

Transport Properties of Alkali Nitrites

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Abstract : Electrolytes with different type of charge carrier can find widely application in different using, e.g. sensors, electrochemical equipments, batteries and others. One of important components ensuring stable functioning of the equipment is electrolyte. Electrolyte has to be characterized by high conductivity, thermal stability, and wide electrochemical window. In addition to many advantageous characteristic for liquid electrolytes, the solid state electrolytes have good mechanical stability, wide working range of temperature range. Thus search of new system of solid electrolytes with high conductivity is an actual task of solid state chemistry. Families of alkali perchlorates and nitrates have been investigated by us earlier. In literature data about transport properties of alkali nitrites are absent. Nevertheless, alkali nitrites MeNO_2 ($\text{Me} = \text{Li}^+, \text{Na}^+, \text{K}^+, \text{Rb}^+$ and Cs^+), except for the lithium salt, have high-temperature phases with crystal structure of the NaCl-type. High-temperature phases of nitrites are orientationally disordered, i.e. non-spherical anions are reoriented over several equivalents directions in the crystal lattice. Pure lithium nitrite LiNO_2 is characterized by ionic conductivity near 10^{-4} S/cm at 180°C and more stable as compared with lithium nitrate and can be used as a component for synthesis of composite electrolytes. In this work composite solid electrolytes in the binary system $\text{LiNO}_2 - \text{A}$ ($\text{A} = \text{MgO}, \gamma\text{-Al}_2\text{O}_3, \text{Fe}_2\text{O}_3, \text{CeO}_2, \text{SnO}_2, \text{SiO}_2$) were synthesized and their structural, thermodynamic and electrical properties investigated. Alkali nitrite was obtained by exchange reaction from water solutions of barium nitrite and alkali sulfate. The synthesized salt was characterized by X-ray powder diffraction technique using D8 Advance X-Ray Diffractometer with Cu K α radiation. Using thermal analysis, the temperatures of dehydration and thermal decomposition of salt were determined.. The conductivity was measured using a two electrode scheme in a forevacuum (6.7 Pa) with an HP 4284A (Precision LCR meter) in a frequency range $20 \text{ Hz} < \nu < 1 \text{ MHz}$. Solid composite electrolytes $\text{LiNO}_2 - \text{A}$ ($\text{A} = \text{MgO}, \gamma\text{-Al}_2\text{O}_3, \text{Fe}_2\text{O}_3, \text{CeO}_2, \text{SnO}_2, \text{SiO}_2$) have been synthesized by mixing of preliminary dehydrated components followed by sintering at 250°C . In the series of nitrite of alkaline metals $\text{Li}^+ - \text{Cs}^+$, the conductivity varies not monotonically with increasing radius of cation. The minimum conductivity is observed for KNO_2 ; however, with further increase in the radius of cation in the series, the conductivity tends to increase. The work was supported by the Russian Foundation for Basic research, grant #14-03-31442.

Keywords : conductivity, alkali nitrites, composite electrolytes, transport properties

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