3
 Fitted parameters for EIS obtained by Zsimpwin software of different samples

Samples	$R_{\rm e}\left(\Omega\right)$	$R_{\mathrm{sf}}\left(\Omega\right)$	$R_{\mathrm{ct}}\left(\Omega\right)$	$R_{\mathrm{total}}\left(\Omega\right)$	$D_{\rm Li}^{+}({\rm cm}^2 {\rm s}^{-1})$
H5	2.72	10.02	152.10	164.84	$2.43 imes10^{-14}$
H10	6.75	8.69	52.79	68.23	$6.23 imes10^{-14}$
H15	2.60	15.05	57.87	75.52	$1.42 imes10^{-13}$
H20	2.78	6.21	82.49	91.48	$5.90 imes10^{-14}$

two ways: (i) the formation of soluble Mn²⁺ through the disproportion reaction of Mn^{3+} ($2Mn^{3+} \rightarrow Mn^{4+} + Mn^{2+}$), and (ii) acid dissolution by HF stemmed from unstable LiPF₆ (LiPF₆ + $H_2O \rightarrow LiF + 2HF + PF_3O$.^{18,60} (2) Phase transition from the original layered structure to a spinel-like structure. Owing to the low theoretical capacity, the presence of the spinel structure would lead to capacity fading. On the other hand, phase transition might result in the corrosion and fragmentation of the layered composite cathode,44,61,62 which would reduce the structural stability. (3) Side reactions at the electrode/electrolyte interface. Due to the overlap of the d-band of the transition metals and the oxygen p-bands, the cathode shows oxygen loss in the form of O2 gas stemmed from the redox reactions between Co⁴⁺ and electrolyte, which may result in the structural instability of electrode materials.^{4,22} (4) The precipitation of the electrolyte decomposition products on the surface of electrode at high voltage could be another important concern.60

4. Conclusions

 $Li_{1.2}Mn_{0.4}Co_{0.4}O_2$ composites were successfully synthesized by a simple gel-combustion method. This method has many merits.

Namely, Li₂CO₃ obtained during the *in situ* burning reaction was homogeneously mixed with metal oxides, which is beneficial for achieving excellent electrochemical properties. The main results could be summarized as follows: (i) sintering at elevated temperatures from 700 to 900 °C improved the crystallinity and layered structure of the samples, further enhancing the electrochemical performance. Excessive sintering at a much higher temperature of 1000 °C led to oversize particles and poor electrochemical performance. 900 °C was determined to be the optimal sintering temperature. (ii) The optimum period of sintering time was determined to be 15 h. Sample H15 delivered the largest capacity, best rate properties, and relatively high cycling performance. When varying the period of sintering time from 5 to 15 h, the impact of the structure and particle size on the electrochemical performance were ignored, while the content of Mn³⁺, electronic conductivity and lithium ion diffusion coefficient in the cycle process are the primary reasons for the different performances of these samples. In addition, large particles, a smaller content of Mn³⁺, relatively low electronic conductivity and lithium ion diffusion coefficient in the cycle process are the dominant factors that resulted in the worst electrochemical performance for the prolonged sintering period of 20 h.

The results reported herein provide a new methodology for obtaining various advanced Li-excess composite materials for use in high-performance energy storage and conversion devices.

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Notes and references

- 1 J. M. Tarascon and M. Armand, Nature, 2001, 414, 359-367.
- 2 Y.-G. Guo, J.-S. Hu and L.-J. Wan, *Adv. Mater.*, 2008, **20**, 2878–2887.
- 3 A. Manthiram, A. V. Murugan, A. Sarkar and T. Muraliganth, *Energy Environ. Sci.*, 2008, **1**, 621–638.
- 4 J. B. Goodenough and Y. Kim, *Chem. Mater.*, 2009, 22, 587-603.
- 5 J. Lu, Q. Peng, W. Wang, C. Nan, L. Li and Y. Li, *J. Am. Chem. Soc.*, 2013, **135**(5), 1649–1652.
- 6 J. N. Reimers and J. R. Dahn, *J. Electrochem. Soc.*, 1992, **139**, 2091–2097.
- 7 T. Ohzuku and A. Ueda, *J. Electrochem. Soc.*, 1994, **141**, 2972–2977.
- 8 D. Luo, G. Li, C. Yu, S. l. Yang, J. Zheng, X. Guan and L. Li, J. Mater. Chem., 2012, 22, 22233–22241.
- 9 K. Kang, Y. S. Meng, J. Bréger, C. P. Grey and G. Ceder, *Science*, 2006, **311**, 977–980.
- 10 T. E. Conry, A. Mehta, J. Cabana and M. M. Doeff, *Chem. Mater.*, 2012, 24, 3307–3317.

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- 11 K. C. Jiang, S. Xin, J. S. Lee, J. Kim, X. L. Xiao and Y. G. Guo, *Phys. Chem. Chem. Phys.*, 2012, 14, 2934–2939.
- 12 Y. Cho, S. Lee, Y. Lee, T. Hong and J. Cho, *Adv. Energy Mater.*, 2011, **1**, 821–828.
- 13 Y. Kim, ACS Appl. Mater. Interfaces, 2012, 4, 2329-2333.
- 14 Y. Wang, E. Hosono, K. Wang and H. Zhou, *Angew. Chem.*, *Int. Ed.*, 2008, **47**, 7461–7465.
- 15 B. Wang, D. Wang, Q. Wang, T. Liu, C. Guo and X. Zhao, *J. Mater. Chem. A*, 2013, 1, 135–144.
- 16 Y. Wang, D. Zhang, X. Yu, R. Cai, Z. Shao, X.-Z. Liao and Z.-F. Ma, *J. Alloys Compd.*, 2010, **492**, 675–680.
- 17 D. Zhang, R. Cai, Y. Zhou, Z. Shao, X.-Z. Liao and Z.-F. Ma, *Electrochim. Acta*, 2010, 55, 2653–2661.
- 18 M. Hirayama, H. Ido, K. Kim, W. Cho, K. Tamura, J. i. Mizuki and R. Kanno, *J. Am. Chem. Soc.*, 2010, **132**, 15268–15276.
- 19 J.-Y. Luo, H.-M. Xiong and Y.-Y. Xia, *J. Phys. Chem. C*, 2008, **112**, 12051–12057.
- 20 M. M. Thackeray, S.-H. Kang, C. S. Johnson, J. T. Vaughey,
 R. Benedek and S. A. Hackney, *J. Mater. Chem.*, 2007, 17, 3112–3125.
- 21 J. Liu, L. Chen, M. Hou, F. Wang, R. Che and Y. Xia, *J. Mater. Chem.*, 2012, **22**, 25380–25387.
- 22 N. Yabuuchi, K. Yoshii, S.-T. Myung, I. Nakai and S. Komaba, *J. Am. Chem. Soc.*, 2011, **133**, 4404–4419.
- 23 G. Singh, R. Thomas, A. Kumar and R. S. Katiyar, *J. Electrochem. Soc.*, 2012, **159**, A410.
- 24 J.-H. Park, J. Lim, J. Yoon, K.-S. Park, J. Gim, J. Song, H. Park, D. Im, M. Park, D. Ahn, Y. Paik and J. Kim, *Dalton Trans.*, 2012, 41, 3053–3059.
- 25 Y. K. Sun, M. G. Kim, S. H. Kang and K. Amine, *J. Mater. Chem.*, 2003, **13**, 319–322.
- 26 C.-C. Wang and A. Manthiram, J. Mater. Chem. A, 2013, 1, 10209–10217.
- 27 J. Liu and A. Manthiram, J. Mater. Chem., 2010, 20, 3961– 3967.
- 28 Q. Y. Wang, J. Liu, A. V. Murugan and A. Manthiram, *J. Mater. Chem.*, 2009, **19**, 4965–4972.
- 29 H. Li and H. Zhou, Chem. Commun., 2012, 48, 1201-1217.
- 30 C. J. Jafta, K. I. Ozoemena, M. K. Mathe and W. D. Roos, *Electrochim. Acta*, 2012, **85**, 411–422.
- 31 D. Luo, G. Li, X. Guan, C. Yu, J. Zheng, X. Zhang and L. Li, J. Mater. Chem. A, 2013, 1, 1220–1227.
- 32 C. Yu, G. Li, X. Guan, J. Zheng and L. Li, *Electrochim. Acta*, 2012, **61**, 216–224.
- 33 B. H. Toby, J. Appl. Crystallogr., 2001, 34, 210-213.
- 34 X. Zhang, D. Luo, G. Li, J. Zheng, C. Yu, X. Guan, C. Fu, X. Huang and L. Li, *J. Mater. Chem. A*, 2013, 1, 9721–9729.
- 35 M. Park, X. Zhang, M. Chung, G. B. Less and A. M. Sastry, J. Power Sources, 2010, 195, 7904–7929.
- 36 A. Abouimrane, O. C. Compton, H. Deng, I. Belharouak, D. A. Dikin, S. T. Nguyen and K. Amine, *Electrochem. Solid-State Lett.*, 2011, 14, A126.
- 37 X. Zhang, C. Yu, X. Huang, J. Zheng, X. Guan, D. Luo and L. Li, *Electrochim. Acta*, 2012, **81**, 233–238.
- 38 C. Yu, H. Wang, X. Guan, J. Zheng and L. Li, *J. Alloys Compd.*, 2013, 546, 239–245.

- 39 X.-J. Guo, Y.-X. Li, M. Zheng, J.-M. Zheng, J. Li, Z.-L. Gong and Y. Yang, *J. Power Sources*, 2008, **184**, 414–419.
- 40 J. M. Zheng, X. B. Wu and Y. Yang, *Electrochim. Acta*, 2011, 56, 3071–3078.
- 41 R. Santhanam, P. Jones, A. Sumana and B. Rambabu, *J. Power Sources*, 2010, **195**, 7391–7396.
- 42 J. Wang, B. Qiu, H. Cao, Y. Xia and Z. Liu, *J. Power Sources*, 2012, **218**, 128–133.
- 43 K. M. Shaju, G. V. Subba Rao and B. V. R. Chowdari, *Electrochim. Acta*, 2002, **48**, 145–151.
- 44 M. Gu, I. Belharouak, J. Zheng, H. Wu, J. Xiao, A. Genc, K. Amine, S. Thevuthasan, D. R. Baer, J.-G. Zhang, N. D. Browning, J. Liu and C. Wang, ACS Nano, 2012, 7(1), 760–767.
- 45 A. R. Armstrong, M. Holzapfel, P. Novák, C. S. Johnson, S.-H. Kang, M. M. Thackeray and P. G. Bruce, *J. Am. Chem. Soc.*, 2006, **128**, 8694–8698.
- 46 Z. Lu and J. R. Dahn, J. Electrochem. Soc., 2002, 149, A815– A822.
- 47 H. Koga, L. Croguennec, P. Mannessiez, M. Ménétrier, F. Weill, L. Bourgeois, M. Duttine, E. Suard and C. Delmas, *J. Phys. Chem. C*, 2012, **116**, 13497–13506.
- 48 Z. Li, Y. Wang, X. Bie, K. Zhu, C. Wang, G. Chen and Y. Wei, *Electrochem. Commun.*, 2011, 13, 1016–1019.
- 49 S. Kim, C. Kim, Y.-I. Jhon, J.-K. Noh, S. H. Vemuri, R. Smith, K. Y. Chung, M. S. Jhon and B.-W. Cho, *J. Mater. Chem.*, 2012, 22, 25418–25426.
- 50 W. He, J. Qian, Y. Cao, X. Ai and H. Yang, *RSC Adv.*, 2012, 2, 3423–3429.
- 51 J. Bareño, M. Balasubramanian, S. H. Kang, J. G. Wen, C. H. Lei, S. V. Pol, I. Petrov and D. P. Abraham, *Chem. Mater.*, 2011, 23, 2039–2050.
- 52 A. W. Moses, H. G. G. Flores, J.-G. Kim and M. A. Langell, *Appl. Surf. Sci.*, 2007, **253**, 4782–4791.
- 53 F. Munakata, H. Takahashi, Y. Akimune, Y. Shichi, M. Tanimura, Y. Inoue, R. Itti and Y. Koyama, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1997, 56, 979–982.
- 54 C. Yu, X. Guan, G. Li, J. Zheng and L. Li, *Scr. Mater.*, 2012, **66**, 300–303.
- 55 S. Ivanova, E. Zhecheva, R. Stoyanova, D. Nihtianova, S. Wegner, P. Tzvetkova and S. Simova, J. Phys. Chem. C, 2011, 115, 25170–25182.
- 56 S. Ardizzone, C. L. Bianchi and D. Tirelli, *Colloids Surf., A*, 1998, **134**, 305–312.
- 57 Q.-H. Wu, M. Liu and W. Jaegermann, *Mater. Lett.*, 2005, 59, 1980–1983.
- 58 D. Andre, M. Meiler, K. Steiner, C. Wimmer, T. Soczka-Guth and D. U. Sauer, *J. Power Sources*, 2011, **196**, 5334–5341.
- 59 G. G. Amatucci, J. M. Tarascon and L. C. Klein, *Solid State Ionics*, 1996, **83**, 167–173.
- 60 K. T. Lee, S. Jeong and J. Cho, Acc. Chem. Res., 2013, 46(5), 1161-1170.
- 61 J. Zheng, M. Gu, J. Xiao, P. Zuo, C. Wang and J.-G. Zhang, *Nano Lett.*, 2013, **13**(8), 3824–3830.
- 62 B. Song, Z. Liu, M. O. Lai and L. Lu, *Phys. Chem. Chem. Phys.*, 2012, 14, 12875–12883.