

## Vibrational Analysis of $\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ ( $0.0 \leq x \leq 0.5$ ) Glass Ceramic Electrolytes Prepared by Acetic Acid-Assisted Sol-Gel Method

M. Hamidi<sup>a</sup>, S. N. Mohamed<sup>a</sup>, R. I. P. R. Mustapha<sup>b</sup>, O. H. Hassan<sup>c</sup>, M. Z. A. Yahya<sup>d,e</sup>

<sup>a</sup>Faculty of Applied Sciences, Universiti Teknologi MARA, 40450, Shah Alam, Selangor, Malaysia.

<sup>b</sup>Faculty of Applied Sciences, Universiti Teknologi MARA (Perak), Cawangan Tapah, 35400, Perak, Malaysia.

<sup>c</sup>Faculty of Art and Design, Universiti Teknologi MARA, 40450, Shah Alam, Selangor.

<sup>d</sup>Faculty of Defence Science and Technology, National Defence University of Malaysia, 57000, Kuala Lumpur, Malaysia.

<sup>e</sup>Institute of Sciences, Universiti Teknologi MARA, 40450, Shah Alam, Selangor, Malaysia.

Corresponding authors: maziidah.h@gmail.com, mzay@upnm.edu.my

### ABSTRACT

In this study,  $\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$  ( $0.0 \leq x \leq 0.5$ ) was prepared by acetic acid-assisted sol-gel method. The structural properties of NASICON phosphates material with chemical formula  $\text{LiTi}_2(\text{PO}_4)_3$  were observed using the Fourier transform infrared spectroscopy. NASICON is a family of crystalline phosphate with a general network system consisting of  $\text{PO}_4$  tetrahedra, thus bands were assigned by vibrations contributed by basic phosphates, in the wavenumber region between  $1300 \text{ cm}^{-1}$  and  $600 \text{ cm}^{-1}$ . Experimental spectra indicated that all  $\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$  ( $0.0 \leq x \leq 0.5$ ), heat treated at  $600^\circ\text{C}$  and  $700^\circ\text{C}$  for 3 hours in air, samples showed the presence of phosphate peaks with shift in frequency as  $\text{Al}^{3+}$  is substituted into the structure, and with increasing temperatures. Some bands broadened and overlapped causing it hard to analyze the arising bands. It however determined the existence of NASICON structure in all of the samples under study.

**Keywords:** NASICON, LATP, glass ceramic, sol-gel, FTIR

### Introduction

The introduction of high energy density lithium ion battery [1] has been a huge milestone for the innovation and discovery of potential lithium-based battery components, both electrodes and electrolytes. Moreover, with the commercialization of lithium ion batteries by SONY in the 1990s [2], countless volumes of research have been done and reported with the aim to produce better batteries with higher density, stable under ambient conditions, safe for consumers, environmentally benign and, of course, being cost efficient [3]. Focusing on the electrolytes, an all solid-state electrolytes are possible substitute for flammable liquid-based electrolytes [4]. Thus, innovation for solid-state ionic conductors is important. Glass-ceramics has great potential as solid electrolytes applied in such batteries [1].

Lithium-based glass ceramic phosphates with structure similar to that of sodium ion conducting compounds,  $\text{Na}^+$  SuperIonic CONductor, which paradoxically is known as NASICON, are excellent lithium ion conductors [5-6]. The NASICON-type structure provides lithium ion mobility forming three dimensional network structures (space group R3c) [7] which enable the glass ceramic electrolyte to achieve high ionic conductivity. One of the most common studied NASICON phosphates is  $\text{LiTi}_2(\text{PO}_4)_3$  has ionic conductivity of  $10^{-6} \text{ S cm}^{-1}$  at room temperature. It is composed of several numbers of octahedral  $\text{MO}_6$  units, where M is the tetravalent cation, Ti, and tetrahedral  $\text{PO}_4$  units, which are joined to each other's O corners and forms P-O-M bridges [7]. The joined units can also be described as a covalent  $[\text{M}_2\text{P}_3\text{O}_{12}]$  skeleton [8]. Attempt to increase the ionic conductivity can be done by partial substitution of cations,  $\text{M}^{\text{III}}$  such as Al, Ga, In, Sc, Y, La, Cr, Fe [9]. The partial substitution changes the chemical formula of  $\text{LiTi}_2(\text{PO}_4)_3$  to  $\text{Li}_{1+x}\text{M}_x^{\text{III}}\text{Ti}_{2-x}(\text{PO}_4)_3$ . The most conductive compound is  $\text{Li}_{1.3}\text{M}_{0.3}^{\text{III}}\text{Ti}_{1.7}(\text{PO}_4)_3$ , with an ionic conductivity up to  $10^{-3} \text{ Scm}^{-1}$ , where the trivalent cation is either Al or Sc [10].  $\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ , abbreviated as LATP, is able to give high ionic conductivity due to its structure whereby, the small sized  $\text{AlO}_6$  octahedra accommodates Li cations through its larger spaces [9]. Xu et al. [1] reported an impressive high room temperature ionic

conductivity of  $10^{-3} \text{ Scm}^{-1}$  for  $\text{Li}_{1.4}\text{Al}_{0.4}\text{Ti}_{1.6}(\text{PO}_4)_3$  glass ceramics, similar with that of LATP as reported by J. Fu (1997) [11].

NASICON structure which is composed of strong P-O bonding is one of the main contributing factors to its high conductive characteristic. The phosphate network can be detected by bands of various vibrations contributed by  $[\text{PO}_4]^{3-}$  polyanions [10]. The LATP structure is built by corner sharing  $\text{Ti}(\text{Al})\text{O}_6$  octahedral and  $\text{PO}_4$  tetrahedral in such a way that the octahedra is surrounded by six tetrahedral, forming Ti-O-P bridges which are also described as a covalent  $[\text{M}_2\text{P}_3\text{O}_{12}]^-$  skeleton [7-8]. These octahedral and tetrahedral connections generate interstitial voids or spaces, known as M1 and M2 sites [8-9]. The M1 sites are located between two octahedral,  $\text{TiO}_6$ , having six coordination of oxygen while M2 sites are located between the ribbons which are formed along the c-axis [8-9]. These sites provide pathways also known as bottlenecks, for the transportation of the conducting mobile ions [7]. M1 sites are filled with cations while M2 sites are empty [12].

Previous work by Xu et. al [1] reported sample preparation of sample by using citric acid as its assisting acid. In this study, however, acetic acid is employed. This study is aimed to determine the vibrational analysis and structural studies of  $\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$  ( $0.0 \leq x \leq 0.5$ ) before and after being sintered at  $600^\circ\text{C}$  and  $700^\circ\text{C}$  for 3 hours in air, by using Fourier transform infrared spectroscopy (FTIR). The ionic conductivity and phase analysis studies of the material have been reported elsewhere [4].

## Experimental

### Sample Preparation

The vitreous  $\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$  ( $0.0 \leq x \leq 0.5$ ) sample was prepared by mixing a stoichiometric amount of  $\text{Al}(\text{NO}_3)_3$  (Bendosen) and  $\text{TiO}_2$  (QReC),  $\text{Li}_2\text{C}_2\text{H}_3\text{O}_2$  (Sigma) and  $\text{NH}_4\text{H}_2\text{PO}_4$  (SigmaAldrich) by sol-gel method. The mixture was dissolved in ethanol and kept magnetically stirred for about 24 hours at  $60^\circ\text{C}$ . Acetic acid was added slowly to maintain pH of 5. The obtained sol was maintained at  $70^\circ\text{C}$  for the release of volatile components. The white colored powder that was achieved was grounded and sintered at  $600^\circ\text{C}$  and  $700^\circ\text{C}$  for 3 hours in air.

### Structural Characterization

The LATP materials were structurally characterized using Perkin Elmer FTIR spectrometer SPECTRUM 2000 at wavenumber region from  $1300 \text{ cm}^{-1}$  to  $600 \text{ cm}^{-1}$ . From this spectrum, the effect of  $\text{Al}^{3+}$  substitution, according to its stoichiometric ratio, was observed.

## Results and Discussion

The six samples prepared,  $\text{LiTi}_2(\text{PO}_4)_3$ ,  $\text{Li}_{1.1}\text{Al}_{0.1}\text{Ti}_{1.9}(\text{PO}_4)_3$ ,  $\text{Li}_{1.2}\text{Al}_{0.2}\text{Ti}_{1.8}(\text{PO}_4)_3$ ,  $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ ,  $\text{Li}_{1.4}\text{Al}_{0.4}\text{Ti}_{1.6}(\text{PO}_4)_3$ ,  $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ti}_{1.5}(\text{PO}_4)_3$  are referred to as LATP 0, LATP 1, LATP 2, LATP 3, LATP 4, and LATP 5, respectively. Ti-O-P bonds and phosphates,  $\text{PO}_4$  bonds are crucial in the identification of the NASICON-type structure before and after being sintered at  $600^\circ\text{C}$  and  $700^\circ\text{C}$ . LATP 0 for each sintering temperature is referred as the reference to identify the occupancies of  $\text{Al}^{3+}$  in the Ti-O-P structure, as Al component was not introduced.

### Before Sintering

Figure 1 shows the FTIR spectra of samples before sintering. From this spectrum, the effect of  $\text{Al}^{3+}$  with different stoichiometric values added to the structure of lithium titanium phosphate was observed. In the present study, the band at  $1045 \text{ cm}^{-1}$  is probably related to the orthophosphate anion  $\text{PO}_4^{3-}$  vibrations, which is in good agreement to A. H. Ahmad, A. K. Arof [14]. Upon addition of  $\text{Al}^{3+}$ , whereby partial substitution of Ti with Al occurred, the orthophosphate band showed a shift to a lower wavenumber ( $1038 \text{ cm}^{-1}$ ). This shift might be due to the presence of  $\text{Al}^{3+}$  in the glass structure causing a complexation by joining into the distorted tetrahedral units. Band spotted at  $1145 \text{ cm}^{-1}$  in LATP 3 is

due to the addition of  $\text{Al}^{3+}$ , indicating that the  $\text{Al}^{3+}$  ion has successfully being incorporated in the structure. Furthermore, the wavenumber shifted to a lower wavenumber ( $1142 \text{ cm}^{-1}$ ) for LAMP 5.

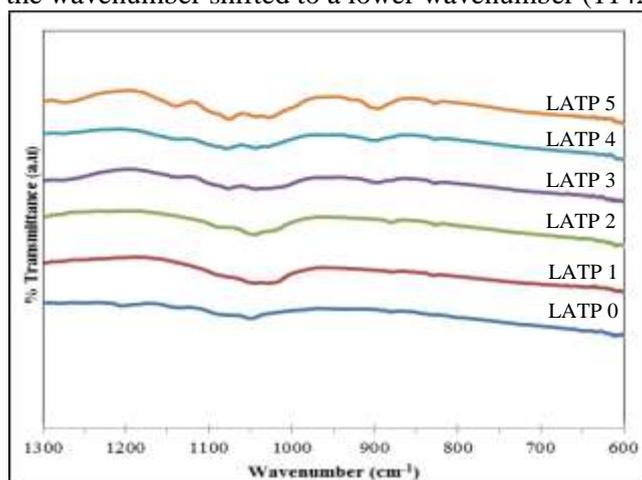


Figure 1 FTIR spectra of LAMP 0, LAMP 1, LAMP 2, LAMP 3, LAMP 4 and LAMP 5, before sintering.

This might be due to the increasing amount of  $\text{Al}^{3+}$ . It also explained the shift of  $\text{PO}_4$  tetrahedral band and increased intensity and peak size of band around wavenumber  $874 \text{ cm}^{-1}$  for LAMP 0 to  $894 \text{ cm}^{-1}$  for LAMP 5. Bands around  $1045 \text{ cm}^{-1}$  represented the existence Ti-O-P bonding, thus it can also be said that the addition of  $\text{Al}^{3+}$  into the material structure resulted in the shift of band to lower wavenumber, which overlapped the band arising from  $\text{PO}_4^{3-}$  orthophosphate tetrahedral [13].

### After Sintering

In order to obtain the NASICON structure for glass ceramic, the samples were sintered at  $600^\circ\text{C}$  and  $700^\circ\text{C}$  for 3 hours in air. More bands associated with phosphates were expected to be obtained. Figure 2 and Figure 3 show the FTIR spectra of LAMP 0, LAMP 1, LAMP 2, LAMP 3, LAMP 4, and LAMP 5, sintered at  $600^\circ\text{C}$  and  $700^\circ\text{C}$  for 3 hours in air, respectively. The absorption band attributing to the bending modes of O-P-O can be identified around  $613 \text{ cm}^{-1}$  for LAMP 0 when annealed at  $600^\circ\text{C}$  and shifted to a higher wavenumber,  $615 \text{ cm}^{-1}$  as annealed at  $700^\circ\text{C}$  [15]. However, the band broadened as well as increased in band intensity with the increase in annealing temperature. This observation was also observed for all other samples annealed at both temperatures.

This shows that as the samples annealed, the NASICON structure of the glass ceramic joined through corners edge leading to the formation of tunnel-like passage ways. All samples heat treated at temperatures  $600^\circ\text{C}$  and  $700^\circ\text{C}$  did not show any sign of  $\text{Al}^{3+}$  band around  $\sim 1146 \text{ cm}^{-1}$  as compared to before the annealing process. This is probably due to the partial substitution of  $\text{Al}^{3+}$  into the structure which occurred due to the annealing process.

The band observed at around  $\sim 740 \text{ cm}^{-1}$  for samples annealed at  $600^\circ\text{C}$  and  $700^\circ\text{C}$  is attributable to the P-O-P linkage which indicated the presence of  $\text{PO}_4$  tetrahedral in the glass ceramics. While bands associated with the asymmetric stretching of  $\text{PO}_4$  was observed at  $885 \text{ cm}^{-1}$  for LAMP 0 annealed at  $600^\circ\text{C}$ , and shifted significantly to  $879 \text{ cm}^{-1}$  as annealing temperature increased. This shows that temperature may result in significant changes on the phosphate in the NASICON structure. While for LAMP 5, this peak showed obvious intensity decrement and slight shift from frequency  $877 \text{ cm}^{-1}$  to  $879 \text{ cm}^{-1}$  with the increase in temperature. The band arising from Ti-O-P was observed for all samples annealed at both temperatures, with bands shifting to lower wavenumber with increasing  $\text{Al}^{3+}$  intensity, from  $1049 \text{ cm}^{-1}$  to  $1045 \text{ cm}^{-1}$  as LAMP 0 was sintered at  $600^\circ\text{C}$  and  $700^\circ\text{C}$ , respectively [13].

The shifting might be due to the partial substitution of  $\text{Al}^{3+}$  with Ti in the structure of NASICON, which is  $\text{LiTi}_2(\text{PO}_4)_3$ . This shift explains the increase in ionic conductivity, as reported elsewhere [4], due to the smaller size of  $\text{AlO}_6$  octahedra when compared to  $\text{TiO}_6$  octahedra leading to a more appropriate pathway to accommodate the  $\text{Li}^+$  mobile ions [9].

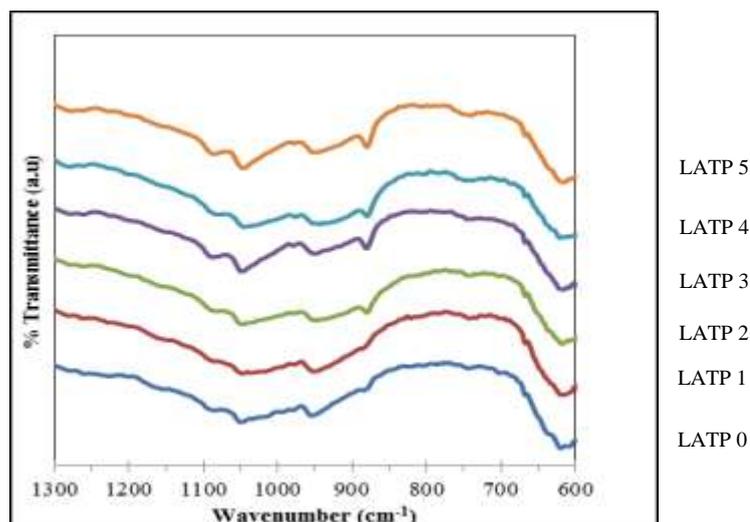


Figure 2 FTIR spectra of LATP 0, LATP 1, LATP 2, LATP 3, LATP 4 and LATP 5, sintered at 600°C for 3 hours in air

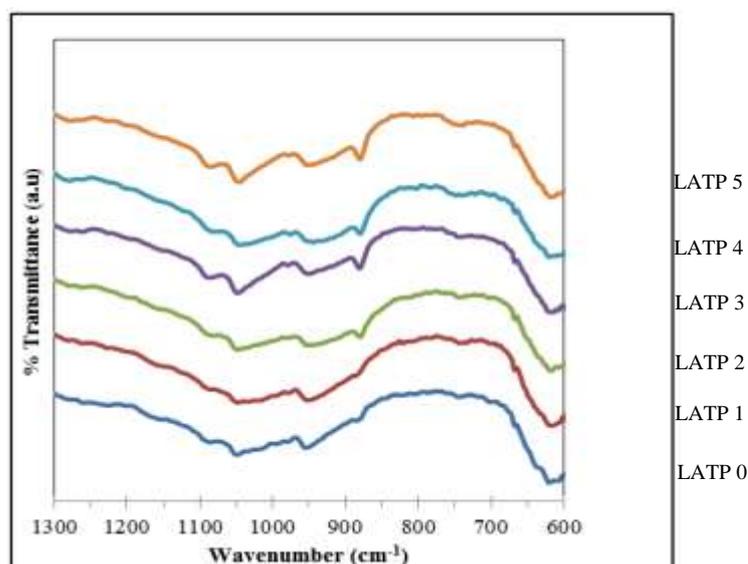


Figure 3 FTIR spectra of LATP 0, LATP 1, LATP 2, LATP 3, LATP 4 and LATP 5, sintered at 700°C for 3 hours in air.

Bands associated with  $[\text{PO}_4]^{3-}$  [16] were seen at  $1087\text{ cm}^{-1}$  for LATP 0 and shifted to  $1083\text{ cm}^{-1}$  for LATP 5 with increasing  $\text{Al}^{3+}$  intensity, as samples annealed at  $600^\circ\text{C}$ . As sintering temperature was increased to  $700^\circ\text{C}$ ,  $[\text{PO}_4]^{3-}$  band was observed at even a lower frequency, for LATP 0, a significant shift to  $1082\text{ cm}^{-1}$  while for LATP 5, a slight shift from  $1083\text{ cm}^{-1}$  to  $1082\text{ cm}^{-1}$ .

## Conclusions

The  $\text{Al}^{3+}$  substitution distorted the structure of NASICON from the studied samples, sintered at  $600^\circ\text{C}$  and  $700^\circ\text{C}$ . Besides, all samples showed the presence of  $\text{PO}_4$  tetrahedral, whereby having NASICON structure provided good lithium ion mobility which is an important aspect in order to achieve high ionic conductivity material.

## Acknowledgment

Authors would like to thank Ministry of Science, Technology and Innovation (MOSTI) Malaysia for funding this research and Ministry of Education (MOE) for supporting this research under the RAGS grant (600-RMI/RAGS 5/3 (28/2012)) and Universiti Teknologi MARA (UiTM) for the facilities provided in the success of this research.

## References

- [1] X. X. Xu, Z. Y. Wen, J. G. Wu, X. L. Yang (2007). Preparation and electrical properties of NASICON-type structured  $\text{Li}_{1.4}\text{Al}_{0.4}\text{Ti}_{1.6}(\text{PO}_4)_3$  glass-ceramics by the citric acid- assisted sol-gel method. *Solid State Ionics*, 178, 29-34.
- [2] P. Berpanda, S. I. Nishimura, and A. Yamada (2012). High-voltage pyrophosphate cathodes. *Advanced Energy Materials*, 2, 841-859.
- [3] G. Q. Tan, F. Wu, L. Li, Y. Liu, and R. Chen (2012). Magnetron sputtering preparation of nitrogen-incorporated lithium-aluminium-titanium phosphate based thin film electrolytes for all-solid-state lithium ion batteries. *The Journal of Physical Chemistry*, 116, 3817-3826.
- [4] M. Hamidi, S. N. Mohamed, A. M. M. Ali, T. Winie, and M. Z. A. Yahya (2012). Preparation and characterization of  $\text{Li}_{1.4}\text{Al}_{0.4}\text{Ti}_{1.6}(\text{PO}_4)_3$  conducting electrolytes. *IEEE Symposium on Business, Engineering and Industrial Applications*, 53-56.
- [5] J. W. Fergus (2010) Ceramic and polymeric solid electrolytes for lithium-ion batteries. *Journal of Power Sources*, 195, 4554-4569.
- [6] Y. Yorozu, M. Hirano, K. Oka, and Y. Tagawa (1987). Electron spectroscopy studies on magneto-optical media and plastic substrate interface. *IEEE Translational Journal on Magnatic Japan*, 2, 740-741.
- [7] A. Nuvulla (2010). Semi sol-gel synthesis, conductivity and luminescence studies of  $\text{Ca}_{0.5}\text{Fe}_{1-x}\text{Eu}_x\text{Sb}(\text{PO}_4)_3$  ( $x=0.1, 0.15$  and  $0.2$ ). *Solid State Ionics*, 181, pp. 659-663.
- [8] M. Cretin, F. Fabry (1997). Detection and selectivity properties of  $\text{Li}^+$  ion selective electrodes based on NASICON-type ceramics. *Analytical Chimica Acta*, 354, 291-299.
- [9] F. E. Mouahid, M. Bettach, M. Zahir, P. Maldonado-Manso, S. Bruque, E. R. Losilla, M. A. G. Aranda (2000) Crystal chemistry and ion conductivity of the  $\text{Na}_{1+x}\text{Ti}_{2-x}\text{Al}_x(\text{PO}_4)_3$  ( $0.0 \leq x \leq 0.9$ ) NASICON series. *Journal of Material Chemistry*, 10, 2748-2753.
- [10] C. R. Mariappan, G. Govindaraj, B. Roling (2005). Lithium and potassium ion conduction in  $\text{A}_3\text{TiB}'\text{P}_2\text{O}_{12}$  ( $\text{A}=\text{Li}, \text{K}; \text{B}'=\text{An}, \text{Cd}$ ) NASICON-type glasses. *Solid State Ionics*, 176, 723-729.
- [11] J. Fu (1997). Superionic conductivity of glass-ceramics in the system  $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{TiO}_2-\text{P}_2\text{O}_5$ . *Solid State Ionics*, 96, 195-200.
- [12] M. J. Bushiri, C. J. Antony, A. Aatiq (2008). Raman and FTIR studies of the structural aspects of Nasicon-type crystals;  $\text{AFeTi}(\text{PO}_4)_3$  [ $\text{A}=\text{Ca}, \text{Cd}$ ]. *Journal of Physics and Chemistry of Solids*, 69, 1985-1989.
- [13] J. Santos-Pena, P. Soudan, M. Cruz-Yusta, S. Franger (2006). Increasing the electrochemical activity of transition metal phosphates in lithium cells by treatment with intimate carbon: The case of titanium phosphate. *Electrochimica Acta*, 51, 4841-4849.
- [14] A. H. Ahmad, A. K. Arof, "XRD, conductivity and FTIR studies on  $\text{LiI}-\text{Li}_2\text{WO}_4-\text{Li}_3\text{PO}_4$  prepared by low temperature sintering (2004). *Ionics*, 3-4, 200-205.
- [15] K. J. Rao, M. Ganguli, M. Harish (1999). Lithium ion transport in  $\text{Li}_2\text{SO}_4-\text{Li}_2\text{O}-\text{P}_2\text{O}_5$  glasses. *Solid State Ionics*, 122, 23-33.
- [16] T. Savitha, S. Selvakarasandian, C. S. Ramya, M. S. Bhuvanewari, G. Hirankumar, R. Bashakaran, O. C. Angelo (2005). Structural and ionic transport properties of  $\text{Li}_2\text{AlZr}(\text{PO}_4)_3$ . *Journal of Power Sources*, 157, 533-536.