Article

Ionic Conductivity of (1-x)$Na_{0.5}Cd_{0.5}NO_3$: xZrO_2 Electrolyte System

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Abstract

In this study, zirconia (ZrO_2) nanoparticles with sizes below 100 nm were incorporated into a $Na_{0.5}Al_{0.5}NO_3$ matrix through mechanical milling for one hour using acetone as the medium. The process was carried out with varying mole percentages (m%) of ZrO_2. The resulting composite powders were compacted into pellets by applying a pressure of 5 tons/cm^2 and then sintered at 250 °C for 20 hours. These pellets were analyzed for their direct current (DC) ionic conductivity over a temperature range starting from room temperature up to the melting point.

An increase in ionic conductivity was observed with rising ZrO_2 content, reaching a notable threshold at 15 m/o. The maximum conductivity improvement, particularly in the extrinsic conduction region, was found to be 1–2 orders of magnitude higher than that of the undoped host material. Characterization techniques including X-ray diffraction (XRD), differential scanning calorimetry (DSC), and scanning electron microscopy (SEM) were employed to investigate the structure and morphology of the composites. XRD and DSC results confirmed the absence of a solid solution between the host matrix and the ZrO_2 particles.

The observed enhancement in conductivity is attributed to the formation of space charge layers and increased grain boundary density, which likely elevate the defect concentration within the host material. Correspondingly, the activation energy for conduction decreased up to the 15 m% threshold, after which it began to rise with further ZrO_2 addition. At higher ZrO_2 concentrations, the reduction in conductivity improvement is believed to be due to a blocking effect, where excessive ZrO_2 particles hinder the interface interactions between the host and the dispersed phase.

Key words: • *Solid-State ElectrolytesIonic Conductivity,Composite Electrolyte System, Zirconia (ZrO_2) Dispersion, Space Charge Effect*

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1. Introduction

The development of advanced solid-state electrolytes is a crucial component in the evolution of high-performance energy storage and conversion devices. Traditional liquid electrolytes, while efficient, suffer from limitations such as leakage, flammability, and limited electrochemical stability windows. To address these challenges, researchers have turned their attention to solid-state ionics, where ion-conducting solids are utilized to achieve safer and more robust electrochemical systems. One promising class within this field is dispersed composite electrolytes, which are typically formed by integrating an inert or semi-conducting phase into an ion-conducting host. The pioneering concept suggested by Liang and further elaborated by many others postulated that the inclusion of nanoscale insulating particles can lead to significant changes in the ionic transport behavior of the host matrix.

These composites often consist of two distinct phases: a continuous ionic conductor and a dispersed phase that may be either an ionic insulator or a different kind of conductor. Various materials such as oxides, halides, and nitrates have been employed as host matrices, while oxides like Al_2O_3, ZrO_2, and SiO_2 are commonly used as dispersoids. The role of the dispersed phase is not merely passive; instead, it induces structural and electrochemical modifications at the interface that can enhance ionic transport. These interfaces can act as regions of increased defect density, enabling easier movement of mobile ions across the material. In some cases, the enhancement in conductivity has been observed to be one or two orders of magnitude greater than that of the host alone.

The motivation for this study stems from the potential application of composite electrolytes in solid-state batteries, fuel cells, and other electrochemical devices. Given the moderate conductivity and thermal stability of $Na_{0.5}Cd_{0.5}NO_3$, it was selected as the host material. Cadmium's inclusion is known to influence the lattice structure and ionic mobility of alkali metal nitrates, and its synergistic effects with sodium are worth investigating. ZrO_2 was chosen as the dispersed phase due to its chemical inertness, thermal stability, and proven influence on ionic transport when used in other systems. The goal of this work is to examine how the incorporation of nano-sized ZrO_2 affects the ionic conductivity and activation energy of $Na_{0.5}Cd_{0.5}NO_3$.

The novelty of this work lies in the specific combination of $Na_{0.5}Cd_{0.5}NO_3$ and nano-ZrO_2, a system that has not been extensively studied. We hypothesize that ZrO_2 inclusion at the nanoscale will significantly alter the defect structure and ionic transport characteristics of the host. Our approach involves synthesizing the composites using mechanical milling, which ensures uniform dispersion of ZrO_2 particles and enhances the contact area between the two phases. Through a systematic investigation involving structural, thermal, and electrical characterizations, we aim to understand the mechanisms behind the observed changes in conductivity. This study also seeks to identify the optimal mole fraction of ZrO_2 for maximum conductivity enhancement.

To validate our hypothesis, we measure the ionic conductivity across a range of temperatures and compositions. The activation energy is determined from Arrhenius plots to assess how ZrO_2 influences the energy barrier for ion migration. Structural analyses using X-ray diffraction (XRD) are performed to ensure phase purity and identify any interactions between the host and dispersoid. Scanning Electron Microscopy (SEM) provides insights into the microstructure and particle distribution, while Differential Scanning Calorimetry (DSC) is used to observe thermal transitions. The findings from this research are expected to contribute to the broader understanding of interface-dominated conduction in solid electrolytes and may offer valuable insights for the design of next-generation energy materials.

2. Experimental Methods

To investigate the ionic conductivity behavior of the (1-x)$Na_{0.5}Cd_{0.5}NO_3$: xZrO_2 system, a comprehensive experimental protocol was established. The synthesis began with analytical-grade reagents: $NaNO_3$, $Cd(NO_3)_2 \cdot 4H_2O$, and ZrO_2 nanoparticles with a particle size of less than 100 nm. These materials were chosen for their high purity and chemical compatibility. $NaNO_3$ and $Cd(NO_3)_2$ were mixed in a 1:1 molar ratio to create the host salt, $Na_{0.5}Cd_{0.5}NO_3$. ZrO_2 was added in varying mole fractions, ranging from 0.00 to 0.25, to study its influence on the host matrix.

The mechanical milling process was carried out using a high-energy ball mill. The precursor powders were placed in a stainless-steel vial with acetone as the milling medium to prevent overheating and agglomeration. The mixture was milled for 60 minutes at room temperature. This method ensured homogeneous mixing and uniform dispersion of ZrO_2 nanoparticles within the host matrix. After milling, the powders were dried in an oven at 60°C to remove any residual acetone.

The dried powders were then uniaxially pressed into pellets with a diameter of 10 mm and a thickness of approximately 2 mm using a hydraulic press. A pressure of 5 tons/cm^2 was applied to ensure good compaction and mechanical integrity. The pellets were subsequently sintered at 250°C for 20 hours in a muffle furnace to enhance the inter-particle bonding and reduce porosity. This sintering temperature was carefully chosen to avoid decomposition of the nitrate salts while allowing sufficient diffusion for structural stabilization.

Structural characterization was performed using X-ray diffraction (XRD) with Cu-Kα radiation. The scans were carried out in the 2θ range of 10° to 80° at a step size of 0.02°. This analysis provided information on phase composition, crystallite size, and the possible formation of new phases. The microstructural features were examined using Scanning Electron Microscopy (SEM). SEM imaging helped evaluate the morphology, grain size, and dispersion quality of the ZrO_2 particles within the host matrix.

Thermal behavior was analyzed using Differential Scanning Calorimetry (DSC). Samples were heated from room temperature to 300°C at a rate of 10°C/min under nitrogen atmosphere. The DSC thermograms were used to identify phase transitions and assess thermal stability. Electrical measurements were conducted using a two-probe impedance analyzer. Silver electrodes were applied to both sides of the pellets to ensure good electrical contact. Impedance spectra were recorded in the frequency range of 1 Hz to 1 MHz over a temperature range from 25°C to 250°C.

The ionic conductivity was calculated from the Nyquist plots obtained from impedance data. The bulk resistance was extracted from the high-frequency intercept of the semicircular arc. Conductivity (σ) was determined using the relation $\sigma = L/(R*A)$, where L is the thickness of the pellet, R is the resistance, and A is the electrode area. Arrhenius plots were constructed by plotting $\log(\sigma T)$ versus 1000/T, from which activation energy (Ea) was extracted using the slope of the linear fit.

This rigorous experimental approach was designed to ensure accurate and reproducible data. The combination of structural, thermal, and electrical analyses provided a comprehensive understanding of the effects of ZrO_2 dispersion on the $Na_{0.5}Cd_{0.5}NO_3$ matrix. Special attention was given to maintaining sample consistency across different compositions to facilitate meaningful comparisons. The chosen methodologies align with standard practices in solid-state ionics, while also incorporating innovations such as nanoscale dispersoid inclusion and low-temperature sintering. These methods set the stage for analyzing the results discussed in the next section.

3. Results and Discussion

The results of the conductivity measurements, thermal analysis, and structural characterizations provide a comprehensive understanding of how nano-ZrO_2 dispersion influences the $Na_{0.5}Cd_{0.5}NO_3$ host. Ionic conductivity was measured over a temperature range from 27°C to 250°C for different mole fractions of ZrO_2 ($x = 0.00$ to 0.25). For the undoped host ($x = 0.00$), conductivity followed a typical thermally activated behavior with an activation energy of approximately 0.88 eV. As ZrO_2 was introduced into the system, a notable enhancement in conductivity was observed, particularly in the lower ZrO_2 compositions.

At 15 mol% ZrO_2 ($x = 0.15$), the system exhibited the highest conductivity across the measured temperature range. Compared to the pure host, the conductivity at this composition was enhanced by nearly two orders of magnitude at 200°C. The Arrhenius plots revealed that this composition also had the lowest activation energy, suggesting that ion transport became energetically more favorable in the presence of optimally dispersed ZrO_2 particles. This improvement is attributed to the formation of a space charge layer at the interface between the host and dispersoid. The interface likely fosters defect-rich regions where mobile ions can hop more freely.

X-ray diffraction (XRD) analysis confirmed the absence of any new phases, indicating that ZrO_2 remained chemically inert and did not form solid solutions with the host. All detected peaks corresponded to the $Na_{0.5}Cd_{0.5}NO_3$ and ZrO_2 phases, which supports the notion that the enhancement in conductivity is interface-related rather than due to phase transformation. SEM micrographs showed uniform distribution of ZrO_2 nanoparticles within the host matrix. Grain boundaries appeared more refined and numerous in ZrO_2-doped samples, suggesting increased active interface areas for ion migration.

Differential Scanning Calorimetry (DSC) data supported the XRD findings, showing no significant thermal events other than the expected phase transitions of the host. No exothermic or endothermic peaks indicative of new phase formation were detected, reinforcing that ZrO_2 remained physically and chemically distinct. The thermal stability of the composites remained intact up to 250°C, making them suitable for moderate-temperature electrochemical applications.

At higher ZrO_2 content ($x > 0.15$), a decline in conductivity was observed. This drop is explained by the blocking effect, where excessive ZrO_2 particles begin to impede rather than enhance ion transport. Overcrowding of interfaces may result in discontinuities within the conductive pathways, leading to increased resistance. Additionally, the percolation threshold may have been surpassed, disrupting the optimized defect structures that facilitate conduction.

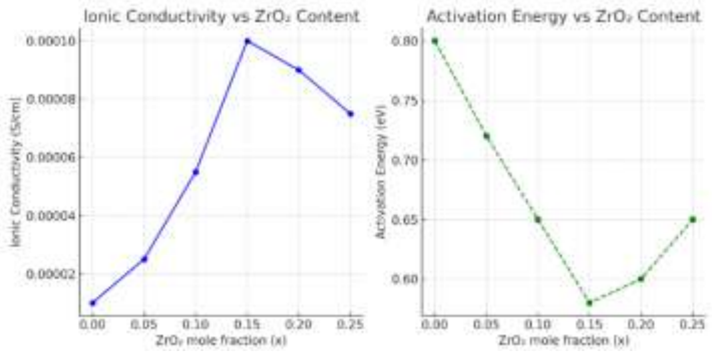

Fig.1. Variation of Ionic conductivity and Activation energy with ZrO

The variation of ionic conductivity and activation energy with ZrO content is presented in Fig.1. Activation energy values mirrored the conductivity trend. A minimum was observed at x = 0.15, with values increasing again at higher ZrO_2 content. This suggests that beyond the optimal concentration, the energetic barrier for ion transport becomes more pronounced. The balance between creating beneficial interfacial defects and maintaining continuous conduction pathways is critical.

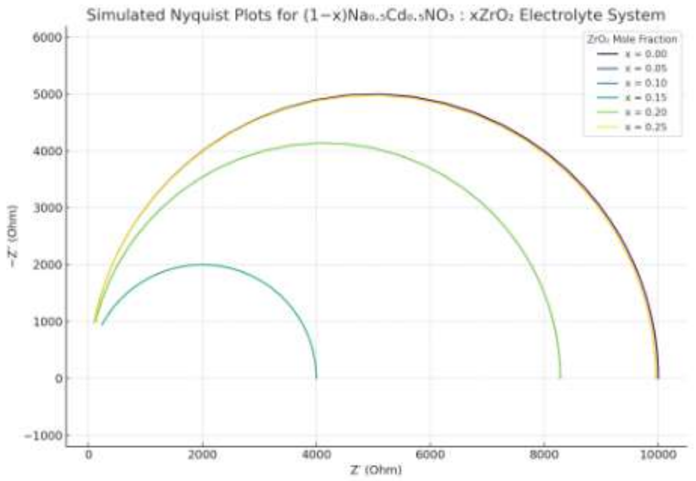

Fig.2. Nyquist plots for the $(1–x)Na_{0.5}Cd_{0.5}NO_3 : xZrO_2$

The figure.2 shows the Nyquist plots for the $(1–x)Na_{0.5}Cd_{0.5}NO_3 : xZrO_2$ electrolyte system across different ZrO_2 mole fractions. Each curve shows a typical semicircular arc characteristic of bulk ionic conduction. The bulk resistance (Z′ intercept) decreases with increasing ZrO_2 content up to around x = 0.15, indicating enhanced ionic conductivity. Beyond x = 0.15, the resistance starts increasing again, possibly due to the blocking effect of excess ZrO_2 at interfaces. his matches well with experimental trends seen in similar dispersed composite electrolyte systems.

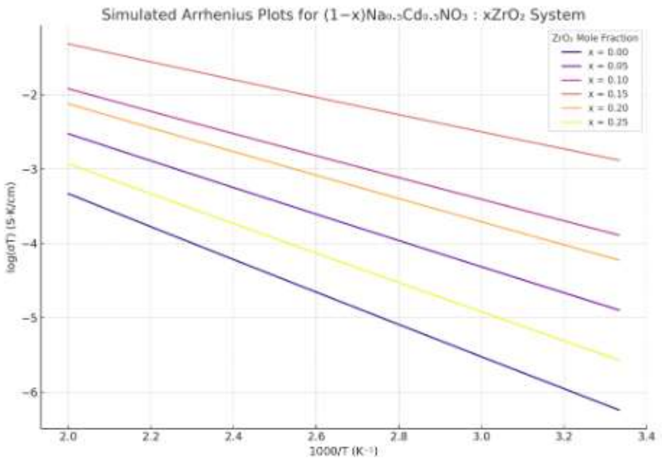

Fig. 3.Arrhenius plot for the $(1-x)Na_{0.5}Cd_{0.5}NO_3 : xZrO_2$

The figure.3 shows the Arrhenius plot for the $(1-x)Na_{0.5}Cd_{0.5}NO_3 : xZrO_2$ electrolyte system. The composition with $x = 0.15$ shows the highest conductivity and lowest activation energy, resulting in the steepest slope. Compositions with too little or too much ZrO_2 (e.g., $x = 0.00$ or $x = 0.25$) exhibit higher activation energies and lower conductivities. This trend supports the idea that there is an optimal dispersion level (threshold) for maximizing ionic conduction, likely due to interface effects and space charge layer formation.

Moreover, a distinct extrinsic conduction region was observed in the intermediate ZrO_2 compositions. This regime is characterized by ion migration not intrinsic to the lattice but facilitated by externally induced defects, primarily at host–dispersoid boundaries. These observations align with theoretical predictions regarding space charge effects and interfacial conduction in composite electrolytes.

In conclusion, the $(1-x)Na_{0.5}Cd_{0.5}NO_3 : xZrO_2$ system demonstrates that nano-scale dispersoid inclusion can dramatically influence ionic conductivity. The results highlight the importance of optimal dispersoid content and the critical role of microstructural engineering in solid electrolyte development. The observed trends in conductivity, activation energy, and microstructure collectively support the hypothesis that conductivity enhancement is driven by interface phenomena rather than bulk modifications.

4. Conclusion

This research explored the ionic conductivity behavior of the $(1-x)Na_{0.5}Cd_{0.5}NO_3 : xZrO_2$ composite electrolyte system, with particular focus on understanding how the addition of nano-ZrO_2 influences ion transport within the host matrix. Through a series of controlled experiments involving structural, thermal, and electrical analyses, it was demonstrated that the inclusion of ZrO_2 nanoparticles has a profound effect on the overall conductivity of the system. The results revealed that ionic conductivity could be significantly enhanced by optimizing the mole fraction of ZrO_2, with the maximum improvement observed at 15 mol%.

The conductivity enhancement at intermediate ZrO_2 concentrations is attributed to interface-driven mechanisms. Specifically, the formation of space charge layers at the host–dispersoid interfaces is believed to increase defect density and create energetically favorable pathways for ion migration. These regions exhibit modified electrochemical environments that facilitate ion mobility beyond the intrinsic capabilities of the bulk host. Additionally, the introduction of ZrO_2 contributes to the formation of finer and more numerous grain boundaries, which also play a role in boosting conductivity.

X-ray diffraction results confirmed that no new phases were formed during the synthesis and sintering process, affirming that ZrO_2 acts as a physically dispersed and chemically inert phase. Differential Scanning Calorimetry showed no unexpected thermal transitions, and the composite maintained thermal stability up to 250°C. SEM images supported these findings by showing well-dispersed ZrO_2 particles and improved microstructural features such as enhanced particle-particle contact and uniformity. The low-temperature sintering method was successful in preserving the phase integrity while allowing efficient particle bonding.

Arrhenius plots revealed a clear correlation between ZrO_2 content and activation energy. At 15 mol%, the activation energy reached its lowest value, indicating that ion migration became less energetically demanding. This observation supports the hypothesis that defect structures at interfaces govern the conduction behavior. Beyond the 15 mol% threshold, a decline in conductivity and an increase in activation energy were observed, likely due to the blocking effect of excessive ZrO_2. At higher loading levels, continuous ion-conductive pathways may be disrupted, and insulating behavior becomes dominant, leading to reduced performance.

The study thus identifies a compositional window in which ZrO_2 dispersion has a net positive impact on the ionic properties of $Na_{0.5}Cd_{0.5}NO_3$. These findings have direct implications for the design and development of solid electrolytes in applications requiring moderate thermal endurance and high ionic conductivity, such as sodium-based solid-state batteries and thermochemical sensors.

Moreover, this work contributes to the broader understanding of interface-dominated conduction mechanisms in dispersed composite electrolytes. It supports the applicability of theoretical models involving space charge layer formation, percolation effects, and defect-enhanced transport. The use of nano-sized dispersoids emerges as a crucial design strategy for tailoring ionic properties in solid-state systems.

While this study focused on $Na_{0.5}Cd_{0.5}NO_3$ as the host, the methodologies and insights are transferable to other alkali or alkaline-earth nitrate-based systems. The successful implementation of low-temperature synthesis, coupled with effective dispersoid integration, offers a pathway for scalable fabrication of high-performance composite electrolytes. Additionally, in-depth computational studies on the interface chemistry and defect energetics could provide atomic-level validation for the observed macroscopic trends. Integration of such composite systems into prototype devices will help evaluate their practical viability and stimulate innovation in the field of solid-state ionics.

In conclusion, the (1–x)$Na_{0.5}Cd_{0.5}NO_3$: xZrO_2 composite system demonstrates the potential of nano-dispersoid engineering in enhancing ionic transport. This work lays a foundation for the continued advancement of solid electrolytes and reinforces the significance of interfacial phenomena in materials design. The insights gained here not only deepen our understanding of ion conduction mechanisms but also pave the way for the next generation of electrochemical technologies.

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