Layered/Layered Homostyrustructure Ion Conductor Coating Strategy for High Performance

Lithium Ion Batteries

Enyue Zhao[†], Minmin Chen[†], Zhongbo Hu[†], Xiaoling Xiao^{*†} and Dongfeng Chen^{**}

[†] College of Materials Science and Opto-electronic Technology University of Chinese Academy of Sciences,

Beijing 100049, P. R. China

^{*} China Institute of Atomic Energy, Beijing 102413, P. R. China

***Corresponding Author:** E-mail: xlxiao@ucas.ac.cn, Tel: +86 10 8825 6655; E-mail: dongfeng@ciae.ac.cn, Tel: +86 10 6935 8015.

Abstract

The Li_2MnO_3 coated $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ electrode has been successfully synthesized through a PVP-chelation and syn-lithiation strategy. X-ray diffraction (XRD) and X-ray photoelectron Spectrometer (XPS) characterizations are applied to verify the existence of the Li_2MnO_3 surface layer. The complete and nanoscale Li_2MnO_3 coating layer strongly adheres to the host material because of the layered/layered homostyruature, improves the content of Mn element on the surface of the electrode and has three-dimensional path for Li^+ -ion diffusion. Due to the numerous unique and dramatic advantages of the Li_2MnO_3 surface layer, the layered/layered homostyruature electrode exhibits superior cycle stability, rate capability and other electrochemical properties. The newly developmental coating material and versatile nanocoating strategy can also be popularized and applied in other electrode materials.

Keywords: Layered cathode materials; Li_2MnO_3 -coated; Lithium-ion conductor; synchronous lithiation strategy

1. Introduction

Layered lithium-mixed transition metal oxides, LiMO_2 ($\text{M} = \text{Ni}, \text{Co}, \text{Mn}$) have appeared to be candidates as cathode materials for lithium-ion batteries, due to their unique advantages such as high energy density, good thermal stability, low cost, and low toxicity [1-6]. However, there are still some drawbacks for layered LiMO_2 materials to prevent their sustainable and high-power applications. For example, the intrinsic lower Li^+ -ion conductivity of layered LiMO_2 materials result in inferior rate performance for lithium-ion batteries [7-10]. The highly reactive Ni^{4+} or Co^{4+} are unstable in organic electrolyte, which could lead to capacity fading and produce a series of safety issues [7, 11].

Based on these existing challenges for LiMO_2 materials, surface modification has been used as an effective strategy to improve their electrochemical properties [12-18]. At present, the mainly coating materials are electrochemically inert oxides and phosphates such as ZrO_2 , Al_2O_3 et al [14,18]. Unfortunately, these coating materials are ion insulator, which are not favorable for both Li^+ -ion conduction of cathode materials and interfacial charge transfer of the electrode [19]. A class of coating materials of ion conductor, such as Li_2TiO_3 , Li_2ZrO_3 and Li_2SiO_3 , can avoid the aforesaid drawbacks because of their unique structure. These coating materials can not only act as a protective layer to stabilize the surface structure of cathode materials, suppress metal-ion dissolution and unfavorable interfacial side reactions, but also have three-dimensional path for Li^+ -ion diffusion which can effectively increase Li^+ -ion conduction [20-26]. For example, we have demonstrated the availability of the Li_2SiO_3 coating material in ameliorating the electrochemical performance of layered cathode materials [25, 26].

Monoclinic Li_2MnO_3 , similar to aforementioned ion conductor coating materials, also has three-dimensional path for Li^+ -ion diffusion [27]. (Figure 1b). More importantly, Li_2MnO_3

possesses some unique advantages in comparison to other coating materials. Firstly, the layered Li_2MnO_3 has the interlamellar (002) d-spacing value of 0.480 nm which can match well with (003) d-spacing of LiMO_2 (0.468 nm). The simultaneous existence of the two phases of Li_2MnO_3 and LiMO_2 in lithium-rich materials further proved the Li_2MnO_3 material, as a surface layer, could bond well with LiMO_2 materials [28,29]. Furthermore, the homostyruce and similar interlamellar d-spacing is favorable for the formation of the Li_2MnO_3 surface layer with ideal crystal structure, which can better preserve the three-dimensional ionic channels. Secondly, the Li_2MnO_3 coating layer can increase the content of Mn element on the surface of the layered LiMO_2 materials, forming a concentration-gradient structure which is advantageous for the improvement of the cycle stability and safety performance [5,30-32]. In this study, we selected Li_2MnO_3 , which possesses numerous dramatic advantages compared with other coating materials, as the coating layer to improve the electrochemical performances of $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$.

As to the coating strategy, It is difficult to establish a uniform, complete and controllable coating layer on the host materials through conventional approaches such as mechanical mixing and so on [33-35]. It has been reported that metal ions tend to entangle onto the backbone of the poly(vinyl pyrrolidone) (PVP) and its long polymeric chain structure will surround the samples [36-38]. Therefore, in our coating strategy, the $\text{Ni}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2(\text{OH})_2$ precursor was first coated with the PVP, then the dissolved Mn^{2+} ions were complexed with the entire PVP backbone previously coated on the hydroxide precursors. In this way, the Mn^{2+} ions can uniformly distribute on the surface of the hydroxide precursor. Finally, a syn-lithiation method was adopted to get the Li_2MnO_3 coated $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$. (Figure 1a) Our studies show that the electrochemical properties of layered $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ materials have been significantly enhanced by coating a

layer of Li_2MnO_3 .

2. Experimental section

2.1. Materials preparation

Firstly, the hydroxide precursor ($\text{Ni}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}(\text{OH})_2$) was prepared by a co-precipitation (CP) method. Stoichiometric amounts of nickel sulfate, manganese sulfate and cobalt sulfate were dissolved in deionized water. The NaOH solution was added into the above solution under violently stirring. The obtained hydroxide precursor was then filtered, washed, and dried at 80 °C overnight. Secondly, 10 mmol of the $\text{Ni}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}(\text{OH})_2$ precursor was mixed with 1 mmol of $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ in deionized water, in which 0.3 g of poly(vinyl pyrrolidone) (PVP) had been previously dissolved at 50 °C for 12 h. The mixed solution was then dried at 80 °C overnight. Finally, the PVP-Mn-coated hydroxide precursor was mixed with stoichiometric amounts of LiOH. One part amounts of LiOH was used to lithiate the hydroxide precursor to form LiMO_2 , the other part was used to lithiate the manganese acetate to form Li_2MnO_3 . The mixtures were then calcinated in the air atmosphere at 800 °C for 12 hours with a heat rate of 5 °C·min⁻¹ to get the Li_2MnO_3 coated $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$. During this syn-lithiation process, the hydroxide precursor $\text{Ni}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}(\text{OH})_2$ was lithiated to $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$, simultaneously the outer manganese acetate was lithiated to Li_2MnO_3 . The pristine $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ was prepared using the same synthesis process without addition of $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$.

2.2. Materials characterization

Powder X-ray diffraction (XRD) was performed on Rigaku Ultima IV-185 with Cu K α radiation between 10 and 80° 2 θ at a scan rate of 1° 2 θ min⁻¹. Elemental analysis measurements were carried out on a SPECTRO ARCOS FHS12 ICP-OES Spectrometer. Particle morphologies

of the prepared powders were observed by scanning electron microscope (SEM, Hitachi S4800) and transmission electron microscopy (TEM, FEI Tecnai G2 F20). XPS spectra was obtained using a Kratos Axis ULTRA X-ray photoelectron Spectrometer under UHV conditions.

2.3. Electrochemical Measurement

For preparation of the positive electrode, 80 wt% active material, 10 wt% carbon black, and 10 wt% polyvinylidene fluoride (PVDF) were grinded to slurry with N-methylpyrrolidinon, and then spread on aluminum foil with doctor blade. The electrodes were dried overnight at 120 °C in a vacuum oven. The loading density of the active material is about 3-4 mg/cm². The 2016-type coin cells were assembled in an Ar-filled glove box using Li foil as the counter electrode. The electrolyte was 1mol/L LiPF₆ in a 1:1 mixture of ethylene carbonate (EC)/dimethyl carbonate (DMC) and the separator was Celgard 2500. Galvanostatic charge-discharge cycling was tested between 3.0-4.3V (vs. Li/Li⁺) using automatic galvanostat (NEWARE). PITT tests were carried out on the Metrohm-Autolab (PGSTAT 302N). All electrochemical measurements were performed at 25 °C.

3. Results and discussion

Figure 2 shows the X-ray photoelectron spectroscopy (XPS) results of the hydroxyl precursor Ni_{0.8}Mn_{0.1}Co_{0.1}(OH)₂. It can be seen that the valences of Ni, Mn and Co in reactants were all 2+ [39]. Although it has been reported that the Mn²⁺ in the Mn(OH)₂ is easily oxidized to Mn⁴⁺ in the aqueous solution, which lead to the appearance of Mn₂O₃ or MnO₂ in the precursor, the content of the Mn⁴⁺ in the precursor is relatively less which would not influence the average valence of Mn element [40]. Figure 3a exhibits the powder XRD patterns of the pristine LiNi_{0.8}Mn_{0.1}Co_{0.1}O₂ and the Li₂MnO₃ coated LiNi_{0.8}Mn_{0.1}Co_{0.1}O₂ materials. Both materials show hexagonal system and a

signal phase of well-defined α -NaFeO₂ structure (space group: R3-m). The splitting of paired diffraction peaks (018)/(110) and (006)/(102) are known to be an indicator of well layered structure [8,9]. It's worth noting that no peaks corresponding to monoclinic Li₂MnO₃ can be found, which may be due to the lower loading content. The characteristic peaks for monoclinic Li₂MnO₃ between 20-22° began to appear with the content of Mn:M(OH)₂ increasing to 50:100 (Figure 3b). This result may prove that the Li₂MnO₃ was formed during the calcination with stoichiometric Li salt, though it was not detected by XRD while the content of Mn:M(OH)₂ is 10:100. In addition, the elemental analysis results show that the actual content of the elements is in good agreement with the theoretical content in the pristine and Li₂MnO₃ coated materials. (Table 1)

The scanning electron microscopy (SEM) pictures of pristine and Li₂MnO₃ coated samples in various magnifications are shown in Figure 4. All the particles are well-crystallized which is consistent with the results of the sharp peaks in the X-ray diffraction (XRD) patterns. It can be seen that there is almost no difference between the pristine and Li₂MnO₃ coated materials, and morphologies of both materials are irregular cake, the average particle size of the particles is about 300-500 nm.

Figure 5a shows the transmission-electron-microscopy (TEM) image of the Li₂MnO₃ coated LiNi_{0.8}Mn_{0.1}Co_{0.1}O₂ sample. It can be seen that there is a clear coating layer on the surface of the host material. The thickness of the coating layer is very uniform, and which is about 5 nm. A high-resolution TEM (HRTEM) image of the Li₂MnO₃ coated sample in the inset in Figure 5a reveals that the inner material and the external coating layer have lattice spacings of 0.47 and 0.43 nm, which can be indexed to the (003) plane of LiNi_{0.8}Mn_{0.1}Co_{0.1}O₂ and the (020) plane of Li₂MnO₃, respectively [7,41,42]. The results of elemental mapping for Ni, Mn and Co in Figure

5c-e indicate that the transition metal elements uniformly distribute in the Li_2MnO_3 coated $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ sample, and can not indicate that there is a clear Li_2MnO_3 coating layer on the surface of the Li_2MnO_3 coated $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ material, which may be due to the ultrathin thickness of the coating layer.

In the similar circumstances, convergent beam electron diffraction and Li^7 MAS NMR have been reported to study the complexity of structure of the $(1-x)\text{LiMO}_2 \cdot x\text{Li}_2\text{MnO}_3$ [34]. Nevertheless, these methods are not suited for the characterization of the coating layer on nanostructures. Instead, X-ray photoelectron spectroscopy (XPS), which only collects photoelectrons from atoms neighboring to the interface within 8–10 nm, has been applied to determine the surface content of elements [39,43]. Figure 5f-h show the result of XPS characterization for the Li_2MnO_3 coated sample. It can be determined that the valences of Ni, Mn and Co are 2+, 4+ and 3+, respectively [39]. In addition, it should be noted that the atomic ratio of Mn:(Ni+Co) determined by XPS is much bigger compared with the original feed ratio in the precursor during synthetic process. (Table 2) The phenomenon again demonstrates that there is a Li_2MnO_3 -rich coating layer on the surface of the layered $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$. In addition, it can be speculated that there is a lithium-rich $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ transitional phase between the host material LiMO_2 and Li_2MnO_3 surface coating layer. (Figure 1c) The unique structure could produce a strong interaction between Li_2MnO_3 and the host material, which can effectively restrain the shedding of Li_2MnO_3 coating layer during the long cycle.

In order to investigate the influence of the Li_2MnO_3 coating layer on the electrochemical properties of $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$. Pristine and Li_2MnO_3 coated $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ cells were charged/discharged galvanostatically between 3.0 and 4.3 V at 25 °C. Figure 6a shows the cycling

performances of the pristine and Li_2MnO_3 coated electrodes at the rate of 1 C (160 mA/g). It is clear that the Li_2MnO_3 coated electrode exhibits higher discharge capacity than that of the pristine $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ material during the whole cycle process. To be specific, the Li_2MnO_3 coated electrode delivered approximately a discharge capacity of 109 mAh/g which increased by 47% compared with that of 74 mAh/g for the pristine sample. The improved specific capacity can be ascribed to the nanoscale Li_2MnO_3 coating layer, which dramatically improves the lithium ions diffusion coefficient. Furthermore, the Li_2MnO_3 modified electrode also shows distinct advantage in cycle stability. The capacity retention of the pristine and Li_2MnO_3 coated $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ electrodes are 69% and 83%, respectively, after 150 cycles. The ameliorative cycle stability of the Li_2MnO_3 coated sample can be ascribed to the reasons that the Li_2MnO_3 coating layer effectively inhibits the decomposition of the electrolyte, reduces the unfavorable interfacial side reactions. Moreover, the Li_2MnO_3 coating layer improves the content of Mn element on the surface of the sample, which could stabilize the structure of the electrode and thus improve the cycle stability [5,30-32].

Further differences of electrochemical performances between the pristine and Li_2MnO_3 modified materials are shown in Figure 6b. It can be clearly observed that the gap between the charge and discharge plateau regions for the Li_2MnO_3 coated electrode is much smaller after 150 cycles than that for the pristine electrode, which indicates that the $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ material modified by Li_2MnO_3 has lower polarization. It has been demonstrated that the Li_2MnO_3 coating layer has preferable crystal structure, which means that the three-dimensional path for Li^+ -ion diffusion could fully exist. The diffusion rate of lithium ions for the Li_2MnO_3 coated electrode can be highly enhanced, and thus reduce its electrode polarization.

Figure 6c and d display the dQ/dV plots of pristine and Li_2MnO_3 coated electrodes, respectively, which are calculated from numerical data observed in discharge profiles of various cycles. During cycle process, the reduction peaks of the pristine electrode shift continuously toward lower potential, whereas the reduction peaks of the Li_2MnO_3 coated electrode are almost overlapping. It is well known that the shift of reduction peaks represents the voltage decline to some extent [44]. More direct results can be found in the insets of Figure 6c and d, the discharge voltage plateau of the pristine and Li_2MnO_3 coated electrodes decreased by 2.6% and 0.5%, respectively. It can be concluded that the existence of Li_2MnO_3 on the surface of the $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ electrode alleviates its voltage drop.

The good rate capability of Li_2MnO_3 coated electrode further demonstrated the advantages of the Li^+ -conductive Li_2MnO_3 coating layer (Figure 6e). Both pristine and Li_2MnO_3 coated materials were characterized at the rate of 0.2 C-5.0 C during 3.0-4.3 V with 5 cycles per step. As shown in Figure 6e, the Li_2MnO_3 coated sample shows high rate capability, while the pristine sample tested for comparison exhibits a poor rate capability, a dramatic capacity drop with the increasing of C-rate. At the rate of 5.0 C, the Li_2MnO_3 coated material delivered a discharge capacity of 48 mAh/g, which increased by 140% compared with the 20 mAh/g of the pristine $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ electrode. The enhanced rate capability is due to the high Li^+ conductive coating layer on the surface of the electrode which made the Li_2MnO_3 coated material has good Li^+ inserting/extracting kinetics.

To better figure out the reasons why the Li_2MnO_3 coated electrode presented more superior electrochemical performances than the pristine sample, a potentiostatic intermittent titration technique (PITT) test was performed. Before measurement, the cells were galvanostatically

charged and discharged in one cycle at the rate of 1 C between 3.0 and 4.3 V at 25 °C. The lithium ions diffusion coefficient (D_{Li} , an important kinetic parameter of intercalation materials) can be obtained by the following equation:

$$D_{Li} = - \frac{d \ln(Q)}{dt} \cdot \frac{4L^2}{\pi^2}$$

in which L is the thickness of the electrode active material on the aluminum foil [45, 46]. The PITT curves of the pristine and Li_2MnO_3 coated $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ electrodes as a function of time between 3.0 and 4.3 V are shown in Figure 7a and b, respectively. On the basis of the PITT measurement and corresponding data calculation, the results of D_{Li} as a function of the charge-discharge voltage can be obtained (Figure 7c and d). During both the charge and discharge processes, the Li_2MnO_3 coated electrode exhibits higher D_{Li} than that of the pristine electrode. In addition, a physical protection layer could not cause the change of D_{Li} [47]. Therefore, the PITT results not only give a convincing explanation for the superior electrochemical performance of the coated cathode material, but also demonstrate the surface phase is epitaxially connected to the host material without any defect.

4. Conclusions

In summary, the Li_2MnO_3 coated $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ electrode has been successfully prepared via a PVP-chelation and syn-lithiation strategy. XPS characterization was applied to demonstrate the existence of the Li_2MnO_3 surface layer. The nanoscale coating layer is confirmed to be responsible for the high capacity, excellent cycling stability, outstanding rate capability, and relieved voltage decay. It is found that (1) the inert and relative uniform Li_2MnO_3 surface layer suppresses the electrochemical side reactions at high voltage; (2) the homostyruecture and similar interlamellar d-spacing strengthens the bonding between the coating layer and the host material; (3)

perfect crystal structure of Li_2MnO_3 surface layer produces the preferably existence of 3D path for Li^+ -ion diffusion and (4) the increased content of Mn^{4+} on the surface is favorable for the structural stability of the electrode material. The newly developmental coating material and versatile nanocoating strategy adopted in this work should inspire the development of other advanced electrode materials with excellent performances for lithium-ion batteries.

Acknowledgements

This work was supported by the Beijing Nova Program (Z141103001814065), the Youth Innovation Promotion Association CAS (2016152), National Science Foundation for Young Scholars of China (21201177), the State Key Project of Fundamental Research (2014CB931900 and 2012CB932504).

References

- [1] F. Lin, I.M. Markus, D. Nordlund, T.-C. Weng, M.D. Asta, H.L. Xin, M.M. Doeff, Surface reconstruction and chemical evolution of stoichiometric layered cathode materials for lithium-ion batteries, *Nat. Commun.* 5 (2014) 3529.
- [2] H. Yu, Y. Qian, M. Otani, D. Tang, S. Guo, Y. Zhu, H. Zhou, Study of the lithium/nickel ions exchange in the layered $\text{LiNi}_{0.42}\text{Mn}_{0.42}\text{Co}_{0.16}\text{O}_2$ cathode material for lithium ion batteries: experimental and first-principles calculations, *Energy Environ. Sci.* 7 (2014) 1068-1078.
- [3] J.B. Goodenough, Y. Kim, Challenges for Rechargeable Li Batteries, *Chem. Mater.* 22 (2010) 587-603.
- [4] J. Wang, C. Du, C. Yan, X. He, B. Song, G. Yin, P. Zuo, X. Cheng, Al_2O_3 Coated Concentration-Gradient $\text{LiNi}_{0.73}\text{Co}_{0.12}\text{Mn}_{0.15}\text{O}_2$ Cathode Material by Freeze Drying for Long-Life Lithium Ion Batteries, *Electrochim. Acta* 174 (2015) 1185-1191.
- [5] Y.K. Sun, S.T. Myung, B.C. Park, J. Prakash, I. Belharouak, K. Amine, High-energy cathode

material for long-life and safe lithium batteries, *Nat. Mater.* 8 (2009) 320-324.

[6] D. Wang, X. Li, Z. Wang, H. Guo, X. Chen, X. Zheng, Y. Xu, J. Ru, Multifunctional $\text{Li}_2\text{O}-2\text{B}_2\text{O}_3$ coating for enhancing high voltage electrochemical performances and thermal stability of layered structured $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ cathode materials for lithium ion batteries, *Electrochim. Acta* 174 (2015) 1225-1233.

[7] J. Lu, Q. Peng, W.Y. Wang, C.Y. Nan, L.H. Li, Y.D. Li, Nanoscale Coating of LiMO_2 (M = Ni, Co, Mn) Nanobelts with Li^+ -Conductive Li_2TiO_3 : Toward Better Rate Capabilities for Li-Ion Batteries, *J. Am. Chem. Soc.* 135 (2013) 1649-1652.

[8] C. Wang, F. Zhou, K. Chen, J. Kong, Y. Jiang, G. Yan, J. Li, C. Yu, W.-P. Tang, Electrochemical properties of $\alpha\text{-MoO}_3$ -coated $\text{Li}(\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13})\text{O}_2$ cathode material for Li-ion batteries, *Electrochim. Acta* 176 (2015) 1171-1181.

[9] W.S. Yoon, C.P. Grey, M. Balasubramanian, X.Q. Yang, J. McBreen, In situ X-ray absorption spectroscopic study on $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ cathode material during electrochemical cycling, *Chem. Mater.* 15 (2003) 3161-3169.

[10] X. Yang, Z. Zuo, H. Wang, Q. Chen, H. Zhang, Z. Huang, B. Wu, H. Zhou, The Contradiction Between the Half-Cell and Full-Battery Evaluations on the Tungsten-Coating $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ Cathode, *Electrochim. Acta* 180 (2015) 604-609.

[11] X. Yang, R. Yu, L. Ge, D. Wang, Q. Zhao, X. Wang, Y. Bai, H. Yuan, H. Shu, Facile synthesis and performances of nanosized Li_2TiO_3 -based shell encapsulated $\text{LiMn}_{1/3}\text{Ni}_{1/3}\text{Co}_{1/3}\text{O}_2$ microspheres, *J. Mater. Chem. A* 2 (2014) 8362-8368.

[12] J. Cho, Y.J. Kim, T.J. Kim, B. Park, Zero-strain intercalation cathode for rechargeable Li-ion cell, *Angew. Chem. Int. Ed.* 40 (2001) 3367-3369.

- [13] J. Cho, Y.W. Kim, B. Kim, J.G. Lee, B. Park, A breakthrough in the safety of lithium secondary batteries by coating the cathode material with AlPO_4 nanoparticles, *Angew. Chem. Int. Ed.* 42 (2003) 1618-1621.
- [14] J. Du, Z. Zhang, J. Peng, Y. Han, Y. Xia, S. Ju, S. Guo, C. Leng, G. Chen, L. Xu, J. Sun, H. Yan, Effects of ZrO_2 Coating on $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ Particle with Microwave Pyrolysis, *J. Mater. Eng. Perform.* 23 (2014) 2159-2163.
- [15] J. Du, Z. Zhang, J. Peng, Y. Han, Y. Xia, S. Guo, S. Ju, C. Leng, G. Chen, L. Xu, J. Sun, H. Yan, Improvement of electrochemical properties of $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ by coating with $\text{La}_{0.4}\text{Ca}_{0.6}\text{CoO}_3$, *J. Solid State Electr.* 18 (2014) 2211-2216.
- [16] H. Lin, J. Zheng, Y. Yang, The effects of quenching treatment and AlF_3 coating on $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ cathode materials for lithium-ion battery, *Mater. Chem. Phys.* 119 (2010) 519-523.
- [17] S.U. Woo, C.S. Yoon, K. Amine, I. Belharouak, Y.K. Sun, Significant improvement of electrochemical performance of AlF_3 -coated $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ cathode materials, *J. Electrochem. Soc.* 154 (2007) A1005-A1009.
- [18] K. Araki, N. Taguchi, H. Sakaebe, K. Tatsumi, Z. Ogumi, Electrochemical properties of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode material modified by coating with Al_2O_3 nanoparticles, *J. Power Sources* 269 (2014) 236-243.
- [19] J.H. Park, J.H. Cho, S.B. Kim, W.S. Kim, S.Y. Lee, S.Y. Lee, A novel ion-conductive protection skin based on polyimide gel polymer electrolyte: application to nanoscale coating layer of high voltage $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode materials for lithium-ion batteries, *J. Mater. Chem.* 22 (2012) 12574-12581.
- [20] E. Zhao, X. Liu, Z. Hu, L. Sun, X. Xiao, Facile synthesis and enhanced electrochemical

performances of Li_2TiO_3 -coated lithium-rich layered $\text{Li}_{1.13}\text{Ni}_{0.30}\text{Mn}_{0.57}\text{O}_2$ cathode materials for lithium-ion batteries, *J. Power Sources* 294 (2015) 141-149.

[21] H. Deng, P. Nie, H. Luo, Y. Zhang, J. Wang, X. Zhang, Highly enhanced lithium storage capability of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ by coating with Li_2TiO_3 for Li-ion batteries, *J. Mater. Chem. A* 2 (2014) 18256-18262.

[22] X. Yi, X. Wang, B. Ju, H. Shu, W. Wen, R. Yu, D. Wang, X. Yang, Effective enhancement of electrochemical performance for spherical spinel LiMn_2O_4 via Li ion conductive Li_2ZrO_3 coating, *Electrochim. Acta* 134 (2014) 143-149.

[23] X. Zhang, S. Sun, Q. Wu, N. Wan, D. Pan, Y. Bai, Improved electrochemical and thermal performances of layered $\text{Li}(\text{Li}_{0.2}\text{Ni}_{0.17}\text{Co}_{0.07}\text{Mn}_{0.56})\text{O}_2$ via Li_2ZrO_3 surface modification, *J. Power Sources* 282 (2015) 378-384.

[24] X. Miao, H. Ni, H. Zhang, C. Wang, J. Fang, G. Yang, Li_2ZrO_3 -coated $0.4\text{Li}_2\text{MnO}_3$ center dot $0.6\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ for high performance cathode material in lithium-ion battery, *J. Power Sources* 264 (2014) 147-154.

[25] E.Y. Zhao, M.M. Chen, D.F. Chen, X.L. Xiao, Z.B. Hu, A Versatile Coating Strategy to Highly Improve the Electrochemical Properties of Layered Oxide LiMO_2 ($\text{M} = \text{Ni}_{0.5}\text{Mn}_{0.5}$ and $\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}$), *ACS Appl. Mater. Interfaces* 7 (2015) 27096-27105.

[26] E. Zhao, X. Liu, H. Zhao, X. Xiao, Z. Hu, Ion conducting Li_2SiO_3 -coated lithium-rich layered oxide exhibiting high rate capability and low polarization, *Chem. Commun.* 51 (2015) 9093-9096.

[27] K. Nakamura, H. Hirano, Y. Michihiro, T. Moriga, Changes in the local structure and Li^+ ion dynamics in lithium manganese oxides prepared by mechanical milling, *Solid State Ionics* 181 (2010) 1359-1365.

- [28] N. Yabuuchi, K. Yoshii, S.T. Myung, I. Nakai, S. Komaba, Detailed Studies of a High-Capacity Electrode Material for Rechargeable Batteries, $\text{Li}_2\text{MnO}_3\text{-LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$, J. Am. Chem. Soc. 133 (2011) 4404-4419.
- [29] C.S. Johnson, N.C. Li, C. Lefief, J.T. Vaughey, M.M. Thackeray, Synthesis, Characterization and Electrochemistry of Lithium Battery Electrodes: $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMn}_{0.333}\text{Ni}_{0.333}\text{Co}_{0.333}\text{O}_2$ ($0 \leq x \leq 0.7$), Chem. Mater. 20 (2008) 6095-6106.
- [30] Y.K. Sun, S.T. Myung, B.C. Park, K. Amine, Synthesis of spherical nano- to microscale core-shell particles $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1})_{1-x}(\text{Ni}_{0.5}\text{Mn}_{0.5})_x\text{O}_2$ and their applications to lithium batteries, Chem. Mater. 18 (2006) 5159-5163.
- [31] Y.K. Sun, S.T. Myung, H.S. Shin, Y.C. Bae, C.S. Yoon, Novel core-shell-structured $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.2})_{0.8}(\text{Ni}_{0.5}\text{Mn}_{0.5})_{0.2}\text{O}_2$ via coprecipitation as positive electrode material for lithium secondary batteries, J. Phys. Chem. B 110 (2006) 6810-6815.
- [32] T. Ohzuku, Y. Makimura, Layered lithium insertion material of $\text{LiNi}_{1/2}\text{Mn}_{1/2}\text{O}_2$: A possible alternative to LiCoO_2 for advanced lithium-ion batteries, Chem. Lett. (2001) 744-745.
- [33] C. Li, H.P. Zhang, L.J. Fu, H. Liu, Y.P. Wu, E. Ram, R. Holze, H.Q. Wu, Cathode materials modified by surface coating for lithium ion batteries, Electrochim. Acta 51 (2006) 3872-3883.
- [34] L.J. Fu, H. Liu, C. Li, Y.P. Wu, E. Rahm, R. Holze, H.Q. Wu, Surface modifications of electrode materials for lithium ion batteries, Solid State Sci. 8 (2006) 113-128.
- [35] J.Q. Zhao, Y. Wang, Ultrathin Surface Coatings for Improved Electrochemical Performance of Lithium Ion Battery Electrodes at Elevated Temperature, J. Phys. Chem. C 116 (2012) 11867-11876.
- [36] M.W. Pitcher, Y.N. He, P.A. Bianconi, Facile in situ synthesis of oriented LiNbO_3 single

crystals in a polymer matrix, *Mater. Chem. Phys.* 90 (2005) 57-61.

[37] S. Lim, J. Cho, PVP-Assisted ZrO_2 coating on LiMn_2O_4 spinel cathode nanoparticles prepared by MnO_2 nanowire templates, *Electrochem. Commun.* 10 (2008) 1478-1481.

[38] Y. Cho, S. Lee, Y. Lee, T. Hong, J. Cho, Spinel-Layered Core-Shell Cathode Materials for Li-Ion Batteries, *Adv. Energy Mater.* 1 (2011) 821-828.

[39] G.E. Muilenberg, C.D. Wagner, Handbook of x-ray photoelectron spectroscopy: a reference book of standard data for use in x-ray photoelectron spectroscopy, Perkin-Elmer Corp., Physical Electronics Division, Eden Prairie, Minn, 1979.

[40] F. Lian, P. Axmann, C. Stinner, Q.G. Liu, M. Wohlfahrt-Mehrens, Comparative study of the preparation and electrochemical performance of $\text{LiNi}_{1/2}\text{Mn}_{1/2}\text{O}_2$ electrode material for rechargeable lithium batteries, *J. Appl. Electrochem.* 38 (2008) 613-617.

[41] L. Li, Q. Yao, Z. Chen, L. Song, T. Xie, H. Zhu, J. Duan, K. Zhang, Effects of lithium-active manganese trioxide coating on the structural and electrochemical characteristics of $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ as cathode materials for lithium ion battery, *J. Alloy. Compound.* 650 (2015) 684-691.

[42] A. Boulineau, L. Croguennec, C. Delmas, F. Weill, Reinvestigation of Li_2MnO_3 Structure: Electron Diffraction and High Resolution TEM, *Chem. Mater.* 21 (2009) 4216-4222.

[43] B. Philippe, R. Dedryvere, J. Allouche, F. Lindgren, M. Gorgoi, H. Rensmo, D. Gonbeau, K. Edstrom, Nanosilicon Electrodes for Lithium-Ion Batteries: Interfacial Mechanisms Studied by Hard and Soft X-ray Photoelectron Spectroscopy, *Chem. Mater.* 24 (2012) 1107-1115.

[44] Q. Li, G. Li, C. Fu, D. Luo, J. Fan, L. Li, K^+ -Doped $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Co}_{0.13}\text{Ni}_{0.13}\text{O}_2$: A Novel Cathode Material with an Enhanced Cycling Stability for Lithium-Ion Batteries, *Acs Appl. Mater. Inter.* 6 (2014) 10330-10341.

- [45] D. Qian, B. Xu, H.-M. Cho, T. Hatsukade, K.J. Carroll, Y.S. Meng, Lithium Lanthanum Titanium Oxides: A Fast Ionic Conductive Coating for Lithium-Ion Battery Cathodes, *Chem. Mater.* 24 (2012) 2744-2751.
- [46] J. Xie, N. Imanishi, T. Matsumura, A. Hirano, Y. Takeda, O. Yamamoto, Orientation dependence of Li-ion diffusion kinetics in LiCoO_2 thin films prepared by RF magnetron sputtering, *Solid State Ionics* 179 (2008) 362-370.
- [47] S. Lee, M. Jeong, J. Cho, Optimized 4 V Spinel Cathode Material with High Energy Density for Li-Ion Cells Operating at 60 degrees C, *Adv. Energy Mater.* 3 (2013) 1623-1629.

Figure captions

Figure 1. (a) Schematic illustration of the preparation process for the Li_2MnO_3 coated $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$; (b) The structure of Li_2MnO_3 , distribution of Li^+ along a-b plane and c axis; (c) Details of the interface between the Li_2MnO_3 surface layer and the LiMO_2 host material.

Figure 2. X-ray photoelectron spectroscopy (XPS) spectra of: (a) Ni $2p_{3/2}$, (b) Mn $2p_{3/2}$ and (c) Co $2p_{3/2}$ for the hydroxyl precursor $\text{Ni}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}(\text{OH})_2$.

Figure 3. (a) The XRD pattern for the pristine and Li_2MnO_3 coated $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ electrodes; (b) The XRD pattern for the Li_2MnO_3 coated LiMO_2 with a Mn:M ratio of 50:100 in mole.

Figure 4. Scanning electron micrographs for (a, b) pristine $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ and (c, d) Li_2MnO_3 coated $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ in various magnification.

Figure 5. (a) TEM images of the Li_2MnO_3 coated $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ and the inset shows the lattice fringes of the inner material and the external coating layer; (b) High-angle annular dark-field scanning TEM (HAADF-STEM) of the Li_2MnO_3 coated $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ sample and elemental mapping results of (c) Ni, (d) Mn and (e) Co; X-ray photoelectron spectroscopy

(XPS) spectra of: f) Ni 2p_{3/2}, (g) Mn 2p_{3/2} and (h) Co 2p_{3/2} for the Li₂MnO₃ coated LiNi_{0.8}Mn_{0.1}Co_{0.1}O₂ sample.

Figure 6. (a) Plots of specific discharge capacity vs. cycle number for the pristine and Li₂MnO₃ coated electrodes; (b) Specific capacity vs. voltage curves for the pristine and Li₂MnO₃ coated electrodes at the 150th cycle. dQ/dV profiles for (c) the pristine LiNi_{0.8}Mn_{0.1}Co_{0.1}O₂ and (d) the Li₂MnO₃ coated electrode calculated from numerical data observed after 1st, 30th, 60th, 100th and 150th cycle at 1 C, insets show the variation trend of discharge voltage after different cycles. (e) The rate performances of the pristine and Li₂MnO₃ coated electrodes.

Figure 7. PITT curves for the (a) pristine LiNi_{0.8}Mn_{0.1}Co_{0.1}O₂ and (b) Li₂MnO₃ coated electrode. Lithium diffusion coefficients (D_{Li}) as a function of the voltage during (c) charge and (d) discharge processes between 3.0 and 4.3 V.

Figure(s)

Figure(s)

Figure(s)

Figure(s)

Figure(s)

Figure(s)

Figure(s)

Table 1.

ICP results (molar percentage content) of the pristine and Li_2MnO_3 coated $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ samples.

	Li	Ni	Mn	Co
$\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$	1.05 %	0.83 %	0.09 %	0.10 %
$\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2@ \text{Li}_2\text{MnO}_3$	1.12 %	0.72 %	0.19 %	0.09 %

Table 2.

Atomic ratios of Mn:(Ni+Co) of the Li_2MnO_3 coated $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ which are obtained from XPS and the precursor, respectively.

	XPS	starting ratio
Mn : (Ni+Co)	3.56 : (5.14+0.48)	2 : (8+1)