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Study of Addition Metal (Ti, Zn) Dopan on The Structure of NASICON as Solid Electrolyte Batteries

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Abstract. This study aims to analysized the effect of addition doped metal (Ti and Zn) on NASICON structure to morphology, materials structure, and electrochemical performance especially ionic conductivity properties. NASICON is a sodium super ionic conductor that it could be as solid electrolyte batteries. One of the problems that exist in the secondary battery is the low working temperature of the electrolyte, which makes it easy to explode when exposed to free air. The common electrolyte in liquid phase, so NASICON as replacement alternative. The synthesis method used is the solid-state reaction method by mixing sodium carbonate, silicon dioxide, zirconium oxide, ammonium dihydrogen phosphate, doped metal (titanium oxide and zinc oxide) and some anhydrous ethanol into a planetary ball mill, dried then calcined. Then the material is pressed to produce pellets and the sintered. The doping used varies from 0 to 5 mol% of titanium and zinc. XRD results showed that all variations in titanium doped had found rhombohedral and monoclinic. whereas in zinc doping also have those phase. The highest ionic conductivity is 7.8x10^{-3} S/m on 2% mol Zinc Addition

Introduction

As is common knowledge, daily-used electronic devices include backup batteries that can be recharged. Due to its high energy density, lengthy lifespans, and performance as free memory, lithium-ion batteries are typically utilized as energy storage [1]. However, LIB also has safety drawbacks because the electrolyte employed is a liquid electrolyte that explodes when it comes into contact with air. As a result, NASICON is an alternative since it is a solid electrolyte [2], is extensively distributed in nature, and also has nearly the same properties as lithium, allowing it to be employed as a battery material with a big capacity [3].

The NASICON type of solid electrolyte, which uses sodium ions instead of lithium ions as charge carriers, is the type that is frequently utilized. The $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$ ($0 \leq x \leq 3$) structure, one of the well-known NASICON kinds, has the benefit of being a stable crystal structure[4]. In order to transmit ions when used in a battery, Na^+ ions in the NASICON type must pass through a bottleneck-like barrier when employed as a Solid State Electrolyte (SSE). By adding the necessary substituents as doping to the NASICON structure, it is a standard practice to increase the bottleneck size, hence increasing the ionic conductivity [2].

NVP (type-NASICON) has undergone structural modification by doping or replacement to enhance the electrochemical performance and energy density. Previous studies found that substituting Ni, Fe, Mo, Al, and Cr improved the electrical conductivity or ion diffusivity, which showed promise for enhancing the electrochemical characteristics. In sodium diffusion channels, for instance, dopant ion substitution can reduce the average bond length or raise the unit cell volume [5]. In addition, research has also been carried out on the addition of doping magnesium by 2% mol with an ionic conductivity value of 8.59 x 10^{-4} S.cm-1[3], Cerium with the addition of 0%, 1% and 5% that the total ionic conductivity value of the sample N0, N1, and N5 respectively, namely 5.02 x 10^{-2}; 4.10 x 10^{-2}; and 4.01 x 10^{-2} S/cm [6], while Yanli Ruan et al. obtained the conductivity value from the NASICON sample with dopant in the form of ytria which has a bulk conductivity value of 7.27×10^{-4} S/cm, while the total conductivity is 6.28 x 10^{-4} S/cm [7].

Vania Mitha Pratiwi et al. investigated the use of titanium oxide as a dopant for the NASICON sample in 2019. The use of titanium varies from 0% to 6% mol. The optimum value for the variation of the addition of 6% mol in the ionic conductivity test was 5.897 x 10^{-5} S/cm [8]. Danchen et al. obtained conductivity values ranging from 0.1 to 0.4 at room temperature (25°C), namely 3.77x10^{-4}, 3.43 x 10^{-4}, 1.12 x 10^{-4}, and 7.19 x 10^{-5} S/cm. Total conductivity, as is well known, is an inherent electrochemical property that is primarily influenced by the geometry of the bottleneck [9]. The effect of adding 1-5 mol% zinc oxide and titanium oxide to the NASICON structure was investigated in this study. The Zr^{4+} cation is expected to be replaced by zinc and titanium.

Experimental Procedure

Solid-state reaction technique was used to create the solid electrolyte Na3Zr2Si2PO12. To begin, combine ethanol with Na_2CO_3, SiO_2, ZrO_2, $NH_4H_2PO_4$, and the dopan (TiO_2; ZnO) in a ball mill. TiO_2 and ZnO are added in amounts ranging from 1% to 5% mole fraction. Ball milling is done for 12 hours at 400 rpm, followed by 12 hours of drying at 80 °C. Then, it is calcined for 12 hours at 1125 °C at a heating rate of 2 °C per minute. A mortar is then used to crush the powder. An X-ray diffraction tester (X'pert PRO PANalytical) and scanning electron microscopy were used to characterize each variant (FEI Inspect S50).

Preparation of Solid Electrolyte $Na_3Zr_2Si_2PO_{12}$ Pellets: A mold with a 10 mm diameter circle was used to produce a pellet out of the weighted NASICON sample. NASICON powder was compressed for 7 minutes. In an alumina crucible, the pellets are sintered for 12 hours at a temperature of 1175°C and a heating rate of 1°C min-1 to stabilize their phase. To determine the ionic conductivity value, all materials were evaluated using an electrochemical impedance spectroscopy tester (CorrTest CS310)

Result and Discussion

To determine the crystalline phase, the samples that were obtained were examined using an X-ray diffraction tester. In accordance with JCPDF Nos. 01-084-1200 (2θ = 13.5°; 27`°; 19°; 30°; 34°; 46°; 53°) and 01-087-0617 (2θ = 22°; 24°; 31.4°; 33.9°; 46°; 51°), respectively, the dominant structures of the produced NASICON on titanium doping were monoclinic at 0, and 5 % mol and rombhohedral at 1; 2; 3; 4 % mol. as with Ti doping According to JCPDF No. 01-084-1200 and 01-087-0617, respectively, the structure of the produced NASICON on zinc doping was rhombohedral at 1; 2; 3; and 4 % mol and monoclinic at 0 and 5% mol. It was discovered that the NASICON crystal structure changed from monoclinic to rhombohedral as a result of the addition of doping material. The aberrations in the crystal structure are the cause of these modifications. The calculation of the XRD diffraction pattern also provides information about the increase in lattice parameters. Monoclinic ZrO_2 (2θ = 28°), Na_2ZrSiO_7 (2θ = 30.6°), and $Na_2ZrSi_4O_{11}$ (2θ = 17°; 27°), are impurities that have been discovered.

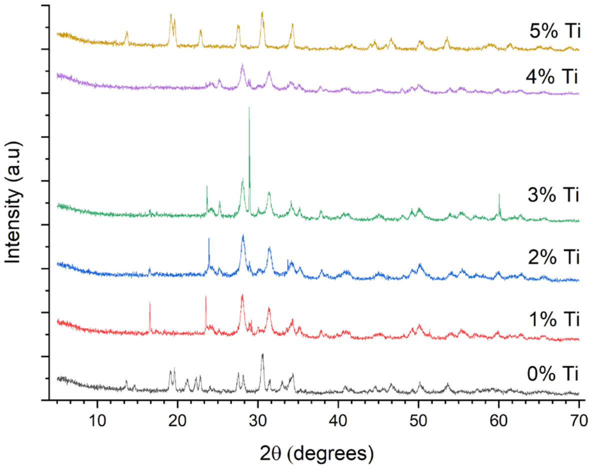

Fig. 1. X-Ray Diffraction Pattern of NASICON doped Ti at 0-5% mol variation

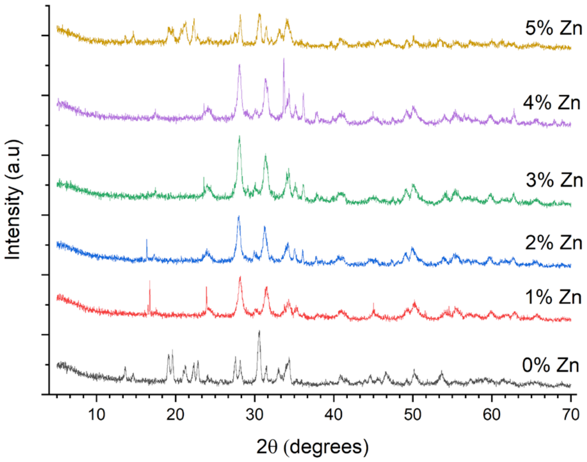

Fig. 2. X-Ray Diffraction Pattern of NASICON doped Zn at 0-5% mol variation

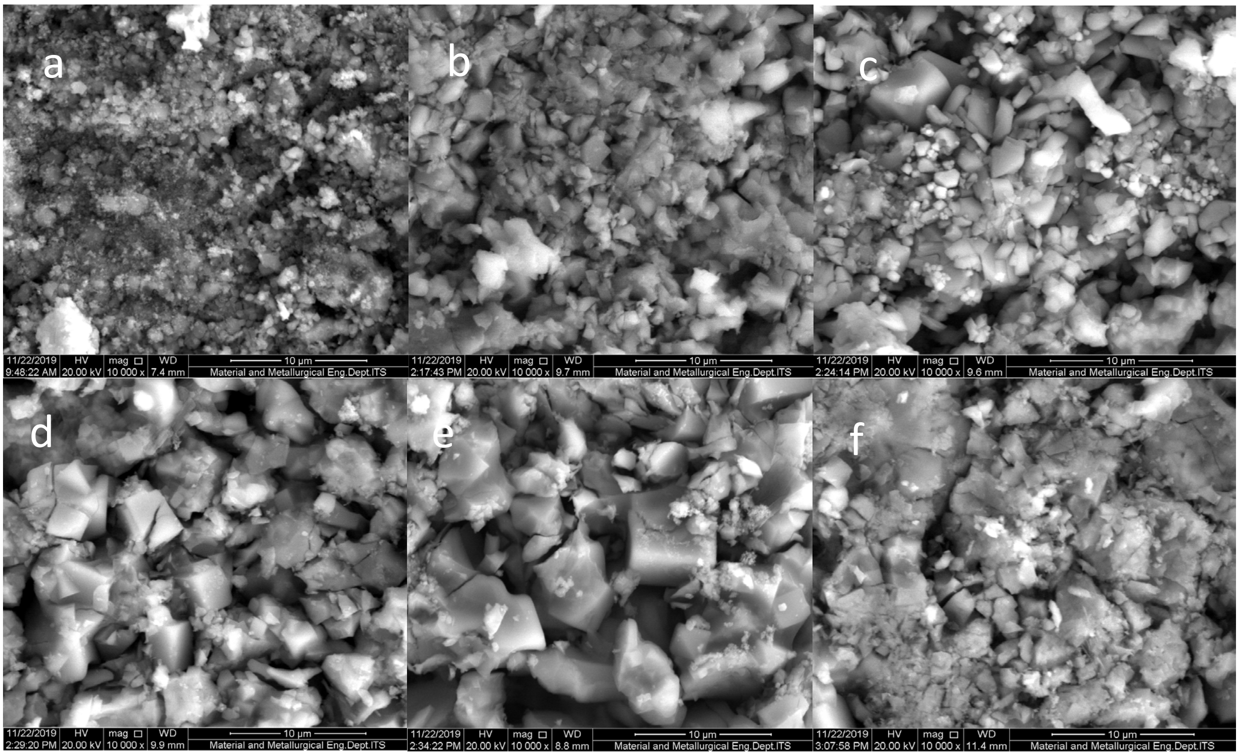

Fig. 3. SEM images of Titanium doped NASICON after sintering with 10000x magnification a) 0 mol%, b) 1 mol%, c) 2 mol%, d) 3 mol%, e) 4 mol% f) 5 mol%

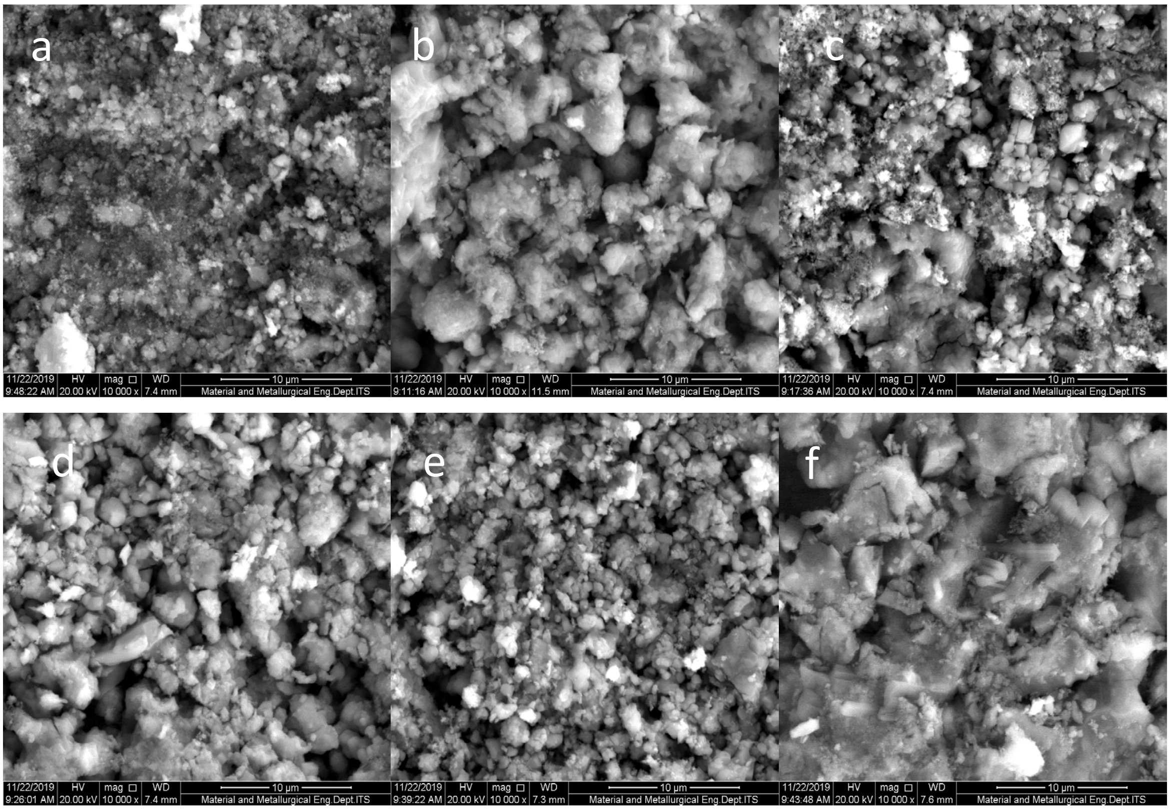

Fig.4. SEM images of Zinc doped NASICON after sintering with 10000x magnification a) 0 mol%, b) 1 mol%, c) 2 mol%, d) 3 mol%, e) 4 mol% f) 5 mol%

In Figure 3, the micro-graph images provided by SEM testing of titanium doped NASICON with variation of mol percentages. The morphology of pellet after sintering which contain 1, 3, and 4% mol has an indicate of good densification owing to less void compared to the other sample. That Figure (Figure 4) shown the morphology powder after calcination, which 2, 3, 4, and 5% mol contain of zinc doping is very good at densification and less void so particle that look dense

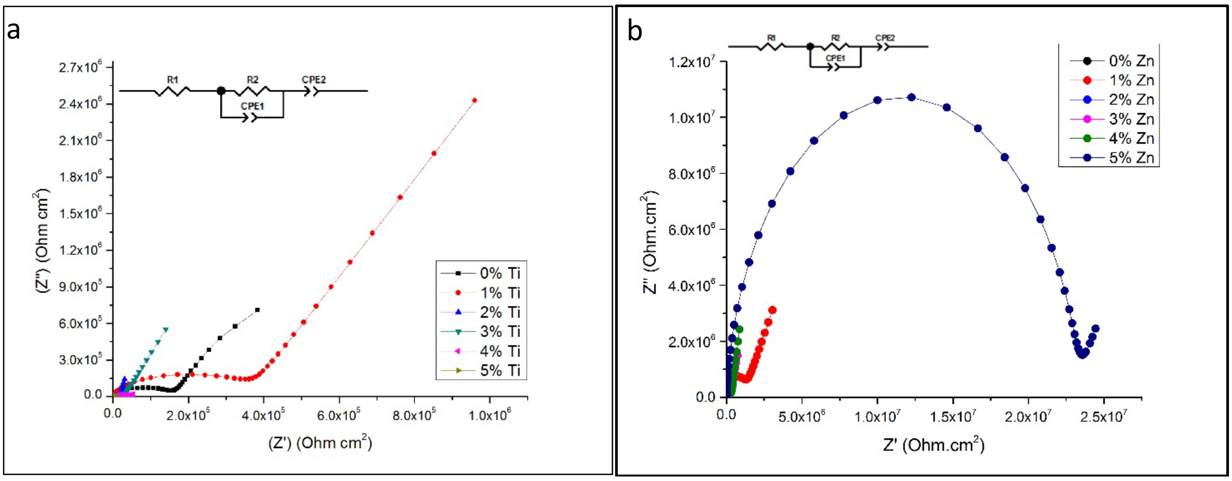

Fig. 5. Result of EIS tester for (a) Titanium doped NASICON (b) Zinc doped NASICON at 0-5% mol addition.

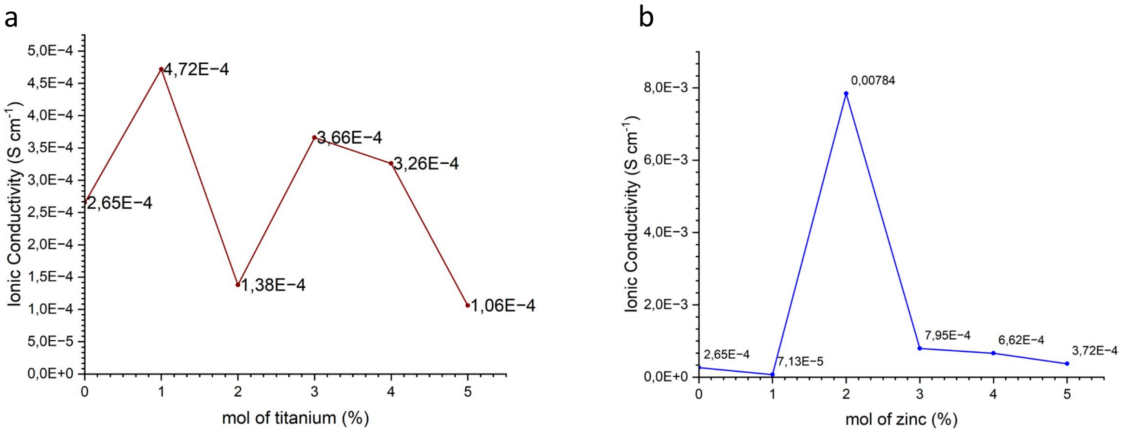

Fig. 6. The conductivity value (a) Titanium doped NASICON (b) Zinc doped NASICON at 0-5% mol addition.

The Nyquist curves of titanium and zinc doped NASICON at 0–5 %mol addition are shown in Figure 5. Samples of electrolyte were sintered for 12 hours at 1175 °C. The sample's total conductivities were calculated by fitting the pattern's data to the data on the CorrTest CS310. Total ion conductivity increases up to a doping concentration of 0.02 as can be observed, but it subsequently declines as the concentration of zinc doping increases. However, there are anomalous data for titanium doping. The NASICON lattice characteristics rise with increasing Ti and Zn doping concentration, as discussed in the XRD analysis, which expands the lithium-ion transmission channels and improves ion conductivity [1].

Grain resistance and grain boundary resistance make to the total resistance for the NASICON electrolyte. Grain resistance and grain boundary resistance exhibit responses in the high- and mid-frequency ranges, respectively. The blocking effect of the electrode ions is shown in the low-frequency region by slanted straight lines. The results of EIS testing for samples with various doping content values are shown in Figure 4.a. All samples initially had a semicircular response, but the addition of doping caused a shift in frequency to the right or to a lower frequency.

As is well known, the geometry of the bottleneck has a significant impact on the total conductivity, which is an inherent electrochemical feature. There are two parts to the impact of various dopants on bulk conductivity. First and foremost, while the dopant level in the valence state drops, bulk conductivity rises. This means that the higher conductivity is a result of the dopant's lower valence state. The sodium ions and dopants will be less attracted to one another due to the low valence cations that are present at the zirconium sites. It requires less energy for the sodium ions to diffuse around the zirconium ions because there is less electrostatic connection between them. As a result, the Ti^{4+} doped NASICON ceramics exhibit an improvement in overall conductivity. Additionally, the Zn^{2+} and Ti^{4+} doped NASICON ceramics create oxygen vacancies and zirconium vacancies to preserve charge neutrality. Na^+ ions can move via openings and voids. The Na^+ ions are allowed to migrate into the empty space, increasing the bulk conductivity [9].

In addition, Figure 6 displays the titanium and zinc doping's ionic conductivity values for all variations. Figure 5 shows that a 2 %mole addition of zinc has a smaller semicircle and lower impedances, which indicates a higher conductivity. The value, 7.8×10^{-3} S/m, is higher than that found in earlier studies [4]. The conductivity of the generated sample ions changes as a result of variations in the crystal structure. There will be more sodium ions in one crystal unit due to an increase in sodium ion sites caused by the electrostatic interaction between sodium ions and the octahedral structure of the crystal diminishing. The ionic conductivity increases with the number of charge carrier ions.

Conclusion

A solid electrolyte of the titanium and zinc-doped NASICON type was successfully synthesized in this study. The crystal structure created in the NASICON sample is known to be rhombohedral, which will later transform into monoclinic depending on the quantity of doping used. The NASICON sample appears to have a compact structure with a reasonably adequate degree of densification as dopant concentrations increase. This influences the sample's ionic conductivity, with increased densification directly enhancing ionic conductivity by decreasing grain resistance and grain boundaries. For 2% mol Zn and 1% mol Ti doping, the greatest ionic conductivity is 7.8 x 10-3 S/m and 4.72 x 10-4 S/m, respectively. The NASICON solid-type electrolyte's high conductivity value has the potential to replace liquid-based electrolytes, lowering the risk of a battery explosion.

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