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ARTICLE

Highly Enhanced Lithium Storage Capability of $LiNi_{0.5}Mn_{1.5}O_4$ by Coating with Li_2TiO_3 for Li-ion Batteries

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A uniform and thin Li_2TiO_3 layer with various amounts was coated on the surface of nanostructured $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) materials by *in situ* hydrolysis of tetrabutyl titanate (TBOT) followed by lithiation process. The morphology and structure of the samples were investigated by X-ray diffraction (XRD) and transmission electron microscopy (TEM) with an energy-dispersive X-ray spectroscope (EDS). Electrochemical tests illustrate that Li_2TiO_3 as Li^+-conductive coating remarkably improved the rate and cycling performance of LNMO spinel cathode. Particularly, the 3 wt. % and 5 wt. % Li_2TiO_3-surface modified samples deliver high discharge capacity of 95 mAh g^{-1} and 90 mAh g^{-1} even at a high current density of 5 C, while the bare one only has a discharge capacity of 70 mAh g^{-1}. At a current density of 1 C at elevated temperature, the 3 wt. % and 5 wt. % Li_2TiO_3-surface modified LNMOsamples show excellent cyclability. After 50 cycles, the capacity retention of 3 wt. % and 5 wt. % Li_2TiO_3 modified LNMO is 88.1% and 94.1%, while only 77.1% for the bare sample.

1. Introduction

Nowadays, the threats caused by energy shortage,environmental pollution and climate change become increasingly obvious. The demands for renewable and clean energy are going up continually.[1-2]To fulfill these requirements, Li-ion batteries (LIBs) with highenergy efficiency,low cost and long cycle life have gained enormous attentions.[3-6] At present, LIBs have been widely used in portable electronic devices, such as mobile phones, cameras and laptops. However, the application of LIBs for electric vehicles (EVs) or renewable energy storage is largely limited due to the finite energy/power density. Substantial research indicates that the energy/power is mainly limited by the cathode material and intensive attempts have been made to develop cathode materials with large capacity or high voltage.[7-10]In this regard, spinel LNMOhas attracted much interest owing to its high operating voltage and relatively high theoretical capacity(147 mAh g^{-1}).[11-14]Moreover, LNMO shows markedly improved cycling performance at ambient temperature compared to $LiMn_2O_4$ because that it could effectively suppress the dissolution of Mn^{3+} and Jahn-Teller distortion.[15] Recently, Jafta *et al* prepared nanostructured$LiMn_{1.5}Ni_{0.5}O_4$ spinel through microwave-assisted synthesis and it exhibits excellent electrochemicalperformance.[16]

Unfortunately, the operation voltage of LNMO exceedsthe superior voltage limit of the conventional electrolyte constituting $LiPF_6$ solute and carbonate solvent. At such a highvoltage (~4.7 V), undesired oxidative decomposition of electrolyte occurs during charging process and the correspondingproducts would cover on thesurface of LNMO cathode, forming a cathode electrolyte interphase (CEI) with

poor conductivity.[17, 18] At room temperature, this side reaction is relatively slow, the cathode exhibits preferable cyclability in a short course of circulation. However, when the temperature is close to 55 ℃, the electrolyte oxidation becomes severely serious. During charge-discharge cyclic process, the CEI film is constantly thickening and LNMO spinel undergoes severe capacity fade.

In order to improve the cycle performance of this material, many efforts have been devoted to addressing these challenges.[19]High potential electrolytes with better electrochemical stability in a wider voltage range have been developed.[20, 21]Moreover, multiple surface coatings havebeen explored, such as SiO_2, ZrO_2, ZnO, Al_2O_3, AlF_3 and $FePO_4$.[22, 23]In addition, some dopant cations (Cr,Fe, and Ga) could segregate preferentially to the surface of LNMO, resulting in amore stable cathode-electrolyte interface and better cyclability.[24, 25]

Among these modifications, surface coating which could stabilize the surface structure of cathode materials has been considered as one of the most effectively ways to ameliorate the electrochemical performance of the spinel. Nevertheless, a majority of oxide coatings are usually poor conductors of lithium and electron, which may bring some negative effect to the rate performance. Recently, solid electrolytes with excellent ionic conductivity have been chosen as the surface cladding. Song *et al* employed polyimide (PI) to wrap the surface of LNMO.[26] Compared to conventional metal oxide-based coatings, the unusual PIwrapping layercould offer facile ion transport channels. Zhou *et al* selected $LiAlO_2$ as lithium-containing surface coating layer of LNMO.[27]The results showed that both rate performance andcycling stability were markedly enhanced.

Lithium titanate (Li_2TiO_3) has attracted many researchers'attentions for its three-dimensional Li^+-iondiffusion path and outstanding structural stability in organic electrolyte, which is capableof stabilizing the structure of high-capacity cathode materials and suitable to be chosen as coating layer for cathode.[28] Moreover, the lithium ionic conductivity of Li_2TiO_3 wouldbe greatly increased when doped with foreign ions, resulting from the formation of vacancies.[29-31] In this work, Li^+-conductive Li_2TiO_3has been employedto coat on thesurface of LNMO cathode. The $LiTi_2O_3$-modified LNMO samples were prepared by two-step strategy that involves *in situ* hydrolysis oftetrabutyl titanate (TBOT) on the LNMO nanoparticles which couldachieve uniform Li_2TiO_3-precursor coating and subsequent lithiation process with Li_2CO_3. It should be noted that the nanoarchitectured Li_2TiO_3 layer could provide facile ion transport channels and suppress the formation of thick CEI layers. The effect of the amount of Li_2TiO_3 on the electrochemical properties was also extensively investigated.

2. Experimental

2.1 Materials Synthesis.

The bare LNMO sample was synthesized by resorcinol-formaldehyde assisted synthesis. 0.1 mol resorcinol and0.15 mol formaldehyde were dissolved in 100 ml distilled water. Afterwards, 0.0206 mol $LiCH_3COO·2H_2O$, 0.01 mol $Ni(CH_3COO)_2·4H_2O$ and 0.03 mol $Mn(CH_3COO)_2·4H_2O$ were added respectively. Then the resultant mixture was heated at 60 ℃ untilviscous and the green gel was formed.Finally, nano-LNMO was obtained by calcination of the obtained products at 750 ℃ for 12 h under air.

To prepare Li_2TiO_3 surface modified LNMO sample, the above-synthesizednano-LNMO was dispersed in ethyl alcohol containing small amounts of aqueous ammonia. And then $Ti(OC_4H_9)_4$ dissolved into ethanol beforehand was dropped in the suspension. Themixture was maintained at 45 ℃ for 24 h and TBOT hydrolyzed slowly. After that, the solvent was evaporated at 60 ℃ and the solid powder was heated at 400 ℃. Eventually, stoichiometric amounts of Li_2CO_3 (corresponding to Li_2TiO_3) was mixed thoroughly and the mixture was calcinated at 800 ℃ for 3 h.

2.2MaterialsCharacterization.

The crystal structure of as-prepared samples were characterized by X-ray diffraction (XRD, Bruker D8 with Cu Kα radiation) in scan rate of 3° min^{-1} over 10° to 80° 2θ range. The morphologies and structural features of the samples were examined by high-resolution transmission electron microscopy (TEM, JEOL JEM-2100).Scanning transmission electron microscopy (STEM) was carried out with Tecnai G2 F30 S-TWIN. The X-ray photoelectron spectroscopy (XPS) analysis was performed on a Perkin-Elmer PHI 550 spectrometer with Al Kα (1486.6 eV) as the X-ray source.

In order to analyze the electrochemical properties of the samples, CR2016-type coin cell was employed to carry out galvanostatic cycling tests. The working electrodes were prepared by mixing 80 wt.% LNMO active materials, 10 wt.% carbon black, 10 wt.% polyvinylidene fluorides (PVDF) in N-methyl pyrrolidinone (NMP) to form homogenous slurry. The mixture was uniformly coated on the aluminum foil current collector and dried under vacuum at 110 ℃ for 12 h. The mass loading of active material is about 1.6-2mg cm^{-1}.Lithium metal

was used as anode and polypropylene (PP) film was acted as separator. The electrolyte was 1.0 M $LiPF_6$ in a 1:1 mixture solution of ethylene carbonate and dimethyl carbonate. Coin cells were assembled in a glove box under argon atmosphere. Galvanostatic tests were performed at different current densities between 3.2 and 5 V (vs. Li/Li^+) using a CT2001A cell test instrument (LAND Electronic Co.). Electrochemical impedance spectroscopy (EIS) date were collected in a frequency range from 100 kHz to 0.01 Hz with an AC amplitude of 5mVon a CHI660C electrochemicalworkstation (Chenhua, Shanghai).

3. Results and discussion
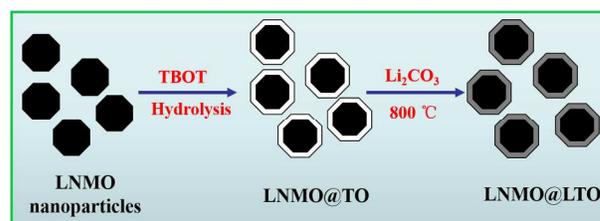
Figure 1. Illustration of the approach for surface modified Li_2TiO_3-LNMO nanoparticles.

The synthetic process of the Li_2TiO_3-LNMO nanoparticles (LNMO@LTO) contains two steps, in which TiO_2-coatedLNMO nanoparticles (LNMO@TO) were first prepared through TBOT-hydrolysis procedure followed by 400 ℃ heat treatment, and then they were mixed with Li_2CO_3 and lithiated to obtain the coated products (Figure 1). LNMO nanoparticles prepared through resorcinol-formaldehyde assisted method were chosen as the precursors, owing to their nano structures with smallparticle size are propitious to be uniformly coated. Samples with progressive proportion of Li_2TiO_3 were obtained by adjusting the amount of TBOT. The LNMO@LTO composites with 3, 5, and 10 wt.% Li_2TiO_3 were referred as LNMO@LTO 3%, LNMO@LTO 5% and LNMO@LTO 10%, respectively.
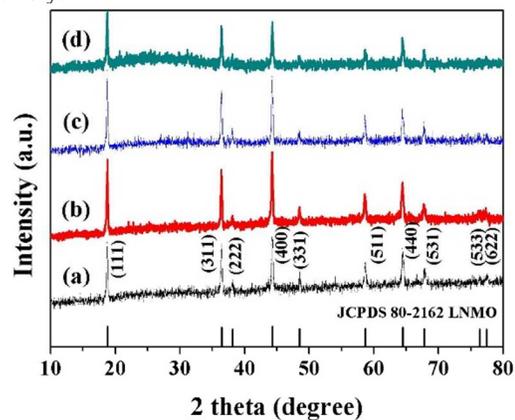
Figure 2. XRD patterns of pristine LNMO and LNMO@LTOcathode materials: (a) LNMO; (b) LNMO@LTO 3%;(c) LNMO@LTO 5%; (d) LNMO@LTO 10%.

Figure 2 compares the XRDpatterns of the bare and Li_2TiO_3-surface modified LNMO samples. All patterns can be assigned to well crystallized cubic spinel LNMO (JCPDS Card No.80-2162), indicating that Li_2TiO_3 incorporationdoes not change the structure.[32,33] No diffraction peaks from Li_2TiO_3 are observed, probably due to thatthe relatively low loading content and layered $Li[Ni_xMn_yTi_z]O_2$ domains in the surface layer of Li_2TiO_3.[30, 31] In order to further illustrate the components of

surface coating, the proportion of Li_2TiO_3 in LNMO@LTO complex was increased to 20 wt. % (LNMO@LTO 20%). Besides, pure Li_2TiO_3 was prepared through the similar manner and the XRD pattern can be perfectly indexed to Li_2TiO_3 (JCPDS Card No.33-0831).[34] As shown in the Figure S 1, different from the bare LNMO, characteristic peaks for Li_2TiO_3 around 43.58° and 63.48° began to appear in the XRD pattern of LNMO@LTO 20% (marked by small black square). In addition, as illustrated in Table S 1, the calculated lattice parameters and unit cell volume of LNMO@LTO became greater with the increase of LTO content, suggesting that Ti^{4+} ions would migrate from surface into the spinel structure as doping ions, which is in agreement with the fact that the ionic radius of Ti^{4+} (74.5 pm) is much larger than that of Mn^{4+} (67 pm).[35, 36]
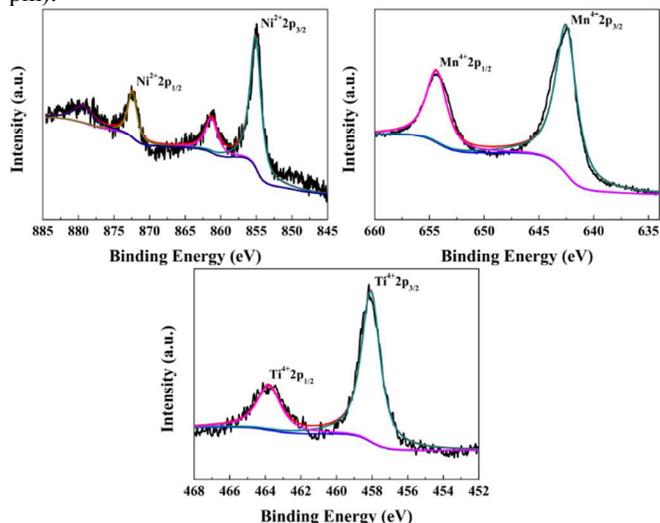

Figure 3. XPS spectra for Ni, Mn and Ti elements of LNMO@LTO 5% sample.

XPS experiments were performed for the coated spinel sample to further evaluate the surface structure of LNMO after Li_2TiO_3-modification. Figure 3 shows the XPS spectra for Ni, Mn and Ti elements of LNMO@LTO 5% sample. The valences of Ni, Mn and Ti are determined to be +2, +4, +4, respectively.[28, 30] Moreover, as for the precursor applied in the synthetic process of LNMO@LTO 5%, the atomic ratio of Ti to (Ni +Mn) is 5: (36+100), while that of LNMO@LTO 5% is 20: (30+100), which suggests Ni^{2+} or Mn^{4+} of LNMO would diffuse from the core to the shell, resulting in the formation of $Li_2Ti_{1-y}M_yO_3$ (M=Mn, Ni) or layered $Li[Ni_xMn_yTi_z]O_2$ domains in the surface layer of Li_2TiO_3 and Li_2TiO_3-rich coating layer was formed on the surface of LNMO nanoparticles indeed.[30, 31] It should be expected that the ionic conductivity of Li_2TiO_3 would be increased when doped with foreign ions (Ni or Mn) and the rate capability of LNMO will be enhanced by the doped-Li_2TiO_3 coating.

The morphology and structure of pristine LNMO and LNMO@LTO 5% cathode materials were confirmed by TEM. As shown in Figure 4a, b, LNMO nanoparticles with an average particle size ranging between 100-200 nm were successfully prepared and the pristine LNMO has smooth planes and well-defined edges. Figure 4c, d shows the TEM images of LNMO@LTO (5%). After modifications, a thin and highly continuous coating was covered on the surface of pristine LNMO. Elemental mapping for Ni, Mn and Ti shows that all the elements are distributed homogeneously throughout the nanoparticles, indicating that the obtained materials were coated

by Li_2TO_3 uniformly (Figure 4 f-h). However, there is hardly any segregation on a scale below the resolution of the EDS technique and the thickness uniformity of coatings could not be obtained. The thickness of coating layer could be analyze perfectly by a high-resolution image or electron energy losss pectroscopy (EELS) mapping.[37, 38]

The discrepancy in crystal structures between the core and shell was evidently demonstrated by a high-resolution (HR) TEM image (Figure 4i) of the black frame region in Figure 4d. The d-spacing of coating layer is 0.480 nm, which is well matched with the d-spacing of (002) plane for the standard monoclinic Li_2TiO_3[31], further suggesting a successful formation of the hierarchical LNMO@LTO as desired. Moreover, it is evident from Figure 4i that the Li_2TiO_3 coating layers with the thickness of approximately 8 nm are distributed on the particle surfaces, which can effectively segregate LNMO from liquid electrolyte.
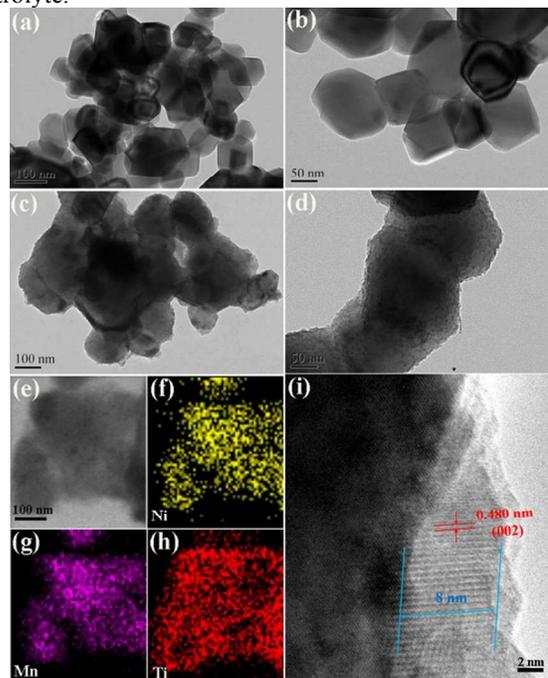
Figure 4. TEM images of LNMO (a, b) and LNMO@LTO 5% (c, d); STEM image of LNMO@LTO 5% (e) and element mapping of Ni (f), Mn (g), Ti (h); HRTEM image of black frame region in Figure 4d for LNMO@LTO 5% (i).

To evaluate the electrochemical performance of LNMO@LTO, CR2016 coin cells were assembled with Li metal as counter electrodes. Meanwhile, bare LNMO sample was also tested in the same condition for comparison. Figure S 2 shows the typical galvanostatic charge/discharge curves of the four samples tested at a current rate of 0.1C (1C = 147 mAh g^{-1}) within a voltage range of 3.2-5.0 V. All the samples exhibit two similar plateaus at about 4.7 V and a small sloping plateau centered at 4.0 V, indicating that the products obtained have a space group of *Fd-3m*.[39, 40] The former plateaus are ascribed to the Ni^{2+}/ Ni^{4+} redox couple, while the latter is associated with Mn^{3+}/Mn^{4+} redox couple. This result demonstrates that the Li_2TiO_3 surface modification does not change the inherent charge and discharge behaviors of LNMO electrode, consistent with the XRD data. The initial discharge capacity of pristine LNMO is 132 mAh g^{-1}. After 3 wt. % and 5 wt. % Li_2TiO_3 coating, the discharge capacities are 128 mAh g^{-1} and 126 mAh g^{-1}, respectively. However, the sample LNMO@LTO 10%

appears a severecapacity loss with a discharge capacity of 115 mAh g^{-1}, which is likely due to the thick coating layer seriously impedes the electron transfer of LNMO. Moreover, itis distinct that the voltagedifference between charge and discharge plateaus becomes smallerafter 3 wt. % or 5 wt. % Li$_2$TiO$_3$ coating, suggesting that the moderate Li$_2$TiO$_3$ coating can bebeneficial to reduce the polarization and internal resistance of the cells. In addition, some amount of Ti^{4+} ions doping could also improve electrochemical activity of LNMO.
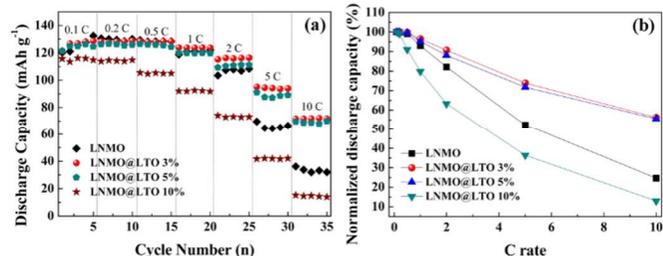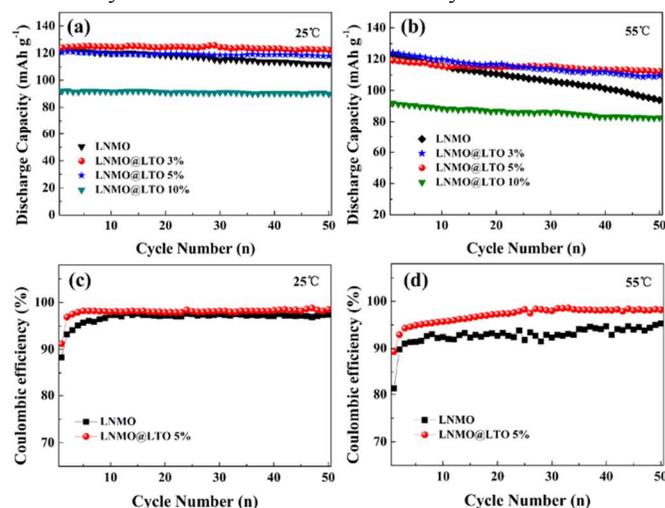

**Figure 5.**Rate performance for LNMO and LNMO@LTOat 25 ℃.

For the purpose of determining the influence of coating layer on rate performance of LNMO cathode materials, all the samples were cycled at different charge discharge rates (0.1, 0.2, 0.5, 1, 2, 5, and 10 C) at room temperature. As shown in Figure 5a, compared to pristineLNMO electrode, Li$_2$TiO$_3$-modified LNMO@LTO electrodes show noevident difference in capacity at a lower discharging rate below 1 C, apart from the LNMO@LTO 10% sample which endured rapidly capacity loss from 0.1 C to 10 C rates.However, when the cells were charged and discharged at larger current densities of 2 C, 5 C, and 10 C, LNMO@LTO 3% and LNMO@LTO 5% still exhibit excellent rate capability while the pristine sample undergoes serious capacity fading. Particularly, at higher current rates of 5 C and 10 C, both LNMO@LTO 3% and LNMO@LTO 5% show considerably higher discharge capacities of 95 and 72 mAh g^{-1} for the former and 90 and 70 mAh g^{-1} for the latter. However, the pristinesample only delivered capacities of 70 and 35 mAh g^{-1} at the samerates. To illustrate the differences in a clearer manner between thepristine and coated samples, we normalized the dischargecapacity values at various *C* rates to the discharge capacityvalue at a 0.1 C rate and plotted in Figure 5b. It is obviously observed that the coated samples with 3 wt. % and 5 wt. % Li$_2$TiO$_3$ show much better capacity retention than the bare one. At large current density of 5 C, the LNMO@LTO 3% and LNMO@LTO 5% can still sustain 73.9% and 71.8% capacity retentionof 0.1 Crate, while the bare LNMO is only 52.2%. The above results indicate that proper amount of Li$_2$TiO$_3$-surface modification cansignificantly improve the rate performance of LNMO spinel

Figure 6a, b compares the cyclability of the bare and surface modified LNMO samples at 1 C rate at different temperatures. At 25 ℃, all the samples exhibit excellent cycle performance with the capacity retention of over 90% after repeated discharge-charge up to 50 cycles. However, at 55 ℃, the first discharge capacity of bare LNMO is 122 mAh g^{-1}, while it decreased to 94 mAh g^{-1} after 50 cycles with only 77.1%capacity retention. Gratifyingly, through surface modifications,all the samples of LNMO@LTO show better capacity retention after 50 cycles at 55℃than the bare one. The capacity retentions of LNMO@LTO 3%, LNMO@LTO 5% and LNMO@LTO 10% are 88.1% 、 94.1% and 90.2%, respectively. Therefore, the Li$_2$TiO$_3$-surface modification offers an effective manner to remarkably improve the cyclability of LNMO cathode at elevated temperature. The Coulombic

efficiency (defined as the ratio of discharge to charge capacity) evolution during cyclic process of bare LNMO and LNMO@LTO 5% was shown in Figure 6c, d. At 25 ℃, the average Coulombic efficiency of both samples are above 95%. When the temperature increased to 55 ℃, the performance of Li$_2$TiO$_3$-modifiedelectrodes did not show apparent decline while the bare electrode distinctly reduced to about 93%. Theresults suggest that the Li$_2$TiO$_3$-coatings could effectivelyalleviate reactions from electrolyte oxidation.[41]

Figure 6. Cycling performance for LNMO and LNMO@LTO at 25 ℃(a) and 55 ℃(b); Coulombic efficiency for LNMO and LNMO@LTO 5% at 25 ℃(c) and 55 ℃(d).
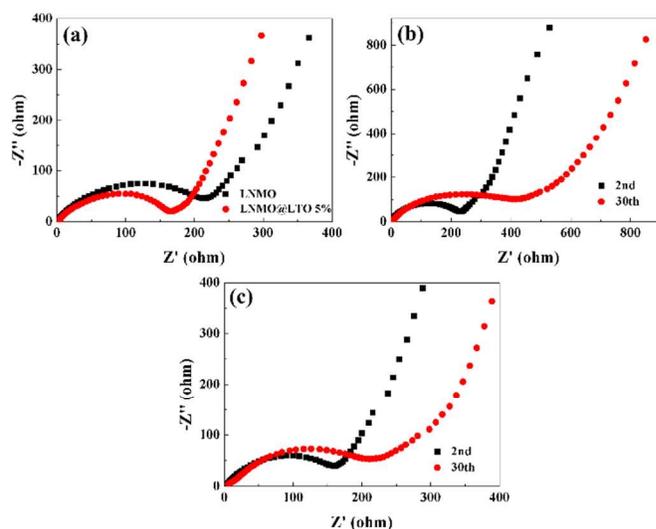

Figure 7. Electrochemical impedance spectra (EIS) of (a) the bare and LNMO@LTO 5% samples afterthe 5th cycle at 25 ℃; (b) the bare sample afterthe 2nd and 30th cycle at 55 ℃; the LNMO@LTO 5% sample after the 2nd and 30th cycle at 55 ℃.

To further understand the difference in the electrochemical performances and polarization behaviors between the bare and the surface-modified samples, the pristine LNMO and LNMO@LTO 5% were analyzed by electrochemical impedance spectroscopy (EIS) after 5th cycle at 25 ℃and 2nd, 30th at 55 ℃. All the cells were in a stable open-circuit voltage value before the EIS measurements. Figure 7a shows theAC impedance test results for pristine LNMO and LNMO@LTO

5% after 5th cycle at 25 ℃. It can be clearly seen that the charge transfer of LNMO@LTO 5% is much smaller than that of theuncoated sample. This result indicates that Li_2TiO_3 as coating layer can effectively reduce the obstacle for Li^+-ion transferat the electrode/electrolyte interface.Thus, the rate performance of LNMO is significantly enhancedwith proper amount of Li_2TiO_3 coated. It may be attributed to that Li_2TiO_3 is a favorable Li^+ conductor and could offer three-dimensional channels for Li^+-ion transmission, also LNMO was doped by some amount of Ti^{4+} ions.[30] As Figure 7b and 7c shown, after 30 cycles at 55 ℃, the bare sample appears drastic increase in battery impedance compared to that at 2nd cycle, while that of LNMO@LTO 5% is of relatively weak increase. It could be ascribed to that Li_2TiO_3-surface modification can effectively restrain the side-reactions between cathode and electrolyte, thus the increase of charge transfer is observably slowed down.[17-18] Hence, Li_2TiO_3 surface modification could be capable to improve the cyclability of LNMO cathode at high cutoff voltage and elevated temperature.

The schematic diagram of the Li_2TiO_3-coated LNMO composite and the mechanism of its role as Li^+-conductive cladding layer to inhibit the unfavorable interfacial side reactions are presented in Figure 8. As previous literature reports, Ni^{4+} ions formed at the charged state of the cathode ($Li_{1-x}Ni_{0.5}Mn_{1.5}O_4$) is active to liquid electrolyte and can induce the oxidative degradation of electrolyte, which is the objective reason to the capacity fading of LNMO during cycle process at high temperature.[24,25] In this work, Li_2TiO_3 as a protecting skin observably suppresses the electrolyte decomposition on electrode/electrolyte interface and thereby improves the capacity retention during iterative charge-discharge cycles.[42,43] Moreover, unlike oxide coatings which may hinder the transportation of Li^+, Li_2TiO_3 could offer a three-dimensional path for Li^+ and the tempo of Li^+-transfer is improved, enhancing the rate capability of LNMO.
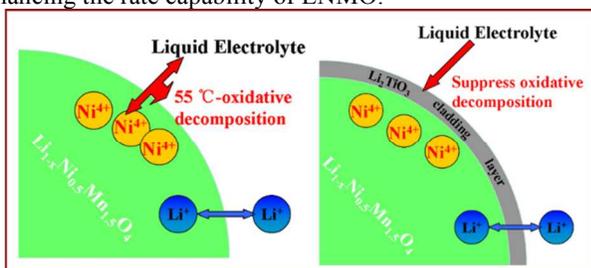
Figure 8. Schematic illustrations of the Li_2TiO_3-coated LNMO and its role as a Li^+-conductive cladding layer to inhibit the unfavorable interfacial side reactions.

As reported previously, the failure of LNMO cells could be mainly attributed to transition metal dissolutionand diffusion to the anode leading to the damage to solid electrolyte interface (SEI) of anode and the cell impedance increase associated with oxidative decomposition of electrolyte.[44, 45] Surface coating which can stabilize the surface structure of cathode materials and mitigate metal-ion dissolution has been considered as one of the most effectively manners to ameliorate the electrochemical performance of the spinel and promote its practical application.[41, 46] In our work, Li^+-conductive Li_2TiO_3 wasemployedto coat on thesurface of LNMO cathode. As a protective layer, it could effectively reduce transition metal dissolution of LNMO and suppress the side reaction between electrode and electrolyte.

4. Conclusions

In summary, a series of Li_2TiO_3-surface modified nanoparticles have been prepared by in situ hydrolysis followed by lithiationapproach. The electrochemical performance of spinel LNMO cathode was significantly enhanced by exploiting nanoscale Li_2TiO_3 layer. The obtained lithium ion conductor not only provides facile ion transport channels, effectively reducing the barrier for lithium ion transfer at the electrode/electrolyte interface, but also suppresses the formation of thick CEI layers during the charge-discharge process. This resultant material exhibits a remarkable rate capability, extremely high capacity, and excellent cycling ability, which may make LNMO materials very attractive for use in batteries for electric vehicles and grid-scale energy storage.

Notes and references

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1. Z. Li, Z. Xu, X. Tan, H. Wang, C. M. B. Holt, T. Stephenson, B. C. Olsen and D. Mitlin, *Energy Environ. Sci.,* 2013, **6**, 871-878.

2. P. G. Bruce, S. A. Freunberger, L. J. Hardwick and J.-M. Tarascon, *Nat Mater*, 2012, **11**, 19-29.

3. W.-K. Shin, Y.-S. Lee and D.-W. Kim, *J. Mater. Chem. A*, 2014, **2**, 6863-6869.

4. L. Zhang, L. Zhou, H. B. Wu, R. Xu and X. W. Lou, *Angew. Chem. Int. Ed.*, 2012, **51**, 7267-7270.

5. J. Lee, A. Urban, X. Li, D. Su, G. Hautier and G. Ceder, *Science*, 2014, **343**, 519-522.

6. J. Ding, H. Wang, Z. Li, A. Kohandehghan, K. Cui, Z. Xu, B. Zahiri, X. Tan, E. M. Lotfabad, B. C. Olsen and D. Mitlin, *ACS Nano*, 2013, **7**, 11004-11015.

7. D. Liu, B. B. Garcia, Q. Zhang, Q. Guo, Y. Zhang, S. Sepehri and G. Cao, *Adv. Funky. Mater.*, 2009, **19**, 1015-1023.

8. A. Kraytsberg and Y. Ein-Eli, *Adv. Eng. Mater.,* 2012, **2**, 922-939.

9. P. Nie, L. Shen, F. Zhang, L. Chen, H. Deng and X. Zhang, *CrystEngComm*, 2012, **14**, 4284-4288.

10. B. Xu, C. R. Fell, M. Chi and Y. S. Meng, *Energy Environ. Sci.,* 2011, **4**, 2223-2233.

11. L. Zhou, D. Zhao and X. Lou, *Angew. Chem., Int. Ed.,* 2012, **51**, 239-241.

12. A. Manthiram, K. Chemelewski and E.-S. Lee, *Energy Environ. Sci.,* 2014, **7**, 1339-1350.

13. J. Liu, W. Liu, S. Ji, Y. Zhou, P. Hodgson and Y. Li, *ChemPlusChem*, 2013, **78**, 636-641.

14. J. Feng, Z. Huang, C. Guo, N. A. Chernova, S. Upreti and M. S. Whittingham, *ACS Appl. Mater. Interfaces*, 2013, **5**, 10227-10232.

15. P. Reale, S. Panero and B. Scrosati, *J. Electrochem. Soc.*, 2005, **152**, A1949-A1954.

16. C. J. Jafta, M. K. Mathe, N. Manyala, W. D. Roos and K. I. Ozoemena, *ACS Appl. Mater. Interfaces*, 2013, **5**, 7592-7598.

17. H. Duncan, D. Duguay, Y. Abu-Lebdeh and I. J. Davidson, *J. Electrochem. Soc.*, 2011,**158**, A537-A545.

18. D. Aurbach, B. Markovsky, Y. Talyossef, G. Salitra, H.-J. Kim and S. Choi, *J. Power Sources*, 2006, **162**, 780-789.

19. B. Li, L. Xing, M. Xu, H. Lin and W. Li, *Electrochem. Commun.*, 2013, **34**, 48-51.

20. Z. Zhang, L. Hu, H. Wu, W. Weng, M. Koh, P. C. Redfern, L. A. Curtiss and K. Amine, *Energy Environ. Sci.,*2013, **6**, 1806-1810.

21. N. P. W. Pieczonka, L. Yang, M. P. Balogh, B. R. Powell, K. Chemelewski, A. Manthiram, S. A. Krachkovskiy, G. R. Goward, M. Liu and J.-H. Kim, *J. Phys. Chem. C*, 2013, **117**, 22603-22612.

22. Y. K. Sun, K. J. Hong, J. Prakash and K. Amine, *Electrochem. Commun.,*2002, **4**, 344-348.

23. D. Liu, Y. Bai, S. Zhao and W. Zhang, *J. Power Sources*, 2012, **219**, 333-338.

24. D. W. Shin, C. A. Bridges, A. Huq, M. P. Paranthaman and A. Manthiram, *Chem. Mater.*, 2012, **24**, 3720-3731.

25. D. Liu, J. Hamel-Paquet, J. Trottier, F. Barray, V. Gariépy, P. Hovington, A. Guerfi, A. Mauger, C. M. Julien, J. B. Goodenough and K. Zaghib, *J. Power Sources*, 2012, **217**, 400-406.

26. J.-H. Cho, J.-H. Park, M.-H. Lee, H.-K. Song and S.-Y. Lee, *Energy Environ. Sci.*, 2012, **5**, 7124-7131.

27. F. Cheng, Y. Xin, Y. Huang, J. Chen, H. Zhou and X. Zhang, *J. Power Sources*, 2013, **239**, 181-188.

28. M. Vijayakumar, S. Kerisit, Z. Yang, G. L. Graff, J. Liu, J. A. Sears, S. D. Burton, K. M. Rosso and J. Hu, *J. Phys. Chem. C*, 2009, **113**, 20108-20116.

29. X. Wu, Z. Wen, X. Xu and J. Han, *Solid State Ionics*, 2008, **179**, 1779-1782.

30. J. Lu, Q. Peng, W. Wang, C. Nan, L. Li and Y. Li, *J. Am. Chem. Soc.*, 2013, **135**, 1649-1652.

31. X. Yang, R. Yu, L. Ge, D. Wang, Q. Zhao, X. Wang, Y. Bai, H. Yuan and H. Shu, *J. Mater. Chem. A*, 2014, **2**, 8362-8368.

32. J. C. Arrebola, A. Caballero, M. Cruz, L. Hernán, J. Morales and E. R. Castellón, *Adv. Funct. Mater.*, 2006, **16**, 1904-1912.

33. K. M. Shaju and P. G. Bruce, *Dalton Trans.*, 2008, 5471-5475.

34. T. Fehr and E. Schmidbauer, *Solid State Ionics*, 2007, **178**, 35-41.

35. R. Alcántara, M. Jaraba, P. Lavela, J. L. Tirado, P. Biensan, A. de Guibert, C. Jordy and J. P. Peres, *Chem. Mater.*, 2003, **15**, 2376-2382.

36. M. Lin, S. H. Wang, Z. L. Gong, X. K. Huang and Y. Yang, *J. Electrochem. Soc.*, 2013, **160**, A3036-A3040.

37. E. Memarzadeh Lotfabad, P. Kalisvaart, K. Cui, A. Kohandehghan, M. Kupsta, B. Olsen and D. Mitlin, *Phys.Chem. Chem. Phys.*, 2013, **15**, 13646-13657.

38. A. Kohandehghan, P. Kalisvaart, K. Cui, M. Kupsta, E. Memarzadeh and D. Mitlin, *J. Mater. Chem. A,* 2013, **1**, 12850-12861.

39. J. Liu and A. Manthiram, *J. Phys. Chem. C*, 2009, **113**, 15073-15079.

40. E. Lee and K. A. Persson, *Energy Environ. Sci.*, 2012, **5**, 6047-6051.

41. J. S. Park, X. Meng, J. W. Elam, S. Hao, C. Wolverton, C. Kim and J. Cabana, *Chem. Mater.*, 2014, **26**, 3128-3134.

42. X. Meng, X.-Q. Yang and X. Sun, *Adv. Mater.*, 2012, **24**, 3589-3615.

43. J. Li, L. Baggetto, S. K. Martha, G. M. Veith, J. Nanda, C. Liang and N. J. Dudney, *Adv. Eng. Mater.*, 2013, **3**, 1275-1278.

44. D. Lu, M. Xu, L. Zhou, A. Garsuch and B. L. Lucht, *J. Electrochem. Soc.*, 2013, **160**, A3138-A3143.

45. X. Xiao, D. Ahn, Z. Liu, J.-H. Kim and P. Lu, *Electrochem. Commun.*, 2013, **32**, 31-34.

46. J. Chong, S. Xun, J. Zhang, X. Song, H. Xie, V. Battaglia and R. Wang, *Chem. Eur. J.* 2014, **20**, 1-8.

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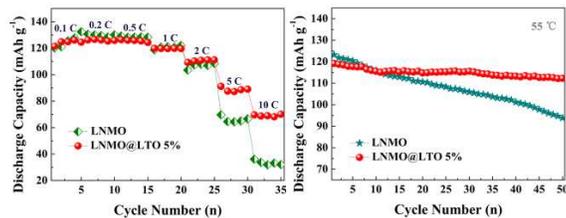
High-voltage $LiNi_{0.5}Mn_{1.5}O_4$ cathode was surface-modified by Li^+-conductive Li_2TiO_3 and proper amount of Li_2TiO_3 can significantly improve the lithium storage capability.