**PHYSICAL CHARACTERIZATION OF NEW LI-ION CONDUCTING NASICON MATERIALS IN THE LI1+2XTA1-XALX+1(PO4)3 SYSTEM**

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**Abstract-** Fabrication of all-solid-state Li battery with non-flammable ceramics electrolyte has been strongly required to overcome safety issues of present Li batteries. One of the promising structures of ceramic electrolyte in solid state battery is the NASICON structure composed of 3 dimensional frameworks (s.g. R-3c). In this study, Li-ion conducting mixed metal phosphate Li1+2xTa1-xAlx+1(PO4)3, L Ta A P-x(x = 0 ~ 0.5) solid electrolyte that possess rhombohedra NASICON structure was prepared via conventional solid state reaction techniques at various sintering temperature ranging from 700 – 1000 °C for 12 h at 5 °C per minute heating and cooling rate. Physical properties of the prepared materials show densification of solid electrolyte at 800 °C sintering temperature and could serve as a solid electrolyte in the application of solid state lithium ion batteries industry.

**Keywords**- Solid State; Electrolyte; Battery; Conductivity; NASICON

**I. INTRODUCTION**

Rechargeable Li batteries at present use conventional liquid electrolyte which had several safety challenges global [14]. The most serious problem is the flammability of the liquid electrolyte [18]. Solid state rechargeable Li batteries with NASICON structure has been identified as one of the alternative technologies to overcome the safety and reliability issues that would greatly contribute to the development of lithium battery industries [19][20]. In order to improve the performance of solid state Li ion batteries, there is need for new solid electrolytes with the following properties: stability against chemical reaction with the electrode material used, high lithium ionic conductivity with low activation energy and material with wide electrochemical window[15-17]. There are several families of inorganic solid electrolytes that exhibit lithium ion conduction for NASICON structure such asLi1+xAlxTi2−x(PO4)3 that exhibit high conductivities over 10−3 Scm−1. This conductivity value is required for practical application in rechargeable lithium batteries and were reported by several authors[7-10].

Regardless of these attractive features, there are some challenges to be conquered before a lithium ion conductor based on the NASICON structure could find application as solid electrolyte material. Researchers are still not clear either the high conductivity of LiTi2(PO4)3 solid electrolyte are intrinsic to the structure or is due to high sintering temperature that eliminate grain boundary resistance. Based on this, Thangadurai [16] with his team reported in their work by replacing Tiiv with Tav and Nbv considering those factors that could enhance conducting properties similar to that of LiTi2(PO4)3. New mixed cation material with stoichiometry chemical formula Li1+2xTa1-xAlx+1(PO4)3 that is relatively stable when having contact with Li metal and does not reduced the cation to its lower ionic level could possess higher lithium ionic conductivities. Al-content within the chemical formula act as sintering aid which resulted into dense material to eliminate the effect of grain boundary [2][3].

In this work, synthesis of LT an AP composition using solid state reaction method at different sintering temperature to observe optimum sintering parameter that will improve ionic conductivity.

**II. EXPERIMENTAL SECTION**

**A. Materials synthesis of **

Li1+2xTa1-xAlx+1(PO4)3 (x = 0 ~ 0.5) bulk ceramic samples were fabricated via solid state reaction method. Materials of AR grade were used as basic starting raw materials, Li2CO3 (99.99 % Alfa Aesar), Ta2O5 (99.99 % Alfa aesar), Al2O3 (99.99 % Alfa Aesar), NH4H2PO4 (98 % Alfa Aesar) in stoichiometric amount. The precursors were manually grounded in an agate mortar for 1 h and calcined at 600 °C for 2 h. The samples were further calcined at 600°C for 2 h for the second time. Two stage of calcination was employed in this system to obtained pure and best electrical properties of the material. The heating and cooling rate were 5°C per minute in both cases. The initial heating was performed to decompose Li2CO3 and NH4H2PO4 with the emission of ammonia, carbon dioxide gases and water vapour. The mixtures were further re-grounded by planetary ball-milling at 450 rpm for 5 h to obtained fine powder of the desired product. The ball-milled powders were pressed into pellets (1.3 cm diameter and 2 - 3 mm thickness) using carver uniaxial hydraulic press at a pressure of 5 tons. The pellets samples were sintered at various temperatures from 700 - 1000°C for 12 h at 5°C per minute heating and cooling rate. These temperatures were chosen to optimize the sintering parameter for further characterization. The synthetic route adopted in this research work is as described by Thangadurai [16], but in this case, the calcination process differ and the duration chosen for planetary ball-milling is lower than the longer period of 24 h adopted by Thangudarai and his team. The bulk densities of the palletized samples were recorded by Mettler Teledo density balance XS64 through Archimedes principle. In all cases, distilled water was used as the immersion liquid and all the measurements were maintaining at room temperature. Samples were label for identification as LTaAP-0.0, LTaAP-0.1, LTaAP-0.2, LTaAP-0.3, LTaAP-0.4 and LTaAP-0.5 respectively in some cases.

**B. Physical and structural characterization**

X-ray powder diffraction patterns were recorded at room temperature with Cu-Kα radiation source (λ = 1.5418 Å) in Bruker D8 Advance diffracto meter on the calcined powders and sintered powder samples to identify correct crystalline phases of the samples. Data were taken in the range of 10° – 80° with 0.02° per step and a count rate of 0.5 s at each step. The analysis and interpretation of the XRD patterns was carried out for all the samples sintered at 800°C from the database of the Inorganic Crystal Structure Database (ICSD) using High Score X-pert plus software package. The microstructures of the sintered samples were studied using Hitachi UI5IO scanning electron microscope (SEM). Samples for SEM was cut in half and mounted on epoxy hardener, grind and polished down to 0.25 μm with diamond paste to obtain a material not affected by surface effects. Samples were gold coated prior to SEM image acquisition. Beam accelerated voltage of 10 kV was maintained for all samples to avoid beam damage during scanning.

**III. RESULTS AND DISCUSSION**

**A. Calcination of mixed powder**

Calcination is a thermal treatment of solids which aims to heat the material at very high temperature in the absence of air or oxygen to bring about a thermal decomposition, phase transition, or removal of volatile fraction. The purpose of calcination is to produce pure powders by eliminating the undesirable compositions. Proper calcinations at the right temperature are therefore necessary to obtain the best electrical and mechanical properties of the material [13]. Fig. 1 shows the mass loss data for the virgin powder of LTaAP composition calcined twice at 600 °C for 2 h in each case. Two stage of calcination process was employed in this research work to obtain the best and pure powder sample. The percentage mass loss for first stage calcination for the samples is found around 5 - 6 % whereas, the second stage calcination of the same samples and heat treatment had mass loss around 0.05 %.



**Fig. 1 Mass loss during calcination at 600 °C for 2 h at different composition of Li1+2xTa1-xAlx+1(PO4)3 (x = 0.0 - 0.5)**

As expected, the volatile constituents of carbon dioxide, ammonia and water molecules are being eliminated completely during this process of second calcinations. This is important for the production of high degree crystalline phase material and minimize the development of impurities [1]. The decreasing and increasing trend of mass loss is due to the fact that the mass of CO2 is heavier than O2.

**B. Bulk density measurement**

Fig. 2 shows the bulk density of various Lithium Tantalum Aluminium Phosphate LTaAP-x (x=0.0 - 0.5) at different sintering temperature ranging from700 - 1000°C. The optimum sintering parameter was at 800°C for the prepared samples which is observed from the density data. This is an indication that Li1+2xTa1-xAlx+1(PO4)3 compounds could attains its best particle compactness at 800°C sintering temperature and result into material densification. [21] reported that varying sintering temperatures have a great impact on densification of ceramics materials and could increase the number of impurity phases which sometimes serve as an advantage for grain boundary conductivity [21]. The trend of bulk density observed from the graph is similar for LTaAP-0.0, LTaAP-0.1, LTaAP-0.2 and LTaAP-0.3 which increase from 700°C sintering temperature to 800°C and suddenly decrease with increase in sintering temperature up to 1000°C, while LTaAP-0.1 tend to increase slightly at 1000 °C sintering temperature. The reason for these trends is most probably because of impurity phases that were present in this composition and could exhibit different crystallization behaviour which may increase or decrease the bulk density of the material. LTaAP-0.4 and LTaAP-0.5 composition follow the same trend with bulk density decreasing with increasing sintering temperature. This suggests that the porosity generated in the samples is increased with increasing sintering temperatures. These materials increase in porosity is strongly agreed with the SEM result obtain in this study where the sample had more pores.



**Fig. 2 Bulk density of Li1+2xTa1-xAlx+1(PO4)3 (x = 0.0 - 0.5) at various sintering temperatures.**

**C. XRD analysis of the sintered powder**

Fig. 3 is the XRD graph for sintered powder at 800 °C for 12 h prepared via solid state reaction techniques. The XRD patterns reported in this study are identical to the Joint Committee on Powder Diffraction Standards file (JCPDS: 98-9539) in all compositions. All the phosphate investigated in this study crystallize in the rhombohedral (R3c) NASICON structure similar to LiTi2(PO4)3 [4],[11][12]. Diffraction peaks were observed at 2θ = 27.1 ° in all the composition (circle with red colour) which is assigned to be a secondary phase known as AlPO4. This phase in LTAP system is unavoidable, because it sometimes aids the sintering effect and serves as a path way for ion percolation. Heat treatment of NASICON materials has great influence in the enhancement of ionic conductivities, and therefore, the samples attain their crystallinity at 800 °C sintering temperature as could be observed generally from the density data [7-10]. From the graph, we observed a peak shift to higher 2θ as the Al content increases, which could be associated with the substitution of Ta5+ (0.73 Å) with smaller Al3+ (0.535 Å) with different ionic radius. Similar observation is also reported for Li-ion composition of LiTi2(PO4)3 by several authors that peak shift towards higher or lower 2θ when doped with different cations cause changes in the lattice parameters [5],[6],[21].



**Fig. 3: XRD pattern of L Ta AP-x (x= 0.0-0.5) sintered powder at 800 °C for 12 h**

We also observed that increase in Al-content split the crystalline peak for the phase with miller indices (024), which could be due to crystalline growth of the samples.

**D. SEM analysis**

Fig. 4(a)-(f) illustrates the surface morphology of the sintered pellets treated at 800°C for 12 h. There are significant changes on surface morphologies for different composition. Fig. 6a-6d shows a polished and gold coated surface of L Ta AP-x (x = 0.0-0.3) and is difficult to discern their crystalline grain. At low magnification of 3k measurement for these compositions, the surface morphology shows no discernible crystalline regions except at some points that shows a crystalline grain growth at the porous region of the micrograph and these points are indicated with arrow on the micrographs. The same magnification of 3k for the sintered polished sample shows region with crystalline grain growing for LTaAP-0.4 (see Fig. 4e). Fig. 4f shows a surface morphology with high crystallinity scattered throughout the surface of the sample. This indicates that LTaAP-0.5 developed large grains that were enough to resolve in the microscope. The crystalline grains that were identifying on the surface of LTaAP-0.5 could be due to Al-content present in large quantity. To our knowledge, this is the first time surface morphology for this kind of composition in NASICON family is reported and discussed.

**IV. CONCLUSION**

We synthesized new material substituted Ta-doped Li1+2xTa1-xAlx+1(PO4)3 (0.0 ≤ x ≤ 0.5) bulk ceramic by solid state reaction techniques. XRD reveal the NASICON structure similar to that of LTP family with secondary phases known to be AlPO4. This phase in LTAP system is unavoidable, because it sometimes aids the sintering effect. SEM morphology revealed NASICON-like structure for the all samples. Our results indicate thatLi1+2xTa1-xAlx+1(PO4)3 is a promising solid electrolyte material for all solid state lithium ion batteries.



**Fig. 4: SEM image of (a) LTaAP-0.0, (b) LTaAP-0.1, (c) LTaAP-0.2, (d) LTaAP-0.3, (e) LTaAP-0.4, (f) LTaAP-0.5 NASICON ceramic sintered at 800°C for 12 h.**

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