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Accomplishment of highly porous-Lithium Lanthanum Titanate through microwave treatment

D. Lakshmi[a], B. Nalini[a]*, K.P. Abhilash[b], P.Christopher Selvin[b]

[a]*Department of Physics, Avinashilingam University for Women, Coimbatore, Tamilnadu*
[b]*Department of Physics, NGM college for arts and science, Pollachi, Tamilnadu*
**E-Mail: jyothsnalalin99@gmail.com*

Abstract: Perovskite structured (ABO_3) lithium lanthanum titanate (LLTO) is a successful electrolyte reported by several scientists in the recent past. It is believed that intercalation and de-intercalation of Li ions inside solid electrolyte can be improved by increasing the porosity of the material. Hence in this research work, an attempt is made to increase the porosity of the LLTO electrolyte by rapid-microwave synthesis route. The microwave prepared LLTO is compared with the sol-gel synthesized LLTO. The prepared samples are analyzed with XRD, SEM, PL and cyclic Voltammetry studies. Morphological analysis proves that microwave synthesized LLTO contains much pores compared to the Sol-gel LLTO. A remarkable difference in its electrochemical property is also demonstrated and analysed with cyclic voltammetric studies and the results are presented.

Keywords: LLTO, porous structure.
PACS: 78.67.Rb; 81.07.Wx; 66.30.Dn; 61.43.Gt.

INTRODUCTION

Lithium lanthanum titanate (LLTO) is a member of oxide class materials exhibiting perovskite structure. LLTO exhibits ionic conductivity in the range of 10^{-3} - 10^{-5} S cm^{-1} in room temperature. It has been identified as the most promising electrolyte material exhibiting high lithium ion conductivity (1,2). In recent times, porous materials have got wide spread attention among researchers since they enhances both the Li^+ and e^- migration which leads to the greater performance of active materials in Li ion batteries. Also, these materials show improved electrochemical behavior compared to the non-porous materials (3,4). The microwave synthesis technique is a rapid, clean and efficient technique for the synthesis of chemical products. This route for synthesizing LLTO is adopted and the results are presented here and it is compared with the conventional sol-gel method.

EXPERIMENTAL

Lithium nitrate and lanthanum nitrate are dissolved in ethylene glycol mono methyl ether and named as solution A. This mixture is stirred well for 45 minutes. Then this solution is treated under microwaves in domestic microwave oven (LG- MC-9283JLR) for 20 sec at a power of 180W which is chosen after several trials. At higher power level, lithium evaporation is experienced using EDX and hence the power level is fixed at 180 W. The solution B which contains, Titanium iso-propoxide and acetyl acetone taken in stoichiometric ratios, is kept in the microwave oven after ensuring complete mixing using magnetic stirrer. Later these two solutions are mixed together drop wise to obtain the gel which is yellow in color. Later, this gel like product is treated in the microwave oven for 45 sec. At this stage the yellow color gel has become intense red color gel then finally it is resulted in the ash like product. This product is collected and tested. This product is made into pellets and embedded in the activated carbon for annealing the prepared sample (4). These pellets are treated in microwave oven at 900W for 60 minutes. This sample is named as M-LLTO. The microwave synthesized powder is compared with the sol-gel synthesized LLTO powder named as S-LLTO.

In Sol-gel synthesis, the above mentioned solution A and Solution B are stirred well in the magnetic stirrer. After ensuring the complete suspension of the

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redox peak. Compared to the S-LLTO sample, M-LLTO powder shows well resolved redox peaks. The reduction peak is suppressed in the S-LLTO sample. The peak separation between oxidation and reduction peaks exhibits the quasi reversible nature of the chosen electrochemical system. The plot between the square root of the scan rate and peak current obeys the linear relationship which can be seen from fig 4. This relationship exhibits the quasi-reversibility of the system.

PHOTOLUMINESCENCE ANALYSIS

Photoluminescence analysis is done for samples synthesized by both techniques. PL emission spectra are recorded in the region of 250 to 450 nm with an excitation wavelength of 230 nm. The emission peak is obtained at 361 nm and 364 nm for S-LLTO and M-LLTO samples respectively. There is a slight shift towards higher wavelength region in emission peak for the M-LLTO sample (fig 5). The blue shifted S-LLTO peak indicates that M-LLTO possess larger crystallite size (6) which supports the XRD result.

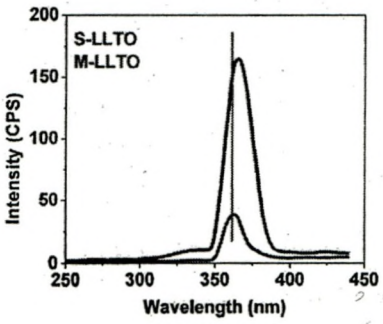

FIGURE 5: PL spectra for LLTO samples.

CONCLUSION

In this research work, preparation of highly porous lithium lanthanum titanate by microwave route is reported. Increased porosity helps to enhance the Li ion motion into the lattice sites. Hence the electrochemical reactions are enhanced in the M-LLTO sample. Hence microwave technique is a versatile technique for synthesizing porous-LLTO ceramics.

ACKNOWLEDGMENTS

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precursor products, they are mixed together and stirred vigorously to obtain the gel like product. This gel is calcined at 900° C for 5 hours in a furnace. Then, the calcined powder is collected and ground well and further annealed at 900° C for an hour. The final product is pure lithium lanthanum titanate.

X-ray diffraction (Panalytical –XPERTPRO diffractrometer with CuKα source), SEM analysis (SEM, -JEOL-JSM 6390), cyclic voltammetry analysis (Bio-logic, SP-150) and the photoluminescence study (Shimadzu- RF5301PC) are carried out in these samples. CV measurements are carried out at different scan rates in the potential range of -0.5 V to +0.5 V in 5M aqueous $LiNO_3$ electrolyte.

RESULT AND DISCUSSION

Structural Analysis

The XRD pattern of M-LLTO is compared with the S-LLTO sample in fig 1. Both the XRD patterns exhibit crystalline planes of the LLTO powder. The peaks are compared with the standard JCPDS data card no-46-0465. The lattice arrangements of both the samples assigned to cubic-perovskite structures with the space group of $Pm\bar{3}m$. The crystallite size of the samples is calculated by Debye-Scherer formula. Employing microwave in the synthesis process has shown only very mild increase in the crystallite size and is not significant to consider as size difference (45 nm for S-LLTO and 53 nm for M-LLTO). This may be due to the internal convection involved during the synthesis process inside the sample due to microwave.

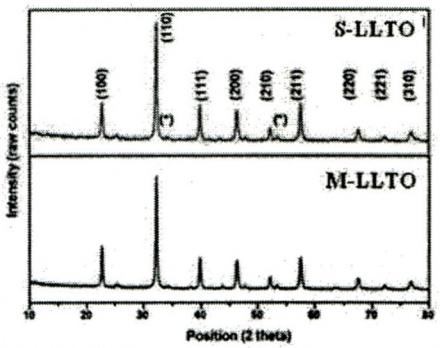

FIGURE 1: XRD pattern of the LLTO nanoparticles.

The lattice constant increases from 0.6533 (S-LLTO) to 0.6786 (M-LLTO). Increased particle size in M-LLTO powder leads to increase in lattice constants and volume of the unit cell. In the XRD pattern, the peaks corresponding to the super lattice structures are marked with (*) symbols (5).

MORPHOLOGICAL ANALYSIS

To elucidate the morphological changes in the LLTO powders synthesized by sol-gel and microwave techniques, SEM analysis is done. Comparing to the S-LLTO sample, M-LLTO has numerous pores in its structure. This is clearly visible in fig 2. These pores can help to increase the ionic motion in the lattice site (3).

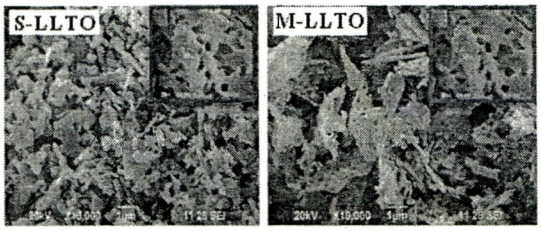

FIGURE 2: SEM images of the LLTO nanoparticles.

ELECTROCHEMICAL ANALYSIS

The CV curves obtained for both the samples are shown in fig 3. Both the powders show single

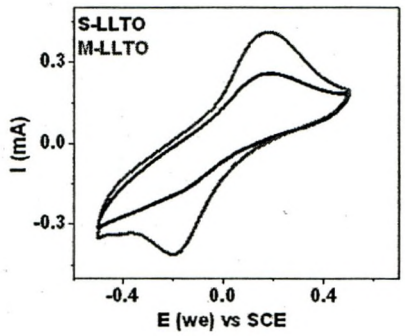

FIGURE 3: CV curve for S-LLTO and M-LLTO.

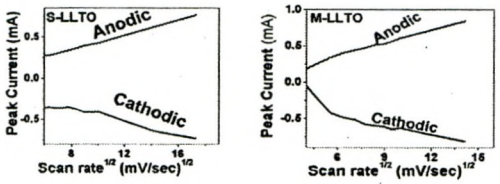

FIGURE 4: Peak current vs square root of scan rate Plot.