Exploring the Influence of V_2O_5 Content on the Mechanism of Electrical Transport in the Na_2O-V_2O_5-Nb_2O_5-P_2O_5 Glass System: A Perspective through Model-Free Scaling Procedures

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Sodium-vanadium-phosphate-based materials have garnered significant interest as cathodes for high-rate sodium-ion batteries, owing to their stable framework, minimal volume change, thermodynamic stability, and excellent sodium storage capacity with fast ion transport kinetics[1]. Furthermore, as these materials consist of both alkali and transition metal (TM) ions, which can exist in various oxidation states (V^{4+}, V^{5+}), these systems can exhibit the mixed ionic-polaronic conduction mechanism. Such feature has proven to be highly effective in facilitating the intercalation and deintercalation of alkali ions[2]. Another crucial property of cathode materials is thermal stability which can be significantly enhanced by incorporating metal oxides such as Nb_2O_5[3]. Based on this premise, the current study focuses on investigating the electrical properties of glasses within the Na_2O-V_2O_5-Nb_2O_5-P_2O_5 system. The P_2O_5 component is gradually replaced by Nb_2O_5 while maintaining constant Na_2O and V_2O_5 content. By varying the concentration of V_2O_5 (10 and 25 mol%), the influence of its content on the electrical transport mechanism is examined, enabling the evaluation of its possible polaronic contribution. Solid-state impedance spectroscopy (SS-IS) is employed to examine electrical transport across a wide frequency (0.01 Hz to 1 MHz) and temperature (–90 °C to 240 °C) range and the conductivity spectra are studied in detail using two model-free scaling procedures, namely Summerfield and Sidebottom scaling. The successful construction of conductivity master curves for all glasses with lower V_2O_5 content (10 mol%) validates the time-temperature superposition (TTS) and confirms a purely ionic conduction mechanism, indicating that V_2O_5 does not contribute to electrical conductivity via a polaronic mechanism. However, master curves cannot be obtained for glasses with higher V_2O_5 (25 mol%) and low Nb_2O_5 content (0 and 5 mol%), suggesting the presence of mixed ionic-polaronic conductivity with a dominant polaronic contribution. Furthermore, with the addition of Nb_2O_5 above 10 mol%, the ionic conductivity mechanism prevails. The findings of this study provide valuable insights into the mixed-conductive glass system and role of V_2O_5 and/or Nb_2O_5, and demonstrate the ability to tune the mechanism of electrical conductivity by adjusting the content of oxide glass and its ratio. Nb_2O_5 content.

ACKNOWLEDGMENTS

This work is supported by the CSF under the projects IP-2018-01-5425 and DOK-2021-02-9665.

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