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Nitridation-Driven Conductive $\text{Li}_4\text{Ti}_5\text{O}_{12}$ for Lithium Ion BatteriesKyu-Sung Park,^{*,†} Anass Benayad,[‡] Dae-Joon Kang,[§] and Seok-Gwang Doo[†]

Energy Group and Analytical Engineering Group, Samsung Advanced Institute of Technology (SAIT), Samsung Electronics Co., Ltd., Yongin 446-712, Korea, and Department of Physics and SKKU Advanced Institute of Nanotechnology, Sungkyunkwan University, 300 Cheoncheon-dong, Jangan-gu, Suwon 440-746, Korea

Received August 4, 2008; E-mail: ks337.park@samsung.com

Recently, because of the record-high oil prices and the serious global warming problems, the development of hybrid electric vehicles (HEVs) is under the spotlight and lithium ion batteries (LIBs) have been a strong candidate for powering them. One of the key safety issues in LIBs for HEVs would be the dendritic lithium growth on the anode surface at high charging current because the conventional carbonous materials approach almost 0 V vs Li at the end of Li insertion.¹ Therefore, a fundamental solution is to use an electrochemical redox couple with higher equilibrium potentials, which makes Li formation thermodynamically less favorable. Among the candidates, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ using the $\text{Ti}^{4+}/\text{Ti}^{3+}$ redox couple (*ca.* 1.5 V vs Li) has showed promising electrochemical properties with structural and chemical stabilities vis-à-vis to the electrolyte.² The electronic structure of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ characterized by empty Ti 3d-states with a band gap energy of ~ 2 eV gives an insulating character to this material.³ Therefore, the high current properties of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ might not be sufficient for high current applications before any materials modifications.

To improve the electrochemical properties of $\text{Li}_4\text{Ti}_5\text{O}_{12}$, we look to previous studies of the LiFePO_4 cathode material because it also shows a two-phase equilibrium reaction between insulating LiFePO_4 and FePO_4 . The most common methods applied are the conductive surface coating and reducing the particle size.⁴ For the conductive coating, it would be desirable to make a thin and dense layer. If a conductive Ti compound like TiN with a metallic conductivity is formed on the surface of $\text{Li}_4\text{Ti}_5\text{O}_{12}$,⁵ it will be dense with good adhesion by forming chemical bondings between N and the surface atoms. For nanosizing, it reduces the Li^+ diffusion path and improves the reaction kinetics. Moreover, it also introduces conductive single phase margins of the voltage plateau, which means mixed-valent $\text{Li}_{\alpha}\text{FePO}_4$ and $\text{Li}_{1-\beta}\text{FePO}_4$, instead of fixed-valent LiFePO_4 and FePO_4 , are in equilibrium and the electronic conductivities must be improved.⁶ The same should be true for $\text{Li}_4\text{Ti}_5\text{O}_{12}$, so we tried to find a new way to introduce mixed-valent end members.

Thermal nitridation has been known to change the oxygen stoichiometry in some oxides and to introduce nitride thin films.⁷ Thus, modification of the surface structure of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ via annealing in NH_3 should change Li insertion/extraction behaviors, and it should also make bonding between surface Ti and N simultaneous. To address this issue, we introduced thermal nitridation to $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and found, for the first time to our knowledge, that it can introduce a mixed-valent intermediate phase, $\text{Li}_{4+\delta}\text{Ti}_5\text{O}_{12}$, and a surface conductive layer, TiN, with a significant enhancement in the battery performances.

After thermal nitridation in NH_3 atmosphere at 700 °C, the color of white pristine $\text{Li}_4\text{Ti}_5\text{O}_{12}$ becomes dark, and it is apparently black

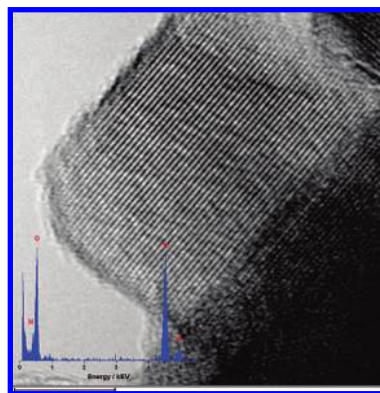


Figure 1. HR-TEM image and corresponding surface EDS spectrum of the nitridated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ for 60 min.

after 1 h of treatment. Surprisingly, the samples with different colors show pure-phase $\text{Li}_4\text{Ti}_5\text{O}_{12}$ patterns with no shift in the diffraction peak positions. This result was corroborated by the high-resolution transmission electron microscopy (HR-TEM) image and the energy dispersive X-ray spectrum (EDS) of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powder after 60-min nitridation (Figure 1). The core region of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles has a well-defined cubic crystalline structure even though the surface region has a glassy structure as small as a few nanometers in thickness. The EDS shows the presence of nitrogen on the particle, and it is expected to be on the surface layer because the bulk crystallographic structure has not been affected by the presence of nitrogen.

The XPS valence band spectra of pristine, 10, 30, and 60 min nitridated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ are shown in Figure 2. All spectra present two main bands. The single band around 22.5 eV corresponds to the specific ionization of the oxygen 2s orbital. The broadband, between 2 and 10 eV, is associated with orbitals mainly involving O 2p but also contains a small amount of Ti 3d. For the pristine material, the upper part of the valence band split on two peaks centered at

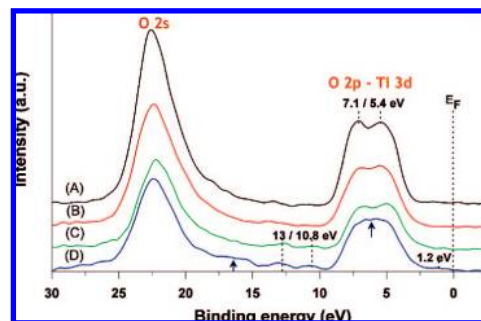


Figure 2. XPS valence bands of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powder (A) before and after (B) 10, (C) 20, and (D) 60-min nitridation.

[†] Energy group, SAIT.

[‡] Analytical engineering group, SAIT.

[§] Sungkyunkwan University.

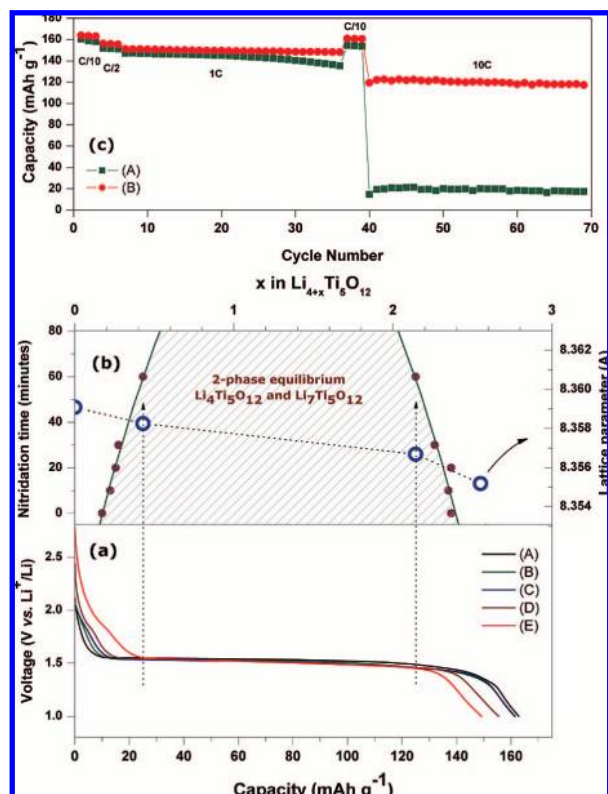


Figure 3. (a) Charging (Li^+ insertion) voltage curves of (A) pristine $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and the nitridated powders at 700°C for (B) 10, (C) 20, (D) 30, and (E) 60 min. (b) shows the corresponding two-phase equilibrium region with different reaction time and the lattice parameters of 60 min-nitridated $\text{Li}_4\text{Ti}_5\text{O}_{12}$. (c) presents the reversible capacities of (A) pristine and (B) 10 min-nitridated $\text{Li}_4\text{Ti}_5\text{O}_{12}$ with different charge/discharge current densities during cycling.

7.1 and 5.4 eV originated from oxygen bonding with three and two Ti atoms within TiO_6 octahedra, respectively.⁸ We note that the empty state just below the Fermi level (between 0 and 2 eV) is in agreement with a formal charge of $4+$ ($3d^0$ configuration) and, thus, the insulator character of $\text{Li}_4\text{Ti}_5\text{O}_{12}$. As the reaction time increases, the valence band spectra show the increase of a new structure around 5.6 eV (shown by an arrow) which is expected from the mixing between Ti 3d and N 2p orbitals.⁹ On the other hand, just below the Fermi level a small band, originated from the partial occupancy of Ti 3d orbitals, was observed. The presence of such a band, after NH_3 treatment, might play an important role in enhancing the surface conductivity of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particle due to the metallic conductivity of TiN species on the surface.¹⁰ We can also recognize two small intensity peaks at 10.8 and 13 eV as well as other characteristics of the presence of Li_2CO_3 on the surface after nitridation.¹¹ From the analysis results, we have evidenced that the surface of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles was decomposed by reacting with NH_3 gas, forming a core/shell system with TiN and Li_2CO_3 species on the surface and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ in the bulk.

Figure 3a shows the voltage curves for Li insertion before and after nitridation at a rate of C/2. The 1C-rate is defined as the current density necessary to fully charge/discharge the battery in 1 h. The pristine $\text{Li}_4\text{Ti}_5\text{O}_{12}$ shows the highest capacity (162 mAh g^{-1}); on the contrary, it decreases for the treated electrodes as the treatment time increases, which should be due to the surface decomposition.

Moreover, the flat voltage curves change to have slopes at the beginning/end of the Li insertion. The sloping voltage curves may indicate a single phase region, and the flat voltage part is a characteristic of two-phase equilibrium, a room temperature miscibility gap, as shown in Figure 3b. The single phase Li insertion is confirmed by the lattice parameter decrease at the outside of the miscibility gap (Figure 3b) which is reported to be almost constant until $\text{Li}_5\text{Ti}_5\text{O}_{12}$ during Li insertion.¹² The increase of the single phase region might be attributed to the locally modified crystal structure near to the surface and the electron state change of Ti as pointed out in Figures 1 and 2. The presence of solid solution outside the miscibility gap indicates a new equilibrium between $\text{Li}_{4+\delta}\text{Ti}_5\text{O}_{12}$ and $\text{Li}_{7-\gamma}\text{Ti}_5\text{O}_{12}$, instead of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and $\text{Li}_7\text{Ti}_5\text{O}_{12}$, and also implies enhanced electronic conductivities during the electrochemical process by increasing the carrier density and hopping probability.

Indeed, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ after nitridation has much better electrochemical properties as shown in Figure 3c. At low current densities below the 1C-rate, the capacities after the nitridation do not differ much from those for pristine $\text{Li}_4\text{Ti}_5\text{O}_{12}$. However, at a high charge/discharge current density of 10C, it could have 6 times larger capacities (*ca.* 120 mAh g^{-1}) even after 10-min nitridation. The mixed-valent intermediate phase, $\text{Li}_{4+\delta}\text{Ti}_5\text{O}_{12}$, and the TiN layer may fully trigger the electrochemical reactions. The cycle performances are also impressive, and the TiN/ $\text{Li}_4\text{Ti}_5\text{O}_{12}$ core-shell powder should retain a robust structure during the electrochemical reactions.

In conclusion, thermal nitridation was adopted to modify $\text{Li}_4\text{Ti}_5\text{O}_{12}$ to make it electronically more conductive. The ammonia gas decomposes surface $\text{Li}_4\text{Ti}_5\text{O}_{12}$ into conductive TiN and Li_2CO_3 without bulk lattice parameter change, and it also may modify the surface structure in a way to accommodate the single phase Li insertion and extraction. Electrochemically induced $\text{Li}_{4+\delta}\text{Ti}_5\text{O}_{12}$ with a TiN surface layer has significantly enhanced the electrochemical properties at high current densities.

Supporting Information Available: Synthetic procedure, characterization methods, powder colors, XRD and XPS data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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