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Solid Hydroxide Eutectics as Self-Organized Nanostructured Electrolytes for Small-Sized and Low- Power Electrochemical Devices at Intermediate Temperatures Range

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Abstract. Nanostructured eutectics (NaOH+KOH),(KOH+KOH.H_2O), (LiOH+NaOH), (KNH_2+$NaNH_2$) have sufficiently more higher ionic (protonic) conductivity than their “parent” individual compounds. Studying such phenomena is useful for physics of nano-materials as well as for promising technological application for synthesis and using for energy storage and conversion.

Introduction

A particular phenomenon was recently discovered, whereby self-organized microheterogeneity of a NaOH+KOH solid eutectic modifies the properties of this proton conductor and thus changes the characteristics of a related “M1|NaOH+KOH|M2” heterostructure. (M1 and M2 are different combinations of electrodes likely Pd, Ti, TiFe, Sn, Ge, C as graphite textile). The basic and applied interest in this phenomenon has related both to a high proton conductivity of the NaOH+KOH solid (!!!) eutectic (10–30 mS/cm). It was several orders of magnitude (!) higher than the conductivity of NaOH and\or KOH individual compounds at moderate temperatures (360–450 K). Moreover the electrochemical activity of such heterostructures was revealed in pioneering special study [1-4]. The much greater conductivity in the indicated temperature range and specific features of the low-frequency impedance spectrum are related to the formation of a microheterogeneous mixture of NaOH and KOH crystals in the course of self-organization accompanying solidification of the eutectic.

Important additional information on the physical nature of structural characteristics of the phase transition was obtained from an analysis of the shapes of peaks in the temperature dependence of the heat capacity of the EA samples measured in the heating and cooling regimes. According to the thermodynamic theory of a self-consistent field in application to shaped smeared first-order phase transitions, numerous fluctuations are localized in a limited volume of the “old” phase so as to form stable nuclei of the “new” phase called the elementary volumes of the transition. The peaks on the differential scanning calorimetry (DSC) curves are asymmetric, which allows one to assume the existence of at least two components characterized by different values. Using two- component fitting, these values were estimated as ~60–80 nm and ~35–40 nm. The almost two-fold difference is probably related to features of the structure of components forming the EA composition. The assignment of these components to KOH and NaOH requires additional investigation. Irrespective of the possible variants, these estimates show that the elementary transformation volumes in the region of the first-order phase transition contain up to 1000 crystal unit cells. This corresponds to a quite large domain, the further growth of which depends on the subsequent treatment of a sample. In concluding, it should be noted that investigations described above form an approach to the search for and creation of nano-heterogeneous ionic conductors employing the phenomenon of self-organization in eutectic mixtures.

The special study on proton transport in all four eutectics (i.d. includingKOH+KOH.H_2O, LiOH+NaOH, KNH_2+$NaNH_2$) will be presented and discussed from points of physics of solid electrolytes in nanoheterogeneous state as well as the properties of electrochemical devices for energy conversion and storage.

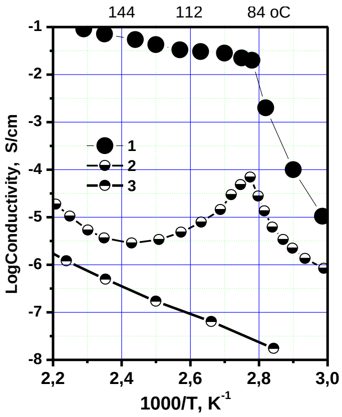

Fig.1. Self-organized eutectic NaOH-KOH as protonic conductors (3) have more higher conductivity than both parents - KOH(2) and NaOH(1) - at T>360 K. It is interesting that phase transition in individual KOH (2) remains in solid mixture

References

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