

Enhanced Ionic Conductivity of Monovalent Cation Halide (AgBr, AgI, LiI) in Mesoporous Alumina

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Abstract

Monovalent ionic conductors (AgI, AgBr and LiI) impregnated in mesoporous alumina were studied in the context of heterogeneous ionic conductors. The crystalline structure and local structure of the ionic conductors were investigated by XRD, DSC and NMR. Enhancement of ionic conductivity strongly depended on the ionic conductors, which was attributed to local structure as well as space charge layer.

Introduction

Enhanced ionic conductivity of ionic conductors by heterogeneous doping of insulating materials (e.g., Al₂O₃, SiO₂) has been qualitatively explained by space charge layer (SCL) model proposed by Maier.^[1] In this context, we fabricated composite ionic conductors of monovalent cationic conductors (AgI, AgBr, and LiI) and mesoporous alumina (MPA) to realize large interface area, interconnected ionic conductive path, and nanosized ionic conductors as schematically shown in Fig. 1. In this paper, the enhancement of ionic conductivity was studied and the influence of the change of the local structure is reported.^[2]

Experimental

MPA was obtained from Sigma-Aldrich (MSU-X type) and used after thermal treatment at 500 °C in Ar (BET surface area: 276 m² g⁻¹, mean pore diameter: 6 nm, crystal structure: γ -Al₂O₃). AgI was impregnated into the pores of by heating the mixture of MPA and AgI in air at 600 °C for 20 h. Nanocomposites of AgI:MPA was characterized by XRD, DSC, N₂ adsorption/desorption isotherms and TEM. Ionic conductivity was obtained by a.c. impedance spectra recorded in Ar from room temperature to 300 °C.

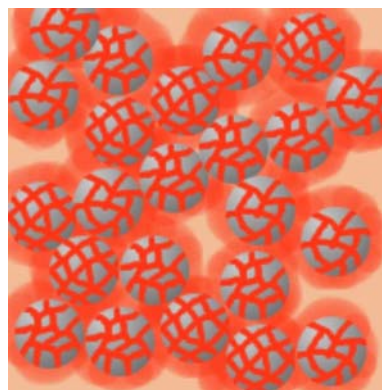


Figure 1. Schematic image of ionic conductor impregnated in mesoporous alumina.

Results and Discussions

The impregnation of ionic conductors in pores of MPA was confirmed by TEM, and indicated by geometrical density, DSC and N_2 adsorption isotherms. From XRD and DSC measurements, it is supposed that AgI in nanopores exhibits stacking disorder of tetrahedral AgI layers, and LiI in nanopores is amorphous. NMR also revealed that Ag^+ in AgI:MPA and Li^+ in LiI:MPA are in a different state from those in pristine materials.

Ionic conductivity was enhanced for all ionic conductors by being impregnated into alumina pores as shown in Fig. 2. For AgBr:MPA, the enhancement of ionic conductivity was proportional to the surface area of alumina and the activation energy was as much as the pristine AgBr, which suggests that the enhancement of the ionic conductivity is well explained by the SCL model. AgI:MPA exhibited higher ionic conductivity than expected from space charge and different activation energy. The enhancement of ionic conductivity is attributed to the structural change. In the case of LiI:MPA, the enhancement of the ionic conductivity was lower than expected from the SCL model and the activation energy for LiI:MPA is as much as that for pristine LiI. It is supposed that amorphous LiI in nanopores that is indicated by XRD and NMR does not contribute to the ionic conduction while ionic conductivity of LiI on the external surface of MPA is enhanced by the SCL mechanism.

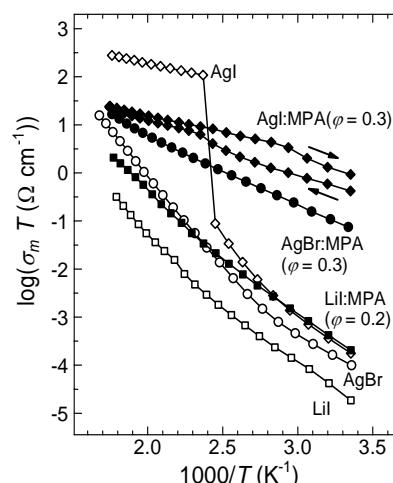


Figure 2. Temperature dependence of conductivities of AgBr:MPA, AgI:MPA and LiI:MPA composites (closed symbols). Conductivities of pristine ionic conductors are also plotted (open symbols).

Conclusion

The ionic conductivity of the heterogenous ionic conductors AgI:MPA, AgBr:MPA, and LiI:MPA was investigated. The enhancement of the ionic conductivity depended on the sort of the ionic conductors: AgBr exhibited the ionic conductivity enhancement that was well explained by the SCL model. The ionic conductivity of AgI:MPA was higher than expected from the SCL model, which was accounted for by the structural change of the AgI. LiI impregnated in nanopores was amorphous that are not an ionic conductor.

Reference

- [1] J. Maier; *Prog. Solid State Chem.*, **23** (1995) 171.
- [2] H. Yamada, A.J. Bhattacharyya, J. Maier; *Adv. Funct. Mater.*, **16** (2005) 525.