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Significantly improving electrochemical performances of TiO_2 coated $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ cathode

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In this paper, we successfully synthesized Ti-coated Ni-rich $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ cathode and microstructure and electrochemical performances for high-energy lithium-ion battery are investigated. The TiO_2-coated $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ delivers excellent cation mixing and there is no big difference in morphology between pristine and TiO_2 coated $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$. The TiO_2-coated $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ has higher electrochemical performances (initial discharge capacity : 201.3 mAh g^{-1}, rate capability : 90.5% at 4.0 C and cyclability : 79.4% after 100 cycles). It can be explained by the positive role of TiO_2 layer on the surface of $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$.

Keywords: Ti-coated Ni-rich layered $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$, microstructure, cation mixing, higher electrochemical performances, TiO_2 layer.

Introduction

Recently, lithium ion batteries (LIBs) are used to electric vehicles (EVs), hybrid electric vehicles (HEVs) and energy storage systems [1-3]. LIBs are required to meet high energy, long cycle life, specific capacity, stability and low cost [4-5]. Until now, $LiCoO_2$ (LCO) is used to the cathode materials of LIBs due to stable discharge plateau and excellent reversibility. However, LCO have some shortcomings such as poor thermal stability, high costs and environmental pollution [6-7].

Hence, LCO need to be replaced by $LiNi_xCo_yMn_zO_2$. Compared with LCO, NCM have various advantages of good thermal stability, low cost and eco-friendly [6-7]. Also, high-Ni content of $LiNi_xCo_yMn_zO_2$ has excellent reversible specific capacity compared to low-Ni content $LiNi_xCo_yMn_zO_2$, which is helpful for commercialization [8-9]. Unfortunately, high-Ni content of NCM (Ni-rich NCM) have poor cycle performance and low coulombic efficiency. This is because, i) the cation mixing is caused by similar radius between Ni^{2+} (0.69 Å) and Li^+ (0.76 Å) and ii) structural instability due to oxygen release from the crystal lattice [10-11]. To solve the problems, effective strategies such as coating and doping are widely used [12-15].

In this paper, we successfully prepared TiO_2 coated $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ and investigated the electrochemical performances. The TiO_2 coated $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ can improve electrochemical performance and structure stability.

Experimental

Spherical $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ powders were synthesized by using co-precipitation method. The $Ni_{0.8}Co_{0.1}Mn_{0.1}(OH)_2$ precursor was prepared using $NiSO_4\cdot6H_2O$, $CoSO_4\cdot7H_2O$, $MnSO_4\cdot H_2O$, Na_2CO_3 and $NH_3\cdot H_2O$. Precipitating agent was prepared using the NaOH and NH_4OH solution. The spherical $Ni_{0.8}Co_{0.1}Mn_{0.1}(OH)_2$ precursor mixed with $LiOH\cdot H_2O$ in a molar ratio 1.05 : 1. Subsequently, the mixture was preheated at 500 °C for 5 h and then calcined 750 C for 15 h in tube furnace under the oxygen flow. The TiO_2 coating layer wasformed on the surface of $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ by the hydroxylation of titanium tetrabutoxide (TBOT) in a mole ratio of Ti:NCM = 0.03 : 1. After that, the sample was sintered at 600 °C for 3 h in air.

The cathode was fabricated by cathode powder (96 wt.%), conductive carbon black (2 wt.%) and polyvinylidene fluoride (PVDF) (2 wt.%). After that, to form slurry, N-methyl-pyrrolidinone (NMP) solvent was added. Aluminum foil coated on the prepared slurry and then dried at 120 °C for 10 h in a vacuum oven. The CR 2032 coin cells were assembled using lithium foil as an anode in glove box filled with argon gas. 1 M $LiPF_6$ in ethylene carbonate (EC), dimethyl carbonate (DMC) and ethyl methyl carbonate (EMC) (with a volumetric ratio 1 : 1 : 1) were used to electrolyte.

The X-ray diffraction (XRD, X'pert MPD DY1219) was used to measure the structural properties of samples. The field emission scanning electron microscopy (FE-SEM, Hitachi S-4800) was prepared to confirm the morphology of the TiO_2 coated sample. An equipment (TOSCAT-3100, Toyo system) was adopted to measure the electrochemical performances.

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Results and Discussion

Fig. 1 presents the XRD patterns recorded on TiO_2 coated $LiNi_{0.91}Co_{0.06}Mn_{0.03}O_2$. It was observed that there is no significant change in peak position and shape of the XRD via TiO_2 coating. This is because the coating does not affect the $LiNi_{0.91}Co_{0.06}Mn_{0.03}O_2$ structure [16]. The XRD pattern of sample demonstrates that TiO_2 coated $LiNi_{0.91}Co_{0.06}Mn_{0.03}O_2$ can be identified by a typical structure of layered hexagonal α-$NaFeO_2$ structure with the space group R-3m. The clear peak splits corresponding to Miller indices of (006)/(102) and (108)/(110) are observed and it indicates the formation of well-crystallized hexagonal layered structure of $LiNi_{0.91}Co_{0.06}Mn_{0.03}O_2$ [17]. The $I_{(003)}/I_{(104)}$ ratio of the TiO_2 coated $LiNi_{0.91}Co_{0.06}Mn_{0.03}O_2$ is 1.56, which is sufficiently higher than 1.2, which is the standard for cation mixing degree. It means superior structure stability and cation ordering of TiO_2 coated $LiNi_{0.91}Co_{0.06}Mn_{0.03}O_2$.

Fig. 2 illustrates the (a) FESEM and (b) TEM images of the TiO_2 coated $LiNi_{0.91}Co_{0.06}Mn_{0.03}O_2$. We can confirm that the TiO_2 coated $LiNi_{0.91}Co_{0.06}Mn_{0.03}O_2$ shows spherical granule shape with an average size of 12.0 μm, consisting of numerous primary particles of approximately 150 - 450 nm. The primary particles contacted each other directly, which can reduce the electrical resistance, thus, it has a positive effect on the electrochemical performance. From FESEM image, it is clearly seen that TiO_2 coating does not change the spherical shape of pristine $LiNi_{0.91}Co_{0.06}Mn_{0.03}O_2$ [18]. Fig. 2(b) exhibits the TiO_2 coating layer. The average thickness of TiO_2 coating layer is approximately 12 nm. Based on structural properties of TiO_2 coated $LiNi_{0.91}Co_{0.06}Mn_{0.03}O_2$, we can infer that TiO_2 coated $LiNi_{0.91}Co_{0.06}Mn_{0.03}O_2$ could deliver excellent electrochemical performances.

To investigate the electrochemical tests of TiO_2 coated $LiNi_{0.91}Co_{0.06}Mn_{0.03}O_2$, the loading level of the sample was adjusted about 14.6 mg/cm^2 because the high areal capacity is necessary for practical application of lithium ion batteries [19]. Fig. 3 shows the initial charge-discharge curves of TiO_2 coated $LiNi_{0.91}Co_{0.06}Mn_{0.03}O_2$ in a potential range of 3.0 - 4.3 V at 0.5 C. The TiO_2 coated $LiNi_{0.91}Co_{0.06}Mn_{0.03}O_2$ has a typical charge-discharge behavior. There is no noticeable additional plateau. It indicates that the TiO_2 coating does not affect the electrochemical activity of the

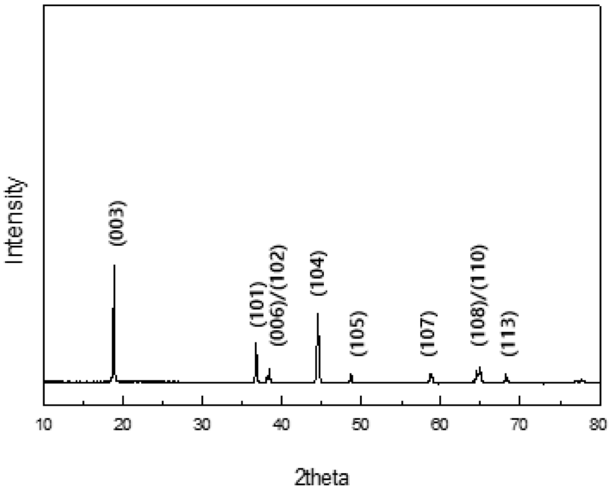

Fig. 1. XRD patterns of TiO_2 coated $LiNi_{0.91}Co_{0.06}Mn_{0.03}O_2$.

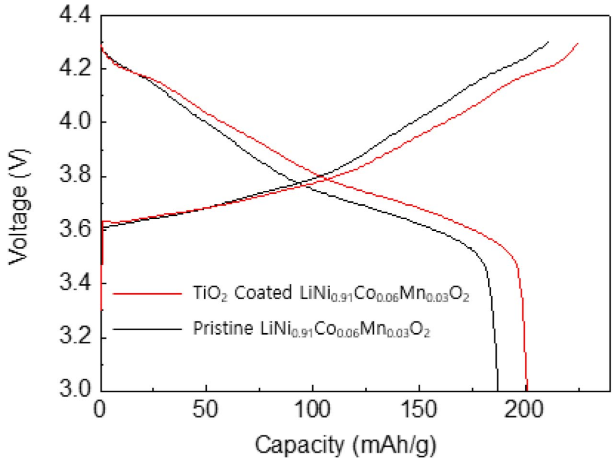

Fig. 3. Initial charge-discharge curves of TiO_2 coated $LiNi_{0.91}Co_{0.06}Mn_{0.03}O_2$.

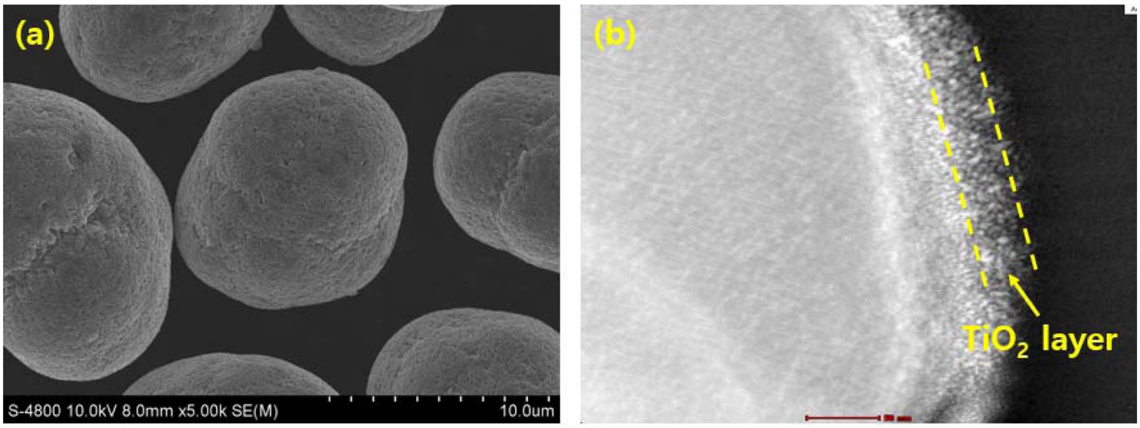

Fig. 2. (a) FESEM image and (b) TEM image of TiO_2 coated $LiNi_{0.91}Co_{0.06}Mn_{0.03}O_2$.

$LiNi_{0.91}Co_{0.06}Mn_{0.03}O_2$. The TiO_2 coated $LiNi_{0.91}Co_{0.06}Mn_{0.03}O_2$ has a discharge capacity of 201.3 mAh g^{-1}, which is higher value compared to pristine sample, resulting from electronically conductive TiO_2 layer [20]. It can be explained by the enhanced conductivity of $LiNi_{0.91}Co_{0.06}Mn_{0.03}O_2$.

Fig. 4 shows the rate performance of TiO_2 coated $LiNi_{0.91}Co_{0.06}Mn_{0.03}O_2$ at various C-rates from 0.1 C to 4.0 C. It is obvious that the capacity retention of TiO_2 coated $LiNi_{0.91}Co_{0.06}Mn_{0.03}O_2$ proportionally decreases with increasing the C-rate. The capacity retention slightly decrease at low C-rates (0.5 and 1.0 C) while the retention of sample is decreased relatively largely at high C-rates (2.0 and 4.0 C). It is associated with the low electrical resistance of TiO_2 coated $LiNi_{0.91}Co_{0.06}Mn_{0.03}O_2$, leading to rapid lithium ion transfer [21].

Fig. 5 shows the long-term cycle performance of TiO_2 coated $LiNi_{0.91}Co_{0.06}Mn_{0.03}O_2$ at 0.5 C rate at 25 °C in the voltage range 3.0 and 4.3 V. The capacity is inversely proportional to the cycle number. However, the TiO_2 coated $LiNi_{0.91}Co_{0.06}Mn_{0.03}O_2$ shows the excellent cycle retention than previously reported pristine sample. The capacity retention of TiO_2 coated $LiNi_{0.91}Co_{0.06}Mn_{0.03}O_2$ is 79.4% after 100 cycles. It is closely associated with the contribution of TiO_2 layer, suppressing the formation of a resistive solid electrolyte interphase (SEI) layer [22]. It causes the increase in charge transfer resistance at the interface between electrolyte and TiO_2 coated $LiNi_{0.91}Co_{0.06}Mn_{0.03}O_2$ cathode. More importantly, TiO_2 layer can alleviate the transition metal elution of $LiNi_{0.91}Co_{0.06}Mn_{0.03}O_2$ cathode to maintain the original layered structure/stable surface chemistry during electrochemical cycling. It was reported that crystalline/amorphous TiO_2 layer can be formed on the surface of $LiNi_{0.91}Co_{0.06}Mn_{0.03}O_2$. Therefore, the protective/conductive TiO_2 layer can suppress the negative unwanted reaction between electrolyte and $LiNi_{0.91}Co_{0.06}Mn_{0.03}O_2$, leading to structural degradation and gassing [23, 24]. It is resulting from O_2 release and electrolyte decay. These phenomenon can be explained by strong bond dissociation energy of Ti-O compared to those of other transition metal ions-O. Moreover, it is well known that coating layer has a positive effect on phase transition (H2→H3) and micro-cracking, which are considered important factors of capacity fading [22, 25].

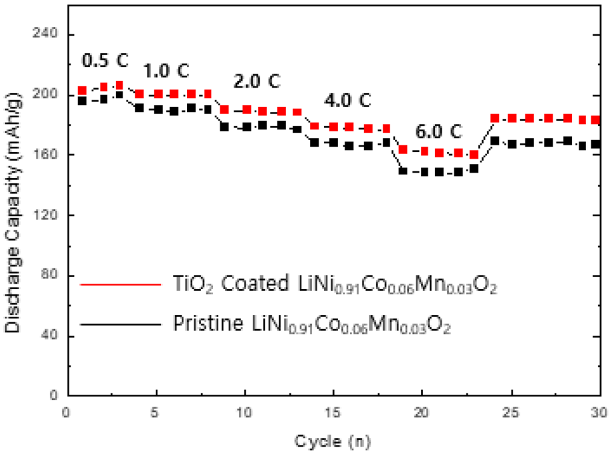

Fig. 4. Rate capability of TiO_2 coated $LiNi_{0.91}Co_{0.06}Mn_{0.03}O_2$.

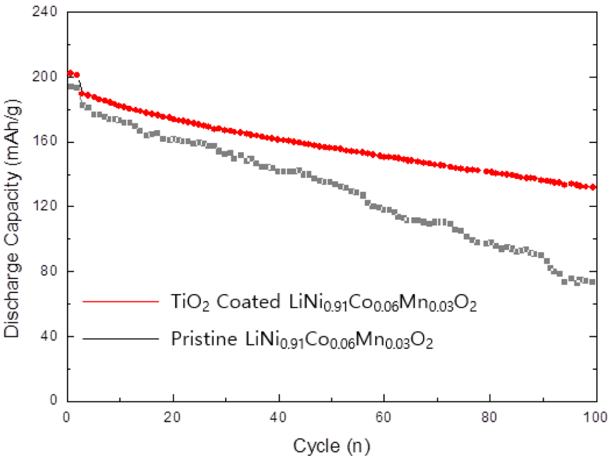

Fig. 5. Cycle performance of TiO_2 coated $LiNi_{0.91}Co_{0.06}Mn_{0.03}O_2$.

Conclusions

We successfully formed TiO_2 coating layer on the surface of $LiNi_{0.91}Co_{0.06}Mn_{0.03}O_2$ cathode via solid-state reaction. The TiO_2 coated $LiNi_{0.91}Co_{0.06}Mn_{0.03}O_2$ cathode shows not only good structural stability but also superior electrochemical performances. The well-crystallized TiO_2 coated $LiNi_{0.91}Co_{0.06}Mn_{0.03}O_2$ cathode maintain original XRD pattern and microstructure of pristine sample. The electrochemical performances of TiO_2 coated $LiNi_{0.91}Co_{0.06}Mn_{0.03}O_2$ cathode surpass pristine sample. It is elucidated that TiO_2 layer could decreases the cation disordering and plays a crucial role in physical on the surface of $LiNi_{0.91}Co_{0.06}Mn_{0.03}O_2$. As a result, it can be concluded that TiO_2 coating layer can be regarded as a breakthrough for high performance and stability $LiNi_{0.91}Co_{0.06}Mn_{0.03}O_2$ cathode.

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