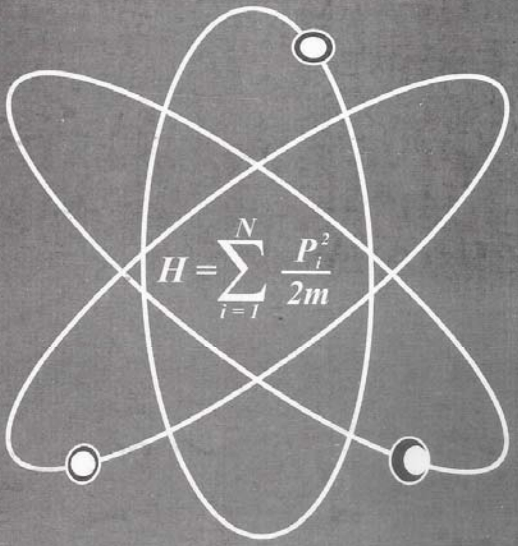
BAYERO JOURNAL OF PHYSICS AND MATHEMATICAL SCIENCES



$$H = \sum_{i=1}^{N} \frac{P_i^2}{2m}$$

VOLUME 5, No. 1
AUGUST, 2013.

Published by: THE DEPARTMENTS OF PHYSICS AND MATHEMATICAL SCIENCES, BAYERO UNIVERSITY, KANO.

MEMBERS OF THE EDITORIAL BOARD

Editor-in-Chief - Dr. A. O. Musa, Dept. of Physics, Bayero University, Kano.
Asst. Editor-in-Chief 1 - Dr. U. M. Gana, Dept. of Physics, Bayero University, Kano.
Asst. Editor-in-Chief 2 - Dr. Aliyu Kiri, Department of Mathematical Sciences, Bayero University, Kano.
Circulation Editor - Dr. Garba Babaji
Business Editor - Dr. Mikaila M. Kashimbila

MEMBERS OF THE BOARD OF TRUSTEE

1. The Head of the Department of Mathematical Sciences, Bayero University, Kano.
2. The Head of Physics Department, Bayero University, Kano.
3. Member of the Editorial Board.

MEMBERS OF THE EDITORIAL ADVISORY COMMITTEE

1. Prof. I. H. Umar, Department of Physics, Bayero University, Kano.
2. Prof. M. Y. Bello, Department of Mathematical Sciences, Bayero University Kano.
3. Prof. A. S. Sambo, Director-General, National Energy Commission of Nigeria, Abuja.
4. Prof. E. U. Utah, Department of Physics, University of Jos, Jos.
5. Prof. B. Osazuwa, Department of Physics, Ahmadu Bello University, Zaria.
6. Prof. N. Hariharan, Department of Physics, Ahmadu Bello University, Zaria.
7. Prof. J. Katande, Department of Electrical Engineering, Bayero University, Kano.
8. Prof. P. N. Okeke, Department of Physics and Astronomy, University of Nigeria, Nsukka.
9. Prof. M. N. Agwu, Department of Physics, Nigerian Defence Academy, Kaduna..
10. Prof. S. S. Duwa, Department of Physics, Bayero University, Kano.
11. Dr. Ado Dan-Isa, Department of Electrical Engineering, Bayero University, Kano..
12. Dr. M. S. Abubakar, Director of Programmes, National Board for Technical Education, Kaduna.
13. Dr. B. S. Galadanci, Department of Electrical Engineering, Bayero University, Kano.
14. Dr. M. B. Yakasai, Department of Mathematical Sciences, Bayero University, Kano.
15. Dr. N. F. Isa, Department of Physics, Bayero University, Kano.
16. Dr. Garba Uba Goje, Dept. of Mathematical Sciences, Ahmadu Bello University, Zaria.
17. Dr. Babangida Sani, Dept. of Mathematical Sciences, Ahmadu Bello University, Zaria.

TABLE OF CONTENTS

BAJOPMAS JOURNAL 5(1): 177 – 194
Printed in Bayero University, Kano - Nigeria.

IMPEDANCE SPECTROSCOPY OF SUPERIONIC CONDUCTORS II: MEASUREMENT AND STUDIES

[1]Ahmadu, U., [2]Musa, A. O. and [3]Isah, K. U.
[1,3]Department of Physics, Federal University of Technology, Minna, Nigeria
[2]Department of Physics , Bayero University , Kano, Nigeria
corresponding author: u.ahmadu@yahoo.com

ABSTRACT

Ionic conducting materials are increasingly playing a crucial role in the search for complimentary sources of energy. They are used in rechargeable batteries for mobile phones and laptop computers for example. However, the most important application of these materials is in the current search for solid oxide fuel cells (SOFC) desperately needed in the transportation sector. The main advantage of these materials as energy storage devices are their being in the solid state, offering portability and flexibility in handling, compared to the traditional liquid electrolytes. Their electrical conductivity at room temperature is comparable to those of the liquid ones. Among the class of ionic materials are the Superionic conductors that have the best conductivity at elevated temperatures. The ultimate challenge in their study is to reduce the temperature to ambient conditions. Various methods have been adopted to achieve this, one of which is by modifications in the stoichiometric compositions of the system or substitution in order to tailor them for targeted applications. One such class of materials is called NASICON, which is sodium Superionic conductor. These compounds have conductivities comparable to the best superionic conductors due to their special structures and wide range of applications, hence the interest in their research. However, the conductivity and impedance spectroscopy of these materials presents challenges from theoretical interpretation of the results. This review therefore briefly explores the impedance spectroscopy results for some NASICON materials in relation to their synthesis conditions. Their general propeties have also been presented.

Keywords: electrical conductivity; impedance spectroscopy; NASICON

1.0 INTRODUCTION

Ionic materials are in recent times at the forefront of materials research. Current trends are in producing materials for various applications, scientific and technological. They are used in various applications, the most ubiquitous being in energy storage as rechargeable lithium batteries for laptop computers, mobile phones, etc., and as electrodes and electrolyte materials. As electrolytes, the materials should have high room temperature ionic conductivity, transference number close to 1 and temperature stability, among others [1-3]. As electrodes, they should have mixed conduction properties, i.e. electronic and ionic. Superionic conductors are class of materials whose conductivity approaches that of the liquid electrolytes at high temperatures and these are the most important in applications and are the focus of this review. The materials may be solid, glassy, or polymer in nature which gives them good advantage over the liquid electrolytes. Glassy materials have become very important superionic conductors and have been widely studied due to their potential applications and high conductivity [1,4].Their conductivity is enhanced on introduction of a crystalline phase into the superionic glass matrix [5]. Many studies have been reported on polymer electrolytes and limited ones on biopolymers by Sarkar, which shows evidence of superionic conduction properties in gum Arabica [6]. The high conductivity in superionic conductors is due to thermal activation (as in semiconductors) often associated with phase transitions to a structural state that enhances conductivity by several orders of magnitude. It has been demonstrated recently that structural phase change could be related to particle size [4] and that effects such as pressure, density and microstructure affect the electrical performance of the materials. We focus our discussions on the family of ionic conductors called NASICON (Na SuperIoni CONductor) which are synthesized by various methods in order to optimize the electrical and microstructural properties of the compounds [7-9].

Lithium-conducting solid electrolytes are the most important due to the special physical properties of lithium such as its small size and low density which leads to increased electrical conductivity on partial as well as full substitutions in the NZP system ($NaZr_2(PO_4)_3$, the basis for the formulation of the NASICONs, resulting in lithium zirconium phosphate $LiZr_2(PO_4)_3$. NZP is thermally stable to 1500°C [10] whereas NASICON, depending on its composition, has melting point higher than 1800°C [11].The substitution of Na becomes necessary since it is not a good ionic conductor for structural reasons [12] .Other compositions are obtained by replacing the Zr with Ge, Sc, In, Ti, etc., with the result that several orders of magnitude increment in conductivity at room temperature is obtained, amongst other substitutions in the P system. There are many studies that have been carried out on the NZP materials reflecting the current applications and indeed potential applications of the compositions such as: in corrosion–resistant coating material for silicon–based ceramics and thermal barrier coatings [11]; in the development of C-C composites due to the matching of its thermal expansion properties [13] and as a nuclear waste demobilization host material [14-16]. Recently, new materials of the NZP family have been developed and structurally characterized showing high ionic conductivity and optical property in particular, an uncharacteristic property of these compounds. Some of these include, $Na_3Al_2(PO_4)_3$

(bulk conductivity 5.10^{-2} s/cm at 600K) [17] , $Rb^3Yb^2(PO^4)_3$ [18] (a cubic system) and $Pb_{0.5}Ti_2(PO_4)_3$ [19] (a hexagonal system of the R-3c space group), respectively. Similarly, new NASICON-related Potassium Iron (III) Pyrophosphate has been synthesized and characterized [20]. A typical member of such novel materials is rhombohedral $Li_3Fe_2(PO_4)_3$, which is a potential electrode insertion material in lithium polymer batteries based on its good ionic conductivity and low cost [21]. The thermal expansion properties of these compounds are very important due to their relevance in the synthesis of the materials and their relationship to microstructure and density, all of which impact on the electrical properties of the compounds. The materials have the lowest tailorable thermal expansion coefficients and exhibit anisotropy in their thermal expansion. Thus several theoretical models have been formulated to explain the thermal properties [14, 22-25] and studies on the coefficients of thermal parameters [26-27] have been carried out.

Microcracking is another phenomenon that occurs in these ceramic polycrystalline materials due to internal stresses among grains, resulting in significant lowering of strength and coefficient of thermal expansion [22].The microcracks begin when a critical grain size of 2μm is exceeded and this is related to the maximum thermal expansion difference between the lattice parameters [28]. In low density ceramics, these microcracks and pores can absorb some expansion thereby causing a reduction in the thermal expansion. It has been suggested that the anisotropic thermal expansion gives rise to poor sinterability [29].The compositions with high degree of thermal anisotropy are the ones prone to microcracking upon cooling at room temperature [23], since the onset of microcracking is related to the sintering temperature and hence grain size .They further suggest that the microcracking may be delayed or enhanced by controlling the atmosphere in which the ceramic is heated and cooled and that thermomechanical properties in general can be improved by compositional and microstructure designs[22], all of which reflects in the way and manner the materials are synthesized in order to obtain high performance materials .Thus the use of appropriate atmosphere is important in the characterization and performance of these materials. NZP materials have space group R-3c and lattice parameters a = 8.815 Å, c = 22.746Å, unit cell volume V= 1530.5$Å^3$ and the number of formula units per unit cell is Z = 6. They also show the possibility of forming solid solutions in some chosen compositions, as reported by [30] in their study of NZP with Strontium (Sr) substituting the Na. They computed the unit cell parameters for NZP with no strontium(x=0.0) as a = 8.803Å, c=22.764Å and unit cell volume, V = 1527.8(2)$Å^3$ and demonstrated that (Na-Sr)-NZP formed solid solutions.

2.0 ELECTRICAL CONDUCTIVITY OF SUPERIONIC MATERIALS

It is important to know how much current can be passed through an electrode-electrolyte interface. Some interfaces are non-polarizable or reversible while others are polarizable or non reversible. A non polarizable interface acts reversibly to the species under consideration. Both ionic and electronic species may cross the interface unobstructed. The polarizable interface acts blocking to the species under consideration and this kind of interface, to a first approximation, acts like a capacitor [31]. There are several methods of measuring ionic conductivity such as far infrared and Raman spectroscopy where the vibration of the atoms can provide hop attempt frequecies; motional narrowing of the NMR absorption lines, among others [32]. All these however, are non ac methods. We shall be limited to ac electrical conductivity [33] measurents in our review and to some extent NMR. Electrical conductivity can be measured over wide range of frequencies and such studies on superionic conductors have been carried out at the dc, low, microwave and far infrared frequencies. However, not much is found in RF range. Conductivity in microwave range through theoretical studies reveal that motion of ions through the lattice in superionic conductors is intimately linked with microwave conductivity and thus frequency range expectedly corresponds to the time scale of ionic motion. Defects or interstitial spaces can provide empty sites through which ions can migrate in a hopping mechanism in which the ions move sequentially into adjacent energy–equivalent vacant sites, or by cooperative motion of the ions. Conductivity may be fully or partly ionic. In the former case it may be due to the positive and negative ion species, while in the latter case it may be due to electronic contribution due to negative electrons and positive holes that may be present. Thus total ionic conductivity may not be the true bulk ionic conductivity due to factors, such as electrode–material contact resistance, generally of negligible fraction of total resistance in high resistance samples. This however, is useful only if it is ensured that the signal makes the electrode-material system linear. There is also the problem of grain-boundary resistance whose only solution is to carry out measurements on single crystals [34]. However, for most superionic conductors the art of growing single crystals is far from developed, measurement are therefore carried out on pressed pellets. Grain boundaries can either increase or decrease the conductivity, depending upon whether or not the activation energy for conduction for the grain boundary conduction is less or more than the bulk conduction. In dc conduction, polarization effects at the nearby electrodes present a major problem in the evaluation of ionic transport. However, static fields are useful in separating electronic components of conductivity.

Some workers [35] have presented a simple mathematical explanation for the ac conductivity based on relaxation concepts. They present a model which is simple in terms of linear equations of motions that illustrates some of the features of the ionic ac conduction in solids and thus helped in clarifying their origin. They also showed how long range motion of the charges can occur in a system composed of ions that are confined by the coulomb potentials of the neighboring ions, however with the condition that the position of these neighbours can also relax. At low frequencies, the long range displacements of carriers give the frequency independent (dc) conduction σ_o. As the frequency increases the conductivity gradually increases and over a frequency range from mHz to GHz it is well approximated by, according to Jonscher and Almond:

$$\sigma(\omega)=\sigma_o\left[1+\left(\omega/\omega_c\right)^s\right] \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

where, w_c is the frequency of the onset of ac conduction and _ is a variable parameter. This equation treats the ac and dc as independent phenomena. However, both contributions should supposedly, arise from the same microscopic mechanism. The authors [36] in their dc and ac impedance study of mixed conduction in lithium vanadate, LixV2O5(x=0.4-1.4), provided another form of the Jonscher's power law to describe the ac behavior as:

$$\sigma(\omega)=\sigma(o)+A\omega^{\alpha} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

the conductivity spectrums of all the samples studied were found to fit the law perfectly. $\sigma(o)$ is the dc conductivity, *A* is a temperature-dependent parameter 0 and 1 has been found to take values between 0 and 1.This law is a universal property of the materials and is related to the dynamics of hopping conduction. According to the jump relaxation model, which takes into account the coulomb interaction between ions, the parameter α can be expressed as:

$$\alpha=\left(\frac{b_r}{s_r}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

where, b_r and s_r are the back hop rate and the site relaxation rate respectively. The back hop rate is the backward motion of the hopping ion to its initial site which is caused by the Coulomb repulsive interaction between mobile ions. The site relaxation is the shift of a site potential to the position of the hopping ion which is caused by a rearrangement of the hopping ions. The authors observed increase of α with lithium content and that it reveals that the backward hopping rate is increasing with lithium composition. They suggest that it may be due to the high repulsive Columbic force between Li^+ ions resulting in high activation energy for Li^+ ion migration in high lithium content samples. There have been two approaches that account for the ac conductivity [35]: the first approach derives conductivity from the effects of a static disordered energy landscape on the ion dynamics while the second approach emphasizes the relevance of Coulomb interaction between carriers. Based on structure and conduction mechanisms [37] classified ionic materials into polymer ionics, considered as soft disordered solids which, together with glassy materials, are amorphous exhibiting no long range structural order and exhibit glass transition temperatures; and on the other hand, ceramic and salt crystalline ionics that conduct because motion pathways are available to the ions often, but not always, by means of ions moving through vacancies.

3.0 Ac IMPEDANCE SPECTROSCOPY STUDIES

Impedance studies are important because by proper choice of the right frequency range, frequency dependence of conductivity can be avoided. They are also important from the point of view of finding the scope of applicability of these materials in various devices and a very useful technique for evaluating the electronic characterization of different materials or processes. The system can be modelled by an equivalent circuit which can consist of series combination of RC branches corresponding to grain interfaces, grain boundaries and electrode polarization. The approach offers opportunity to separate several physico-chemical processes involved in all solid state electrochemical systems. The overall electrical behavior is a result of several contributions: bulk electrolyte and grain boundary impedance, electrode-electrolyte interfacial impedance and measuring lead impedance.

Two main parameters determine impedance: frequency and temperature. Temperature dependence is through the Arrhenius equation:

$$\sigma T = C^* exp\left({E_o}/{k_B T} \right) \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \qquad (4)$$

here, C* is pre-exponential factor. The plot of real and imaginary parts of the impedance as a parametric function of frequency on an Argand plane shows a low frequency region, characterized by a straight line due to surface charge polarization and a high frequency region, due to electrical properties of the bulk. In order to determine the real part of the complex impedance the high frequency region is approximated to a semi circle. The dc value of the resistance on the other hand corresponds to the intersection of this semi circle and the real axis.

4.0 IMPEDANCE SPECTROSCOPY MEASUREMENT

This can be carried out by the application of a small periodic voltage perturbation (sinusoidal) while registering the magnitude and phase shift of the corresponding current over a wide range of frequencies. For a sinusoidal varying perturbation of the form:

$$V(t) = Voe^{iwt} \text{ ....} \quad (5)$$

where, V is a vector quantity, the resulting current response has in general the form:

$$I(t) = Ioe^{(iwt-i\phi)} \quad \text{.......................} \quad (6)$$

The complex admittance & is defined as the ratio of the complex current $I(t)$ over the complex voltage perturbation $V(t)$ applied to the system. The complex impedance Z is the reciprocal of the complex admittance. Thus considering (7) and (8)

$$Y(t) = {I(t)}\big/{V(t)} \text{ ....} \quad (7)$$

$$Z(t) = \left(Y^{-1}\right) = {I(t)}\big/{I(t)} = {Vo}\big/{Ioe^{(i\phi)}} \quad \text{..............} \quad (8)$$

Thus both complex admittance and impedance are independent. We write the impedance with its real and imaginary parts as: $Z = Z' + iZ''$. If the real and imaginary parts of the admittance and impedance are known, the complex admittance and impedance are well defined. Alternatively, the admittance and impedance vectors could be realized if the phase angle and modulus are known.

The real and imaginary parts of are:

$$\mathrm{Re}(Z) = Z' = |Z|cos\phi \quad \text{..............................} \quad (9)$$

$$\mathrm{Im}(Z) = Z'' = |Z| c\sin\phi \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (10)$$

The phase angle and modulus are:

$$\varnothing = \tan^{-1}\left(Z''/Z'\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (11)$$

$$|Z| = \sqrt{(Z')^2 + (Z'')^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (12)$$

Impedance is generally a complex quantity and is only real when =0, that is purely resistive, in that case it is also frequency independent. As mentioned earlier, the interface, electrode-electrolyte can be regarded to a first approximation as parallel plate capacitor, the rate of charging of which is determined by the bulk ionic resistance of the electrolyte.

5.0 IMPEDANCE SPECTROSCOPY STUDIES

There are works that have been reported on NASICON, for example, some workers have reported [38] extensive studies on lithium conducting $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_{3-x}(Z = V, Nb)$ system(LATP) and reported that Gromov *et al* substituted V and Nb for Phosphorus in it and observed an increase in the conductivity of the system. Previous work shows the grain boundary component of impedance producing an arc extending from well above 1678 down to the KHz region, however, literature could not provide clear information on the mechanism of conductivity enhancement, i.e., whether the grain boundary or the bulk conductivity of the system is enhanced. The nature of the electrodes was crucial in resolving the grain boundary arc in the cole-cole plot, as observed previously by Inaguna. Accordingly [38] compared graphite, silver and gold electrodes, as well as their combinations in order to obtain well defined impedance arcs. They observed that graphite alone was too resistive and tends to dominate the impedance values, whilst silver ink did not produce good adherent electrodes even though the film resistance was quite low. It was also difficult to apply Gold-sputtered electrodes in sufficiently thick layer to overcome the surface roughness of the pellets as a result of which the cole-cole plots could not be resolved, due to electrode impedance. The best electrodes were thus obtained by a combination of sputtered gold layer over which a silver ink was applied.

Scanning electron microscopy (SEM) is used in determining the morphology as well as the extent of grain boundary sintering which affects the grain boundary resistance and hence overall conductivity. Evidence of large porosity (>10%) was found, implying that sintering is incomplete; hence a large grain boundary resistance was inevitable. It has been demonstrated in the study of Li_{1+x} $[Al_xGe_{2-x}(PO_4)_3]$ glass ceramics that heat treatments with shorter nucleation times leads to higher grain size and subsequently higher ionic conductivity[39]. XRD, another complimentary tool used in the characterization, provides confirmation of the purity of the phases synthesized, such as the presence of some minor phases. A correlation exists between the extent of sintering and total conductivity as demonstrated by [40] in their study of two NASICON compositions. Previous reports showed that the substitutions investigated in their work leads to an increment in densification, attributed to the extra intergranular low melting or glassy phases which can act as fluxes to improve sinterability and connectivity, as demonstrated by the effect of atmosphere on the value of conductivity. The use of Ar and O_2 atmospheres in their work resulted in lower conductivities. The effect of atmosphere was also studied by [41] on impedance and conductivity characteristics of series of co-doped nanocrsytalline ceria compositions, $Ce_{1-x}M_xBi_{0.4}O_{2.6-x}$(M=Ca, Sr and Ba; x = 0.01- 0.15) which were hydrothermally synthesized at 240oC. The oxygen ionic conductivity in air, oxygen and helium were investigated. It was found that Oxygen gas had a great influence on the low frequency electrode response but had no effect on the grain and grain boundary conductivity .Work by [42] have also shown that Lithium-ion conducting ceramics (the LATP–Lithium Aluminum Titanium Phosphate system) and glasses, have advantage over polymer based systems because their conduction can be solely attributed to the lithium species. In addition, high room temperature conductivities (up to $1x10^{-3}$S/cm) have been reported, including reports that the ionic conductivity can be altered by controlling the channel sizes via one or more substitutions (Al, Sc, Nb and V), as the lattice dimensions depends on the size of the structural cations.

With NMR technique, it is possible to predict changes in ionic conductivity by measuring the mobility of Lithium ions in these materials through 7LiNMR. With increasing V content the 7Li static line width was found to steadily increase, indicative of decreasing lithium ion mobility [42]. The authors subsequently predicted that V substitutions in LATP will not enhance the bulk conductivity of the electrolyte. A study was conducted by [43] on lithium ion conductor with composition Li_xMPO_4(M=Mn,Fe,Co,Ni, etc.) and having the NASICON structure in Ar atmosphere. A 4-probe point conductivity measurement showed that the higher sintering temperature of the sample at 850°C ensured higher sample density and they therefore exhibited highest absolute value of conductivity at a given temperature. Three of the undoped samples showed different values of conductivity however and this they attribute to the measurement method and suggest that differences in the absolute values of carrier concentration may be due to heat treatment conditions. Activation energies for all samples were within 0.39-0.50eV, pointing to a common mechanism of conduction due to its narrow range. The use of blocking electrodes in dc measurements, they suggest, makes the conductivity predominantly electronic. The authors [44] studied compounds $LiM_2(PO_4)_3$,where(M = Ge, Zr, Ti) that belong to the NASICON-type structure and found that ionic conductivity of the system is greatly enhanced when Zr^{4+} in the $LiZr_2(PO_4)_3$ is replaced by a smaller Ti^{4+} ion, since the tunnels in the $LiTi_2(PO_4)_3$ are more suitable in size for the Li ion migration. Partial substitutions of Ti^{4+} by Sc^{3+} and Cr^{3+} ions in the NASICON-type structure of $LiTi_2(PO_4)_3$ is known to also cause an increase of the value of the Li ion conductivity of the substituted systems. Substitution of Zr^{4+} by Ti^{4+} and trivalent ion Sc^{3+} in the $LiZ_2(PO_4)_3$ compound causes a drastic increase of σ at room temperature in comparison with the values of ionic conductivity of $Li_{1+x}Zr_{2-x}Ti_x(PO_4)_3$ compound. The authors give the zoom temperature values of σ for $Li_1{+}_{1.2}Sc_{0.6}Z_{0.6}\,Ti_{1.6}(PO_4)_3$ as 1.2×10^{-2} S/cm which they said increases with temperature and the activation energy as $E_q = 0.33$eV. The crystal structure of $LiZr_2(PO_4)_3$ depends on technological condition of its preparation. The x-ray pattern of $LiZr_2PO_4)_3$ prepared at 1323K-1373K greatly differs from rhombohedral and is thought to possibly correspond to a triclinic cell[44]. At 1423-1473K however, sintered $LiZr_2(PO_4)_3$ pellets belong to rhombohedral symmetry with lattice parameters, a = 8.860Á and c = 22.13Á. At room temperature the values of the ionic conductivity of $LiZr_2(PO_4)_3$ is lower than 10^{-7}S/m. The authors [44] observed two dispersion regions in all the investigated samples, high frequency part attributed to the relaxation time in grains, and a low frequency part which corresponds to the grain boundary processes which are thermally activated. They also observed the shifting of the dispersion regions towards higher frequencies with increase of temperature. An impedance spectroscopy study in solution by [45] of NASICON ionic conducting material in aqueous solution (0.1M NaCl for different times) used Randle's equivalent circuit for the modeling and the ion exchange method. They distinguished three semicircles: the first at high frequency (HF) they attributed to the bulk electrical properties of the material and because of inhomogeneity of the sample, as it did not show an ideal semicircle shape, but a flattened one. The second one at medium frequency (MF) is thought to be contributed by the NASICON/solution interface process, which was also not a perfect semicircle and became flatter when the ion exchange time increased. The third semicircle at low frequency (LF) is generally assigned to slow transport processes such as diffusion. The authors found that the bulk resistance increased while the bulk capacitance decreased when ion exchange time increased and ascribed these to leaching of Na^+ ions from NASICON with a resulting increase in charge carrier concentration of electrolyte as reported by Nga and Son. The constant phase element (CPE) exponent decreased and they suggest that it is due to growth of pores in the material. By contrast, the interface resistance decreased while the interface capacitance increased and this has been attributed to the collection of Na^+ ions at NASICON/solution interface as earlier suggested by Nga and Son.

A recent work [46] synthesized NASICON through hot-press sintering to prepare the sodium superionic conductor, $Na_3Zr_2Si_2PO_{12}$ ceramics using the sol-gel method. The results showed that samples contain mainly monoclinic NASICON and no ZrO_2 phase was found, no matter the sintering temperature. At the sintering temperature of 1150°C for example, they observed that ionic conductivity of the sample has the highest value of 3.6×10^{-3}S/cm, which they attribute to its having the highest density and the least grain boundary due to the large crystal size of the ceramics. Recently a variant of the sol-gel method has been reported, the so-called 'drop generation' method. This is said overcome limitations due to conventional compacting method of ceramics which leads to structural modifications as a result of variations in size, density and non uniformity in shape etc., caused by the processing parameters [47]. A comparison of sintering techniques has been studied by [48] on NASICON compounds through solid state reaction technique by sintering them by *Spark Plasma Sintering* (SPS) and conventional sintering (CS). The SPS gave dense materials with high electrical conductivity at relatively low sintering temperature of 1100°C while highest conductivity of 1.8×10^{-13} 3S/cm was achieved for the stoichiometric SPS composition, a value they emphasize is comparable to the best results reported in literature, 2.0×10^{-3}S/cm (Ahmad et al, Fuentes et al). Specifically, two NASICON compositions were compared, $Na_3Z_2S_2PO_{12}$ and 5Na5P (5% excess of Na and P). They observed three distinct regions: a straight line at low frequency, representing an electrode–ceramics interface phenomenon and a semicircle which is associated with the grain boundary. The high frequency arc has been attributed to bulk effect and could not be well distinguished or observed in some cases. In principle however, the bulk contribution could be determined by extrapolating the grain-boundary semicircle, even in the absence of a high frequency arc. It was not possible to determine precisely the bulk resistance due to the inevitable inductance contribution from the lead wire. Because the grain boundary resistance contributes to the total resistance, the evaluation of bulk resistance was also difficult. The total resistance of the NASICON ceramics was therefore determined from the intercept of the electrode and grain boundary arc.

It was also found that the sample from low temperature sintering has visible grain boundary arc, while the bulk contribution could only be estimated from the high frequency intercept of the grain boundary arc. With increasing temperature the grain boundary arc became smaller and the grain arc became more visible. At 1150°C the grain boundary arc and the grain arc were both semicircles with good shape. The dc conductivity of the samples was thus calculated using the bulk resistances determined from the complex plots. With increment of sintering temperature, the d c conductivity improved and reached 5.64 $\times 10^{-3}$S/cm at 1150°C, higher than the reported results. For the sintered NASICON ceramics the impedance from the crystal boundary dominated, because the crystals from these samples were very small. Density of sample sintered at 1000°C was the lowest and crystal size the smallest, thus the impedance from the crystal boundary is the highest and the ion conductivity of the sample is the lowest. As the sintering temperature increased the crystal size grew slowly while the impedance from crystal boundary became weaker with concomitant increased ion conductivity. A report on the comparative study of the effect of different Zirconia precursors on the electrical properties of NASICON [49] reveals a great deal of information. NASICON, $Na_3Si_2Zr_2(PO_4)_3$ and NASICON-TZP ($Na_3Zr_{1.94}Y_{0.06}Si_2PO_{12}$) were studied. The NASICON was found to exhibit different grain sizes and the presence of a liquid phase was confirmed, suggestive of the consequence of high sintering temperature which results in low temperature ion–blocking phenomenon. It was found necessary to carry out low temperature measurements at 0oC in order to distinguish the bulk from the grain boundary contribution for both the NASICON and NASICON-TZP due to the higher impedance of the NASICON pellets. However, even at this temperature only the grain boundary arc is clearly seen and the bulk contribution was estimated from the high frequency intercept of the grain boundary arc in the case of the NASICON. The NASICON–TZP was also found to have the advantage of sintering to full densification at lower temperatures. The computed conductivities and activation energies for the NASICON and NASICON-TZP are respectively, 4.10^{-4}S/cm at 0.39eV, and $2.1.10^{-3}$S/cm at 0.36eV, at room temperatures. Some workers have also studied zirconia precursors [49-50] and found, in the case of hydrated and nanocrsytalline zirconia, that ion conductivity of the hydrated zirconia could be increased by thermal treatment by one order of magnitude or more. Other workers report correlation studies [40] carried out in which they correlated the sintering temperature, time, density and cooling mode (air or furnace) to conductivity. They called the Hong et al NASICON, $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}(0<x<3)$, H-type and the Von–Alphen type NASICON, $Na_{1+x}Zr_{2-x/3}Si_xP_{3-x}O_{12-2x/3}$, Atype, with little ZrO_2 second phase. Several works have shown that most sintered NASICON contain certain amount of ZrO_2 second phases, and have a monoclinic-tetrahedral phase transition at 1100°C below the usual sintering temperature of NASICON compounds. The monoclinic-rhombohedral phase transition of crystalline NASICON around 200°C has however been associated with a dilatometric anomaly unfavourable for applications [40]. One suggestion to overcome the problems is by various modifications in the compositions, as reported by von-Alphen, H. Kohler, S. Fujitstu et al, to improve its microstructure and physical properties. Impedance measurements carried out at different frequencies together with conductivity measurements for the H-type and for A-type samples found significant change in the activation energy (9; for Na^+), the highest of which occurred at about 200°C, attributed to the structural change between monoclinic (C2/c) and rhombohedral (R3c) crystal systems, as against a second-order transition that has previously been suggested by other workers. The authors [51] studied lithium conducting NASCON-type materials, $LiM_2(PO_4)_3$(where M=Ge, Zr, Ti) and synthesized $Li_{1.3\ 1.7}Sc_{0.3}Ce_{1.7}(PO_4)_3$ by solid state reaction method. Three dispersion regions were found in the σ spectra which all shifted toward higher frequencies with increase of temperature. The low frequency dispersion ranges were attributed to the blocking Pt electrodes and the complex conductivity plots show that the higher frequency part of the spectrum correspond to the relaxation in grains, while the lower frequency part correspond to grain processes. At 650K the values of total conductivity (σ_t) and grain conductivity (σ_g) conductivities of the investigated ceramics were found to be σ_t = 8.59 $x10^{-4}$S/m and σg=1.95 $x10^{-3}$S/m respectively, with corresponding activation energies for the total and grain, E_t = 1.34eV and 0.73eV.

The study [52] of lithium conductivity in the system $LiTi_2(PO_4)_3$(~10-6S/cm at RT) found that the conductivity may be increased from this value by at least two orders of magnitude upon partial substitutions of Ti^{4+} by trivalent cations such as Al, Ga, In, Sc,Y,La,Cr or Fe. The increase of ionic conductivity is due to a higher charge carrier number which they attributed to the lower porosity of the pellets. The conductivities of $Li_{1+x}Ti_{2-x}Al_x(PO_4)_3$materials on the other hand can be as high as 10^{-3}S/cm at RT. This they argued could mean that the ionic radius of Al^{3+} is likely to lie within the tolerability limit of the NASICON framework and that the maximum amount of Titanium that can be replaced with Al^{3+} with the concomitant insertion of Lithium to balance the charges, is 0.4 per formula unit. The experimental results indicate clear blocking phenomena at grain boundaries and electrode characteristics of ionic conductors. The complex impedance plots at high temperatures show well developed spikes characteristic of blocking electrodes which are observed at low frequencies. At lower temperatures they observed a depressed/deformed semicircle which they suggest may be related to the presence of a second semicircle at lower frequencies due to partial blocking (*constriction effect*) of the grain boundaries. The grain boundary contribution, they hypothesized, probably results from the relatively low pellet density which is an indication of a very good connectivity between grains probably resulting from small amount of Li_3FePO_4 impurity phase acting as an intergrain binder.

The authors [53] have also studied Lithium ionic conductive solid electrolyte based on the NASICON–type $Li_{1+x}Ga_xTi_{2-x}(PO_4)_3$(x = 0.1-0.9) and obtained a maximum conductivity of 7.3 x 10^{-4}S/cm at 303K and activation energy of 0.30eV, for $Li_{1+1.25}Ga_{0.25}Ti_{1.75}(PO_4)_3$. Addition of Li_3PO_4 or TiO_2 (rutile–type) as binder did not increase the conductivity in all the samples, rather they became lower. Thus they argue it indicates that these materials have no effect on the values of the measured parameters, even though such phases may be present in the synthesized materials. Some authors [54] have also studied new NASICON-type materials of composition, $Li_{3-2x}Al_{2-x}Sb_x(PO_4)_3$ (x = 0.6 to 1.4) and their dc conductivities. Impedance studies carried out at different frequencies and temperatures showed Arrhenius behaviour for all compositions, using d.c. conductivity measurements. The Cole–Cole plots obtained from impedance data do not show any spikes on the lower frequency side, indicating negligible electrode effects. A maximum conductivity of 4.5×10^{-6} S cm^{-1} at 573 K was obtained for x = 0.8 of the $Li_{3-2x}Al_{2-x}Sb_x(PO_4)_3$ system. The presence of a single peak in the plots of both log f vs. Z″ and log f Vs. M″ (M″ electric modulus.) were said to indicate bulk conductivity and absence of any grain boundary contribution to impedance. The complex impedance plot does not show semicircles up to 323K but as the temperature increased the curves attained greater curvature and became perfect semi circles, terminating at the origin and indicative of the absence of series resistance in the equivalent circuit model of the sample. All the semicircles start on the real impedance axis at the lowest frequency and this point is found to decrease with increase in temperature. The low frequency intercepts of these semicircles gives the resistance of the samples at the temperature of the cole-cole plots. Frequency variation of conductivity shows two shapes at all temperatures of the measurements and the authors suggest that the low frequency and low temperature conductivity could be due to intrinsic defects and charge agglomerations present in the sample, therefore the variation of slope with conductivity plots at lower frequency is an indication of presence of such defects.

6.0 CONCLUSION

The application of superionic materials in various electronic devices, particularly, NASICON and its multifaceted applications, offer opportunities for increased exploitation for hitherto insulating materials, in terms of cost and environmental friendliness, amongst others. Lithium-conducting materials, despite their enormous application in thermal and energy storage systems are grossly lacking in fundamental work in the area of optical characterizations, in the light of current nanoionics initiatives related to miniaturization.. The synthesis and characterization of NASICON materials also shows that microcracking can be reduced or controlled due to its relationship with grain size and density through novel sintering techniques and synthesis. The conductivity and impedance spectra emphasizes the need for correlation studies of conductivity from various techniques, such as NMR, Raman and infrared spectroscpies.This should be correlated with studies on the correlation of nucleation times, and sintering temperatures in order to arrive at specific parameters regarding the synthesis of these materials to improve performance. The research in the RF range has also been inadequate in the light of the complimentary role these materials could play in this age of communications. The conductivity and impedance spectra of NASICON have generally shown three regions of dispersive behaviour and obeyed Arrhenius character in their temperature-dependent conductivity, except of course in some cases were high/low frequency semicircles may be absent as a result of in homogeneities, relaxation times, etc., emphasizing their characteristic behaviour.

ACKNOWLEDGEMENT

The authors wish to thank Prof. Masaru Aniya, department of Physics, Kumamoto University, Japan for providing relevant literatures in the field of theoretical models for superionic conductivity and Dr. Tomas Salkus, Faculty of Physics, Vinius University, for literatures on impedance characterization of NASICON.

REFERENCES

[1] E. Kartini, T. Sakuma, A. Purwanto, T. Kamiyama and M. F. Collins, conductivity and structure of superionic compound (AgI)0.6(NaPO3)0.4 ,p.27

[2] D.R. Sadoway and A. M. Mayes (eds.), *MRS Bulletin*, August, 2002.

[3] G. Pasciak, J. Chmielowiec and P. Bujlo, *Materials Science-Poland*, 23(2005)209-219

[4] S. Sumiata, E. K. Mariyanto and Ari Adi, Pressure dependence of crystal structure and ionic conductivity of composite (AgI)0.7(AgPO4)0.3 P.111-125

[5] J. L. Nowinski, M. Mrocczkwoska, J. E. Garbarczyk and M. Wasiucionek, *Material Science-Poland,* 24(2006)

[6] H. Mallick and A. Sarkar, *Bull. Mater. Sci.,* 23(2000)319-324

[7] M. K. Dongare,P. Singh and P.M. Suryavanshi, *Mater. Res. Bull.*, 27(1992)637-645

[8] http:www.netl.doe.gov/publications/processing/03/ucr-hcbu/Brown.pdf. Accessed, August, 2009

[9] A. H. Naik, N. V. Thakkar, S. R. Darwadkhar, K. D. S. Mudher and V. Venegopal, *Journal of Thermal analysis and Calorimetry,* 78(2004)707-713.

[10] P. Brown, Nanostructured ceramics and composites, final progress report, Penn state University, 2005

[11] W. Y. Lee, K. M. Cooley, C. C. Berndt, D. L. Joslin and D. P. Stinton, *J. Am. Ceram. Soc.*, 79, (1996)2759

[12] http:www.eng.hawaii.edu/¬ssi II/SSI-II papers/A44.pdf.Accessed, August, 2009

[13] D. K. Agrawal,G. Harshe, E. Breval and R. Roy,*J. Mater. Res.*, 11 (1996)3158

[14] R. M. Hazen, L. W. Finger, D. K. Agrawal, H. K. McKinstry and A. A. Parrotta, *J. Mater. Res.,* 2(1987)329-337

[15] S. Nakayama and K. Itoh, *J. Nucl. Sci. Tech.*, 40 (2003)631-633

[16] http:library.iem.ac.ru/exper/vol10-1/151-152.pdf. Accessed, August, 2009

[17] F. Brunet, N.Bagdassarov and R. Miletich, *Solid state Ionics,* 159(2003)35-47

[18] J. J. Carvajal, I. Pareu, R. Sale, X. Solarus, F. Dianz and M. Aguilo, *Chem. Mater.*, 17(2005)6746-6754

[19] A. El Bouari and A. El Jazouli, *Phosporus Research Bulletin*, 15(2004)136

[20] G. S. Gopalakrishna, B.H. Doreswamy, M.J. Mahendra, M.A.Sridhar,J.S. Prasad and K.G.Ashamanjari, *Bull. Mater. Sci.*, 28 (2005)1-7

[21] A. S. Andersson,B. Kalska,P. Jonson, L. Hagstrom, P. Nardhblad, P. Tellgreen and J. O. Thomas, *J.Mater. Chem.*, 10 (2000)2542

[22] Z. Biao, G. Jingkum and Z. Peinan, *Science in China* (series E), (1996)337-339

[23] http:www.osti.gov./bridge/servelets/purl/102178-4Smo9M/102178.pdf. Accessed, August, 2009

[24] S. N. Achary, O. D. Jayakumar, S. J. Patwe, A. B. Shinde, P. B. R. Krishna, S. K. Kulshreshtha and A. K. Tyagi, *PRAMANA J. Phys.*, 71(2008)941-946

[25] C.Huang, D.K.Agrawal, H.A. McKinstry and S.Limaye, *J.Mater. Res.* 9(1994)2005-2013

[26] R. M. Hazen, L.W.Winger, D. K. Agrawal and H.A. McKinstry, J. *Mater. Res.,* 2 (1987)329-337

[27] D.A. Woodcock, P.Lightfoot and C. Ritter, *Chem. Commun.*, (1998)107-108

[28] B. Angadi,V.M .Jali, M.T. Lagare, N.S.Kini and A.M. Umarji, *Bull.Mater. Sci.*, 25(2002)191- 196

[29] P. S. Tantri, K.Gheeta, A. M. Umarji and S.K. Ramasesha, *Bull.Mater.Sci.* 23(2000)491-494

[30] A. R. Kotelnikov, A. M. Kovalskii, E. G. Karyaeva, A. I. Orlova, V. I. Petkov, G .M. Akhmedzhanova, and T. V. Ushakovskaya, *Crystal growth, structure and physical properties of crystals,* 7(2009) 68-69

[31] E. D. Tsagarakis, PhD Thesis, Kiel University, 2004.

[32] Jen's Thesis, chapter 1: Oxygen ion conductivity measurements: brief summary and introduction

[33] H. Jaeger, M.J. Pechan and D. K. Lottis, *Am. J. Phys.*, 66(1998)728-729

[34] P. P. Kumar, and S. Yashonath, J. *Chem. Sci.,* 118(2006)135-154

[35] J. Bisquert, V. Halparn, and F. Hern, *J. chem. Phys.,* 122 (2005) 151101

[36] M. Vijayakumar, and S. Selvasekarapandian, *Crystal Research Technolology,* 39 (2004)611-616

[37] M. A, Ratner, P. Johansson, and D. F. Schriver, *Mater. Res. Soc. Bull.*, March (2000)

[38] http:www.eng.hawaii.edu/¬ssi II/SSI-II papers/C55/C55.pdf. Accessed, August, 2009

[39] A. M. Cruz and A. C. S. Rodriques, *Ceramica* 53(2007) 180

[40] H. B. - Kang, and N. H. Cho, *J. Mater. Sci., 34* (1999)5005-5013

[41] H. Zhao and S. Feng, *Chem. Mater,* 11 (1999) 958-964

[42] M. Forsyth, S. Wong, K. M. Nairn, D. R. MacFarlene, P.J. Newman and A.S. Best, *J. Mater. Chem.*, 8(1998) 2199

[43] Y. Nian Xu, S.Y. Chung, J. T. Bloking, Y. M. Chiang and W. Y. Ching, *Electrical and solid state letters* 76 (2004)A131-A134

[44] T. Salkus, A. Dindune, Z. Kanepe, J. Ronis, A. Kazeonisand, and A. E. Orliukas, *Lithuanian Journal of Physics, 46* (2006) 361-366

[45] N. T. Nga, and T. Son, *Communication in Physics, 4* (2004)105-110

[46] Z. Dong-mei, L. Fa, X. Zang-long, Z. Wang-Cheng, *Transactions of nonferrous Metal Society of China*, 17 (2007) S1156-S1159

[47] J. Judes and V. Kamaraj, *Materials Science-Poland,* 27(2009)407

[48] J. S. Lee, C. M. Chang, Y.I. Lee, J.H. Lee and S. H. Hong, *J. Am. Ceram. Soc., 87* (2004)305-307

[49] R. O. Fuentis, F. M. B Marques and J. I. Franco, *Bol. Soc. Esp. Ceram. Vidrio,* 38(1999)631-634

[50] V.A.Tarnopolsky, A. D. Aliev, B. R. Churagulov, A. A. Burukhin, S. A. Novikova and A. B. Yaroslavtsev, *Sold State Ionics,* 162-163(2003)225-229

[51]T. Salkus , A. Dindune, Z. Kanepe, J. Ronis, A. Kezionis,E. Kazakevicius, L.J. Gaukckler, U. P. Mucke and A. F. Orliukas, *Lithuanian Journal of Physics, 46* (2006)483-488

[52] F. E. Mouahid, M. ,Zahir, P.M. Maldonado-Manso,S. Bruque, E. R. Losilla, M.A.G. Aranda, A. Rivera, C. Leona and J. Santamaria, *J. Mater.Chem.,11* (2001)3258-3263

[53] K. Oda, S. Takase and Y. Shimizu, *Material Science Forum, 544-545* (2007)1033-1036

[54] N. Anantharamulu, G. Prasad and M. Vithal, *Bull. Mater. Sci.,* 31(2008)133-138