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Preparation and Characterisation of LAITP/PVDF Composite Solid Electrolyte for Lithium Battery

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Highlights

- It is doped indium to the lithium aluminum titanium phosphate (LATP) solid electrolyte.
- The structure of LATP doped indium (LAITP) is analysed.
- PVDF and LAITP electrolytes are combined to form a composite.
- LAITP/PVDF solid composite electrolyte is analysed with regard to structure and impedance.

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Keywords

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Abstract

This study investigates the potential of LAITP/PVDF composite electrolytes to improve the safety and performance of lithium-ion batteries. The study focuses on the synthesis and characterization of composite solid electrolyte consisting of indium-doped lithium aluminum titanium phosphate (LAITP) ceramic material and $LiClO_4$ salt with polyvinylidene fluoride (PVDF) as the polymer matrix. The LAITP ceramic, synthesized via solid-state synthesis, demonstrates high ionic conductivity, thermal stability, and mechanical robustness. PVDF provides electrochemical and thermal stability to the composite. The composite electrolytes were prepared by integrating LAITP into the PVDF matrix through the solution casting method. Various characterization methods were employed to assess the properties of the resulting composite. X-ray diffraction (XRD) was used to examine the crystal structure, while scanning electron microscopy (SEM) provided insights into the morphological features. Ionic conductivity measurements were conducted using electrochemical impedance spectroscopy (EIS), enabling an evaluation of the composite's electrochemical performance. The LAITP-reinforced PVDF-based composite solid electrolyte exhibited an ionic conductivity of 1.7×10^{-5} S cm^{-1} at room temperature.

1. INTRODUCTION

The increasing demand for portable electronic devices has driven rapid advancements in rechargeable lithium-ion batteries, now essential for powering a wide range of consumer electronics. Although widely utilized, conventional lithium-ion batteries present significant safety concerns primarily due to their use of liquid electrolytes, which are susceptible to leakage, flammability, and thermal runaway factors that can result in fire or explosion during operation [1-3]. Although thermal management solutions can mitigate some of these risks [3, 4], all-solid-state lithium batteries (SSBs) are emerging as a fundamentally safer alternative. Unlike conventional batteries, SSBs use solid electrolytes, which are non-flammable, structurally stable, and effectively resist lithium dendrite formation that can cause short circuits [5-9]. These properties position SSBs as promising candidates for safer, more reliable energy storage. However, challenges such as improving ionic conductivity, increasing stability, and minimizing interfacial resistance between electrolyte and electrode must be addressed for the practical deployment of SSBs [10]. Researchers have made significant strides in improving the performance of SSBs since the initial discovery of solid electrolyte materials.

Lithium-ion batteries utilize electrolytes that can be broadly classified into three types based on their composition: liquid, inorganic solid, and polymer-based electrolytes. While liquid electrolytes are widely

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*Corresponding author, e-mail: oksuzogluf@gmail.com used, they carry substantial safety concerns due to thermal runaway risks [11, 12]. In contrast, inorganic solid electrolytes comprising sulfides, oxides, and halides offer superior ionic conductivity and safety but often require challenging processing conditions and suffer from high interface impedance [13]. Among these, polymer electrolytes stand out due to their ability to combine multiple advantages, such as high ionic conductivity, robust mechanical properties to suppress dendrite formation, and stable performance under chemical and thermal stresses [14-17]. Researchers have investigated a variety of polymers such as, including PEO (poly(ethylene oxide) [18, 19], PVDF (poly(vinylidene fluoride) [20, 21], PVDF-HFP (poly(vinylidene fluoride-hexafluoropropylene) [22-24], PAN (polyacrylonitrile) [25, 26] and PMMA (poly(methyl methacrylate) [27] as matrices for these electrolytes. These polymer matrices are often paired with lithium salts such as lithium hexafluorophosphate ($LiPF_6$), lithium bis(fluorosulfonyl)imide (LiFSI), and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) to improve ion mobility and optimize the electrochemical properties of the battery. The ongoing development of these materials highlights their critical role in advancing the performance and safety of solid-state batteries [28, 29].

While individual polymer electrolytes such as PVDF or ceramic electrolytes such as garnet-type $Li_7La_3Zr_2O_{12}$ (LLZO) [30-33] and NASICON-type $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ (LATP) [20, 34-36] offer unique advantages, none of them alone meets all the requirements for commercial viability. Therefore, the composite structure obtained by using ceramic and polymer electrolyte together can provide advantages that can meet expectations. This research focuses on developing a composite solid electrolyte tailored for lithium solid-state batteries by utilizing a PVDF polymer matrix integrated with NASICON-type indium-doped $Li_{1.3}Al_{0.3}In_xTi_{1.7-x}(PO_4)_3$ (LAITP) ceramic filler. The PVDF matrix was selected due to its exceptional thermal and electrochemical stability, as well as its mechanical resilience, which is further enhanced by its electron-withdrawing fluorine groups. These properties make PVDF highly effective at promoting the ionization of lithium salts, thereby facilitating ion transport [37, 38].The incorporation of active ceramic fillers such as LATP into the PVDF matrix can significantly improve the composite's ionic conductivity, thermal stability, and mechanical properties. LATP itself is characterized by high ionic conductivity but suffers from a brittle nature and poor interfacial compatibility [39]. By doping titanium sites in LATP with indium, forming LAITP, it is possible to increase the lattice volume due to the larger ionic radius of indium [40]. This modification is expected to further enhance its ionic conductivity, optimizing the performance of the electrolyte.In this composite system, lithium perchlorate ($LiClO_4$) is chosen as the lithium salt owing to its high ion mobility, superior dissociation constant, strong hydrolytic and electrochemical stability, and cost-effectiveness [41, 42]. Unlike other commonly used lithium salts such as $LiPF_6$ and $LiBF_4$, $LiClO_4$ is resistant to hydrolysis and does not generate HF, which can corrode battery components and degrade performance [43]. Moreover, by avoiding the potential release of toxic fluorinated byproducts during thermal runaway events, the use of $LiClO_4$ addresses critical safety concerns associated with fluorinated salts [44, 45]. As a result, the flexible solid electrolyte produced from the combination of LAITP ceramic filler, PVDF matrix and $LiClO_4$ lithium salt can provide high performance in next-generation lithium batteries by combining the above-mentioned advantages of all the materials constituting this structure.

In the literature, LATP/PVDF composite electrolytes have been mainly investigated using lithium salts such as LiTFSI [21] and $LiPF_6$ [20], and to the best of our knowledge, the study involving $LiClO_4$ [39] salt is limited to one. Yaddanapudi, A. [39] investigated LATP-based composite electrolyte membranes fabricated using a casting method, wherein $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ (LATP) was incorporated into a lithiated polymer matrix consisting of polyvinylidene fluoride (PVDF) and lithium perchlorate ($LiClO_4$). The study revealed that the curing temperature significantly influences the ionic conductivity of the composite membranes, with excessively high casting temperatures leading to the thermal degradation of PVDF. Furthermore, the incorporation of an optimal LATP content was shown to enhance both the ionic conductivity and mechanical strength of the membrane, while preserving its flexibility. Lancel et al. [46] developed a novel hybrid membrane that integrates an ionically conducting inorganic phase, $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ (LATP), with a poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF−HFP) polymer matrix to achieve both efficient Li^+ ion transport and mechanical integrity, including water resistance. The membrane architecture features a three-dimensional interconnected network of crystalline LATP fibers, fabricated via a combination of sol–gel synthesis and electrospinning, followed by thermal treatment. Subsequent impregnation with PVDF−HFP yielded hybrid membranes with varying polymer volumetric fractions. These membranes demonstrated watertight properties and exhibited Li^+ ion conductivities in the range of 10^{-5} to 10^{-4} mS/cm. In particular, the combination of indium-doped LATP (LAITP) and PVDF polymer matrix with lithium salt $LiClO_4$ has never been reported before. In the present study, we introduce this novel composite system for the first time by integrating LAITP as a ceramic phase into PVDF matrix and using $LiClO_4$ as lithium source. This unique combination aims to investigate the synergistic effects of indium doping and $LiClO_4$ usage on the structural and electrochemical performance of the composite electrolyte.

2. MATERIAL METHOD

2.1. LAITP Solid Electrolyte Synthesis

The LAITP solid electrolyte, with the composition $Li_{1.3}Al_{0.3}In_xTi_{1.7-x}(PO_4)_3$ with x = 0.1, was synthesized via a solid-state reaction method as reported in previous work [47]. The synthesis procedure, illustrated schematically in Figure 1, began with precise stoichiometric measurements of Li_2CO_3, Al_2O_3, TiO_2, In_2O_3, and $NH_4H_2(PO_4)_3$. These precursor materials were thoroughly mixed in a ball mill at 250 rpm for 2 hours to ensure uniform distribution. The resulting homogeneous mixture underwent an initial calcination step at 450 °C for 2 hours, which facilitated the decomposition of ammonium phosphate and partial reaction between the components. Subsequently, the material was subjected to a second calcination at 900 °C for 5 hours to promote the formation of the desired NASICON-type phase. After completing the calcination process, the calcined powders were reground in the ball mill for an additional 5 hours to refine the particle size and ensure consistency. The fine powders were then compressed into pellet forms using a uniaxial press. These pellets were sintered in an alumina crucible at 900 °C for 5 hours, resulting in the final LAITP solid electrolyte with improved density and structural integrity. This method ensured the production of a high-quality ceramic electrolyte suitable for advanced energy storage applications.

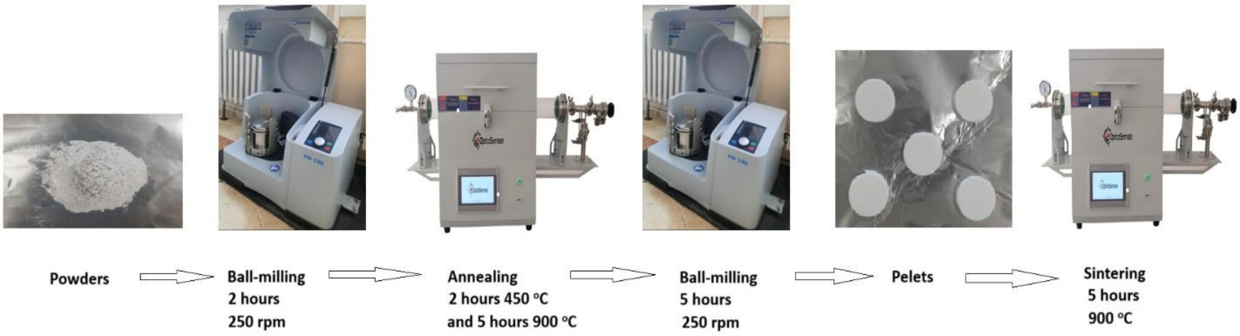

Figure 1. *Procedure for solid-state synthesis preparation*

2.2. Production of Composite Solid Electrolytes

Composite solid electrolytes were fabricated using the solution casting method, with polyvinylidene fluoride (PVDF) serving as the polymer matrix and lithium perchlorate ($LiClO_4$) as the lithium salt. Initially, PVDF and lithium salt were dissolved in N-Methyl-2-pyrrolidone (NMP) in a 5:95 molar ratio and stirred for 4 hours to ensure complete dissolution. Following this, lithium salt was introduced to the polymer solution at a vinylidene fluoride polymer (VDF)/$LiClO_4$ weight ratio of 20:1. The resulting mixture was heated and stirred at 80 °C for 5 hours to achieve a homogeneous solution. To prepare the composite material, 20 wt% LAITP powder was added to the polymer/lithium salt mixture, and the solution was stirred thoroughly to ensure uniform dispersion of the ceramic filler. The slurry was then poured into a Teflon mould, smoothed to obtain a uniform thickness and placed in an oven at 80 °C to evaporate the solvent. After approximately 24 hours in ambient conditions, the solvent was completely removed, forming a dense, solid composite electrolyte. The final appearance of the prepared LAITP/PVDF composite electrolyte is depicted in Figure 2.

The composite material was subjected to a series of characterization techniques to assess its structural and electrochemical attributes. X-ray diffraction (XRD) was conducted to identify the crystalline phases present and to examine the material's structural integrity. The morphological features and the dispersion of ceramic components within the polymer matrix were examined through scanning electron microscopy (SEM), offering insight into microstructural uniformity and interfacial interactions. Electrochemical impedance spectroscopy (EIS) was utilized to investigate the ionic transport properties of the composite, yielding data relevant to its applicability in solid-state battery systems. Together, these methods facilitated an in-depth evaluation of both the structural configuration and electrochemical behavior of the prepared composite electrolyte.

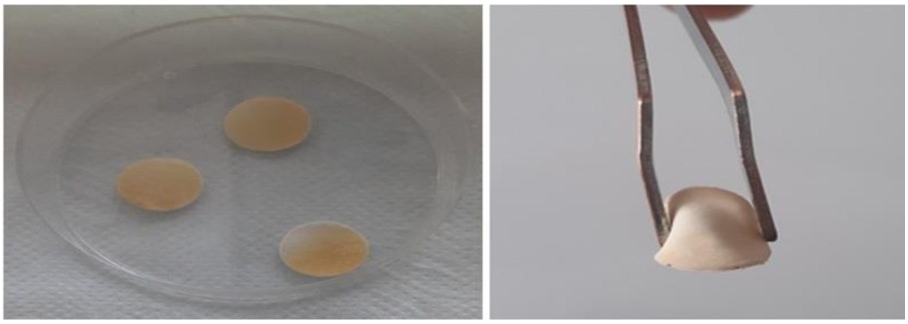

Figure 2. *Image of LAITP/PVDF composite solid electrolyte*

2.3. Material Characterisation and Impedance Analysis

X-ray diffraction (XRD) analysis of LAITP and LAITP/PVDF materials was carried out using a Bruker D8 X-ray diffractometer with a CuKα radiation source, within a 2θ range of 10° to 60°. LATP electrolyte was synthesized in a previous study, its structural properties were investigated and presented here for comparison [48]. Figure 3 shows the XRD patterns of LATP, In-doped LATP (LAITP) electrolytes and LAITP/PVDF based composite electrolyte. Rietveld refinement was carried out using the MAUD software to analyze the crystal structure, and the crystallite size (D) of the synthesized samples was determined through the Scherrer equation Equation (1)

$$D_{\text{crystallite}}=\frac{K\lambda}{\beta\cos\theta} \tag{1}$$

In the given equation, the Scherrer constant (K) assumes a value of 0.94, while λ (1.5406 Å) denotes the wavelength of the incident X-ray radiation. The term β represents the full width at half maximum (FWHM) of the observed diffraction peak. Furthermore, the dislocation density (δ), quantified in units of 10^{-3} lines/nm^2, was derived using the Williamson-Smallman relation, offering a measure of the crystalline defect concentration within the material

$$\delta = \frac{1}{D^2} \ . \tag{2}$$

Micro strain (ε) for sample,

$$\varepsilon = \frac{\beta}{4\tan\theta} \tag{3}$$

is calculated using the relation.

The microstructure of the samples was examined using a ZEISS EVO LS10 scanning electron microscope (SEM). The ionic conductivity of the composite solid electrolyte comprising LAITP and PVDF was evaluated through AC impedance spectroscopy. Symmetrical cells were assembled, and the measurements were conducted at ambient temperature using a Gamry PCI4/750 Potentiostat. The impedance characteristics of the composite electrolyte were assessed using an alternating current (AC) signal of 100 mV amplitude, with frequency variations from 0.1 Hz to 1 MHz. The total ionic conductivity (σ) was obtained using the equation given below,

$$\sigma=\frac{d}{R\,S} \tag{4}$$

here, d is the thickness of the electrolyte layer, R represents the bulk resistance extracted from the impedance data, and S is the surface area of the electrolyte.

3. THE RESEARCH FINDINGS AND DISCUSSION

In this study, we explored the effects of incorporating In-doped LATP (LAITP) ceramic electrolyte within a PVDF polymer matrix on the resulting electrolyte's structural and electrical properties. Our characterization techniques, including XRD, SEM, and EIS, have yielded critical insights into the material composition, crystallinity, and ionic conductivity of the composite solid electrolyte.

$LiTi_2(PO_4)_3$ (LTP) peaks identified in Figure 3 correspond to the LATP sample sintered at 900 °C as reported in our previous research [48]. This phase identification is consistent with NASICON-type LTP, which is indexed to the rhombohedral phase with space group $R\overline{3}c$ (COD ID: 7222155). Table 1 shows the crystal structure analysis results of the LAITP sample. From Figure 3 and Table 1, it can be seen that the LAITP sample contains two impurity phases, 0.85 wt% $LiTiPO_5$ and 0.6 wt% $AlPO_4$. It has been reported that $AlPO_4$ secondary phase formation may occur due to solubility differences in aluminium and phosphate sources [49, 50]. The XRD results also provided insights into the crystallinity of the PVDF matrix. Pristine PVDF showed high crystallinity, with strong γ-phase peaks at 18.5°, 20.4°, and 26.6°, which are associated with its robust mechanical and thermal properties [51]. However, the addition of LAITP disrupted the crystalline structure of PVDF, significantly reducing its crystallinity. This reduction is likely due to LAITP acting as a solid plasticizer, which introduces amorphous regions within the PVDF matrix. These increased amorphous sites are advantageous for ion transport, as they reduce the ordered structure of PVDF and enhance ionic mobility. This improved ionic conductivity in the LAITP/PVDF composite suggests that the integration of LAITP in the PVDF matrix not only affects crystallinity but also optimizes the material for potential solid-state electrolyte applications [52].

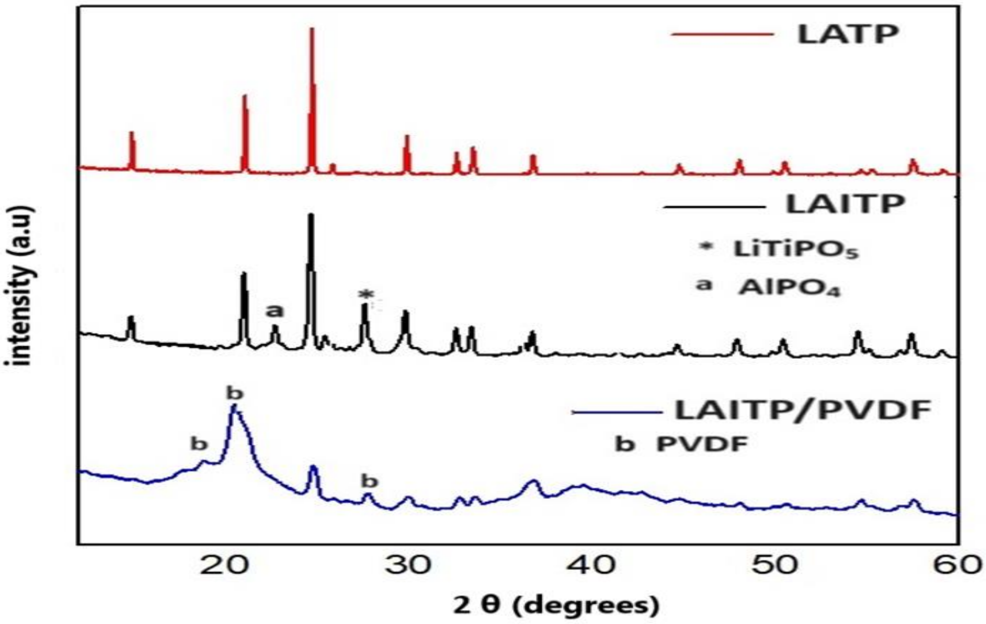

Figure 3. *XRD diffraction pattern of LAITP/PVDF solid electrolyte*

Table 1. *Crystal Structure Characterization Findings of the LAITP Sample*

Sample	**Crystal**	**α**	**β**	**γ**	**a (Å)**	**b (Å)**	**c (Å)**	**Geometry**	**%(Weight)**
LAITP	$LiTi(PO_4)_3$	90	90	120	8.454	8.454	20.906	Rhombohedral ($R\bar{3}c$)	98.55 ± 0.0
	$AlPO_4$	90	90	90	18.521	32.124	8.400	Monoclinic (Cm:b1)	0.60 ± 0.41
	$LiTiPO_5$	90	90	90	7.529	7.529	7.230	Orthorhombic (P222)	0.85 ± 0.24

Table 2. *The values of structural parameters for the LAITP/PVDF sample*

2θ (degrees)	20.55	24.88	27.72	30.04	32.8	33.68	36.87	54.71	57.33
FWHM (rad)x10^{-3}	1.49	0.5	0.48	1	0.66	1.26	1.15	0.87	0.62
D (nm)	5.56	19.94	17.30	8.29	12.58	6.58	7.24	9.53	13.38
δx10^3 $(1/nm)^2$	32.34	2.51	3.34	14.55	6.31	23.09	19.23	11.01	5.58
ε (x10^{-3})	67.52	27.57	29.30	67.08	48.56	95.34	95.83	112.52	84.73

Key structural parameters such as D crystallite size, δ dislocation density, and ε microstrain for the LAITP/PVDF composite solid electrolyte are outlined in Table 2. These parameters are essential for assessing the structural characteristics and mechanical durability of the material, which are critical for its functionality in advanced energy storage systems.

The crystallite size directly impacts the mechanical and electrochemical properties of solid electrolytes. For the LAITP/PVDF composite, the average crystallite size was determined to be 11.15 nm. This nanoscale size is advantageous, as it increases the material's surface area, potentially enhancing ionic conductivity. Dislocation density, a measure of the dislocations per unit volume within the crystal lattice, serves as a key indicator of structural quality. A lower dislocation density signifies fewer lattice defects and better crystal quality. In the case of the LAITP/PVDF sample, the dislocation density was measured at 13.10 nm, indicating a satisfactory crystal structure. Microstrain, which represents the distribution of internal strain within the crystallites, arises from lattice distortions and defects. This parameter significantly affects the mechanical stability of the material. For the LAITP/PVDF composite, the average microstrain value was calculated to be 69.82, reflecting the internal stresses present in the crystal lattice. Together, these structural parameters provide valuable insights into the composite's crystallographic integrity and its potential for energy storage applications. The findings summarized in Table 2 demonstrate the material's suitability for advanced electrochemical systems, where mechanical robustness and high ionic conductivity are essential.

The surface morphology of LAITP/PVDF solid electrolytes was analysed by SEM. The SEM images presented in Figure 4 provide important information about the microstructural properties of these composite materials at various magnification ratios. Detailed examination of the SEM images reveals a homogeneous distribution of LAITP ceramic particles within the PVDF matrix. This homogeneous distribution is an indication that LAITP particles were successfully incorporated into the PVDF matrix and a homogeneous composite material was obtained. Although no significant phase separation was observed, microcracks were observed in the structure. Microcracks observed along the grain boundaries after the sintering process can be attributed to the pronounced thermal expansion anisotropy of LATP. During the cooling phase, variations in thermal contraction between different grains lead to uneven shrinkage, which induces localized stresses. These stresses accumulate at the grain boundaries, ultimately causing the formation of microcracks [53-55]. The presence of the $AlPO_4$ impurity phase can be shown as an enhancing cause of these cracks. In addition, the $AlPO_4$ phase acts as a passive layer for the lithium diffusion pathway [39].

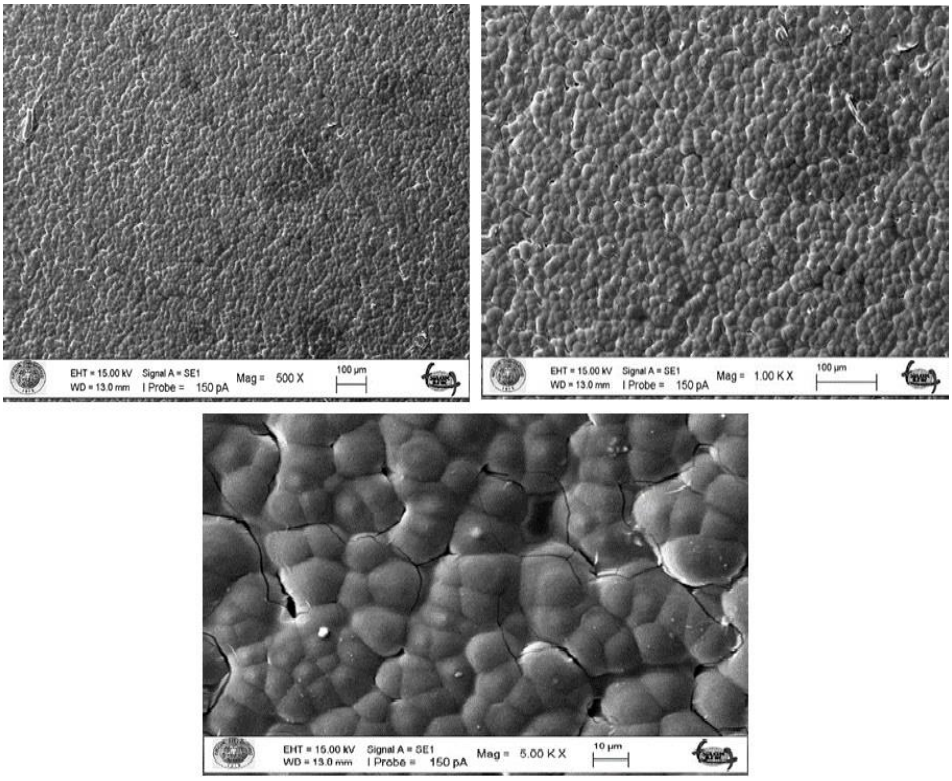

***Figure 4**. SEM images of LAITP/PVDF solid electrolyte at different magnifications*

The impedance spectra for the LAITP/PVDF composite electrolyte, analyzed using an equivalent circuit model, are presented in Figure 5. In the high-frequency region, the spectra exhibit a semicircular arc, corresponding to ionic transport within the bulk material. This arc is associated with R_g grain resistance and R_{gb} grain boundary resistance, which provide insights into the distinct contributions of grains and grain boundaries to the overall ionic conductivity of the composite. To account for the material's non-ideal capacitive behavior, a constant phase element (CPE) was included in the equivalent circuit model. This element enhances the accuracy of the fit by capturing deviations from ideal capacitance often observed in heterogeneous materials. At lower frequencies, the impedance spectra show a linear feature, characteristic of Warburg-type impedance. This slope reflects Li-ion diffusion at the interface between the solid electrolyte and the counter electrode. The Warburg element (W) in the circuit represents this diffusion-controlled process and is essential for evaluating R_{ct} charge transfer resistance at the interface between the electrolyte and the electrode. The parameter Q, representing the CPE with units of S·sec, quantifies the capacitive behavior within the composite [53]. Together, these features of the impedance spectra provide a comprehensive understanding of the ionic transport and interfacial properties of the LAITP/PVDF composite solid electrolyte.

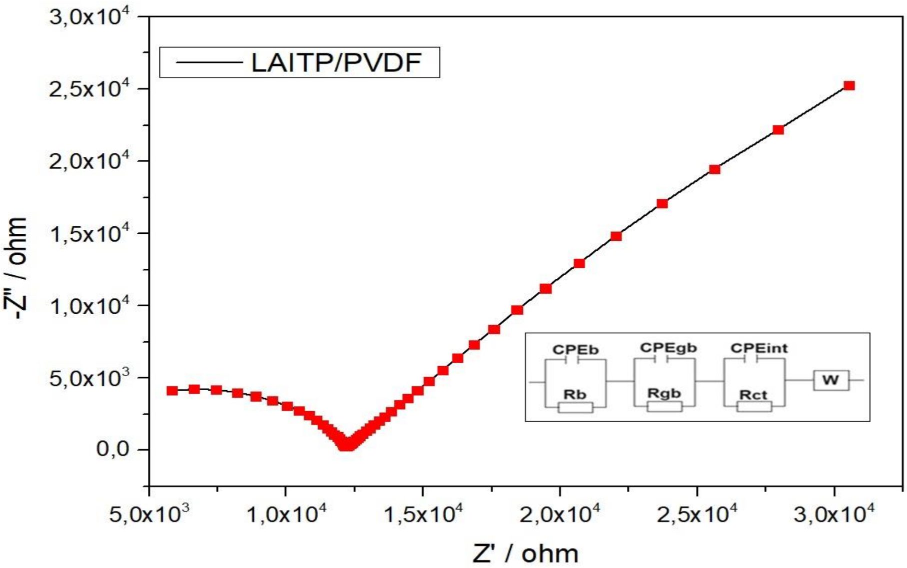

Figure 5. *Nyquist plot and corresponding equivalent circuit for the LAITP/PVDF solid electrolyte*

Table 3. *Fit values of LAITP/PVDF solid electrolyte*

Sample	**R_b(Ω)**	**Q_b (S.s^n)**	**R_{gb}(Ω)**	**Q_{gb} (S.s^n)**	**R_{ct} (Ω)**	**Q_{int}(S.s^n)**	**Warburg**	**χ^2**
LAITP/PVDF	1.14×10^3	1.19×10^{-4}	12.1×10^3	3.98×10^{-10}	82.3×10^3	7.12×10^{-4}	54.19×10^{-5}	2.94×10^{-4}

During the experimental phase of this study, while forming composite solid electrolyte materials, LAITP ceramic filler materials were added to the polymer matrix at 10, 15 and 20 wt% separately and it was observed that the highest ionic conductivity value was obtained when 20 wt% LAITP was added. Electrochemical impedance spectroscopy revealed that the samples containing 10 wt% and 15 wt% LAITP exhibited relatively low ionic conductivities, on the order of 10^{-7} S·cm^{-1} at room temperature. The ionic conductivity of 20 wt% LAITP/PVDF composite electrolyte was determined using the Nyquist plot given in Figure 5 and the resistance values listed in Table 3 obtained by fitting to the equivalent circuit. The obtained ionic conductivity of 1.7×10^{-5} S cm^{-1} at room temperature indicates the moderate ion transport ability typical for polymer-ceramic composite electrolytes. This value is within the expected range (10^{-7}-10^{-4} S cm^{-1}) reported in literature studies and demonstrates the consistency and reliability in the synthesis and measurement approach [39, 56].

4. RESULTS

In this study, a novel LAITP/PVDF composite solid electrolyte using $LiClO_4$ as lithium salt was successfully synthesized by a solution casting method. The aim of the composite was to improve the electrochemical performance by utilizing the synergistic advantages of ceramic and polymer components by incorporating 20 wt% indium-doped LATP (LAITP) ceramic in the PVDF polymer matrix. The structural integrity, morphological features, and ionic transport properties of the synthesized composite were systematically investigated using X-ray diffraction (XRD) for crystallographic analysis, scanning electron microscopy (SEM) for microstructural characterization, and electrochemical impedance spectroscopy (EIS) to assess conductive behavior. XRD analysis confirmed the successful substitution of indium into the LATP lattice, indicating the formation of the targeted LAITP phase. SEM micrographs revealed that ceramic particles were largely homogeneously distributed within the PVDF matrix; however, small microcracks were observed along the grain boundaries. Impedance spectroscopy measurements showed that the composite containing 20 wt% LAITP had an ionic conductivity of 1.7×10^{-5} S cm^{-1} at room temperature. Compared with previous studies on LATP/PVDF composites reported in the literature depending on the ceramic content and processing conditions, the present results are promising and indicate that indium doping plays a beneficial role in stabilizing the structure and enhancing lithium ion mobility. However, the presence of residual impurity phases and microstructural defects slightly reduced the expected conductivity improvements and highlighted the critical role of synthesis optimization.

This work represents the first successful integration of indium-doped LATP with a PVDF matrix and paves the way for further investigation of doped NASICON-type ceramics in polymer composite electrolytes. Future research should focus on improving the doping strategy, enhancing particle dispersion, and reducing microstructural defects to fully realize the potential of such composites in high-performance solid-state lithium batteries.

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CONFLICTS OF INTEREST

No conflict of interest was declared by the authors.

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