Research Article

Structure and Electrochemical Properties of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ Prepared via Low-Temperature Precipitation

Le Thanh Nguyen Huynh ¹, Cam Thanh Duy Ha,¹ Viet Dung Nguyen,¹
Dinh Quan Nguyen,² My Loan Phung Le ^{1,3} and Van Man Tran^{1,3}

¹Applied Physical Chemistry Laboratory (APCLAB), VNUHCM-University of Science, 227 Nguyen Van Cu Street, District 5, Ho Chi Minh City, Vietnam

²Biomass Laboratory, VNUHCM-University of Technology, 268 Ly Thuong Kiet street, District 10, Ho Chi Minh City, Vietnam

³Department of Physical Chemistry, Faculty of Chemistry, VNUHCM-University of Science, 227 Nguyen Van Cu street, District 5, Ho Chi Minh City, Vietnam

Correspondence should be addressed to My Loan Phung Le; lmphung@hcmus.edu.vn

Received 3 March 2019; Revised 21 May 2019; Accepted 10 June 2019; Published 25 August 2019

Guest Editor: Nguyen Van Noi

Copyright © 2019 Le Thanh Nguyen Huynh et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

This work aimed to prepare the spinel phase $\text{Li}_4\text{Ti}_5\text{O}_{12}$ by a combination of the low-temperature precipitation technique and assisted calcination step. X-ray diffraction (XRD) revealed that the intermediated phase was Li_2TiO_3 , and the spinel phase could be evidently formed at 700°C for 12 to 20 hours. The morphology of spinel powder, determined by SEM and TEM, exhibited a good distribution at the submicrometric scale that promoted a fast kinetic of Li migration and an excellent performance at the high-rate cycling test. The stable performances were achieved in the charge-discharge test at different current densities: 80 mA/g (165 mAh/g), 320 mA (160 mAh/g), and 1600 mA (145 mAh/g) upon 100 cycles. Moreover, we observe a capacity retention of 48% (corresponding 80 mA/g) at a high rate of 5000 mAh/g. The cyclic voltammetry measurement displayed a reversible system and revealed the lithium diffusion coefficient of $1.15 \times 10^{-11} \text{ cm}^2/\text{s}$.

1. Introduction

Spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ has become an attractive anode material for high-power and fast-charging Li-ion battery because of its excellent cycle performance, structural stability, and little change in the unit cell volume during lithium intercalation/deintercalation. The spinel structure of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ provides a three-dimensional network for Li migration [1, 2]. The process of lithium insertion/extraction occurs as the two-phase mechanism at 1.55 V (vs. Li^+/Li), characterized by a long flat plateau in the voltage profile. The voltage plateau happens to be much above the reduction potentials of most common electrolyte solvents mitigating the formation of the solid electrolyte interface (SEI). In spite of these beneficial properties, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ does not yet meet all the requirements for successful use in fast-charging applications caused by its

poor electrical conductivity and sluggish diffusion of lithium ions. [3, 4].

In the literature, many efforts have been aimed to overcome these disadvantages by doping or carbon coating of particles [5, 6] to enhance the conductivity of LTO particles; or alternative synthesis methods fabricate the nano-size LTO with controlled and regular morphologies aiming to shorten the lithium diffusion pathway. It has been reported that nanocrystalline $\text{Li}_5\text{Ti}_5\text{O}_{12}$ electrode materials have excellent performance even at high charging rate and high temperature; therefore, they are useful when applied in high-rate charge/discharge Li-ion batteries. Different synthesis methods have been investigated such as sol-gel processes, high-temperature annealing treatment, solution-combustion, and hydrothermal to improve the phase purity and electrochemical performance. Hao et al. [7] synthesized

$\text{Li}_4\text{Ti}_5\text{O}_{12}$ particles by a sol-gel method with citric acid as a chelating agent and Li_2CO_3 and tetrabutyl titanate as starting materials. Mixtures of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and rutile- TiO_2 were observed after heating at 800°C for 20 hours in air, while the pure $\text{Li}_4\text{Ti}_5\text{O}_{12}$ phase with an average particle size of 500 nm was obtained at 850°C for 24 hours. Li et al. [8] prepared $\text{Li}_4\text{Ti}_5\text{O}_{12}$ with nanotubes and nanowires morphology by a hydrothermal lithium exchange processing. XRD analysis showed a trace of anatase- TiO_2 in spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanotubes calcinated at 350°C for 2 hours. The $\text{Li}_4\text{Ti}_5\text{O}_{12}$ spinel was synthesized by a sol-gel method using titanium isopropoxide, LiOH , and 2-methoxy ethanol and subsequent treatment with high ball milling by Kim et al. [9] It was also notified that a trace of rutile- TiO_2 was observed for the powder annealed at 850°C for 5 hours. According to previous studies, the heat treatment at high temperature in synthesizing the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ spinel obviously led to the formation of rutile or anatase- TiO_2 , and these impurities are detrimental to the electrochemical performance of the spinel phase. Consequently, low-temperature synthesis or minimum heat treatment by employing a suitable aqueous particulate sol-gel route or intermediate precipitate phase has been recently suggested. Chui and coworker [10, 11] utilized the extreme excess ratio of Ti versus Li (Ti:Li = 6:1) to prepare the spinel phase $\text{Li}_4\text{Ti}_5\text{O}_{12}$ through the intermediated phase lithium titanate hydrate $\text{Li}_{1.81}\text{H}_{0.19}\text{Ti}_2\text{O}_5\cdot 2\text{H}_2\text{O}$ (LTH).

Our work aimed to prepare the nanosized spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ powder from the intermediated cubic phase Li_2TiO_3 which was obtained from a low-temperature precipitation. The effect of temperature and duration of calcination on the formation of the spinel phase was regarded. The structural and morphological properties were characterized by powder X-ray diffraction, Raman spectroscopy, and scanning/transmission electronic microscopy (SEM/TEM). The high-rate performance through galvanostatic charge-discharge and the diffusion coefficient of lithium ions (D_{Li}) in the host $\text{Li}_4\text{Ti}_5\text{O}_{12}$ were measured and compared with the bulk material.

2. Experimental

2.1. Synthesis of Nanostructured $\text{Li}_4\text{Ti}_5\text{O}_{12}$. Spinel-type $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was prepared via a low-temperature precipitation method combining with the calcining process from 600 to 800°C . Titanium butoxide $\text{Ti}(\text{OBu})_4$ with a normal purity of 97% (Sigma Aldrich, $d = 1.491 \text{ g/mL}$ at 20°C , $M = 340.39 \text{ g/mole}$) and lithium hydroxide monohydrate $\text{LiOH}\cdot\text{H}_2\text{O}$ with a normal purity of 99.95% (Sigma Aldrich) were used as titanium and lithium precursors. 10.50 mg $\text{Ti}(\text{OBu})_4$ was dropped into 25 mL solution of 1 M LiOH solution under vigorous stirring at 5°C with the molar ratio Li:Ti of 1:1.33. Then, the produced powder was collected by centrifugation and washed several times with deionized water to neutral pH to eliminate the excess of LiOH and dried at 120°C for overnight. The as-prepared powder was annealed at 600 – 800°C for 12 hours.

2.2. Structural Characterizations. The structure of samples was identified by X-ray diffraction (XRD) in D8-Advance (Bruker) diffractometer using $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). XRD patterns were collected in the range 10° – 70° with a step of 0.029° per second. Lattice parameters were calculated by software CelRef. Raman spectra were measured with a XploRA Raman microspectrometer (Jobin-Yvon-Horiba), using a He:Ne laser (632.8 nm) as the excitation source. The morphologies and the distribution of grain size were determined by using scanning electron microscope (FE-SEM S4800 Hitachi, Japan) and transmission electronic microscopy (TEM, JEOL 1400, Japan).

2.3. Electrochemical Characterizations. The electrochemical performance, including rate capability and charge/discharge capacity of spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$, was evaluated at room temperature with the coin-cell type CR-2025 in which a metallic lithium foil was used as the counterelectrode. The composite electrodes were made of the active material (80 wt.%), conducting acetylene black (7.5 wt.%), carbon graphite (7.5 wt.%), and polyvinylidene fluoride (PVdF) binder (5 wt.%) homogeneously dispersed in *N*-methyl-2-pyrrolidone (NMP) solvent. The slurry was coated on an aluminum foil and cut to pieces with diameter of 10 mm (an area surface of 0.785 cm^2) and then dried at 120°C in vacuum for 12 hours. The coin cell was assembled in an argon-filled glove box (M. Braun Co., $[\text{O}_2] < 1 \text{ ppm}$ and $[\text{H}_2\text{O}] < 1 \text{ ppm}$). The employed organic electrolyte was a mixture of 1 M LiPF_6 with ethylene carbonate (EC) and dimethyl carbonate (DMC) at volumetric ratio 2:1.

A constant current protocol in the range of 20 mA/g to 5000 mA/g was used for formation cycles in a potential range of 1 – 2.5 V (vs. Li^+/Li). The cyclic voltammetry (CV) was performed at different scan rates between the voltage of 10 and $120 \mu\text{V/s}$ to evaluate the lithium coefficient diffusion related to the charge/discharge process.

3. Results and Discussion

3.1. Structure and Morphology. Considering the structure of $\text{Li}_4\text{Ti}_5\text{O}_{12}$, the previous studies [1, 2, 4] demonstrated a cubic spinel (unit cell $a = 8.3557 \text{ \AA}$) with a space group of F3dm. The three ions Li^+ are situated at the tetrahedral 8a site, the other ions Li^+ and ions Ti^+ randomly locate in the octahedral 16d sites with a ratio of 1:5, and the oxygen atoms totally are located at the 32e site; this suggests that $[\text{Li}_3]^{8a}[\text{Li}_1\text{Ti}_5]^{16d}[\text{O}_{12}]^{32e}$ is the probable structure. Figure 1 compares the XRD patterns of the intermediated phase and final samples calcinated at different temperatures from 500°C to 800°C for 12 hours. The intermediate phase can be indexed in the orthorhombic phase Li_2TiO_3 (JSPDS: 00-003-1024). At 500°C , the spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ phase was apparently formed, but the transformation was uncompleted; the remaining of the intermediate phase was still observed in the XRD diagram. At 600°C , XRD patterns provided the main peaks of the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ phase (JSPDS: 000-049-0207) [12], indicating the

FIGURE 1: XRD patterns of samples at different calcination temperatures.

complete transformation from the intermediated phase to $\text{Li}_4\text{Ti}_5\text{O}_{12}$ phase. However, it was noticed in the samples thermally treated, and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ presents wide peaks, which indicated the formation of the small crystalline material. The pure spinel phase $\text{Li}_4\text{Ti}_5\text{O}_{12}$ was obtained at 700°C and 800°C, and it could be obviously observed that the crystallinity degree of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ improved with increase in calcination temperature. In contrast, the calcination at 800°C led a trace of rutile- TiO_2 . When the calcinating temperature was raised from 600°C to 700°C, the lattice parameter a slightly increased: 8.3477 Å (600°C) to 8.3599 Å (700°C). Colbow et al. [1] reported $a = 8.357$ Å, and Harisson et al. [13] also reported $a = 8.358$ Å which is in good agreement with our value at 700°C. The sample calcinated at 800°C exhibited unexpectedly the high value of the lattice parameter and 8.3716 Å due to the emergence of the TiO_2 rutile phase, respectively.

In order to examine the impact of calcination time, the sample at 700°C was treated at variable scheduling (Figure 2). The remaining intermediate phase was still observed for 4 hours and 8 hours, while the pure phase $\text{Li}_4\text{Ti}_5\text{O}_{12}$ only appeared at the duration from 12 hours to 20 hours. However, with 24 hours of calcination, the TiO_2 anatase phase was merged in the LTO phase. XRD patterns of samples at 12, 16, and 20 hours are identical and indexed to the pure spinel phase. The lattice parameter a can be determined to be 8.3595 Å which is in good agreement with the reported standard values even though the wide XRD peaks indicated the small crystallite of LTO. The crystallite size of the LTO phase was, respectively, calculated from their reflections using the Scherrer equation based on the full width at half maximum (FWHM) of diffraction peaks:

$$d_{hkl} = \frac{k\lambda}{\beta \cos \theta} \quad (1)$$

where d_{hkl} is the average crystallite size, k is the constant depending on the crystalline shape (0.9), λ is the radiation X-ray wavelength of Cu (1.5406 Å), β is the FWHM of the most intense peak, and 2θ is the diffraction angle. The rough estimation of crystallite size is around 40 nm for all three

FIGURE 2: XRD patterns of samples at different calcination times at 700°C.

samples. The submicrometric LTO could suggest a fast kinetic of lithium insertion due to shortening of the lithium pathway diffusion.

Raman active modes of spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ involve F_{2g} , E_g , and A_{1g} following the calculation of symmetry group O_h^2 , which represented the stretching and bending vibration of Ti-O bonds in $[\text{TiO}_6]$ octahedra and Li-O bonds in $[\text{LiO}_4]$ and $[\text{LiO}_6]$ polyhedra. [14, 15] At high frequency, two vibration modes A_{1g} at 671 cm^{-1} and 740 cm^{-1} were assigned to the vibrations of Ti-O bonds, while the stretching vibrations of the Li-O bonds were attributed by two modes in region medium frequency 430 cm^{-1} and 374 cm^{-1} . The last modes in low frequency (235 cm^{-1}) were attributed to the bending vibrations of O-Ti-O bonds. In brief, we succeeded to produce the pure phase $\text{Li}_4\text{Ti}_5\text{O}_{12}$ treated at 700°C for three schedules (12, 16, and 20 hours) without structural difference.

Figure 3 shows the SEM and TEM morphology of the sample $\text{Li}_4\text{Ti}_5\text{O}_{12}$ treated at 700°C for 16 hours. It can be seen that the sample consists of submicro-scaled primary particles with a homogeneous size distribution, which are in turn composed of larger particles of 100 μm . From the TEM image, the primary particles consist of nanorods of 10 nm in length (Figure 4).

3.2. Electrochemical Performance. The electrochemical performance of the spinel nanosized $\text{Li}_4\text{Ti}_5\text{O}_{12}$ as anode materials for lithium ion batteries has been investigated. Figure 5(a) illustrates the voltage profiles at low current density 20 mA/g of three samples $\text{Li}_4\text{Ti}_5\text{O}_{12}$ calcinated at 700°C for 12, 16, and 20 hours. The samples delivered a first discharge capacity of 178 mAh/g with a cutoff value of 1.0 (vs. Li^+/Li). This is in line with the theoretical capacity of 175 $\text{mAh}\cdot\text{g}^{-1}$ meaning that the excess lithium ions were intercalated into LTO, and no SEI film formed during the first charge which is usually formed in the range 0.2–0.8 V vs. Li^+/Li [8]. In the subsequent cycles, the capacity discharge was stabilized at 167 mAh/g without obvious capacity fading. A flat plateau at 1.65 V vs. Li^+/Li precisely corresponding to the $\text{Ti}^{3+}/\text{Ti}^{4+}$ redox reaction means that is the insertion/

FIGURE 3: Raman spectroscopy of $\text{Li}_4\text{Ti}_5\text{O}_{12}$.

FIGURE 4: SEM images (a) and TEM image (b) of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ treated at 700°C for 16 hours.

FIGURE 5: (a) Typical charge-discharge curves at current density of 20 mA/g and (b) cycling performance of samples $\text{Li}_4\text{Ti}_5\text{O}_{12}$ calcined at 700°C for 12 hours, 16 hours, and 20 hours.

FIGURE 6: (a) Typical charge-discharge curves at current density: 80, 320, and 1600 mA/g and (b) cycling performance of $\text{Li}_4\text{Ti}_5\text{O}_{12}$.

extraction of lithium ions during the charge/discharge process. In addition, a small electrode polarization of about 0.02 V (below 20 mV) is observed between charge and discharge curves indicating the existence of good interparticle electrical contacts and better ion transport owing to the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ nanoparticles and good stability of the spinel structure during Li migration. Furthermore, all three spinel samples exhibited excellent cycling stability with a capacity retention of 100% upon 100 cycles (Figure 5(b)).

Spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is subjected to cycling at different charge-discharge rates such as 80 mA/g, 320 mA/g, and 1600 mA/g to evaluate the capacity-rate relationship (Figure 6(a)). The charge-discharge curve at current 320 mA/g seems to quasi-superimpose on the one at current 80 mA/g without potential difference. The sample exhibited a capacity value of 165 mAh/g (80 mA/g) and 160 mAh/g (320 mA/g), a value close to the theoretical value of 175 mAh/g. At extremely high current of 1600 mA/g, there is a slight drop in capacity values (12.5% decrease) together with a drop in the discharge voltage plateau at 1.5 V (vs. Li^+/Li) which causes high electrode polarization (140 mV). However, the cycling performance upon 100 cycles at all three constant current show an excellent Coulombic efficiency; typically, the capacity retention remained 100% after 100 cycles with the capacity of 165 mAh/g, 160 mAh/g, and 135 mAh/g, respectively.

The rate capability is also important parameter for evaluating an electrode material addressed to the battery as well as supercapacitor application. A constant current discharge test was performed on $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrodes varying the rate from 20 mA/g to 5000 mA/g during discharge in the voltage range of 1.0–2.5 V, with the voltage profiles visible in Figures 7(a)–7(c). The charge-discharge profiles at rates below 1000 mA/g (Figure 7(a)) show a low polarization from 20 mV (40 mA/g) to 90 mV (960 mA/g) indicating the electron transfer efficiency and lithium diffusion pathway.

Our spinels exhibit the better rate capability than those reported in the literature [16]. A capacity of 145 mAh/g was achieved at current 400 mA/g, and this capacity amounts to 85% of capacity at the low current of 20 mA/g. From the current density above 1200 mA/g, we observe the critical impact of rates on the voltage profiles and the specific capacity. The more the current density applied, the more the discharge plateau shortened. Traditionally, the lithium insertion/extraction into host $\text{Li}_4\text{Ti}_5\text{O}_{12}$ occurred via a two-phase mechanism; herein, it showed a sloping voltage curve similar to that of a one-phase reaction due to the large electrode polarization.

Figure 7(d) illustrates the electrode polarization and specific capacity as function of the C-rate, and the highest current 5000 mA/g corresponds to rate 30°C. In the high current density performance, the electrochemical profiles significantly depended on the electronic conduction, which served as the electrode polarization. The drastic increase of polarization voltage from 100 mV to 350 mV was observed when the currents applied varied from 1200 mA/g to 5000 mA/g. Our spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ still shows an impressive performance at such high current densities. At three highest currents 4500 mA/g (26°C), 4750 mA/g (28°C), and 5000 mA/g (30°C), the capacities 90 mAh/g, 85 mAh/g, and 80 mAh/g were achieved, respectively. It is noteworthy that the capacity (80 mAh/g) obtained with nanosized LTO at 30°C rate is much higher than that obtained at the 5°C rate (95 mAh/g) with bulk LTO. Indeed, the morphology of mesoporous and nanoparticle LTO powders provide a short diffusion path for Li and pore fill of electrolytes ensuring a high flux of Li.

Cyclic voltammetry analysis has been carried out to further investigate the electrochemical properties of spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$. Figure 8(a) shows the cyclic voltammetry curve at different scan rates to determine the kinetic of Li-migration process. The pair of anodic/cathodic peaks of spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$,

FIGURE 7: (a–c) Charge-discharge profile of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ at various current densities from 40 mA/g to 5000 mA/g and (d) electrode polarization and specific capacity as the function of C-rate.

FIGURE 8: (a) CV curves under various scan rates from 10 $\mu\text{V/s}$ to 120 $\mu\text{V/s}$ and (b) current density as a function of the square root of the scan rate $v^{1/2}$.

located at 1.62 V/1.55 V at the scan rate of 10 μ V/s, demonstrate reversible lithium intercalation and deintercalation of host $\text{Li}_4\text{Ti}_5\text{O}_{12}$, respectively. The peak separation increases with the increasing scan rate that indicated the effect of electrode polarization owing to the limited diffusion process. The plot of cathodic peak current density (i_{pc}) as a function of the square root of the scan rate ($\nu^{1/2}$) in Figure 8(b) shows a good linear relation between i_{pc} and $\nu^{1/2}$ ($R = 0.9999$). Herein, the equation Randles–Sevcik [17] can be applied to determine the diffusion coefficient of lithium ions (D_{Li}), characterized as the kinetics of the lithium insertion process. The diffusion coefficient of lithium ions was calculated to be $1.15 \times 10^{-11} \text{ cm}^2/\text{s}$.

4. Conclusion

In summary, spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ has been successfully prepared through a low temperature precipitation process to obtain a particle-size distribution at the submicrometric scale. The electrochemical measurements show that spinel LTO exhibited the discharge capacity of 178 mAh/g at 0.1°C in the first discharge and favorable cyclic reversibility at different current rates of 20, 80, 320, and 1600 mA/g with a capacity of 167, 165, 160, and 135 mAh/g upon 100 cycles. Furthermore, the spinel samples show an excellent performance at extremely high rate, which is capable of delivering a capacity of 80 mAh/g at current 5000 mA/g.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

This research was funded by the Department of Science and Technology in Ho Chi Minh City (DOST) under contract no. 135/2017/HĐ-SKHCN.

References

- [1] K. M. Colbow, J. R. Dahn, and R. R. Haering, "Structure and electrochemistry of the spinel oxides LiTi_2O_4 and $\text{Li}_{43}\text{Ti}_{53}\text{O}_{40}$," *Journal of Power Sources*, vol. 26, no. 3-4, pp. 397–402, 1989.
- [2] T. Ohzuku, "Zero-strain insertion material of $\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4$ for rechargeable lithium cells," *Journal of The Electrochemical Society*, vol. 142, no. 5, p. 1431, 1995.
- [3] D. Li and H. Zhou, "Two-phase transition of Li-intercalation compounds in Li-ion batteries," *Materials Today*, vol. 17, no. 9, pp. 451–463, 2014.
- [4] I. A. Leonidov, O. N. Leonidova, L. A. Perelyaeva, R. F. Samigullina, S. A. Kovyazina, and M. V. Patrakeev, "Structure, ionic conduction, and phase transformations in lithium titanate $\text{Li}_4\text{Ti}_5\text{O}_{12}$," *Physics of the Solid State*, vol. 45, no. 11, pp. 2183–2188, 2003.
- [5] C. H. Chen, J. T. Vaughey, A. N. Jansen et al., "Studies of Mg-substituted $\text{Li}_{4-x}\text{Mg}_x\text{Ti}_5\text{O}_{12}$ spinel electrodes ($0 \leq x \leq 1$) for lithium batteries," *Journal of The Electrochemical Society*, vol. 148, no. 1, pp. A102–A104, 2001.
- [6] K.-S. Park, A. Benayad, D.-J. Kang, and S.-G. Doo, "Nitridation-driven conductive $\text{Li}_4\text{Ti}_5\text{O}_{12}$ for lithium ion batteries," *Journal of the American Chemical Society*, vol. 130, no. 45, pp. 14930–14931, 2008.
- [7] Y.-J. Hao, Q.-Y. Lai, D.-Q. Liu, Z.-U. Xu, and X.-Y. Ji, "Synthesis by citric acid sol-gel method and electrochemical properties of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode material for lithium-ion battery," *Materials Chemistry and Physics*, vol. 94, no. 2-3, pp. 382–387, 2005.
- [8] J. Li, Z. Tang, and Z. Zhang, "Controllable formation and electrochemical properties of one-dimensional nanostructured spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$," *Electrochemistry Communications*, vol. 7, no. 9, pp. 894–899, 2005.
- [9] H.-J. Kim, M.-H. Oh, W.-K. Son, T.-I. Kim, and S.-G. Park, "Novel synthesis method and electrochemical characteristics of lithium titanium oxide as anode material for high power device," in *Proceedings of the 2006 IEEE 8th International Conference on Properties Applications of Dielectric Materials*, pp. 464–467, Denpasar, Indonesia, June 2006.
- [10] H.-C. Chiu and G. P. Demopoulos, "A novel green approach to synthesis of nanostructured $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode material," *ECS Transactions*, vol. 50, no. 26, pp. 119–126, 2013.
- [11] H.-C. Chiu, N. Brodusch, R. Gauvin, A. Guerfi, K. Zaghib, and G. P. Demopoulos, "Aqueous synthesized nanostructured $\text{Li}_4\text{Ti}_5\text{O}_{12}$ for high-performance lithium ion battery anodes," *Journal of the Electrochemical Society*, vol. 160, no. 5, pp. A3041–A3047, 2013.
- [12] D. Tsubone, T. Hashimoto, K. Igarashi, and T. Shimizu, "Electrical characterization of phase changes in lithium titanate," *Journal of the Ceramic Society of Japan*, vol. 102, no. 1182, pp. 180–184, 1994.
- [13] M. R. Harrison, P. P. Edwards, and J. B. Goodenough, "The superconductor-semiconductor transition in the $\text{Li}_{1+x}\text{Ti}_{2-x}\text{O}_4$ spinel system," *Philosophical Magazine B*, vol. 52, no. 3, pp. 679–699, 1985.
- [14] D. Z. Liu, W. Hayes, M. Kurmoo, M. Dalton, and C. Chen, "Raman scattering of the $\text{Li}_{1+x}\text{Ti}_{2-x}\text{O}_4$ superconducting system," *Physica C: Superconductivity*, vol. 235–240, pp. 1203–1204, 1994.
- [15] C. M. Julien, M. Massot, and K. Zaghib, "Structural studies of $\text{Li}_4/3\text{Me}_5/3\text{O}_4$ (Me = Ti, Mn) electrode materials: local structure and electrochemical aspects," *Journal of Power Sources*, vol. 136, no. 1, pp. 72–79, 2004.
- [16] M. V. Tran, N. L. T. Huynh, T. T. Nguyen, D. T. C. Ha, and P. M. L. Le, "Facile solution route to synthesize nanostructure $\text{Li}_4\text{Ti}_5\text{O}_{12}$ for high rate Li-ion battery," *Journal of Nano-materials*, vol. 2016, Article ID 4261069, 7 pages, 2016.
- [17] D. Y. W. Yu, C. Fietzek, W. Weydanz et al., "Study of LiFePO_4 by cyclic voltammetry," *Journal of The Electrochemical Society*, vol. 154, no. 4, pp. A253–A257, 2007.