

## Synthesizing and Structural Characterization of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ Anode Nanomaterials for Lithium-Ion Batteries

Allison-Bruce Samuel Adonye<sup>1\*</sup>, Wokoma Biobele Alexander<sup>2</sup>

<sup>1</sup>Department of Physics, Rivers State University, Port Harcourt, Nigeria

<sup>2</sup>Department of Electrical/Electronic Engineering, Rivers State University, Port Harcourt, Nigeria

**\*Corresponding Author**

**E-Mail Id:** bruceallis@yahoo.com

### ABSTRACT

A simple and an effective method for synthesizing high density, high capacity  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  electrode material within a very short period of time, using homemade starch as carbon source is presented in this study. Lithium Titanate ( $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{C}$ ) was synthesized by using a simple microwave assisted hydrothermal method, with  $\text{LiCO}_3$  and  $\text{TiO}_2$  as precursors in which different concentrations of homemade starch was employed as carbon source. The samples were characterized by three different techniques, namely powder X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray (EDX). The results show mixed phase material containing  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ,  $\text{TiO}_2$  and  $\text{Li}_2\text{Ti}_3\text{O}_7$ . The estimated particle size calculated using XRD results showed that the material produced were on the nanometer scale. It also showed that the sample with 5% starch produced the smallest particle size of 36.31 nm. The SEM images of the control sample (without starch) showed a flat continuous crystallite surface while that of the samples with starch showed discrete macron sized crystallites. The EDX spectra indicated that all the constituent elements were present.

**Keywords:** Lithium-ion Batteries, anode material,  $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{C}$ , LTO, synthesized electrode

### INTRODUCTION

In the classification of anode materials, composite  $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{C}$  is regarded as the most promising Li-ion battery anode materials due to its high equilibrium potential which does not allow the formation of lithium dendrite [1-3]; therefore, ensuring safety of the battery at high operating voltages.  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  exhibits excellent cycling ability with no solid electrolyte interphase (SEI) formation and with a working voltage of 1.55 V gives an electrode material with longer life time than the conventional once such as graphite [4-7].

The low capacity ( $175 \text{ mAh}^{-1}$ ) and low electronic conductivity ( $10^{-13} \text{ S cm}^{-1}$ ) has limited its practical applications, especially

for upcoming electric vehicles. However, improvement in the conductivity of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  can be achieved through various ways, such as decreasing the particle size, surface coating with conductive material such as carbon and cation substitution. In this work, homemade starch has been chosen as the carbon source.

The technology required to synthesize electrode materials are essential for successful production of a more efficient and cost-effective battery becomes it controls the structure, morphology, and particle size and particle size distribution.

In studying synthesis methods, it is obvious that performance of electrodes is very much influenced by the method of

preparation. Studies have shown that  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  prepared by conventional methods require, high calcination temperature, prolong calcination time and an inert environment (i.e., needed to be performed in a nitrogen or argon gas stream) which increases cost of production. [8], observed that samples of electrode materials synthesized at low temperature show better cyclability but low capacity than those prepared at high temperature.

Several methods of synthesizing electrode materials are widely known in the industrial sphere which can be classified into two broad approaches; the conventional (solid state/ the solution chemistry) approaches and microwave synthesis [9-11]. Microwave assisted synthesis seems to be a very simple approach, cost effective and can easily produce electrode material with a high degree of control of particle size, within a short period of time.

However, solution chemistry also known as wet chemistry preparation routes give rise to materials in which particle size can be controlled [12-15]. Solution chemistry ensure higher purity and better electrochemical performance. It includes hydrothermal/solvo-thermal, sol-gel, co-precipitation, micro emulsion drying and spray pyrolysis methods. However, microwave assisted hydrothermal method was employed in the synthesis of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ .

## EXPERIMENT

Stoichiometric amount of the precursors, 0.689 g of  $\text{LiNO}_3$  and 1.120 g of  $\text{TiO}_2$  were weighed and each dissolved in 100 ml of distilled water. The solutions were mixed together in a beaker and heated on a hot plate with a magnetic stirrer for continuous stirring of the mixture. The mixture was heated to dryness. The deposit

was grounded and pressed into a pellet using a hydraulic press. Finally, after 5 minutes of calcining the pellet in a domestic microwave oven, nano porous  $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{C}$  was produced without the use of inert gases ( $\text{Ar}/\text{H}_2$ ). Different concentration of starch was used in the nucleation process.

## Material Characterization

Powdered X-Ray Diffraction (XRD) equipment model EMMAGBC was used to identify the crystalline phase of the samples using  $\text{Cu K}\alpha$  radiation wavelength  $\lambda = 1.5406 \text{ \AA}$ . Scanning electron microscopy (SEM) characterization was achieved using an SEM model ASPEX3020 equipment attached with an Energy Dispersive X-Ray (EDX).

## RESULT

The XRD spectra of the four samples with different starch concentrations (LTO1 = 0% starch, LTO2 = 5% starch, LTO3 = 8% starch and LTO4 = 10% starch) synthesized by microwave assisted hydrothermal method is shown in Figure 1. It illustrates mixed phase materials containing  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ,  $\text{TiO}_2$  and  $\text{Li}_2\text{Ti}_3\text{O}_7$  as identified by using the JCPDS database, probably due to the quality of precursors used and environmental effects.

From Table 1, LTO2 containing 5% starch gave the smallest particle size 36.31nm as calculated from XRD result, based on Scherrer's equation. This result shows that 5% concentration of starch is the optimum required to give best result.

The SEM images are illustrated in Figure 2. LTO1 which is the control (without starch) showed a continuous crystallite surface, while LTO2, LTO3 and LTO4 which contained starch showed discrete macron sized crystallites. The corresponding EDX plots are shown in Figures 3. The EDX plot indicated that

there are impurities or artefacts in them. EDX plot shows some level of impurities probably due to impurities in the precursors used since they are not analytical grade. However, very high temperature above 800 °C under Argon gas is required in the synthesis of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  [14].

Average particle sizes were calculated using XRD result data. Average particle size calculation is based on Scherrer's

equation as indicated in equation 1. The calculated values are shown in Table 1.

$$L = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$

were:

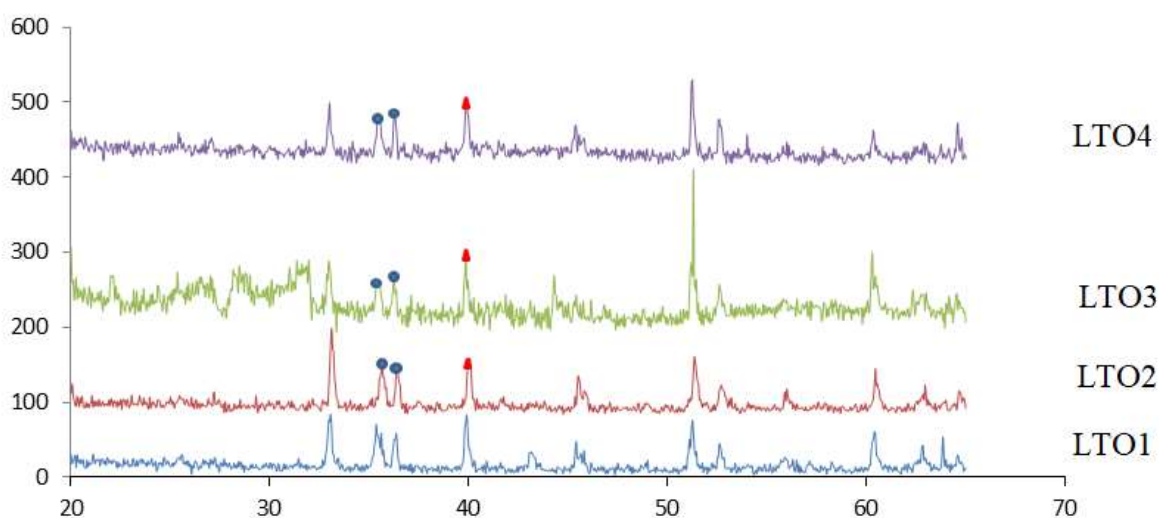
L is the crystal size

K is the shape factor of the normal crystallite generally assigned the value of 0.9

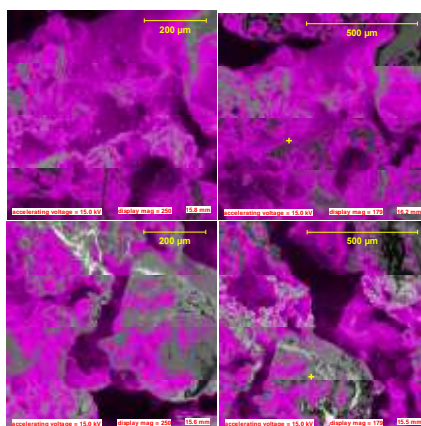
$\beta$  is the full width at half maximum (FWHM) in radians

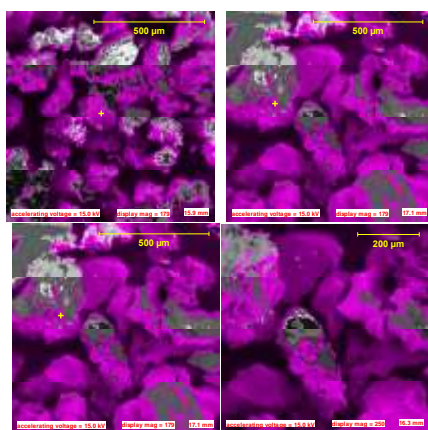
**Table 1:** Effect of starch on the particle size of  $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{C}$  samples.

Samples	Starch (wt. %)	Average particle size (nm)
LTO1	0	44.30
LTO2	5	36.31
LTO3	8	56.55
LTO4	10	45.98

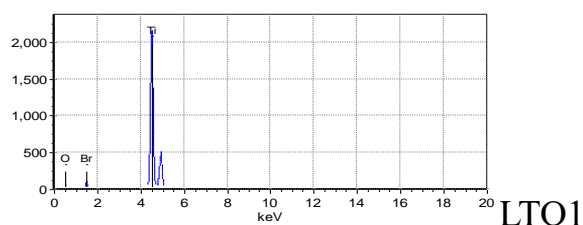


**Fig. 1:** XRD Spectra of the  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ .

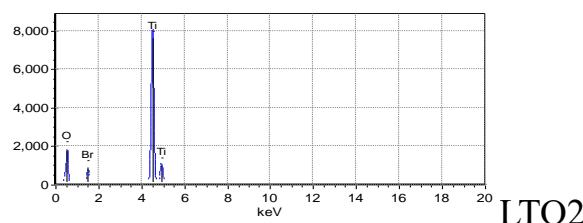




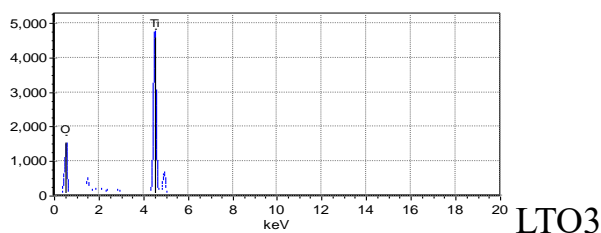
**Fig. 2:** SEM images of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ .



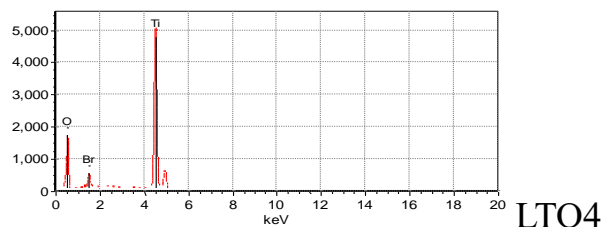
LTO1



LTO2



LTO3



LTO4

**Fig. 3:** EDX plots of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ .

## CONCLUSION

The first attempt in synthesizing  $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{C}$  anode nanomaterial using starch as carbon source, by microwave assisted hydrothermal method without inert gas environment has been carried out. In this experiment it has been shown that;

- Microwave method is a quick way of producing  $\text{Li}_4\text{Ti}_5\text{O}_{12}/\text{C}$  anode material under ambient temperature.
- Starch has been used in the control of morphology and particle size of micro porous electrode materials.

This work has clearly revealed that home-made starch can significantly improve the purity of electrode materials; by acting as a reducing agent that can suppress the growth of impurity phases. Also, starch significantly reduced crystal particle size to nano scale, which is the basic requirement for high conductivity of Li-ion cell.

The estimated particle size calculated using XRD results showed that  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  produced were on nanometer scale. It also showed that sample LTO2 with 5% starch produced the smallest particle size of 36.31 nm, which indicates that 5% starch in this work is the optimum.

However, EDX plots of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  show some level of impurities probably due to impurities in the precursors used, since they are not of analytical grade.

Also, synthesis of  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  requires very high temperature above  $800^\circ\text{C}$  under Argon gas, which was not possible to attain under the prevailing conditions.

The EDX and XRD results indicated that the targeted electrode material ( $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ) was synthesized with its constituent elements present.

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