

Sol-Gel Synthesis of Nanocomposite $\text{Cu-Li}_4\text{Ti}_5\text{O}_{12}$ Structures for Ultrahigh Rate Li-Ion Batteries

A. ERDAS*, S. OZCAN, M.O. GULER, H. AKBULUT

Sakarya University, Engineering Faculty, Department of Metallurgical & Materials Engineering,
Esentepe Campus, 54187, Sakarya, Turkey

In this study, spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ materials were successfully synthesized by a simple and facile sol-gel process and electroless copper deposition techniques. The characteristics of the as-prepared $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and $\text{Cu-Li}_4\text{Ti}_5\text{O}_{12}$ were examined by X-ray diffraction and scanning electronic microscopy, while the electrochemical performances including charge/discharge and rate performance tests were also investigated. $\text{Cu-Li}_4\text{Ti}_5\text{O}_{12}$ electrode demonstrated the superior initial discharge capacity and rate capability to $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrode, cycled between 1.0 and 2.5 V. The enhanced rate capability can be attributed to the higher Li^+ diffusivity and lower charge-transfer resistance due to the electroless deposition of copper. Moreover, when both electrodes discharged with 80 °C state of discharge conditions, the reversible capacities were further increased $\sim 70 \text{ mAh g}^{-1}$ with excellent cycling stability and almost no irreversible capability was observed during cycling.

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1. Introduction

Due to the technological improvements, portable consumer electronics, such as mobile phones and notebook computers require more energy. That makes lithium-ion batteries the dominant power source. In addition, to meet the global environmental concerns, lithium-ion batteries are also in the focus for electric vehicle and hybrid electric vehicle, to save oil and to decrease exhaust emissions. Development of new materials for lithium ion batteries has been attractive for investigators, because of the increasing demands for high-energy density and high-power density of batteries. Nowadays, spinel lithium titanate, $\text{Li}_4\text{Ti}_5\text{O}_{12}$, has attracted great interest as anode material for rechargeable lithium-ion batteries, due to its unique characteristics, including the zero-strain feature and the flat Li insertion voltage at about 1.55 V versus Li. As a consequence, a theoretical specific capacity of 175 mAh g^{-1} is expected [1, 2]. It is revealed that spinel host has an excellent structural stability and a very small volume change during cycling. However, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ is a poor electrical conductor with a conductivity of only $10^{-13} \text{ S cm}^{-1}$ at room temperature. To develop high rate lithium storage devices, nano structured active materials have attracted great interests, owing to their shorter transport length for Li^+ and electronic transport, larger electrode-electrolyte contact area and better accommodation of the strain of Li^+ insertion/extraction. The use of nanosized $\text{Li}_4\text{Ti}_5\text{O}_{12}$ has been shown to improve the rate capability [3, 4]. In this study, we aimed to produce porous spinel lithium titanate anode materials with high electronic conductivity. Copper is known as a good ma-

terial because of its low resistivity and high resistance to electromigration [5]. $\text{Li}_4\text{Ti}_5\text{O}_{12}$ spinel structure is produced via facile sol-gel method and the surfaces of the spinel structure are then coated with Cu via electroless coating techniques. The effect of copper coating on the electrochemical properties is investigated.

2. Experimental details

LTO powders were produced via sol-gel method, using citric acid (Merck, purity: > 99%) as a chelating agent. 5 mmol of titanium isopropoxide, $\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4$ (Sigma Aldrich, 99.999% trace metal basis), was dissolved in 150 ml of 2-propanol (Merck, Emsure) to obtain a saturated solution. 4 mmol of lithium nitrate, LiNO_3 (Merck, purity: 99.995% Suprapur), was then added with mild stirring. A saturated aqueous citric acid ($\text{C}_6\text{H}_8\text{O}_7$, Merck, > 99%) was then added at a molar ratio of 9 mmol. pH of the final solution was kept at 7.0 by adding ammonium hydroxide (Alfa Aesar, 25% Solution). The solution was then heated to 90 °C with vigorous stirring to remove the excess ammonia and water, until a transparent gel was obtained. The gel was then kept for 12 h in air oven at 120 °C in order to obtain metal citrate precipitation. After drying process, the precursors were decomposed at 450 °C for 4 h and 850 °C for 7 h in air in order to eliminate organic contents.

LTO powders were used as the cores of the composite powders in the electroless plating. Before starting the deposition process, the surfaces of the anode active powders had to be pre-treated as follows, (i) the surfaces of the as-synthesized powders were cleaned by immersing powders into 1 M sodium hydroxide (Merck, Titripur) solution for 10 min, (ii) the cleaned LTO powders were then immersed into boiling hydrochloric acid (Merck, 1N) for 15 min to coarsen their surfaces. The coarsened surfaces will also help to improve the adhesion between the LTO-based powders and copper parti-

*corresponding author; e-mail: aslihan_erdas@hotmail.com

cles. (iii) since the surfaces of LTO powders were non-conductive, an activation process was needed in order to improve the catalytic properties. One-step sensitization and activation process was performed in this study. The etched particles of LTO were immersed in a palladium activation solution consisting of palladium dichloride (Merck, PdCl₂) (0.3 g/l), stannous chloride (Merck, SnCl₂·2H₂O, > 99.9%) (16 g/l), sodium chloride (Merck, NaCl, > 99.99%) (150 g/l) and hydrochloric acid HCl (Merck, 1N) (60 ml/l), and stirred strongly at room temperature for 15–20 min. After each pre-treatment process, particles of LTO were repeatedly washed by using bidistilled water until pH had reached 7. The pre-treated powders were then dried after the activation step in an oven at 80 °C for 12 h.

The resulting samples were characterized by means of X-ray diffraction (XRD, Rigaku D/Max 2200) with monochromated Cu K_α radiation at a scanning rate of 1 °min⁻¹ in the range of 10–80°. The morphology of the synthesized materials was examined using a scanning electron microscopy (SEM, Jeol 6060 LV). Galvanostatic charging and discharging tests were performed using CR2016 coin type cells by using MTI BST8A battery tester system. The positive electrode was prepared by blending active material, carbon black (Alfa Aesar, > 99.9%) and polyvinylidene fluoride (Alfa Aesar, > 99.9%) (80:10:10) in N-methyl-2-pyrrolidone (Alfa Aesar, > 99%) with a weight ratio of 8:1:1 in N-methyl pyrrolidinone. The aluminum foil was then coated with the slurry using “doctor blade” technique. The weight of active material was ~ 1.786 mgcm⁻². Coin type (CR2016) test cells were assembled in an argon-filled glove box (Mbraun, Labstar) using a microporous polypropylene film as a separator, 1 M LiPF₆ (Sigma Aldrich, ≥ 99.99%) in ethylene carbonate (Sigma Aldrich, 99%) and dimethyl carbonate (Sigma Aldrich, ≥ 99%) (EC/DMC, 1:1 vol) as electrolyte, and Li foil as the counter and reference electrodes. Constant current charge/discharge was performed at various rates within a voltage window of 1–2.5 V (versus Li⁺/Li).

3. Results and discussion

The X-ray diffraction patterns of the synthesized powders are shown in Fig. 1. All sharp diffraction peaks can be indexed on the basis of a cubic spinel structure, Li₄Ti₅O₁₂ (JCPDS file no. 26-1198). The peaks at $2\theta = 18.4^\circ$, 35.6° , 43.3° , 47.4° , 57.2° , 62.8° , 66.1° , 74.3° and 79.3° , which correspond to (111), (311), (400), (331), (511), (440), (531), (533) and (444) planes, respectively, of a face-centered cubic spinel LTO, with *Fd3m* space group. This suggests that high purity LTO can be prepared by firing the sol-gel derived precursors at 850 °C for only 1 h. No trace amount of impurity Li phase can be detected, as shown in Fig. 1.

Surface morphologies of the LTO and Cu/LTO powders calcined at 850 °C are presented in Fig. 2. A typical SEM image in Fig. 2a shows that the sample has polyhedron morphology and a uniform particle size distribution. Higher magnification SEM image in the inset

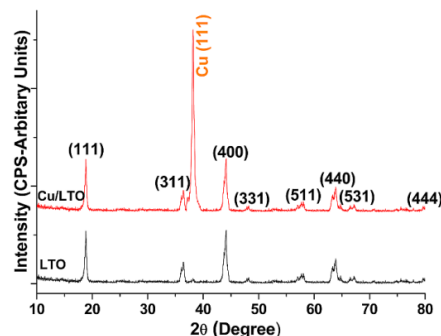


Fig. 1. XRD patterns of the (a) pristine LTO (b) Cu coated LTO spinel samples.

of Fig. 2a indicates that the polyhedron structures are composed of subgrains that have particle size ranging from 60 to 90 nm, which is in agreement with the XRD result. Figure 2b shows the SEM images of Cu-coated as-synthesized LTO powders with EDS dot map analysis. No free copper particles and uncoated surface of pristine LTO particles are found in powders. From the Fig. 2a and 2b it can also be concluded that surfaces of polyhedrons have not been changed after electroless deposition process. In addition, EDS dot map analysis also confirm that surfaces of the LTO powders were coated uniformly with Cu. The Cu film growth on the surfaces of LTO can be explained by the layer growth, in which the nucleation starts spreading both in the vertical and horizontal directions.

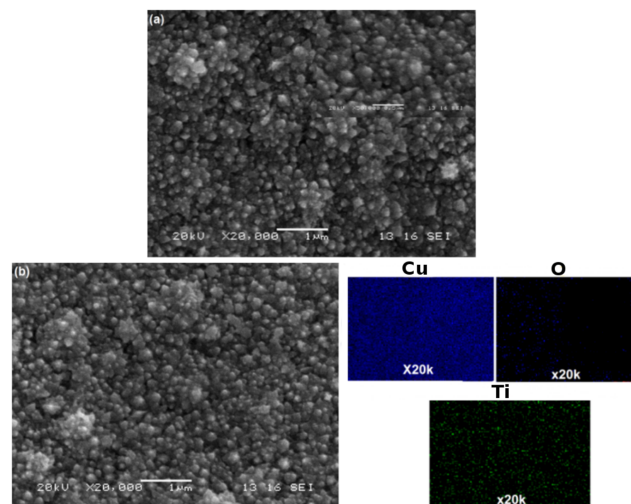


Fig. 2. SEM images of the (a) pristine LTO (b) Cu coated LTO with EDS dot map analysis of spinel samples.

Galvanostatic charge/discharge curves of pristine LTO and Cu/LTO as anode electrodes for Li-ion batteries are evaluated and given in Fig. 3. The electrode density and percentage of the active mass were adjusted to be similar for all samples, to compare the relationship be-

tween the particle size and morphology. The cells were cycled between 1 and 2.5 V at 1 C rate and an initial capacity of 170 mAh g^{-1} was obtained for both samples, which is closer to the theoretical discharge capacity of LTO spinels. Even at 1 C state of charge conditions, the difference between the capacity of the pristine LTO and Cu/LTO is still not so large. This is reasonable because Li^+ insertion/extraction is sufficient at this relatively low current rate. The Li grains in the inner part of the aggregated micron-sized particles are still electrochemically active due to the long diffusion time. However, with increasing the discharge-charge current rate, the difference between the lithium storage capacities of these two samples becomes evident. A specific capacity of 102 mAh g^{-1} and 163 mAh g^{-1} after 100 cycles for pristine LTO and Cu/LTO nanocomposite anode electrodes, shows that the Cu coating on LTO samples has significantly improved the electronic conductivity of LTO spinels.

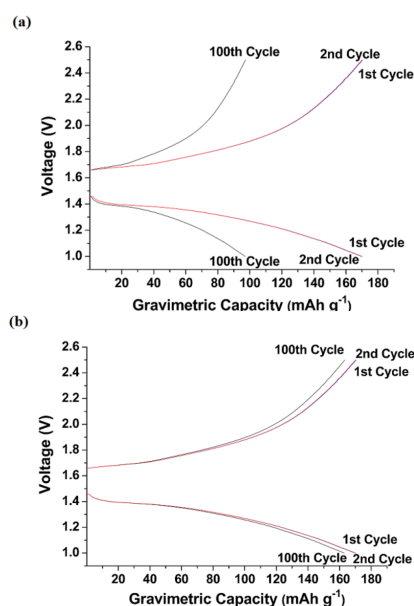


Fig. 3. Galvanostatic charge/discharge curves of the (a) pristine LTO (b) Cu coated LTO spinel samples.

Discharge capacity vs. cycle curves of the pristine LTO and Cu/LTO samples are given in Fig. 4a. It can also be concluded from the figure, that the Cu/LTO electrodes show higher lithium storage capability than those made of the pristine powders. On the contrary, very uniform electrochemical reaction may take place in the well-dispersed LTO nano composite electrode, which leads to a very smooth capacity-cycle profile with an average capacity fading by 2% per cycle within the first 50 cycles and no capacity fading has been observed after 50 cycles. Capacity vs. cycle number at various current densities for pristine LTO and Cu/LTO composites is shown in Fig. 4b. The Cu/LTO samples show much better cycle stability and much better rate capability than pristine samples at the same discharge rate. Upon completion of

the 100th charge/discharge cycle, the current density lowers to 1 C again, while the discharge capacity decreases for the first 1 C rate cycle with a capacity loss of 11% only for Cu/LTO composites, while the capacity loss of 47% for pristine LTO samples was observed.

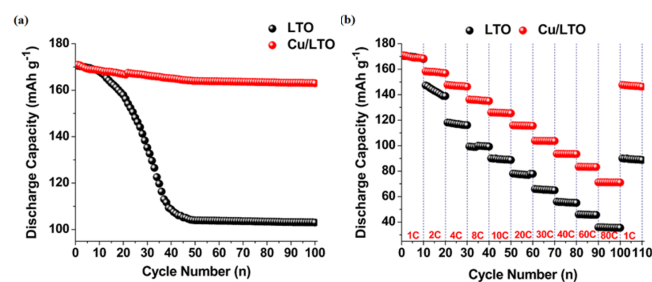


Fig. 4. (a) Galvanostatic charge/discharge vs cycling number curves of the pristine LTO and Cu coated LTO spinel samples, (b) rate performance of pristine LTO and LTO/Cu composites.

4. Conclusion

In this study, LTO anode active electrodes were produced via a facile sol-gel process and Cu/LTO composite electrodes were also prepared using electroless coating process. A pure spinel structure LTO can be obtained by calcination at 850°C for 1 h. The intimate contact between Cu coating and LTO nanoparticles not only affords a highly conductive matrix for Li ion insertion but also suppresses the agglomeration and growth of LTO nanoparticles after the calcination process. The confinement of LTO particles in Cu coating reduces lithium ion and electron transport diffusion resistance. The capacity of Cu/LTO synthesized via electroless coating techniques is 170 mAh g^{-1} at 1 C rate and it retains more than 79% and 42% of its capacity at the discharge rate of 20 C and 80 C. Irrespective of the rate used, Cu/LTO basically retain their initial capacity up to 100 cycles at 1 C state of charge conditions. Cu/LTO nanocomposite synthesized at 850°C is a superior lithium storage material and it has a promising application in power lithium ion batteries.

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