

Influence of aliovalent Cr^{3+} substitution on the structural, ionic conductivity and electrochemical properties of $\text{Mg}_{0.5+1/2x}(\text{ZrSn}_{1-x})\text{Cr}_x(\text{PO}_4)_3$ NASICON-type solid electrolyte

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Abstract

In this work, $\text{Mg}_{0.5+1/2x}(\text{ZrSn}_{1-x})\text{Cr}_x(\text{PO}_4)_3$ (MZSCP) novel NASICON-type solid electrolytes, with compositions ranging from $0.0 \leq x \leq 0.3$, were synthesized via a water-based citrate sol-gel method. The structural, electrical, and electrochemical behaviors of the synthesized materials were systematically investigated. Rietveld refinement of X-ray diffraction (XRD) data confirmed that the polycrystalline compounds crystallize in a monoclinic NASICON-type structure with a $P21/n$ space group. Field emission scanning electron microscopy (FESEM) revealed a uniform particle size distribution, with average grain sizes ranging from 56.06 nm to 117.40 nm. Among the investigated compositions, the $x = 0.10$ substitute exhibited the optimized electrochemical performance, yielding a maximum ionic conductivity of $\sigma_{500^\circ\text{C}} \sim 2.26 \times 10^{-4} \text{ Scm}^{-1}$ and a wide electrochemical stability window ($\sim 4.81 \text{ V}$). These significantly enhanced electrical and electrochemical properties demonstrate that the Cr-doped MZSCP ($x = 0.10$) is a highly promising solid electrolyte candidate for next-generation magnesium-ion energy storage devices.

1. Introduction

Rechargeable battery technologies, particularly lithium-ion batteries (LIBs), are the most widely used due to their high energy density and reliability. However, their widespread application, especially in large-scale energy storage systems, is hindered by significant challenges, including high costs and safety concerns. These limitations have driven interest in alternative technologies such as magnesium-ion batteries (MIBs), which are considered a promising next-generation energy storage solution. Magnesium offers several advantages over lithium, including natural abundance, low cost, higher specific capacity (2205 Ah kg^{-1}), superior volumetric capacity (3833 mAh/cm^3), and greater atmospheric stability, making it safer for use in high-energy-density rechargeable batteries [1]. Despite their potential, MIB technology faces significant obstacles, primarily due to the lack of practical electrolytes. These challenges include low reversible capacity, limited magnesium-ion mobility, and poor operating voltage. To address these issues, researchers have explored various magnesium-based electrolytes, including liquid electrolytes, solid-state electrolytes (such as inorganic and polymeric electrolytes), and molten salt systems (ionic liquids and high-temperature molten salts). However, these systems present additional hurdles, such as high volatility, flammability, air reactivity, low thermal stability, and inadequate ionic conductivity [2].

Although incorporating ionic liquids into solid electrolytes can enhance certain properties, such as ionic mobility, their high cost and toxicity make them an impractical standalone solution [3]. Among inorganic solid electrolytes, NASICON materials have garnered significant attention due to their unique combination of properties. These include broad electrochemical stability, lightweight structure, excellent thermal stability, and high ionic conductivity. Recent studies have demonstrated sodium-ion conductivities as high as $3.2 \text{ mS}\cdot\text{cm}^{-1}$ at 25°C , making NASICON a promising candidate for advancing MIB technology [4]. The well-known Na^+ superionic conductor (NASICON) is widely recognized for its ability to facilitate sodium-ion mobility, attributed to its robust three-dimensional network structure. This

framework comprises ZrO_6 octahedra corner-sharing with PO_4 tetrahedra, forming interconnected channels that allow the migration of Mg^{2+} cations with low activation energy [5]. As a result, there is significant interest in developing multivalent ionic conductors with NASICON-type structures, represented by $\text{MZr}_4(\text{PO}_4)_6$ (where $\text{M} = \text{Ca}^{2+}, \text{Sr}^{2+}, \text{Mg}^{2+}, \text{Ba}^{2+}$). Among these, magnesium zirconium phosphate ($\text{Mg}_{0.5}\text{Zr}_2(\text{PO}_4)_3$), has been extensively studied as a potential NASICON solid electrolyte for battery applications [6].

Further research on $\text{Mg}_{0.5}\text{Zr}_2(\text{PO}_4)_3$ solid electrolytes has extensively focused on aliovalent cation substitution across various oxidation states (mono- to pentavalent) and ionic radii. This strategic doping aims to enhance ionic conductivity via three synergistic mechanisms: introducing charge-compensating interstitial ions or vacancies (defect engineering), tailoring grain size/grain-boundary density, and modifying lattice parameters to expand the structural bottlenecks for optimized ion migration. For instance, pentavalent substitution by Nb^{5+} at the tetravalent Zr^{4+} site in $\text{Mg}_{0.5}\text{Zr}_2(\text{PO}_4)_3$ crystallizing in a $\beta\text{-Fe}_2(\text{SO}_4)_3$ -type framework—yielded an ionic conductivity of $7.7 \times 10^{-4} \text{ S cm}^{-1}$ at 600°C , marking a sixfold increase over the pristine parent phase [7]. Similarly, using co-precipitation to introduce Mg^{2+} into the Hf^{4+} site in $\text{HfNb}(\text{PO}_4)_3$ created NASICON-type conductors exhibiting high performance ($10^{-4} \text{ S cm}^{-1}$), underscoring the efficacy of subvalent hosting [8]. Trivalent and divalent substitutions have proven equally vital for low-temperature optimization. Replacing Zr^{4+} with Fe^{3+} in $\text{Mg}_{0.5}\text{Zr}_2(\text{PO}_4)_3$ generated interstitial Mg^{2+} carrier ions, boosting room-temperature conductivity to $1.24 \times 10^{-5} \text{ S cm}^{-1}$ [9]. Multi-component doping strategies have further amplified this effect; co-substituting smaller Zn^{2+} and Al^{3+} ions into the Zr^{4+} site to form $\text{Mg}_{0.5+x+0.5y}\text{Zn}_x\text{Al}_y\text{Zr}_{2-x-y}(\text{PO}_4)_3$ enhanced conductivity by two orders of magnitude over undoped counterparts [10]. Notably, the highest ambient-temperature bulk conductivity reported for this material class ($1.54 \times 10^{-4} \text{ S cm}^{-1}$) was achieved via trivalent Al^{3+} substitution in $\text{Mg}_{0.5}\text{Si}_2(\text{PO}_4)_3$ [11]. Conversely, the impact of larger tetravalent cations like Ce^{4+} in $\text{Mg}_{0.5}\text{Ce}_x\text{Zr}_{2-x}(\text{PO}_4)_3$ demonstrated that while a composition of $x = 0.2$ maximized pellet density and phase purity, it yielded lower conductivities ($2.6 \times 10^{-9} \text{ S cm}^{-1}$ for pellets; $2.0 \times 10^{-10} \text{ S cm}^{-1}$ for thin films) [12]. Recent investigations into $\text{Mg}_{0.5(1+x)}\text{Fe}_x\text{Zr}_{2-x}(\text{PO}_4)_3$ revealed that although iron doping altered the localized bottleneck dimensions to reduce total resistance, excessive loading ($x = 0.2$) produced a relatively low room-temperature conductivity of $1.8 \times 10^{-7} \text{ S cm}^{-1}$ [13]. Collectively, these precedents confirm that tailored partial substitutions dictate electrochemical performance by strategically increasing mobile Mg^{2+} carrier concentrations and geometrically tuning structural channels to facilitate unhindered ion transport. The impacts of aliovalent substitution on $\text{Mg}_{0.5}\text{Zr}_2(\text{PO}_4)_3$ -type solid electrolytes are summarized in Table 1.

Table 1
Summary of the impact of aliovalent substitution on $\text{Mg}_{0.5}\text{Zr}_2(\text{PO}_4)_3$ -type solid electrolytes

Composition	Dopant Ion & Target Site	Mechanism	Conductivity Performance	References
$\text{Mg}_{0.5}\text{Zr}_{2-x}\text{Nb}_x(\text{PO}_4)_3$	Nb^{5+} (Pentavalent) at Zr^{4+} site	Structural modification ($\beta\text{-Fe}_2(\text{SO}_4)_3$ -type framework).	$7.7 \times 10^{-4} \text{ S cm}^{-1}$ at 600°C (6 times higher than undoped parent phase).	[7]
$\text{HfNb}(\text{PO}_4)_3$	Mg^{2+} (Divalent) at Hf^{4+} site	Subvalent hosting in NASICON-type framework.	$\sim 10^{-4} \text{ S cm}^{-1}$ (High performance via co-precipitation).	[8]
$\text{Mg}_{0.5+x}\text{Zr}_{2-x}\text{Fe}_x(\text{PO}_4)_3$	Fe^{3+} (Trivalent) at Zr^{4+} site	Charge-compensating and generate interstitial Mg^{2+} carriers).	$1.24 \times 10^{-5} \text{ S cm}^{-1}$ at room temperature.	[9]
$\text{Mg}_{0.5+x+0.5y}\text{Zn}_x\text{Al}_y\text{Zr}_{2-x-y}(\text{PO}_4)_3$	Zn^{2+} & Al^{3+} (Co-doping) at Zr^{4+} site	Double substitution using smaller ionic radii.	$3.97 \times 10^{-4} \text{ S cm}^{-1}$ at room temperature.; $5.82 \times 10^{-4} \text{ S cm}^{-1}$ at 500°C	[10]
$\text{Mg}_{0.5+x/2}\text{Si}_{2-x}\text{Al}_x(\text{PO}_4)_3$	Al^{3+} (Trivalent) at Si^{4+} site	Interstitial carrier modulation.	$3.78 \times 10^{-5} \text{ S cm}^{-1}$ room temperature.	[11]
$\text{Mg}_{0.5}\text{Ce}_x\text{Zr}_{2-x}(\text{PO}_4)_3$	Ce^{4+} (Tetravalent) at Zr^{4+} site	Size mismatch (Larger cation alters framework packing).	$(2.6 \times 10^{-9} \text{ S cm}^{-1}$ pellets; $2.0 \times 10^{-10} \text{ S cm}^{-1}$ films).	[12]
$\text{Mg}_{0.5(1+x)}\text{Fe}_x\text{Zr}_{2-x}(\text{PO}_4)_3$	Fe^{3+} (Trivalent) at Zr^{4+} site	Geometric bottleneck tuning (Reduces total localized resistance).	$1.8 \times 10^{-7} \text{ S cm}^{-1}$ at 25°C .	[13]

Composition	Dopant Ion & Target Site	Mechanism	Conductivity Performance	References
$\text{Mg}_{0.5}\text{Zr}_x\text{Sn}_{1-x}(\text{PO}_4)_3$	Sn^{4+} at Zr^{4+} site	Size mismatch (Larger cation alters framework packing).	$2.47 \times 10^{-5} \text{ S cm}^{-1}$ at 500°C	[14]

In our previous work, we reported that isovalent substitution between Sn^{4+} and Zr^{4+} within the NASICON-structured $\text{Mg}_{0.5}\text{Zr}_x\text{Sn}_{1-x}(\text{PO}_4)_3$ (MZSP) matrix successfully enhanced ionic conductivity by modification of lattice parameters [14]. Building upon those findings, this work transitions to an aliovalent doping strategy, exploring the influence of replacing Sn^{4+} with trivalent Cr^{3+} to synthesize a series of novel $\text{Mg}_{0.5+1/2x}(\text{ZrSn}_{1-x})\text{Cr}_x(\text{PO}_4)_3$ (MZSCP) NASICON-type solid electrolytes. The integration of subvalent Cr^{3+} potentially introduces a distinct, dual-action mechanism: it deliberately injects charge-compensating interstitial Mg^{2+} carrier ions into the framework while geometrically dilating the structural bottleneck channels to lower the activation energy for ion hopping.

To the best of our knowledge, no published literature currently addresses this specific $\text{Mg}_{0.5+1/2x}(\text{ZrSn}_{1-x})\text{Cr}_x(\text{PO}_4)_3$ architecture. To systematically evaluate how these atomic-scale modifications translate to macroscopic electrochemical performance, a comprehensive characterization suite was deployed. Phase evolution, vibrational characteristics, and surface morphologies were analyzed using X-ray Diffraction (XRD), Fourier Transform Infrared (FTIR) spectroscopy, and Field Emission Scanning Electron Microscopy (FESEM). Concurrently, the underlying ion transport kinetics, carrier dominance, and electrochemical stability windows were thoroughly interrogated via Impedance Spectroscopy (IS), and Linear Sweep Voltammetry (LSV).

2. Experiment

2.1 Synthesis of $\text{Mg}_{0.5+1/2x}(\text{ZrSn}_{1-x})\text{Cr}_x(\text{PO}_4)_3$, (MZSCP)

The synthesis $\text{Mg}_{0.5+1/2x}(\text{ZrSn}_{1-x})\text{Cr}_x(\text{PO}_4)_3$ compound with composition of $x = 0.05, 0.10, 0.15, 0.20$ and 0.30 were carried out via water-based citrate sol gel method. The stoichiometric amounts of high purity precursor of magnesium acetate tetrahydrate ($\text{MgCH}_3\text{COO}_2)_2 \cdot \text{H}_2\text{O}$, Sigma Aldrich), ammonium phosphate monobasic (NH_4PO_4 , Merck Millipore), zirconium (IV) acetate hydroxide ($\text{Zr C}_6\text{H}_{10}\text{O}_7$, Sigma Aldrich), tin (IV) chloride pentahydrate ($\text{SnCl}_4 \cdot \text{H}_2\text{O}$, Sigma Aldrich) and chromium (III) acetate hydroxide ($(\text{CH}_3\text{CO}_2)_7\text{Cr}_3(\text{OH})_2$, Sigma Aldrich) were weighted and dissolved separately in deionized water except $\text{ZrC}_6\text{H}_{10}\text{O}_7$ were dissolved in acetic acid. Citric acids ($\text{C}_6\text{H}_8\text{O}_7$, Merck) as chelating agent with molar ratio 1:3 for citric acids to metal were used to assist the gelation process. Magnesium acetate and ammonium phosphate solution were mixed while continuously stirring to form the homogeneous sol. Following, other solutions were added to the homogeneous sol. Lastly, zirconium acetate and tin

chloride solutions were added dropwise through the burette and transferred into a reflux system and continuously stirred for 24 hours at 80 °C to obtain homogeneous colloidal solutions. The stepwise and dropwise of mixing solutions is crucial to obtain a homogeneous gel and to avoid the residual chloride salt excess and minimize the secondary phase formation [14]. Then, the solutions were vaporized for 6 hours at 80 °C. The resulting gel were then dried at 120 °C for 24 hours to form precursor powders and were calcined at 400 °C for 4 hours to remove acetate, citrate and chloride organic groups. The calcined powders were ground and sieved in order to obtain very fine powder. Finally, 0.5 g powder was put into cylindrical steel mould with a diameter of 13 mm and pelletized using conventional uniaxial hydraulic press at 133 MPa before sintered in furnace at 800 °C (2 °C step/min) for 24 hours.

2.2 Characterization

X-ray diffraction (XRD) was measured using PANalytical-Empryan with Cu-K α radiation wavelength of 1.5406 Å in range from $2\theta = 5^\circ - 90^\circ$ at a rate of 0.026° step size at room temperature. The XRD pattern were refined by Rietveld refinement using HighScore Plus 3.0 software for detail structural. Lattice parameters of the monoclinic compound were determined using the following equations:

$$\frac{1}{d^2} = \frac{1}{\sin^2\beta} \left(\frac{h^2}{a^2} + \frac{k^2 \sin^2\beta}{b^2} + \frac{l^2}{c^2} \right) - \frac{2hl\cos\beta}{ac} \text{) and } d = \frac{\lambda}{2\sin\theta} \quad (1)$$

Where d is the interplanar spacing, λ is the X-ray wavelength, θ is the diffraction angle, hkl are the Miller indices, a , b , and c are lattice parameters, and β is the monoclinic angle. Crystallite size (D) was estimated using the Scherrer equation: $D = K\lambda / (\beta \cos \theta)$, where K is the Scherrer constant (0.94), λ is the X-ray wavelength, θ is the diffraction angle, and β is the full width at half maximum of the XRD peak. The morphology and the composition were characterized using field emission scanning electron microscopy (FESEM) which were carried out using cold field emission source of FESEM (Hitachi SU8220 series) with acceleration voltage of 2.0 kV. Fourier-transform infrared (FTIR) analysis was obtained by Perkin Elmer Frontier Spectrometer in the wave number range from 500 cm^{-1} to 4000 cm^{-1} with a resolution of 2 cm^{-1} at room temperature. The temperature dependent of impedance measurements (EIS) were determined by impedance analyzer (Solartron 1260) using two-blocking stainless steel electrode cells sandwiching the sample pellet over frequency range from 1 Hz to 10^6 Hz and temperature ranging from 300 °C to 500 °C at 25°C step. The impedance fitting analysis was performed using ZView software. The transference number measurement was performed using DC polarization method with magnesium metal electrodes were used as non-blocking electrodes. The electrochemical measurement was done at room temperature using the multichannel electrochemical workstation potentiostat (ZIVE Lab). Linear sweep voltammetry (LSV) was employed on samples sandwiched between two stainless steel electrodes with potential sweep between 0 and 8 V at 5 mV step to evaluate the samples' electrochemical stability window.

3. Result and discussion

3.1 XRD analysis

Figure 1 (a) shows the XRD patterns of MZSCP with different composition of $x = 0.00, 0.05, 0.10, 0.15, 0.20, 0.30$ and Fig. 1 (b) shows the Rietveld refinement of pure MZSCP for $x = 0.05$ and 0.10 . From the figures, the spectra at $x = 0.05$ and 0.10 indexed to a single phase of ordered NASICON-type structure belonging to the monoclinic phase with a space group $P2_1/n$. This suggests that the partial aliovalent substitution ($\text{Cr}^{3+} + 1/2\text{Mg}^{2+} \rightarrow \text{Sn}^{4+}$) has completed in the framework of MZSCP with respective compositions. Meanwhile, the XRD patterns for the composition of $x \geq 0.15$ detected a small amount of Cr_2O_3 secondary phase impurity peaks at $24.5^\circ, 33.6^\circ$ and 36.2° . The intensity of these impurity peaks (Cr_2O_3) increases with the addition of more Cr^{3+} . Rietveld refinement determined the percentage of the Cr_2O_3 impurity to be 1.8%, 2.3%, and 11.2% for compositions (presumably Cr^{3+} doping levels) of 0.15, 0.20, and 0.30, respectively. This suggests that the allowable concentration of Cr^{3+} in the doped MZSCP material is limited. Table 2 summarizes the refinement reliability factors.

Table 2
Rietveld refinement reliability factors and percentage of secondary phase.

Composition x	0.05	0.10	0.15	0.20	0.30
Agreement factor					
Weighted R-profile, R_{wp}	5.68	4.93	5.38	4.91	4.55
R-profile, R_p	5.44	4.41	5.40	4.60	4.62
Good of fitness, χ^2	1.23	1.06	1.56	1.18	1.13
Other phase, %					
Cr_2O_3	0%	0%	1.8%	2.3%	11.2%

The structural parameters, unit cell volumes, average crystallite sizes, and densities derived from the Rietveld refinement are summarized in Table 3. The structural parameters obtained from the Rietveld refinement demonstrate that substitution significantly influences the lattice geometry, phase purity, and crystallization behavior of the MZSCP solid electrolytes. In the lower doping regime ($0.05 \leq x \leq 0.10$), the material exhibits high phase purity with a 0% secondary phase, characterized by a marginal contraction of the unit cell volume from $941.928 \text{ \AA}^3$ to $941.805 \text{ \AA}^3$. This contraction is attributed to the successful substitution of host ions by the smaller ionic radius of Cr^{3+} , alongside an optimal goodness of fitness ($\chi^2 = 1.06$ at $x = 0.10$) indicating highly reliable structural convergence. However, beyond the solubility

limit ($x \geq 0.15$), a solubility transition occurs where unreacted Cr^{3+} precipitates as a Cr_2O_3 secondary phase, which climbs substantially to 11.2% at $x = 0.30$. This phase segregation disrupts the host matrix, triggering a sharp expansion of the unit cell volume to $949.607 \text{ \AA}^3$ and an increase in theoretical density to 3.73 g/cm^3 , likely due to interstitial structural distortions or localized strain induced by the secondary phase. Furthermore, the fluctuations in crystallite size ($256.8 \text{ \AA}$ to $323.1 \text{ \AA}$) reveal that the introduction of Cr^{3+} alters the nucleation energy and grain growth kinetics during the sol-gel process, with the $x = 0.10$ composition marking the critical threshold before secondary phase formation impacts structural integrity [15].

Table 3
Unit cell parameters and the agreement factors obtained from Rietveld refinement of $\text{Mg}_{0.5+1/2x}(\text{ZrSn}_{1-x})\text{Cr}_x(\text{PO}_4)_3$ with different composition of x .

Composition x	a [Å]	b [Å]	c [Å]	V [Å ³]	Density [g/cm ³]	Crystallite size [Å]
0.05	12.2977	8.8110	8.6930	941.928	3.36	322.5
0.10	12.2971	8.8060	8.6929	941.805	3.36	256.8
0.15	12.2969	8.7950	8.6820	941.059	3.05	323.1
0.20	12.2935	8.7910	8.6910	943.651	3.59	311.3
0.30	12.2817	8.7910	8.6740	949.607	3.73	302.8

3.2 FTIR analysis

Figure 2 displays the FTIR spectra of MZSCP compounds with varying Cr^{3+} ion compositions of $0.05 \leq x \leq 0.30$ in the spectral range of 500 to 2000 cm^{-1} , providing chemical insights into the compounds. The orthophosphate PO_4 functional groups were identified by absorption bands between 1200 and 961 cm^{-1} for samples with Cr^{3+} ion substitution. The absorption band seems to shift to higher wavenumber as the composition of Cr^{3+} increases. These indicated that the substitution of Cr^{3+} successfully in MZSP. The distortion of the PO_4 tetrahedral bonds is attributed to the successful Cr^{3+} ion substitution, consistent with lattice parameter changes observed in the XRD analysis. While the transmission peak positions remained largely unaffected by the varying chromium ion compositions, the PO_4 stretching vibration peaks shifted slightly to higher wavenumbers with increasing Cr^{3+} substitution. This shift is attributed to the shortening of the P-O bond distance caused by the substitution of Cr^{3+} ions into the Zr^{4+} sites, inducing a distorted tetrahedral structure [16]. Additionally, the O-P-O vibration of the phosphate group was observed around 750 cm^{-1} across all samples [17]. These findings confirm the successful incorporation of Cr^{3+} ions and the presence of phosphate groups within the MZSCP compounds.

3.3 FESEM & EDX, Particle sizer analysis

The FESEM micrographs of the sintered MZSCP ceramics with varying Cr^{3+} compositions reveal notable changes in microstructure as the concentration of Cr^{3+} increases as shown in Fig. 3 (a) – (e). A clear trend is observed where the grain size becomes progressively larger with higher Cr^{3+} content. This suggests that Cr^{3+} ions act as effective grain growth inhibitors, restricting the excessive growth of MZSCP grains. The microstructure of the ceramics exhibits well-defined crystallization with minimal porosity and no significant voids. The grain sizes of MZSCP ceramics were measured to range between 56.06 nm and 117.40 nm, reflecting the influence of Cr^{3+} doping on grain refinement. The relative density of the ceramics, determined using the Archimedes method, increases from 3.24 g/cm³ to 3.98 g/cm³ as the Cr^{3+} concentration rises, achieving 98% of the theoretical density. This indicates the successful synthesis of high-density ceramics. The incorporation of Cr^{3+} ions with varying valences introduces lattice defects, which enhance the nucleation of grains and contribute to a reduction in grain size. However, a slight increase in grain size was observed in the composition with $x = 0.05$, implying that higher Cr^{3+} concentrations effectively suppress grain growth while minimizing void formation. Overall, the results highlight the role of Cr^{3+} in controlling the microstructure and enhancing the densification of MZSCP ceramics

3.4 Electrochemical Impedance analysis (EIS) analysis

The influence of Cr^{3+} substitution on the ionic transport properties of MZSCP was evaluated via electrochemical impedance spectroscopy (EIS) across the composition range of $0.05 \leq x \leq 0.30$. Measurements were systematically performed at elevated temperatures (300°C to 500°C) to probe the thermally activated ionic conduction regime. For magnesium-based NASICON systems, reliable impedance data are typically accessible only above 300°C [14]. Below this thermal threshold, the total resistance increases drastically because the rigid coordination environment within the NASICON framework severely restricts Mg^{2+} ion mobility. Consequently, low-temperature ionic transport becomes negligible, yielding noisy spectra dominated by electrode polarization that obscures the distinct bulk and grain-boundary contributions. Such behavior is characteristic of oxide-based ceramic electrolytes, which demand higher thermal activation energies to facilitate cation hopping. Accordingly, all EIS profiles in this study were acquired at temperatures 300°C. As illustrated in Fig. 4, the Nyquist plots for all compositions feature two overlapping, depressed semicircles at high-to-intermediate frequencies, followed by an inclined spike in the low-frequency region. Notably, the diameters of these semicircles contract progressively with increasing temperature, confirming a thermally activated conduction process. The two semicircles represent bulk resistance (R_b) at high frequencies and the grain boundaries resistance (R_{gb}) at middle frequencies and incline spikes in the low frequency ascribe to an ion diffusion due to the blocking electrode. As the temperature increase, the reduction of the semicircles diameter or resistance, result in an increase in ionic conductivity [18].

The bulk (σ_b), grain boundary (σ_{gb}) and total (σ_t) ionic conductivities of the MZSCP solid electrolytes were determined using the following relationships:

$$\frac{1}{\sigma_t} = \frac{1}{\sigma_b} + \frac{1}{\sigma_{gb}}$$

2

where $\sigma_b = \frac{t}{AR_b}$ and $\sigma_{gb} = \frac{t}{AR_{gb}}$. In this equation, t is sample thickness and A is sample area.

Table 4 summarizes this compiled conductivity values for all compositions evaluated at 500°C. As tabulated, the total ionic conductivity of the MZSCP system exhibits a non-monotonic, volcanic trend as a function of Cr^{3+} dopant concentration. The maximum total conductivity reaches $2.26 \times 10^{-4} \text{ S cm}^{-1}$ at $x = 0.10$, representing a significant enhancement over the $x = 0.05$ composition. Remarkably, this optimized value is nearly one order of magnitude higher than that reported for the pristine, undoped parent framework, $\text{Mg}_{0.5}\text{Zr}_x\text{Sn}_{1-x}(\text{PO}_4)_3$ [14].

This maximum at $x = 0.10$ is governed by a critical trade-off between interstitial charge carrier concentration and structural transport dynamics within the NASICON framework. The aliovalent substitution of Sn^{4+} by the lower-valent Cr^{3+} introduces additional interstitial Mg^{2+} ions into the conduction channels to maintain electrostatic charge neutrality. This effectively elevates the density of mobile charge carriers while preserving an open, unperturbed bottleneck pathway for efficient ion hopping. Conversely, further Cr^{3+} doping ($x \geq 0.15$) leads to a progressive decline in ionic conductivity. This degradation is strongly correlated with the precipitation of the secondary Cr_2O_3 phase verified via Rietveld refinement; these insulating impurities segregate preferentially along the grain boundaries, serving as highly resistive physical barriers that obstruct long-range three-dimensional (3D) cation migration. Nevertheless, the electrochemical performance of the optimized MZSCP ($x = 0.10$) solid electrolyte remains highly competitive with other state-of-the-art, high-temperature Mg^{2+} isostructural NASICON materials reported in literature, including $\text{Mg}_{0.5-x}(\text{Zr}_{1-x}\text{Nb}_x)_2(\text{PO}_4)_3$, $x = 0.15$ ($\sigma_{600^\circ \text{C}} = 6.9 \times 10^{-5} \text{ S cm}^{-1}$) [19], $\text{Mg}_{0.9}\text{Fe}_{0.4}\text{Zr}_{1.6}(\text{PO}_4)_3$ ($\sigma_{500^\circ \text{C}} = 7.18 \times 10^{-5} \text{ S cm}^{-1}$) [9], $\text{Mg}_{1.05}\text{Zn}_{0.4}\text{Al}_{0.3}\text{Zr}_{1.3}(\text{PO}_4)_3$ ($\sigma_{500^\circ \text{C}} = 5.82 \times 10^{-4} \text{ S cm}^{-1}$) [10], and $\text{Mg}_{0.5}\text{Ce}_x\text{Zr}_{2-x}(\text{PO}_4)_3$ ($\sigma_{500^\circ \text{C}} = 8.0 \times 10^{-5} \text{ S cm}^{-1}$) [12].

Table 4
Bulk, grain boundary and total conductivity values for $\text{Mg}_{0.5+1/2x}(\text{ZrSn}_{1-x})\text{Cr}_x(\text{PO}_4)_3$ with different composition of x at 500°C

Composition of x	Bulk conductivity, (S cm^{-1})	Grain boundary conductivity, (S cm^{-1})	Total conductivity, (S cm^{-1})
0.05	4.75×10^{-4}	5.32×10^{-5}	4.76×10^{-5}
0.10	6.53×10^{-4}	3.46×10^{-4}	2.26×10^{-4}
0.15	5.72×10^{-4}	7.75×10^{-5}	6.82×10^{-5}
0.20	6.53×10^{-4}	5.02×10^{-5}	5.81×10^{-5}
0.30	2.24×10^{-4}	2.87×10^{-6}	2.84×10^{-6}

Figure 5 illustrates the temperature dependence of the highest ionic conductivity compound, MZSCP ($x = 0.10$). The conductivity behaviour follows the classical Arrhenius relationship:

$$\sigma_t = A \exp\left(\frac{-E_a}{k_B T}\right)$$

3

Where σ_t represents the total DC conductivity, E_a is the activation energy, k_B is the Boltzmann constant, T is the absolute temperature, and A is the pre-exponential factor. The linear Arrhenius plot of $\log \sigma_t$ versus $1000/T$ demonstrates a highly linear relationship ($R^2 = 0.99$) over the measured temperature range (300°C to 500°C), confirming that a single, thermally activated hopping mechanism governs the long-range migration of magnesium ions within the framework. From the negative slope of this fitted regression line, the activation energy (E_a) was calculated to be 0.55 ± 0.03 eV. This relatively low energy barrier for a divalent cation conductor indicates that the aliovalent substitution of Sn^{4+} by Cr^{3+} successfully optimized the interstitial configuration and the bottlenecks within the NASICON structural channels.

3.5 A.C conductivity

The AC conductivity behavior of the MZSCP ($x = 0.10$) sample was analyzed as a function of frequency and temperature (Fig. 6) using Jonscher's universal power law, defined as:

$$\sigma_{ac}(\omega) = \sigma_{dc} + A\omega^s$$

where σ_{dc} is the frequency-independent DC conductivity, A is a temperature-dependent constant, and s is the frequency exponent, which provides insight into the conduction mechanism and the nature of the

interaction between mobile ions and the surrounding lattice [20]. Table 5 shows the variation of the frequency exponent s_1 with temperature for MZSCP ($x = 0.10$) composition. The values of s_1 decrease gradually from 0.663 at 325°C to a minimum of 0.482 at 475°C, before slightly increasing again to 0.492 at 500°C. This non-monotonic trend reflects changes in the ion dynamics and lattice interaction as the thermal energy increases [21]. The decrease in s_1 with increasing temperature (up to 475°C) suggests a correlated barrier hopping (CBH) conduction mechanism, where ions hop between localized states over potential barriers that are thermally modulated. In this model, the decrease in s with temperature indicates that the hopping becomes easier due to thermal agitation, which reduces the energy barriers between neighboring sites. At higher temperatures (beyond 475°C), the slight increase in s_1 may be associated with saturation effects or changes in the relaxation dynamics due to increased ion-vacancy interactions or possible microstructural changes such as grain boundary softening [22]. It may also indicate a deviation from purely thermally activated hopping to a more mixed conduction regime or even the onset of long-range ion transport [23]. Moreover, the relaxation behavior observed in this system wherein ions may return to their original positions within short time periods contributes to the sublinear frequency dependence ($s < 1$), consistent with dispersive transport mechanisms dominated by localized hopping. In summary, the temperature-dependent variation of the frequency exponent s_1 supports the CBH model as the dominant conduction mechanism in the MZSCP ($x = 0.10$) sample. The findings complement the EIS and activation energy results, affirming that Cr^{3+} substitution not only enhances ionic conductivity but also influences the dynamic interaction between mobile Mg^{2+} ions and the crystal lattice [24].

Table 5
variation of the frequency
exponent s_1 for the
 $\text{Mg}_{0.55}(\text{ZrSn}_{0.90})\text{Cr}_{0.10}(\text{PO}_4)_3$
for temperature from 325°C
to 500 °C.

Temperature (°C)	s_1
325	0.663
350	0.636
375	0.603
400	0.569
425	0.569
450	0.593
475	0.482
500	0.492

3.6 Linear sweep voltammetry

Linear sweep voltammetry (LSV) was employed to determine the electrochemical stability windows of the solid electrolytes. The sharp onset of anodic current in the high-voltage region signifies the onset of oxidative electrolyte decomposition, with this critical potential establishing the upper operating limit of the material's electrochemical stability. LSV measurements were conducted for all compositions across a potential window from 0.0 V to 8.0 V at a scan rate of 5 mV. At low applied voltages, a negligible and steady leakage current was recorded. Beyond a critical threshold, a sharp exponential rise in current occurred, denoting electrolyte oxidation. The precise decomposition voltage was determined by the intersection of the linear extrapolation lines from the low-current baseline region and the high-current decomposition region.

As shown in Fig. 7 (a), the un-doped MZSP baseline matrix exhibits an electrochemical stability window up to 4.16 V. In comparison, the optimized MZSCP ($x = 0.10$) sample evaluated between asymmetric blocking electrodes and detailed further via the magnesium-metal symmetric configuration shown in Fig. 7 (b) reaches a significantly higher critical oxidation onset of 4.81 V. This represents an impressive 15.6% widening of the electrochemical stability window alongside the previously noted enhancements in ionic conductivity. This simultaneous improvement in both transport and electrochemical stability is primarily attributed to the contraction of the unit cell volume upon Cr^{3+} substitution. The lattice shrinkage effectively yields a denser, robust, and structurally stable NASICON framework that resists early oxidative breakdown.

The wide potential stability of the optimized than MZSCP ($x = 0.10$) electrolyte compares favorably against other previously reported inorganic magnesium solid electrolytes. For context, the decomposition voltage of a recently developed, $\text{Mg}_{1+x-2y}(\text{Zr}_{1-y}\text{Nby})_4\text{P}_6\text{O}_{24} + x\text{Zr}_2(\text{PO}_4)_2$ system was limited to approximately 2.2 V (vs. Mg) [25], while a complex hydride-based electrolyte, $\text{Mg}(\text{BH}_4)(\text{NH}_2)$ demonstrated a stability window of around 3.0 V (vs. Mg) [26]. Furthermore, standard MZP exhibits a breakdown potential of approximately 2.5 V [17], and while $\text{Mg}_{0.5}\text{Si}_2(\text{PO}_4)_3$ caps out near 3.2 V [27]. Consequently, the superior oxidative stability (4.81 V) achieved by MZSCP ($x = 0.10$) ceramic electrolyte indicates that it can be safely and reliably paired with high-voltage cathode materials in next-generation, high-energy-density solid-state magnesium batteries.

4. Conclusions

In summary, a series of novel $\text{Mg}_{0.5+1/2x}(\text{ZrSn}_{1-x})\text{Cr}_x(\text{PO}_4)_3$ (MZSCP) NASICON-type solid-state electrolytes ($0.05 \geq x \geq 0.30$) was successfully synthesized via a water-based citrate sol-gel method. Structural analysis verified that the aliovalent substitution of Sn^{4+} by Cr^{3+} successfully preserves the monoclinic framework lattice ($P2_1/n$ space group), with minor Cr_2O_3 secondary phase segregation occurring only beyond the solubility limit ($x \geq 0.15$). Microstructural investigations revealed uniform particle distributions, with grain sizes exhibiting progressive growth as a function of chromium concentration. Electrochemical evaluations demonstrated that Cr^{3+} tuning significantly drastically lowers the activation energy barrier ($E_a = 0.55 \pm 0.03$ eV), yielding an optimized total ionic conductivity of $2.26 \times$

$10^{-4} \text{ S cm}^{-1}$ nearly an order of magnitude improvement over the un-doped MZSP baseline matrix ($2.47 \times 10^{-5} \text{ S cm}^{-1}$). Furthermore, linear sweep voltammetry measurements expanded electrochemical stability window extending up to 4.81 V for the optimized $x = 0.10$ composition. This simultaneous enhancement in structural stability, charge carrier transport dynamics, and anodic oxidation resistance demonstrates that Cr^{3+} substitution is a highly effective strategy for engineering high-performance NASICON frameworks, positioning the optimized MZSCP electrolyte as a highly promising candidate for next-generation, high-energy-density, and inherently safe solid-state magnesium-ion batteries.

Declarations

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Author Contribution

All authors contributed to the study conception and design. S.B.R. S Adnan: Data curation, Writing – original draft, preparation. Mazni Mustaffa: Data curation. F.M Salleh & Mazni Mustaffa : Data curation and review English language and All authors reviewed the manuscript

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Figures

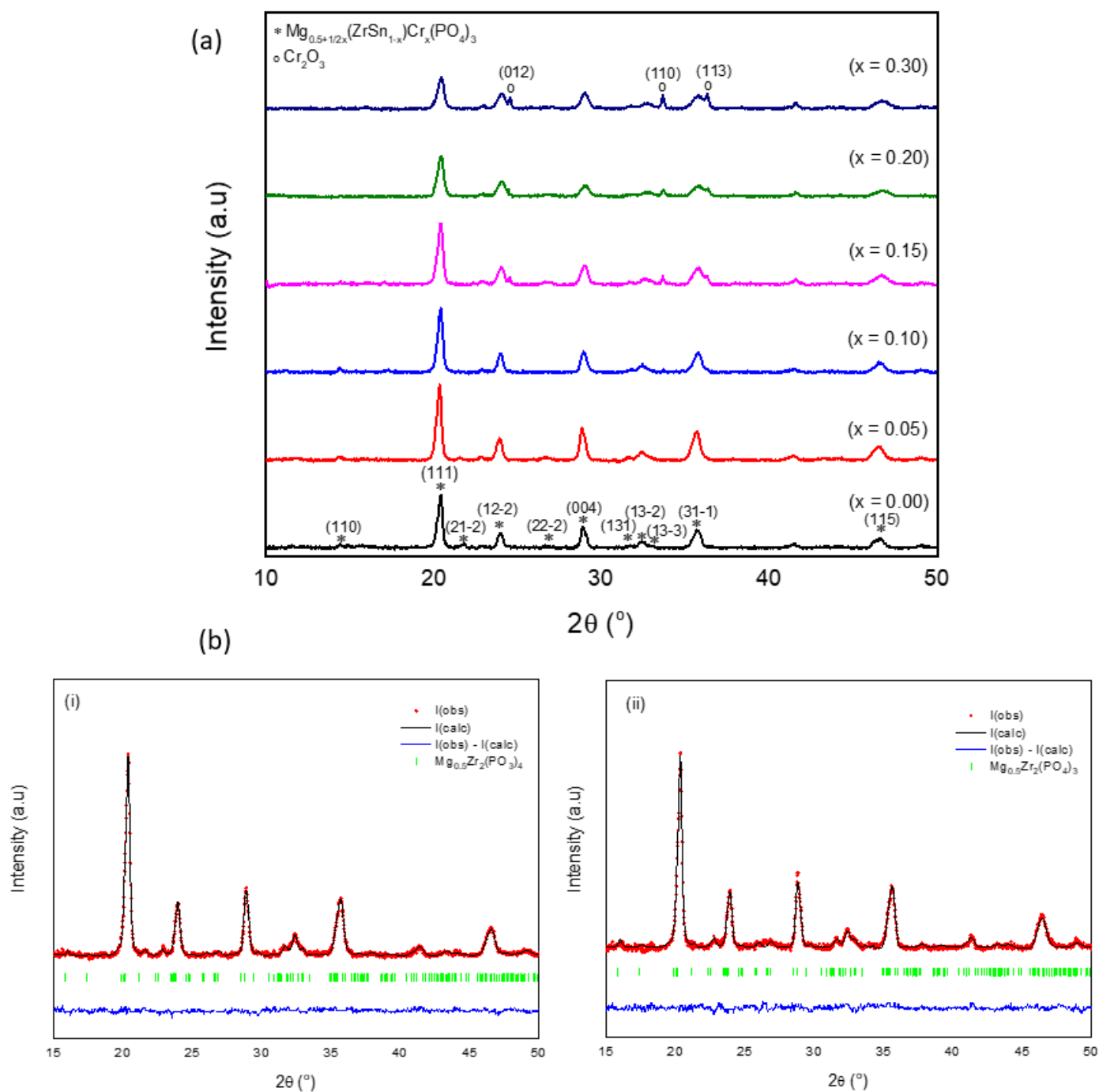


Figure 1

(a) The XRD spectrum for $\text{Mg}_{0.5+1/2x}(\text{ZrSn}_{1-x})\text{Cr}_x(\text{PO}_4)_3$ with different composition of x (b) Rietveld refinement plot for $\text{Mg}_{0.5+1/2x}(\text{ZrSn}_{1-x})\text{Cr}_x(\text{PO}_4)_3$ ((i) $x = 0.05$ and (ii) 0.10).

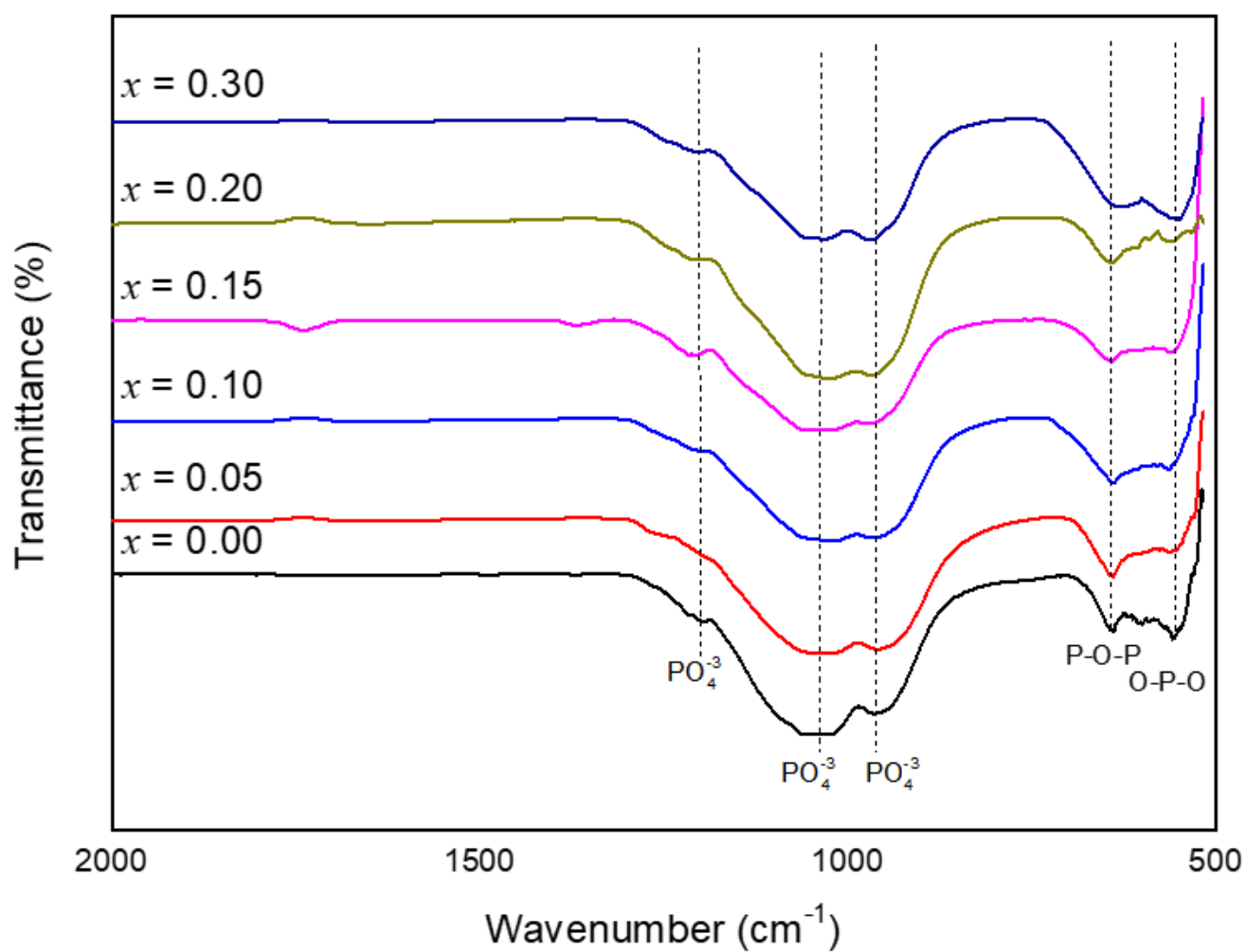


Figure 2

The FTIR spectrum of $\text{Mg}_{0.5+1/2x}(\text{ZrSn}_{1-x})\text{Cr}_x(\text{PO}_4)_3$ with different composition of x sintered at temperature of 800 °C in the spectral region from 500 cm^{-1} to 2000 cm^{-1} .

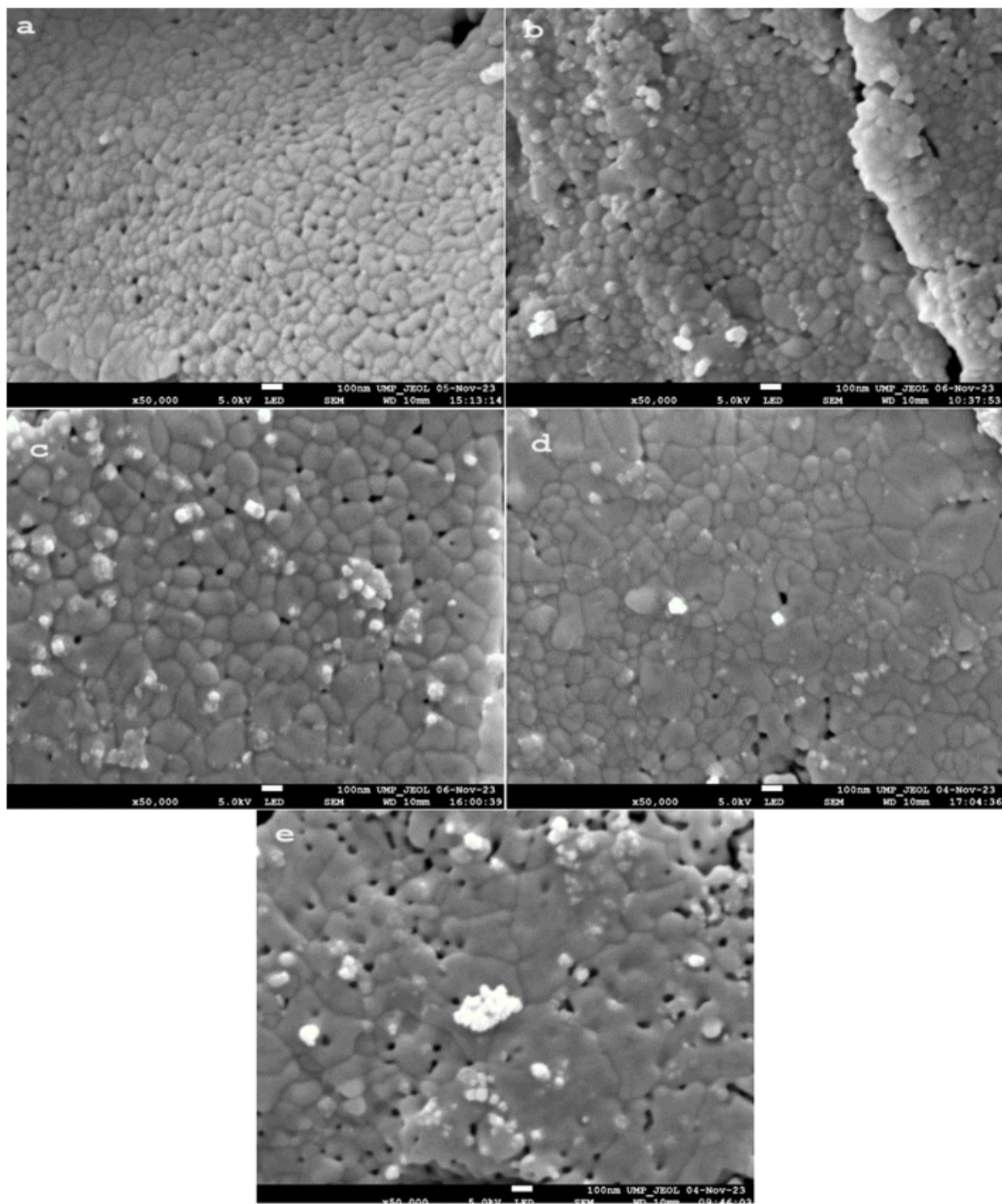


Figure 3

FESEM images for $\text{Mg}_{0.5+1/2x}(\text{ZrSn}_{1-x})\text{Cr}_x(\text{PO}_4)_3$ with different composition of x (a) 0.05, (b) 0.10, (c) 0.15, (d) 0.20 and (e) 0.30

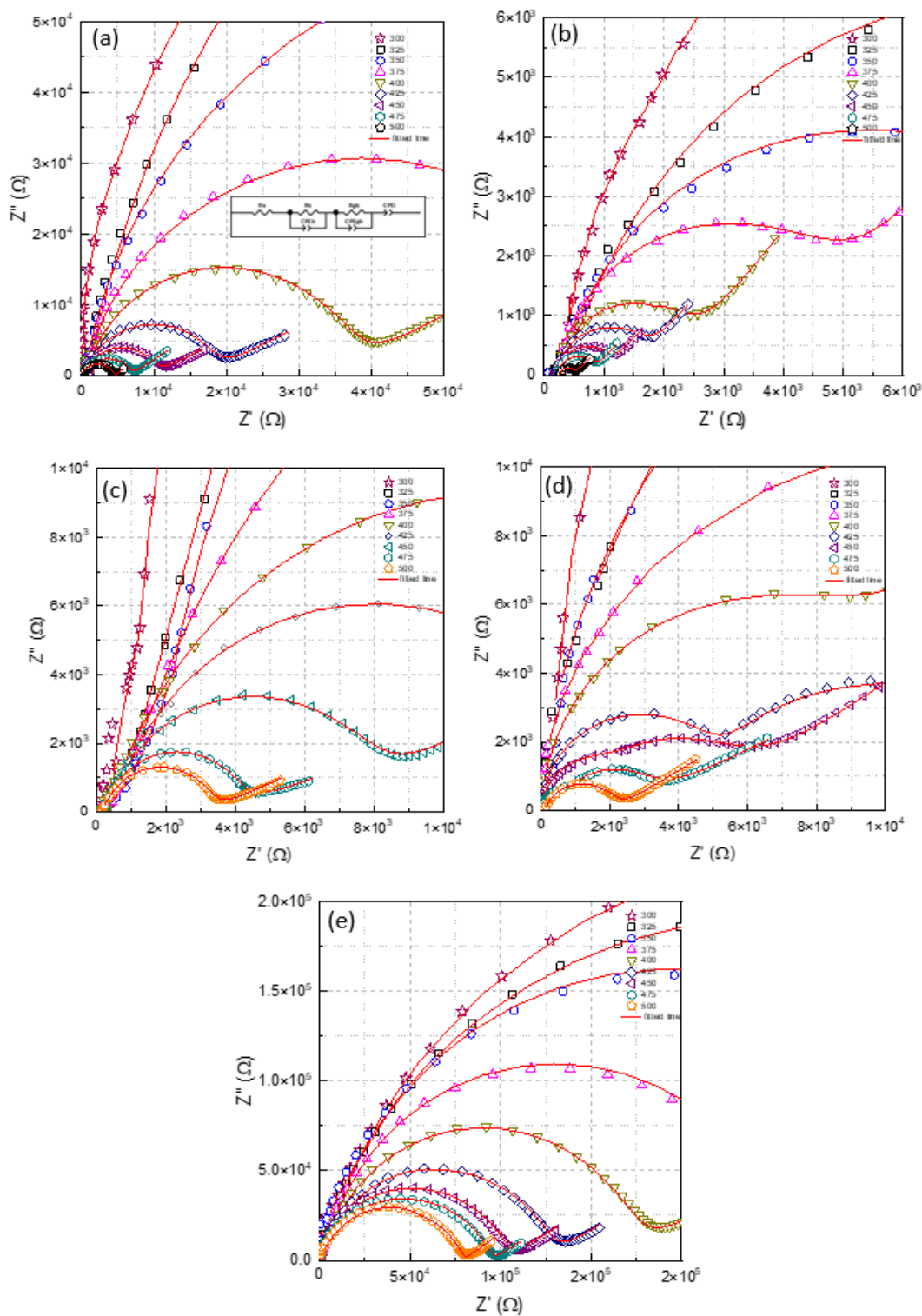


Figure 4

Complex impedance plot of $\text{Mg}_{0.5+1/2x}(\text{ZrSn}_{1-x})\text{Cr}_x(\text{PO}_4)_3$ with x (a) 0.05, (b) 0.10, (c) 0.15, (d) 0.20 and (e) 0.30 sample at high temperature.

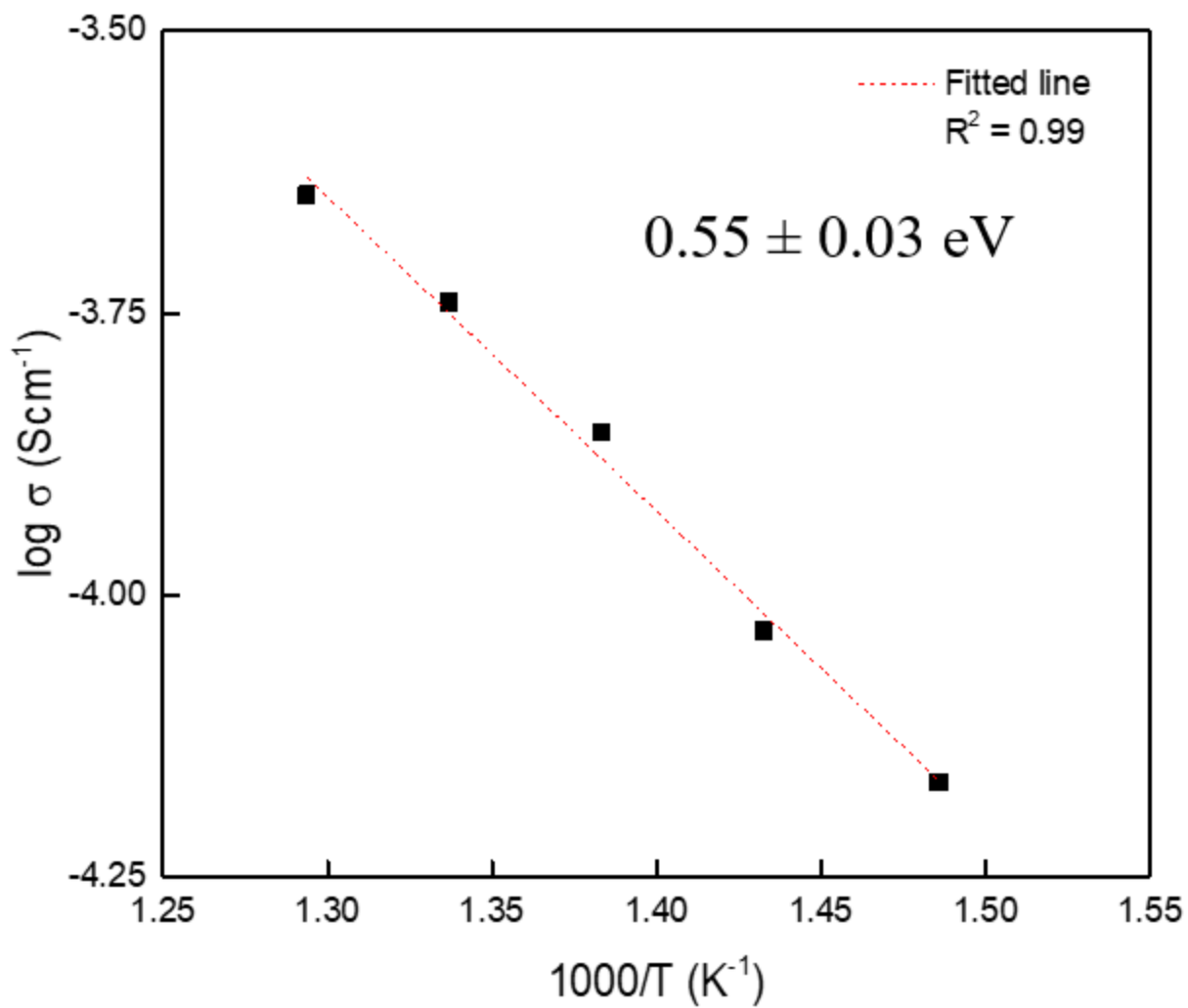


Figure 5

Temperature dependence of conductivity of $\text{Mg}_{0.5+1/2x}(\text{ZrSn}_{1-x})\text{Cr}_x(\text{PO}_4)_3$ with $x = 0.10$

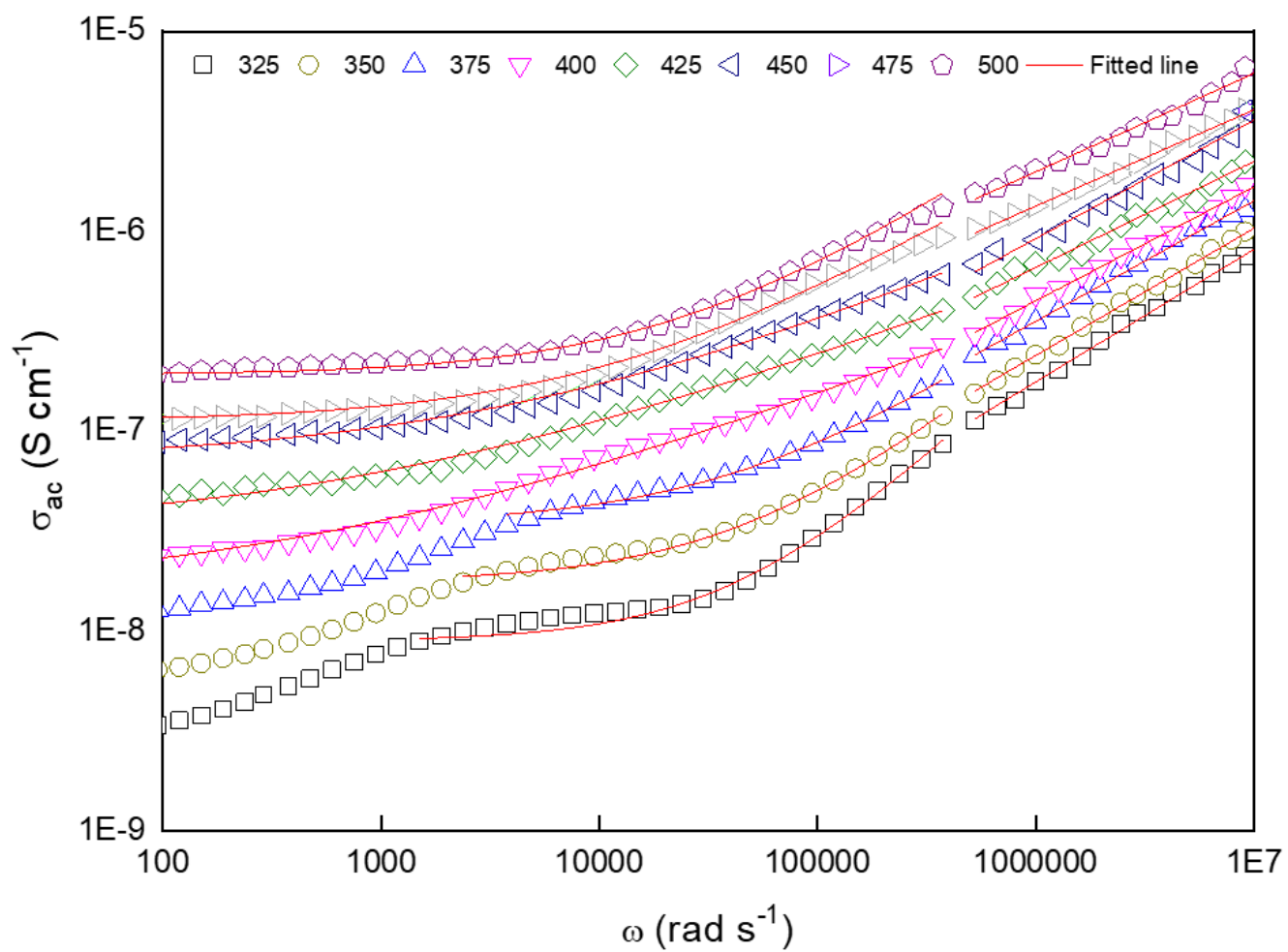


Figure 6

Log σ_{ac} vs. frequency at different temperatures for $\text{Mg}_{0.55}(\text{ZrSn}_{0.90})\text{Cr}_{0.10}(\text{PO}_4)_3$ compound.

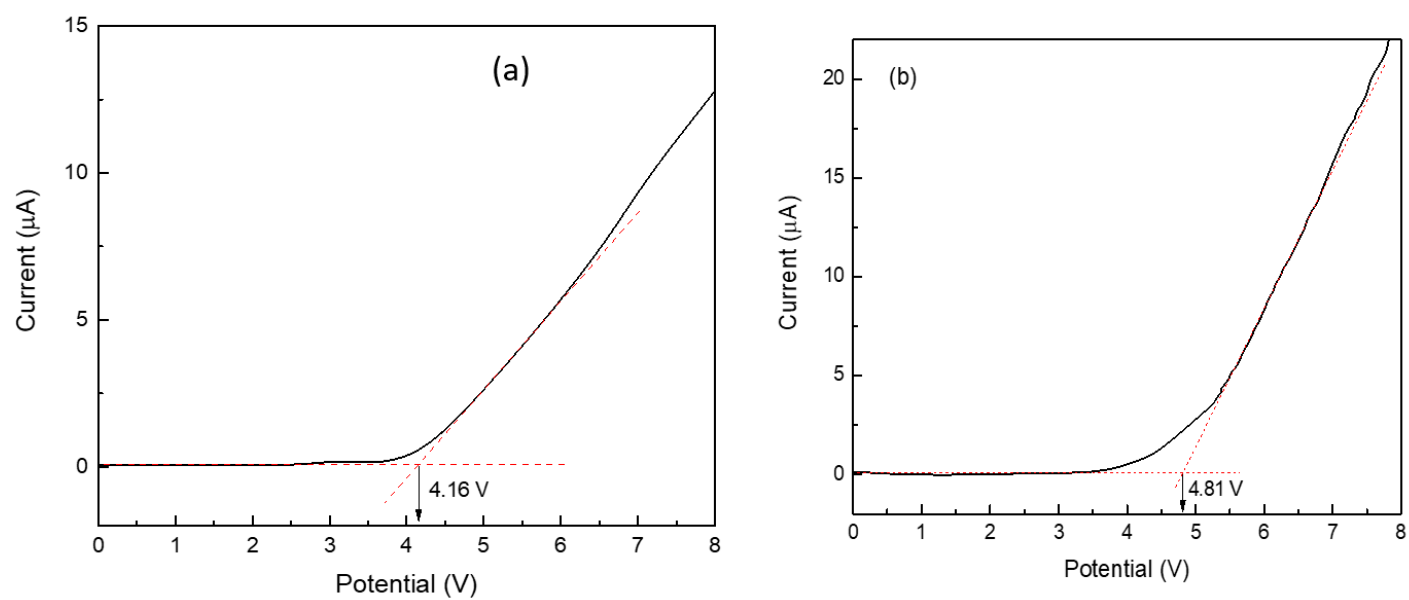


Figure 7

Linear Sweep Voltammetry of (a) $\text{Mg}_{0.5}\text{Zr}_x\text{Sn}_{1-x}(\text{PO}_4)_3$ (b) $\text{Mg}_{0.55}(\text{ZrSn}_{0.90})\text{Cr}_{0.10}(\text{PO}_4)_3$ ceramic electrolytes.