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STUDY OF STRUCTURE AND ELECTRONIC PROPERTY OF SPINEL $Li_4Ti_5O_{12}$ ANODE MATERIAL

© ***Sarantuya L.,*** Institute of Physics and Technology,
Mongolian Academy of Sciences,
Ulaanbaatar, Mongolia,
E-mail: saraa.ipt@gmail.com

© ***Tsogbadrakh N.,*** Department of Physics,
National University of Mongolia,
Ulaanbaatar, Mongolia,
E -mail: Tsogbadrakh@num.edu.mn

© ***Sevjidsuren G.,*** Institute of Physics and Technology,
Mongolian Academy of Sciences,
Ulaanbaatar, Mongolia

© ***Altantsog P.,*** Institute of Physics and Technology,
Mongolian Academy of Sciences,
Ulaanbaatar, Mongolia

We have performed the study of electrochemical properties of the spinel $Li_4Ti_5O_{12}$ anode materials in Li-ion batteries. The $Li_4Ti_5O_{12}$ was successfully synthesized by a solid state reaction method at different temperatures according to the $Li_4Ti_5O_{12}$ cubic spinel phase structure. The synthesized samples were characterized by X-ray diffraction (XRD). In this study, we used a first principle method, based on the density functional theory to explore electronic structure. We have shown that the $Li_4Ti_5O_{12}$ anode material exhibits an insulating behavior with the band gap of 3.3 eV and the $Li_7Ti_5O_{12}$ becomes metallic as Li atoms inserted in $Li_4Ti_5O_{12}$ anode material.
*Keywords:*Li- ion battery, spinel structure, intercalation voltage, solid state reaction method.

Introduction

$Li_4Ti_5O_{12}$ compound is known for its very good electrochemical performance as anode material for lithium ion batteries. It possesses advantages such as good safety, environmental friendliness, and good cycling

performance. $Li_4Ti_5O_{12}$ has been identified as a zero-strain anode material [1]. The material exhibits minimal change in cell volume upon intercalation and de-intercalation (less than 1%), which helps maintain its structural stability, and it also has good thermal stability [2].$Li_4Ti_5O_{12}$ spinel is a very interesting intercalation compound with potential applications as electrode material for Li ion batteries [3]. The compound has a cubic structure with space group symmetry Fd3m. Within the spinel structure, lithium atoms occupy all the 8a sites and 1/6 of the 16d sites, while the remaining 5/6 of the 16d sites aretaken by Ti atoms and all the 32e sites are occupied with O atoms. So this structure is always denoted as$[Li_3]^{8a}[Li_1Ti_5]^{16d}O_{12}$ [4]. At the end of the intercalation process, an additional 8 Li atoms are intercalated into one spinel unit cell and locate at the octahedral (16c) sites. Normally, this material works between the delithiated state $Li_4Ti_5O_{12}$ and lithiated state $Li_7Ti_5O_{12}$, possessing very flat charge/discharge potential plateaus at about 1.5 V [3]. In the present work, we present the structural and electronic properties of the $Li_4Ti_5O_{12}$ compound is studied both theoretically and experimentally. Some of the calculated results are compared with available experimental data, and the others are given as reference to the experiments.

Experimentaland Computational details

$Li_4Ti_5O_{12}$ has been synthesized by a solid state method. The precursors of $Li_4Ti_5O_{12}$ powder samples were synthesized using Li_2CO_3(Sigma–Aldrich, 99.9%), anatase TiO_2(Sigma–Aldrich,99%) as starting materials. Stoichiometric amounts of TiO_2 and Li_2CO_3 (Ti/Li = 5:4) were mixed in ethanol (99.9%). After ball milling for 10 h, the mixed slurry was oven-dried at 80℃. In order to obtain the final $Li_4Ti_5O_{12}$, the mixed precursors were heat-treated at 800, 850, 900, and 1000℃for some time under air atmosphere. The synthesized samples were characterized by X-ray diffraction (XRD).

Our calculation part is based on the plane wave self-consistent field (PWscf) method using the generalized gradient approximation (GGA) by Perdew, Burke and Enzerhof (PBE) [5] within the framework of density functional theory (DFT) [6,7] as implemented in the QUANTUM ESPRESSO package [8]. The following electronic state is treated as valence: Li ($1s^2\ 2s^1$), Ti ($3s^2\ 3p^6 3d^1 4s^2$) and O ($2s^2 2p^4$) for atoms. The interaction between the ions and valence electrons is expressed as the ultrasoft pseudopotential [9]. The wave functions are expressed as plane waves up to a kinetic energy cutoff of 30 Ry. The summation of charge densities is done using the special *k*-points generated by the 5 x 5 x 5

Monkhorst-Pack meshes [10]. We used the tetrahedral method [11] when we evaluate the electronic density of state (DOS). For the self-consistent cycle the total energy convergence is 10^{-4} eV. The occupation numbers of electrons are expressed Gaussian distribution function with an electronic temperature of kT = 0.001 Ry. The atomic ionic positions are relaxed at the fixed lattice parameters until the residual forces are less than 0.05 eV/Å.

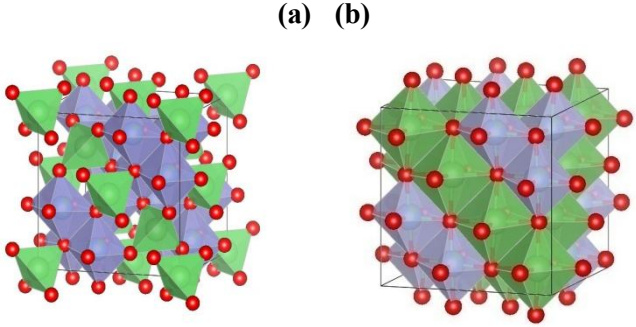

Fig. 1. Unit cells of the (a) $Li_4Ti_5O_{12}$ and (b) $Li_7Ti_5O_{12}$ phases, where the green tetrahedrons, green octahedrons, blue octahedrons, and red spheres represent Li ions at the 8a site, Li ions at the 16c site, Li and Ti ions at the 16c site, and O ions at the 32e site, respectively.

Results and Discussion

Atomistic models — Figures 1a and 1b show the unit cells of $Li_4Ti_5O_{12}$ and $Li_7Ti_5O_{12}$ defect spinel, which belong to Fd3m space group (No. 227). For the $Li_4Ti_5O_{12}$ phase, as shown Fig. 1a, the green spheres represent Li ions at the 8a sites. For the $Li_7Ti_5O_{12}$ phase, as shown in Fig. 1b, the green spheres represent the Li ions at the 16c sites. The red spheres represent the O ions at the 32e sites. The blue spheres represent the Li and Ti ions occupying randomly at the 16d sites.

Structural properties — Equilibrium lattice parameters of both $Li_4Ti_5O_{12}$ and $Li_7Ti_5O_{12}$ phases that were obtained from ab initio calculations using the most stable structures proposed in this work and experimental value are summarized in the Table I. It can be seen that our results are in good agreement with experimental results. For the $Li_4Ti_5O_{12}$ phase, the lattice parameter of the proposed structure is 8.374 A^0 and is in good agreement with the experimental value 8.359 A^0 with an error of 0.17%. For the $Li_7Ti_5O_{12}$ phase, the lattice parameter of the proposed structure is 8.291 A^0 and its error is 0.74% in comparison eith experi-

mental value. This results indicates that the small change in cell volume upon lithiation is one of the advantageous properties that make this material a good candidate for use as an anode material.

Table I

Lattice parameters of spinel $Li_4Ti_5O_{12}$ and $Li_7Ti_5O_{12}$ in Angstroms (A^0)

Lattice constant	**$Li_4Ti_5O_{12}$**	**$Li_7Ti_5O_{12}$**
Experimental value	8.359	8.353
Our result	8.374	8.291

Average intercalation voltage. — The average intercalation voltage can be obtained from an ab initio calculation using the Nernst equation according to Eq. (1) [12].

$$V = -\frac{\Delta G}{nF} \tag{1}$$

Where, n is the number of electrons being transferred during the intercalation process, F is the Faraday constant, ΔG is the Gibbs free energy ($\Delta G = \Delta E - T\Delta S + P\Delta V$). The intercalation potential can be approximated as given in Eq. (2):

$$V \approx -\frac{\Delta E}{nF} \tag{2}$$

The change in internal energy ΔE of intercalation between $Li_4Ti_5O_{12}$ and $Li_7Ti_5O_{12}$. ΔE can be calculated according to Eq. (3):

$$\Delta E = E[Li_7Ti_5O_{12}] - E[Li_4Ti_5O_{12}] - 3E_{BCC}[Li] \tag{3}$$

The calculated results indicate that the average voltage of lithiation/delithiation in relevant electrode materials can be obtained by calculating the total energy differences before and after electrochemical reactions. The average intercalation voltage of 1.9V during charging/discharging were obtained. Our results are summarized in the Table II. All the predicted structural and electrochemical properties agree closely with the experimental findings in literature.

Table 2

Intercalation potentials of theoretical and experimental studies

	Intercalation voltage (Volts)
Experiment	1.55
Our result	1.9

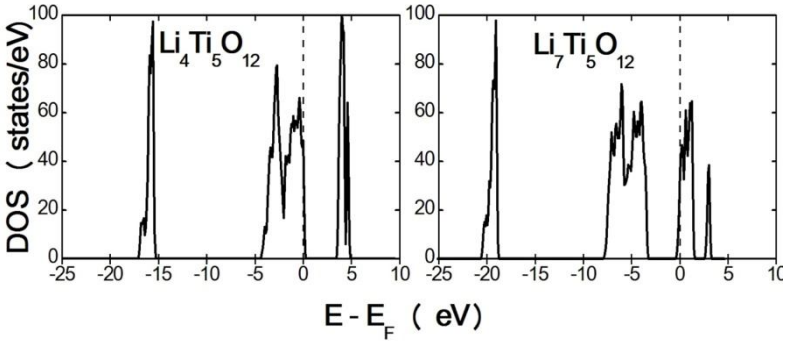

Fig. 2. Total density of states (DOS) for (a) $Li_4Ti_5O_{12}$ and (b) $Li_7Ti_5O_{12}$. The dashed line corresponds to the Fermi level

We have presented the total density of states for $Li_4Ti_5O_{12}$ and $Li_7Ti_5O_{12}$ materials. The figure 2 is shown that the $Li_4Ti_5O_{12}$ material exhibits an insulating behavior [2] with the band gap of 3.3 eV and the $Li_7Ti_5O_{12}$ becomes metallic as Li atoms inserted in $Li_4Ti_5O_{12}$ anode material.

Conclusion

We have investigated the electrochemical properties of the spinel $Li_4Ti_5O_{12}$ anode materials in Li-ion batteries using the GGA — PBE within the framework of DFT as implemented in the QUANTUM ESPRESSO package. Our result is shown that the average intercalation voltage is 1.9V during charging/discharging. The $Li_4Ti_5O_{12}$ material exhibits an insulating behavior with the band gap of 3.3 eV and the $Li_7Ti_5O_{12}$ becomes metallic as Li atoms inserted in $Li_4Ti_5O_{12}$ anode material.

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ИССЛЕДОВАНИЕ СТРУКТУРЫ И ЭЛЕКТРОННЫХ СВОЙСТВ АНОДНОГО МАТЕРИАЛА — ШПИНЕЛИ $Li_4Ti_5O_{12}$

Л. Сарантуя, Институт физики и технологии,
Монгольской академии наук,
Улан-Батор, Монголия,
Электронная почта: saraa.ipt@gmail.com

Х. Цогбадрах, физический факультет,
Национальный университет Монголии,
Улан-Батор, Монголия,
E -mail: Tsogbadrakh@num.edu.mn

Г. Седживсурен, Институт физики и технологии,
Монгольской академии наук,
Улан-Батор, Монголия

П. Алтанцог, Институт физики и технологии,
Монгольской академии наук,
Улан-Батор, Монголия

Мы провели исследование электрохимических свойств шпинели $Li_4Ti_5O_{12}$как анодных материалов для литий-ионных батарей. $Li_4Ti_5O_{12}$успешно синтезировали твердотельным методом реакции при различных температурах. Синтезированные образцы были охарактеризованы с помощью рентгеновской дифракции (XRD). В данном исследовании мы использовали первый принцип метода, основанный на теории функционала плотности для объяснения электронной структуры. Мы показали, что материал анода $Li_4Ti_5O_{12}$ демонстрирует диэлектрическое поведениес шириной запрещенной зоны 3,3 эВ и $Li_4Ti_5O_{12}$ становится проводником по мрере внедрения атомовLi.
Ключевые слова: Li- ионная батарея, структура шпинели, интеркаляции напряжения, твердотельный реакционный метод.