SYNTHESIS AND MODIFICATION OF THIN NASICON SOLID ELECTROLYTES USING ION BEAMS

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https://doi.org/10.37904/nanocon.2025.5197

Abstract

Solid electrolytes (SEs) for sodium-based superionic conductors (NaSICON) were first introduced in 1976 and quickly recognized for their excellent ionic conductivity. While considerable effort has been made to develop thin electrolytes for all-solid-state batteries (ASSBs), only a few sodium-based SEs have been successfully fabricated as thin films. These thin films are particularly desirable for their reduced electrical resistance, which typically increases with the thickness of the SE. By reducing the thickness of the SEs to the nanometer scale, their ionic conductivity can be significantly enhanced.

In this study, the NASICON composite was initially prepared in the form of pellets using the mixed oxide technique with a planetary ball mill and synthesized by the solid-state method at 1300 °C. The resulting pellets were used as sputtering targets in a low-energy ion facility to prepare continuous NASICON nanofilms. To explore the effect of ion implantation on the electrical properties of NASICON, the prepared films were bombarded with Ni ions at 1.1 MeV and varying fluences, using the Tandetron accelerator at the CANAM infrastructure (NPI Řež). The electrical properties of both the synthesized and implanted films were analyzed through electrochemical impedance spectroscopy (EIS). The results, describing the impact of irradiation on NASICON's properties, are presented here.

Keywords: Energy storage systems, ion beam modifications, nanofilms

1. INTRODUCTION

NASICON-type (sodium-based superionic conductors) solid electrolytes are among the most studied ceramic based ion conductor thanks to their high ionic conductivity and chemical stability and nowadays are playing a crucial role for advanced of energy storage technologies [1, 2]. In the energy storage field, lithium ion batteries currently dominate the market due to their excellent electrochemical performance and mature large-scale production technology. However, the limited availability and uneven geographical distribution of lithium pose significant challenges to the long-term sustainability of global energy infrastructure. In this context, sodium-based all-solid-state batteries have emerged as a promising alternative, benefiting from the natural abundance and low cost of sodium. The use of NASICON-based solid electrolytes is considered a key enabling factor for such systems. Despite their favorable intrinsic properties, the ionic conductivity of NASICON electrolytes is highly sensitive to composition, defect chemistry, and microstructure. Among NASICON compounds, $Na_3Zr_3Si_3PO_{12}$ (NZSP) has recently attracted considerable attention as a solid electrolyte for sodium-ion rechargeable batteries operating at low and room temperatures, owing to its comparatively high ionic conductivity and chemical stability [3]. While various synthesis and doping strategies have been explored to improve its performance [4], a systematic study on thin films with high defect controll, is still missing. Ion beam based techniques are suitable methodologies for this purpose. Ion beam sputtering method enables the growth of dense, uniform thin films, while ion implantation provides a method for precise, depth-resolved stoichiometric modification and defect engineering without altering the overal morphology. In this study, NZSP thin films were synthesized using ion beam sputtering and systematically modified through ion implantation to improve lattice quality and tailor stoichiometry. Elemental composition was analyzed using ion beam-based methods, while electrochemical testing provided insights into performance improvements. The NASICON thin films were also examined to explore the impact of sample miniaturization on ionic conductivity and the potential for tuning their properties. This study compares conventional and nuclear-assisted synthesis and analytical approaches, highlighting their effects on material properties and device performance.

2. METHODOLOGY

The NASICON material, $Na_3Zr_2Si_2PO_{12}$ (NZSP), was produced using the solid state reaction method at ITAE, Messina. Pellets were produced using different procedures to achieve varying grain sizes in the final product. The synthesis process can be divided into three main phases: In the first phase, the precursors (SiO_2, ZrO_2, Na_2CO_3, $NH_4H_2PO_4$) in powder form were ball-milled to obtain a uniformly mixed fine powder. In the second phase, the fine powder was pressed into pellets and annealed at 1150°C to form the NZSP phase. In the final phase, the annealed pellets were crushed, ball-milled again, and then re-pelletized before undergoing a final sintering at 1250°C to improve the crystallinity of the NZSP pellets. Three pellets were produced: NASICON 2, made with commercial NZSP powder; NASICON 4, produced by mixing the reagents as described; and NASICON 5, prepared with the same procedure as NASICON 4, but without the second sintering step. Thin films of NASICON were then produced from these pellets using the ion beam sputtering (IBS) technique, with the pellets serving as targets for the sputtering. The ion beam sputtering was performed at the LEIF facility in NPI Řež. LEIF (Low Energy Ion Facility) is a laboratory ion beam system that generates Ar ions in the energy range of 1-100 keV and operates within the CANAM infrastructure [5]. The Ar ion beam was directed into a multipurpose vacuum chamber, where it impinged on the NASICON pellet at a 45° angle, sputtering the pellet material. Silicon wafers, placed parallel to the target (but out of the beam's direct path in a distance of about 15 cm), served as substrates. In IBS process, the sputtered material was deposited onto the substrates, forming thin NASICON films.

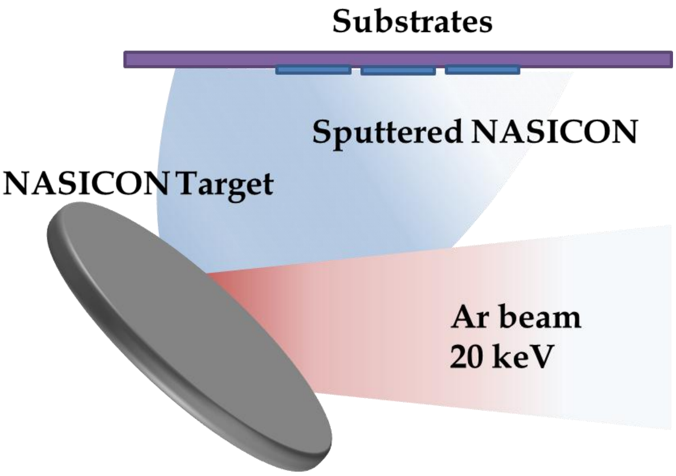

Figure 1 Sketch of thin film deposition by ion beam sputtering

To determine the elemental composition of the prepared films, RBS measurements were performed. Given the novelty of the Ion Beam Sputtering (IBS) method for preparing NASICON ultrathin films, one of the primary goals was to determine the elemental ratios and identify any potential contaminants. RBS is widely used for studying thin films and multilayer systems, with thicknesses ranging from nanometers to micrometers. It enables the determination, with some limitations, of both the atomic mass and concentration of elemental constituents as a function of depth beneath the surface [6].

The RBS measurements were carried out at the Tandetron MC 4130 accelerator within the NPI CANAM infrastructure. In the experiment, He^+ ions with an energy of 2 MeV and a low current (~100 nA) were used to minimize radiation damage to the material. The backscattered particles were detected using a partially-depleted ORTEC ULTRA detector with an active area of 50 mm² and a 300 μm thick depletion layer. The detector was positioned at a backscatter angle of 170°, in accordance with the Cornell geometry.The thin films were modified by ion implantation to alter their electrical properties (ion implantation is a technique used to modify the material at shallow depths by doping it with selected atoms). Implantation was performed using 1.1 MeV Ni ions, with three different fluences (1E14 Ni/cm^2, 5E14 Ni/cm^2, and 1E15 Ni/cm^2) for three different samples.

Both as-deposited and implanted samples were then investigated for changes in their electrical properties using Electrochemical Impedance Spectroscopy (EIS). The EIS study was conducted using a Biologic Potentiostat, operating in the frequency range of 7 MHz – 1 Hz. For the measurements, the samples were placed in a custom-made holder connected to the potentiostat electrodes.

3. RESULTS

The RBS analysis was performed on samples produced from three different pellets. The experimental data were evaluated using the SIMNRA code, which allowed for the estimation of the relative percentages of the composing elements [7]. The evaluation revealed no contaminants; however, a higher amount of oxygen was detected in pellet 5, suggesting that the stoichiometry of the NASICON layer was disturbed due to additional oxidation of the constituent elements.

Table 1 Elemental composition of produced thin films from the RBS analysis.

	NASICON 2	**NASICON 4**	**NASICON 5**
Na (%)	16,39	15,86	8,83
Si (%)	11,11	10,65	6,67
P (%)	5,46	4,84	2,94
Zr (%)	11,29	10,64	6,62
O (%)	55,74	58,02	74,93

Electrochemical impedance spectra of the as-deposited NASICON thin films (**Figure 2a**) show clear differences depending on the pellet used as sputtering target. Among the three samples, NASICON 4 exhibits the lowest overall impedance, followed by NASICON 5, while NASICON 2 (commercial powder) shows the highest impedance. This trend suggests that the synthesis route of the sputtering target plays a decisive role in determining the electrical performance of the deposited films. In particular, the two-step annealing procedure used for NASICON 4 likely results in improved crystallinity and more favorable Na-ion conduction pathways, which are partially preserved during the sputtering process, leading to a memory effect of the original microstructure. **Figures 2b, c and d** illustrate the effect of Ni ion implantation on the impedance response of the three NASICON films. For all samples, low fluence implantation (1E14 Ni/cm^2) leads to a pronounced increase in impedance compared to the as-deposited state, indicating a reduction of ionic conductivity. This could be due to the initial formation of structural damage that disrupts the ionic transport pathways in the amorphous NZSP. However, with increasing implantation fluence (5E14 and 1E15 Ni/ cm^2), a gradual reduction in impedance is observed for all samples. This behavior suggests a competition between beneficial doping effects and ion-induced lattice damage. While moderate Ni concentrations enhance conductivity, higher fluences introduce excessive structural disorder, defect clustering, or partial amorphization, which ultimately hinder ion transport. A comparison among the three samples reveals that NASICON 4 maintains the lowest impedance across all implantation conditions, indicating a higher tolerance to irradiation-induced damage.

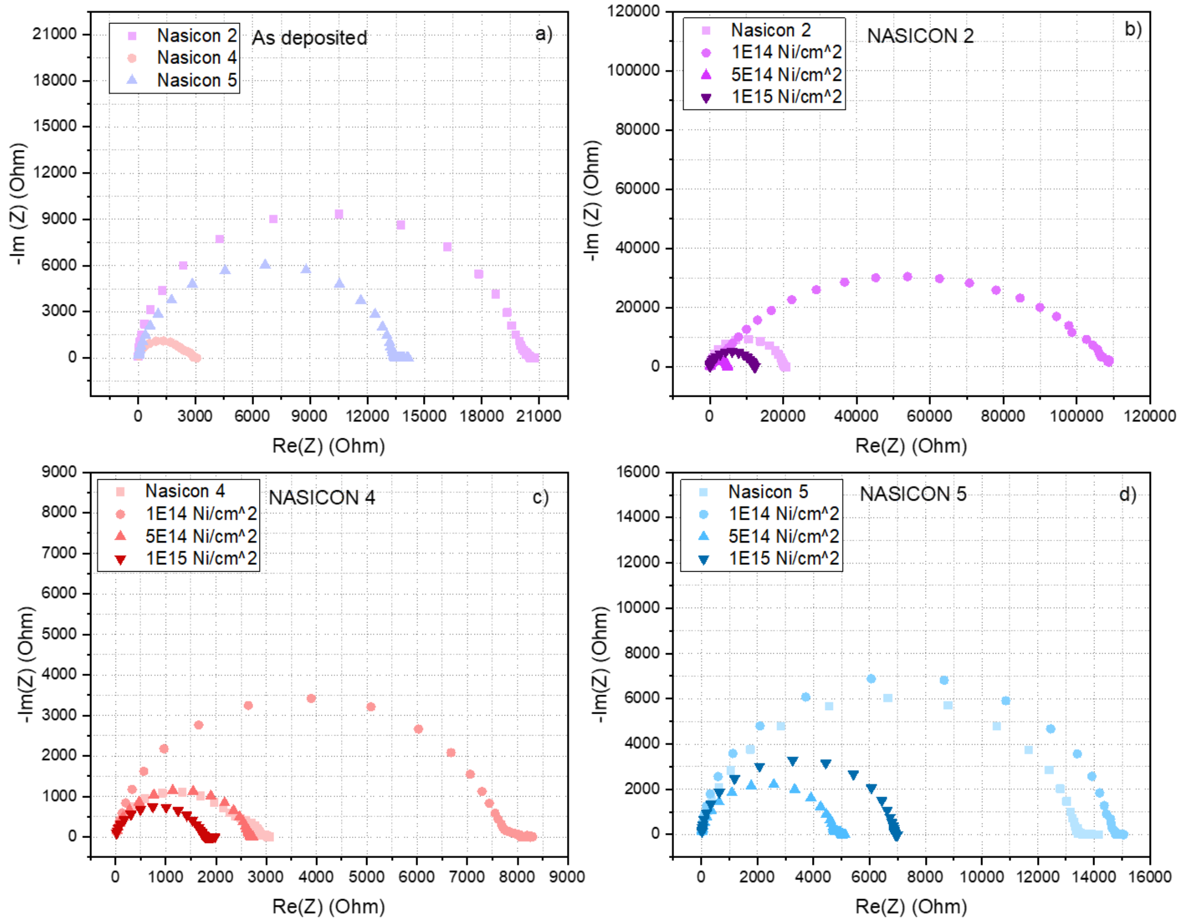

Figure 2 Experimental impedance spectra for the NASICON thin films: a) shows the comparison between as prepared films, b), c) and d) show the changes in impedance in different NASICON after ion irradiation.

4. CONCLUSION

NASICON thin films were produced by ion beam sputtering from a NASICON pellet synthesized using the solid state reaction method. The films exhibited good homogeneity and no contamination (except for higher oxidation observed in one sample). The films were then irradiated with MeV Ni ions to modify their electrical properties. Electrochemical Impedance Spectroscopy (EIS) revealed that the changes in impedance were not linear with ion fluence; higher fluences also led to a reduction in the improvement of conductivity. Overall, Ni incorporation enhanced the synthesized film conductivity, significantly reducing the impedance for all NASICON films tested.

ACKNOWLEDGEMENTS

This work was supported by the Ministry of Education, Youth and Sports (MEYS) CR under the project OP JAK CZ.02.01.01/00/22_008/0004591. The authors acknowledged also the support of Czech Academy of Science Mobility Plus Project, Grant No. CNR-25-01.

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