

Short communication

Improved electrochemical performance of LiCoO₂ surface treated with Li₄Ti₅O₁₂

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Abstract

The LiCoO₂ cathode material was surface treated with the Li₄Ti₅O₁₂ particles by a simple mechano-thermal process, followed by calcination at 723 K for 10 h in air. The X-ray diffractometer (XRD) patterns showed a single-phase hexagonal α -NaFeO₂-type structure for the surface treated LiCoO₂ without any structure modification and new phase formation. The transmission electron microscope (TEM) image exposed a uniform layer Li₄Ti₅O₁₂ particulate over the surface of the LiCoO₂ particles that had an average thickness of \sim 20 nm. The electrochemical performance studies indicated that a 1.0 wt.% Li₄Ti₅O₁₂ coated LiCoO₂ sample heated at 723 K for 10 h in air exhibited an initial discharge capacity of 171 mAh g⁻¹ and excellent cycle stability of about 148 cycles for a cut-off voltage of 80% when cycled between 2.75 and 4.40 V. The differential capacity plots for LiCoO₂ surface treated with Li₄Ti₅O₁₂ confirmed that the enhanced performance can be attributed to slower impedance growth and increased resistance to Co dissolution into the electrolyte during the (de)intercalation processes.

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1. Introduction

Lithium-ion batteries have attracted the most attention because of their excellent properties such as high voltage and energy density, durable cycling characteristics, reversibility, and rate capability. The electrochemical performance of a Li-ion battery is mainly based on the cathode material that has a major influence on high specific capacity, cycle stability and safety characteristic [1–3]. Among the available cathode materials, LiCoO₂ is used frequently in commercial Li-ion batteries, even though it suffers major drawbacks during the (de)lithiation process where only 0.5 mol of Li ion can be extractable with a maximum capacity of 137 mAh g⁻¹ between the voltage range 3.0 and 4.2 V [4]. On the other hand, the extraction of more lithium ions (>0.5) when charged at higher voltages [5] leads to capacity loss during cycling accompanied by a structural degradation, dissolution of strongly oxidized Co⁴⁺ ion species into the acidic electrolyte (HF) and faster impedance growth on the surface of the cathode materials [6,7].

In order to improve the electrochemical performance, a surface coating technique has been adapted to surmount the shortcomings practiced by the unprotected LiCoO₂ cathode material. This technique protects the surface of the cathode from faster impedance growth and dissolution (3d metal ion) into the acidic electrolyte, to achieve high specific capacity and thermal stability when cycled beyond 4.2 V. Major surface coating materials used are inert oxides such as ZrO₂ [6–9], Al₂O₃ [5–11], TiO₂ [8,9,11], SiO₂ [7,12], and Co₃O₄ [13]. Many researchers have also attempted to use the electrochemical active oxide materials such as LiCoO₂ [14] and LiMn₂O₄ [15,16] for coating the cathode materials, which enhanced specific capacity, cycle stability and thermal stability compared to their pristine materials. Thus, surface treatment with different coating materials could improve electrochemical properties of the pristine cathode materials. Another interesting electrode material is a Li-ion intercalated Li₄Ti₅O₁₂ compound that has excellent Li-ion insertion/extraction reversibility and exhibits zero-strain insertion, very flat discharge–charge plateau and high cycle stability during charge–discharge cycling. Intensive studies have demonstrated that this so-called zero-strain material offers excellent cycle stability without capacity fade for prolonged cycling. Moreover, Li₄Ti₅O₁₂ may not form a solid electrolyte interface (SEI) that

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protects against electrolyte reactivity when fully charged. The power density depends on the rate capability of the intercalated compound which is associated with the Li-ion diffusion coefficient and the diffusion distance in the intercalated compound particle. These features could allow a cell based on $\text{Li}_4\text{Ti}_5\text{O}_{12}$ spinel to operate very well at both low and high temperatures [17,18]. Therefore, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ spinel material was coated over unstable LiCoO_2 electrode material to attempt to prevent the Co ions from dissolving into the harmful acidic liquid electrolyte, which led to an improvement in the electrochemical performance of the coated LiCoO_2 and cycle stability. The advantages of this compound focused our attention to preparing $\text{Li}_4\text{Ti}_5\text{O}_{12}$ material as a coating material on the commercial LiCoO_2 particles by a simple mechano-thermal process and studying its electrochemical cell performance when charged at a higher voltage.

2. Experiment

Lithium titanate was synthesized by following the procedure as described by Nakahara et al. [19]. Chemicals used during the coating process were LiCoO_2 powder (commercial product of FMC), $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (as prepared above), to form 0.5, 1.0 and 2.0 wt.% of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ coated LiCoO_2 , and pure ethanol. The calculated amount of 0.02 g of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (1.0 wt.%) was dispersed in 50 mL ethanol after 1 h sonication, followed by continuous stirring at 300 K for 10 h. 1.98 g of LiCoO_2 was dispersed in 25 mL ethanol by a 1 h sonication, and stirred for 3 h. The dispersed $\text{Li}_4\text{Ti}_5\text{O}_{12}$ solution was added dropwise to the LiCoO_2 solution after sonication for 1 h and stirred for 10 h at 300 K, followed by heating at 353 K with continuous stirring. After the removal of excess ethanol, a thick black slurry was formed. The obtained slurry was dried in an oven at 383 K for 12 h to form a dry black powder, which was heated at a ramp of 4 K min^{-1} to 623, 723, 823 and 923 K and retained for different time periods 5, 10 and 20 h in air to form a thin coating layer of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ on LiCoO_2 . The weight ratios of coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ to LiCoO_2 , formed during calcination were 0.5:99.5, 1.0:99.0 and 2.0:98.0.

Structural analysis was carried out using a powder X-ray diffractometer (XRD), Siemens D-5000, Mac Science MXP18, equipped with a nickel-filtered $\text{Cu K}\alpha$ radiation source ($\lambda = 1.5405 \text{ \AA}$). The diffraction patterns were recorded between scattering angles of 15° and 80° in steps of 0.05° . The coated layer morphology of the particle was examined by a JEOL JEM-200FXII transmission electron microscope (TEM) equipped with a LaB_6 gun.

The cathodes for electrochemical studies were prepared by a doctor-blade coating method as described in our previous work [13]. The coin type cells of the 2032 configuration were assembled in an argon-filled VAC MO40-1 glove box. The prepared circular disk of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ coated LiCoO_2 was used as the cathode, lithium metal (Foote Mineral) as the anode and a 1 M LiPF_6 in 1:1 by volume ethylene carbonate/diethyl carbonate, EC/DEC (Tomiya Chemicals), as the electrolyte with a Celgard membrane as the separator. The cells charge–discharge cycles were performed at a 0.2 C rate between 2.75 and 4.40 V at 298 K, in a multi-channel battery tester (Maccor 4000).

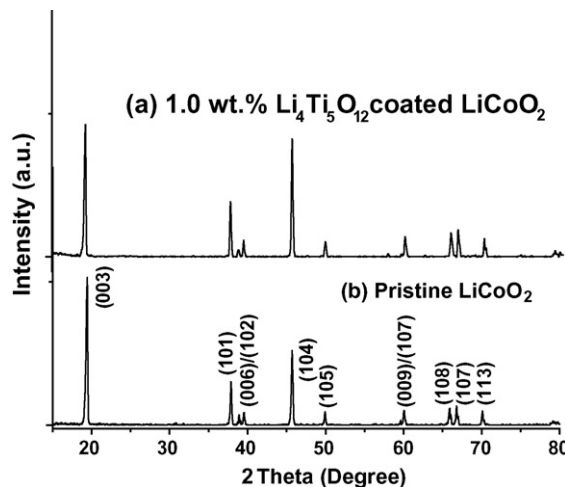


Fig. 1. X-ray diffraction patterns of (a) 1.0 wt.% of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ coated and (b) pristine LiCoO_2 .

3. Results and discussion

Fig. 1a and b represents the XRD patterns of 1.0 wt.% $\text{Li}_4\text{Ti}_5\text{O}_{12}$ coated LiCoO_2 heated at 723 K for 10 h in air and pristine LiCoO_2 , respectively. It is observed that the XRD patterns of 1.0 wt.% $\text{Li}_4\text{Ti}_5\text{O}_{12}$ coating materials exposed the absence of secondary phase peaks in the range of the diffraction patterns corresponding to $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and this may be attributed to very low concentrations. The XRD patterns of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ coated LiCoO_2 particles conform to a single-phase hexagonal $\alpha\text{-NaFeO}_2$ -type structure of the cathode material. There is no basic change in the a and c lattice parameters, the 2θ values of the peaks and their $I(003)/I(104)$ ratios upon coating, which indicates $\text{Li}_4\text{Ti}_5\text{O}_{12}$ does not interact with the core material to form a solid solution during the heat treatment at 723 K for 10 h in air.

Fig. 2 depicts the TEM images of a 1.0 wt.% $\text{Li}_4\text{Ti}_5\text{O}_{12}$ coated LiCoO_2 particle. The coating was a thin compact layer formed of distinguished bright translucent $\text{Li}_4\text{Ti}_5\text{O}_{12}$ par-

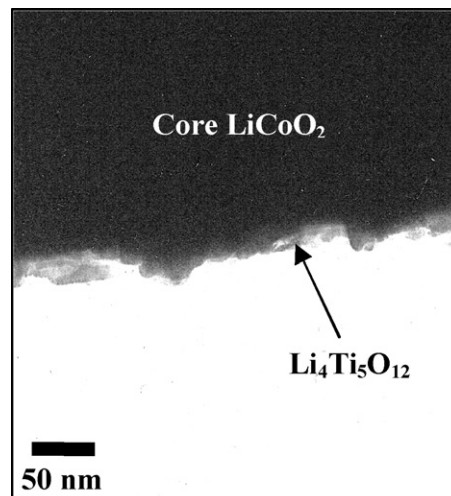


Fig. 2. TEM image of 1.0 wt.% $\text{Li}_4\text{Ti}_5\text{O}_{12}$ coated LiCoO_2 particle.

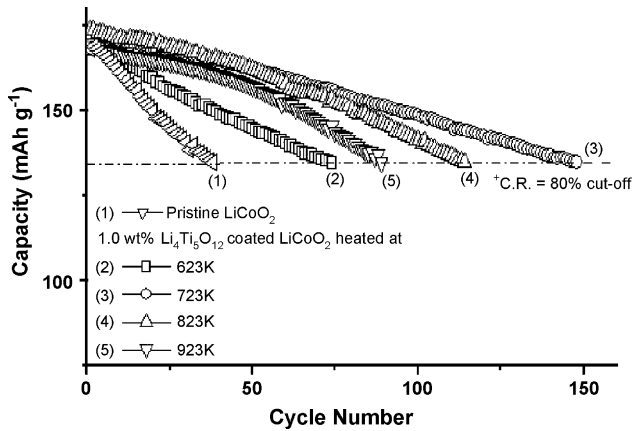


Fig. 3. Cycling performance of pristine and 1.0 wt.% Li₄Ti₅O₁₂ coated LiCoO₂ samples heated at different temperatures for 10 h; charge–discharge: 4.40–2.75 V; 0.2 C rate.

ticulates over the surface of LiCoO₂ particles that had an average thickness of ~20 nm. The TEM image revealed that the Li₄Ti₅O₁₂ coating remained on the surface of the core particles after calcination at 723 K.

The cycle performance studies were carried out with two different strategies in order to establish the conditions required for an excellent Li₄Ti₅O₁₂ coating on the LiCoO₂ samples as (a) heat treatment at 623, 723, 823 and 923 K for 10 h as shown in Fig. 3 and (b) heat treatment at 723 K for 5, 10 and 20 h as shown in Fig. 4. Cell performance studies were also carried out for pristine LiCoO₂ and 0.5, 1.0 and 2.0 wt.% of Li₄Ti₅O₁₂ coated LiCoO₂ between 2.75 and 4.40 V, as shown in Fig. 5. The cycle efficiency and stability effects of Li₄Ti₅O₁₂ coating on the cycle performance of Li⁺/Li were compared based on a preset cut-off value of 80% capacity retention (C.R.) and calculated with respect to the first-cycle discharge capacity of the material.

From Fig. 3, it is observed that the cut-off regime was 134 mAh g⁻¹ for the pristine LiCoO₂ (168 mAh g⁻¹) material and it could sustain just 38 cycles, whereas the coated samples heated at 623, 723, 823 and 923 K exhibited a cycle stability of 74, 148, 114 and 89 number of cycles, respectively. From Fig. 4, it is observed that the coated samples heated at 723 K for 5, 10 and 20 h sustained 105, 148 and

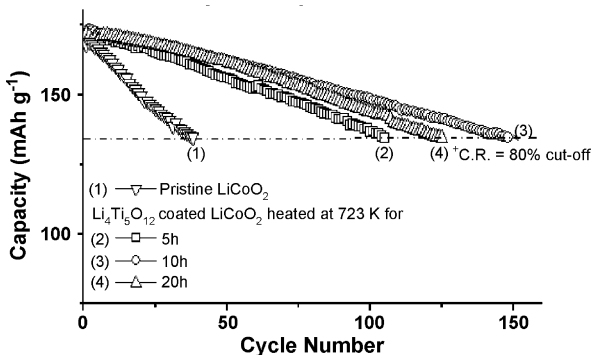


Fig. 4. Cycling performance of pristine and the 1.0 wt.% Li₄Ti₅O₁₂ coated LiCoO₂ samples heated at 723 K for 5, 10 and 20 h; charge–discharge: 4.40–2.75 V; 0.2 C rate.

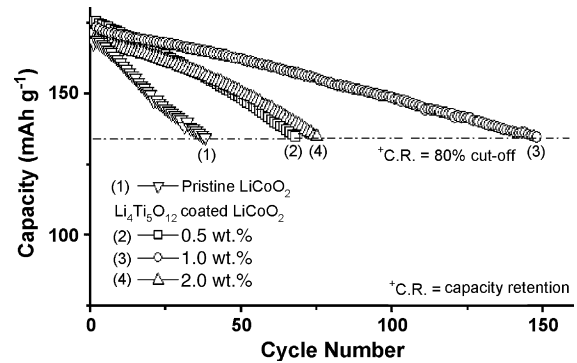


Fig. 5. Cycling performance of pristine and various wt.% Li₄Ti₅O₁₂ coated LiCoO₂; charge–discharge: 4.40–2.75 V at a 0.2 C rate.

125 cycles, respectively. Therefore, from the charge–discharge cycle stability data, it is concluded that the Li₄Ti₅O₁₂ coated LiCoO₂ cathode materials heated at 723 K for 10 h had a well-adhered coating surface and that resisted harmful interaction with the liquid electrolyte. Thus, from the above studies, the optimal heat treatment conditions were then followed to prepare the various wt.% coated Li₄Ti₅O₁₂ coated LiCoO₂ cathode materials.

From Fig. 5, it is observed that the 0.5, 1.0 and 2.0 wt.% Li₄Ti₅O₁₂ coated samples exhibited enhanced cycling stability. In Fig. 5, the number of cycles sustained by 1.0 wt.% Li₄Ti₅O₁₂ coated LiCoO₂ (171 mAh g⁻¹) was 148 cycles compared to the 0.5 wt.% (175 mAh g⁻¹) and 2.0 wt.% (169 mAh g⁻¹) coatings that sustained 68 and 75 cycles, respectively. Therefore, it could be concluded that the 1.0 wt.% coating level is the optimum for this material to form a compact adhesive uniform layer, which results in enhanced cycling performance by resisting the inclination of Li_{1-x}CoO₂ to lose Co and O ions from the lattice by chemical interaction with the harmful acidic electrolyte solution, resulting in excellent cycle stability [6,7,9].

Fig. 6 represents the rate capability study for pristine LiCoO₂ and the Li₄Ti₅O₁₂ coated LiCoO₂ cathode materials when cycled between 2.75 and 4.40 V at different *c*-rates. From Fig. 6, it is observed that for *c*-rates 0.1, 0.2 and 0.4 C, the discharge capacities for pristine LiCoO₂ were 179, 172 and 159 mAh g⁻¹ and for the Li₄Ti₅O₁₂ coated LiCoO₂ cathode materials were

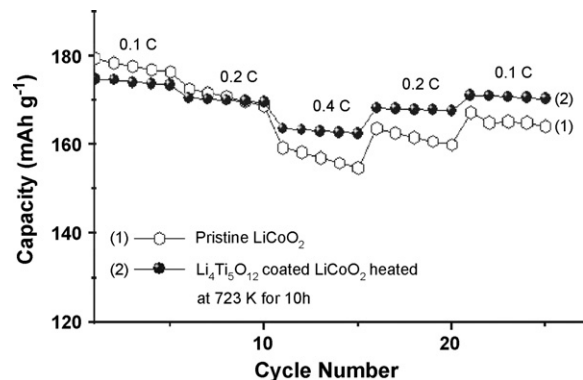


Fig. 6. Cycling performance of pristine and 1.0 wt.% Li₄Ti₅O₁₂ coated LiCoO₂; charge–discharge: 4.40–2.75 V; different *c*-rates: 0.1, 0.2 and 0.4 C.

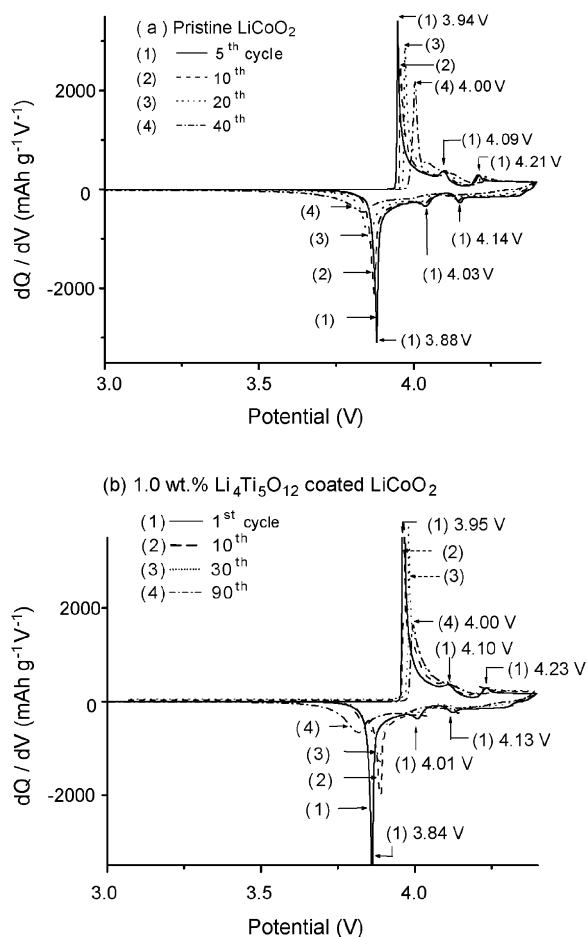


Fig. 7. The dQ/dV vs. voltage curves of (a) pristine LiCoO_2 and (b) 1.0 wt.% $\text{Li}_4\text{Ti}_5\text{O}_{12}$ coated LiCoO_2 ; charge–discharge at 4.40–2.75 V at a 0.2 C rate.

175, 171, and 163 mAh g^{-1} , respectively. On the other hand, when the c -rates were applied in a descending order as 0.4, 0.2 and 0.1 C, the cell showed a different effect on the discharge capacities, which demonstrated the rate capability as shown in Fig. 6.

Thus, the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ coated LiCoO_2 cathode materials demonstrated a significantly higher rate capability compared to pristine LiCoO_2 material since the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ coating facilitated a channel for Li-ion diffusion that was not hindered at the surface. Therefore, we conclude that the surface coating layer of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ organized to protect the surface from faster impedance growth during the (de)intercalation processes at higher current densities, resulting in smaller capacity fades. Fig. 7a and b shows the dQ/dV versus voltage plots for the pristine LiCoO_2 and the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ coated LiCoO_2 cathode material between 2.75 and 4.40 V for 5, 10, 20 and 40 cycles and 1, 10, 30 and 90 cycles, respectively.

From Fig. 7a and b, it is observed that the charge and discharge processes accompanied by transitions from hexagonal to monoclinic to hexagonal phases for both the pristine and the coated samples. During the first cycle, the charge–discharge peaks were narrow and sharper and were centered at 3.94 and 3.88 V, respectively, which corresponds to the oxidation process accompanied by delithiation of lithium ions from the lattices.

However, after 40 cycles the transition peaks became broader and shifted to 4.00 and 3.82 V for pristine LiCoO_2 .

On the other hand, in Fig. 7b, the charge–discharge peaks corresponding to the phase transitions were narrow and sharper and were centered at 3.95 and 3.84 V, respectively. After 90 continuous cycles, the peaks shifted to 4.00 and 3.80 V with slight shift redox potentials compared to the initial potential. Thus, the pristine sample exhibited a large shift between the reduction (lithiation process) peaks (~ 0.06 V) for 40 cycles, compared to the coated samples the reduction peaks which shifted less (~ 0.04 V) for 90 cycles [6,7].

Thus, it is evident that slower impedance growth on the surface of the coated core materials was due to the presence of $\text{Li}_4\text{Ti}_5\text{O}_{12}$, which protects the loss of 3d metal ions and oxygen when the cells are charged at higher voltages [6,7], whereas pristine LiCoO_2 had faster impedance growth caused by some side reactions with the liquid electrolyte involved at the surface. The surface side reaction was supported by XPS results reported by Edstrom et al. [20], that the cathode material surface reacts with the electrolyte to form a passive surface film of organic species and lithium-salt anion (polycarbonates, polymeric hydrocarbons, Li_2CO_3 , LiF , Li_xPF_y and $\text{Li}_x\text{PF}_y\text{O}_z$) dependent on electrode material type (LiCoO_2 , $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ and LiFePO_4). Therefore, it is important to control the harmful reaction of the PF_6 anion and other contaminants (CH_3COO^- , HF and PF_5) with the electrode surface. The results agree with the reports of Aurbach et al. [21], where upon cycling, LiCoO_2 undergoes a major capacity fade due to the formation of surface films on the cathode that electronically isolates the components from each other and from the current collector.

4. Conclusions

LiCoO_2 was coated with $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles by a simple mechano-thermal method. XRD results revealed that the surface of the LiCoO_2 was coated with $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles without any modification of crystal structure and lattice parameters of the core material, and thereby confirmed that the coating particles remained on the surface. The TEM images exposed that the LiCoO_2 surface layer is formed of coated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles. Cycle performance studies revealed that the 1.0 wt.% $\text{Li}_4\text{Ti}_5\text{O}_{12}$ coated LiCoO_2 cathode material was about 3.9 times more stable than pristine LiCoO_2 . The differential capacity plots demonstrated that the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ surface coating protected the cathode from faster impedance growth and dissolution of strongly oxidized Co ions during the cycling process. Therefore, capacity retention and cycle stability were enhanced. This paper is the first report for clarifying the effectiveness of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ coating.

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