

Nanocrystalline versus Microcrystalline $\text{Li}_2\text{O}:\text{B}_2\text{O}_3$ Composites: Anomalous Ionic Conductivities and Percolation Theory

Sylvio Indris,¹ Paul Heitjans,¹ H. Eduardo Roman,^{2,3} and Armin Bunde³

¹*Institut für Physikalische Chemie und Elektrochemie, Universität Hannover, Callinstraße 3-3A, 30167 Hannover, Germany*

²*I.N.F.N., Sezione di Milano, Via Celoria 16, 20133 Milano, Italy*

³*Institut für Theoretische Physik III, Justus-Liebig-Universität Giessen, Heinrich-Buff-Ring 16, 35392 Giessen, Germany*

(Received 16 August 1999)

We study ionic transport in nano- and microcrystalline $(1-x)\text{Li}_2\text{O}:x\text{B}_2\text{O}_3$ composites using standard impedance spectroscopy. In the nanocrystalline samples (average grain size of about 20 nm), the ionic conductivity σ_{dc} increases with increasing content x of B_2O_3 up to a maximum at $x \approx 0.5$. Above $x \approx 0.92$, σ_{dc} vanishes. By contrast, in the microcrystalline samples (grain size about $10 \mu\text{m}$), σ_{dc} decreases monotonically with x and vanishes above $x \approx 0.55$. We can explain this strikingly different behavior by a percolation model that assumes an enhanced conductivity at the interfaces between insulating and conducting phases in both materials and explicitly takes into account the different grain sizes.

PACS numbers: 61.82.Rx, 05.40.-a, 05.70.Jk, 66.30.Dn

Nanocrystalline materials are polycrystals with a grain size of a few nanometers [1]. In recent years nanocrystalline ceramics have attracted considerable attention due to their broad potential applications as advanced materials with controlled chemical, mechanical, electrical, magnetic, and optical properties [1,2]. Many of the properties can be attributed to the enhanced fraction of grain boundaries in these materials: The fractions of atoms being located in these boundaries can be up to 50% [2].

By reducing the grain size, the conductivity of some ionic conductors could be raised, for example in nanocrystalline CaF_2 [3]. However, the experiments were done so far only for nanocrystalline monophase materials. Grain boundaries with an enhanced ionic conductivity are known to occur also in microcrystalline diphase systems, where an insulator is added to a poorly conducting material [4]. These systems are called dispersed ionic conductors (DIC). The enhanced ionic conductivity may have different origins (see, e.g., [5–7]) and can lead to a pronounced maximum in the total ionic conductivity as a function of the insulator content [4–10].

These dispersed ionic conductors are prepared by melting the ionic conductor and adding the insulator (mainly Al_2O_3) to it. In this paper, we study diphase micro- and nanocrystalline materials, which are prepared by mixing the two different powders and pressing them together to a pellet, combining both aspects of nanocrystalline as well as of DIC materials. This enables us to modify the grain size of the ionic conductor as well as of the insulator (i) independently, and (ii) over 3 orders of magnitude (from micrometers to nanometers). We find that in the nanocrystalline systems the conductivity can be increased strongly by adding the insulator, while in the microcrystalline mixtures the conductivity decreases monotonically. The activation energy remains almost constant in both cases. We can explain the surprising result by a continuum percolation model that explicitly takes into account the effect of the different grain sizes on the ionic conductivity.

The source materials of our samples were Li_2O (99.5%, Johnson Matthey) and B_2O_3 (99.9%, Johnson Matthey) powders, where the grains have an average diameter of about $10 \mu\text{m}$. In the composite samples, the former represents the conductor (Li being the charge carrier) and the latter the insulator. The microcrystalline samples were prepared from the original powders by carefully mixing and then compressing them under 1 GPa uniaxial pressure at room temperature (300 K). The nanocrystalline powders were produced in a high energy ball mill (Spex 8000) by milling the microcrystalline powders for 16 h (Li_2O) and 8 h (B_2O_3). The line broadening of x-ray diffraction (XRD) patterns (Fig. 1) indicates that the milling results in an average grain size of about 20 nm for both materials. To achieve a good mixing of the nanocrystalline powders, the two materials were milled together in the ball mill for 15 min. The resulting nanocrystalline powders were then

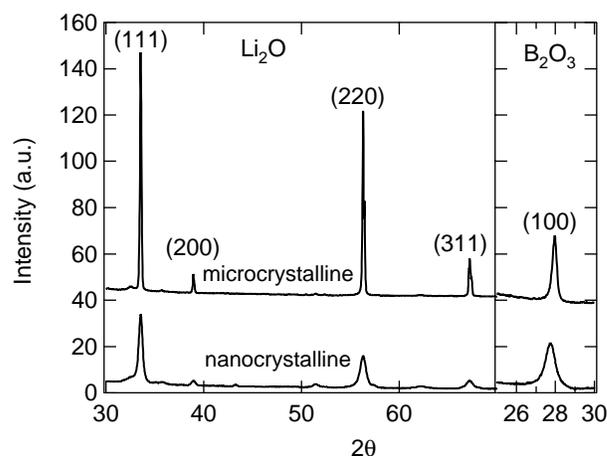


FIG. 1. XRD diffraction patterns of pure Li_2O on the left side and B_2O_3 on the right side. The upper curves belong to the microcrystalline materials and the lower curves show the line broadening in the nanocrystalline materials due to the reduced grain size (angle 2θ refers to $\text{Cu } K\alpha$ radiation).

pressed to pellets like the microcrystalline samples. In all cases the electrical contacts were pressed from platinum powder. The cylindrical samples typically have a diameter of 8 mm and a thickness of about 2 mm. All preparation steps were performed in argon atmosphere.

Experimental difficulties arise from the nature of the materials: Li_2O is unstable in air, the nanocrystalline materials tend to anneal (leading, e.g., to grain growth), and the two substances Li_2O and B_2O_3 react together, yielding lithium borate with various stoichiometries, at higher temperatures. For these reasons, we have performed differential thermal analysis (DTA), XRD, and annealing experiments to detect a suitable temperature range for our impedance spectroscopy studies. The results show that below a temperature of 500 K no irreversible changes occur in the samples. Besides these difficulties, the advantage of our samples is that the diffusivity of Li can be examined directly using standard NMR techniques [11,12].

The impedance measurements were carried out in an argon atmosphere using a standard HP 4192A impedance analyzer in the frequency range from 5 Hz to 13 MHz, for temperatures in the range from 300 to 500 K. Figure 2 shows typical conductivity spectra of the measured samples, here, as an example, for pure nanocrystalline Li_2O . At low frequencies, all samples show a very distinct plateau which represents the dc conductivity of the material, σ_{dc} . At higher frequencies, the spectra exhibit a strong dispersion due to the restricted motion of the Li ions in the disordered structures. From the data, we can extract the activation energy E_{act} , defined by the Arrhenius behavior $\sigma_{\text{dc}} \cong \sigma^{(0)} \exp(-\beta E_{\text{act}})$, with $\beta = 1/k_{\text{B}}T$, which turns out to scatter around 1 eV, $E_{\text{act}} = (1.0 \pm 0.2)$ eV, for all x .

Although the activation energy remains almost constant, the ionic conductivity of the nanocrystalline samples rises strongly as the content x of B_2O_3 is increased. As is shown in Fig. 3 for three different temperatures, the conductivity, plotted versus insulator concentration p [13], reaches a

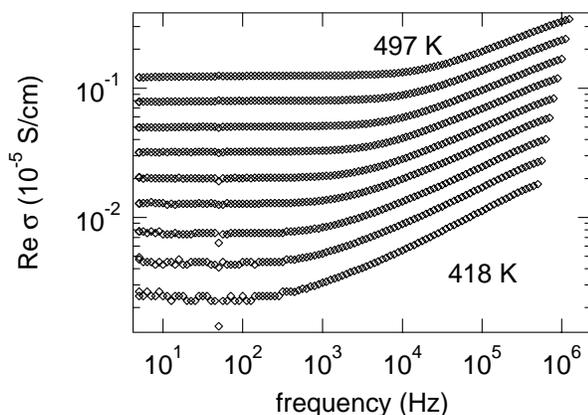


FIG. 2. Conductivity spectra of pure nanocrystalline Li_2O in the temperature range from 418 to 497 K showing the dc plateau and the dispersive region at higher frequencies.

maximum at $x \approx 0.5$ ($p \approx 0.7$) and decreases with further increasing B_2O_3 content. Above $x = 0.92$ ($p \approx 0.96$), the dc conductivity becomes smaller than 10^{-9} S/cm and cannot be detected by our impedance apparatus. It is remarkable that, contrary to the conventional DICs, a tiny volume fraction (≈ 0.04) of the ionic conductor is sufficient to obtain a dc conductivity that is higher than that of the pure ionic conductor. The figure also shows that the behavior of the nanocrystalline samples differs drastically from the behavior of the microcrystalline samples, where the conductivity decreases monotonically with increasing B_2O_3 content. In this case, the decrease of the conductivity is much faster than the decrease of the charge carrier concentration, suggesting that the mobility of lithium ions is decreased by adding the insulator. Above $x = 0.55$ ($p \approx 0.7$), the dc conductivity becomes smaller than 10^{-9} S/cm, for all temperatures considered. The differences between micro- and nanocrystalline composite materials are quite remarkable in view of the fact that for micro- and nanocrystalline pure Li_2O materials the conductivities are approximately equal [14].

To explain these surprising experimental observations, we assume that, similarly to dispersed ionic conductors, (i) B_2O_3 acts as an insulator for the lithium ions, (ii) the mobility of the Li ions along the diphas boundaries between ionic conductor and B_2O_3 is larger than in the bulk lithium oxide, and (iii) the thickness λ of this highly conducting interface is independent of the grain size.

The experimental results shown in Fig. 3 strongly suggest the existence of two different percolation thresholds for the conduction paths, $p_c \approx 0.7$ for microcrystalline samples and $p_c \approx 0.96$ for nanocrystalline ones, above which the dc conductivity of the composite vanishes. These different thresholds can be understood by simple geometrical arguments. In the case of microcrystalline samples, the highly conducting region at the interface between B_2O_3 and Li_2O grains does not play a role since its width is negligible compared to the grain sizes, and conducting paths can open up only when two Li_2O grains get in direct contact to each other. Qualitatively, we can expect a percolating conducting path when the Li_2O concentration gets larger than 0.3 (i.e., $p = 0.7$), which is between the percolation threshold of spheres in a three-dimensional continuum percolation model (≈ 0.28 [15]) and the percolation threshold of sites in the simple cubic lattice (≈ 0.31 [15]). In the case of nanocrystalline samples, however, the situation is quite different since the width of the highly conducting interface becomes comparable to the grain sizes. In this case, the highly conducting region can act as a bridge between two Li_2O grains not in direct contact to each other, opening up additional paths for Li ions. A percolating conducting path can be disrupted at much higher concentrations of B_2O_3 than for micrometer sized grains. Again, we expect the critical value to be between that of site percolation ($p_c \approx 0.90$) and overlapping spheres ($p_c \approx 0.97$) [15].

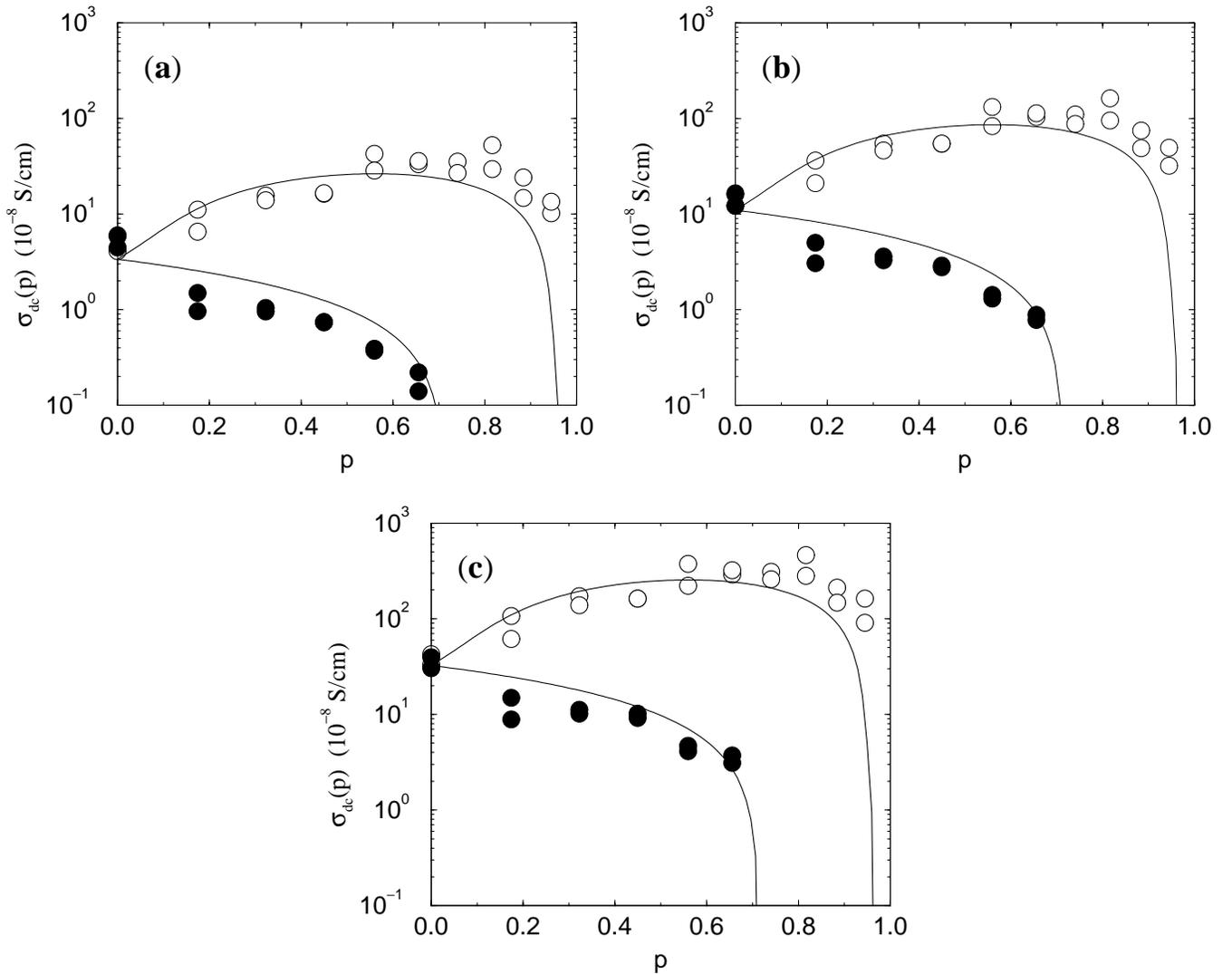


FIG. 3. Plot of the dc conductivities of the micro- and nanocrystalline composites vs insulator volume fraction p at three different temperatures: (a) $T = 433$ K, (b) $T = 453$ K, and (c) $T = 473$ K. The conductivity of the nanocrystalline samples (open circles) shows an enhancement up to a maximum at $p \approx 0.7$ ($x \approx 0.5$), while the conductivity of the microcrystalline composites (full circles) decreases monotonically. The lines show the dc conductivities obtained from the continuum percolation model discussed in the text.

To describe the dependence of the dc conductivity of $\text{Li}_2\text{O}:\text{B}_2\text{O}_3$ composites, $\sigma_{\text{dc}}(p)$, on the insulator concentration p , we employ a continuum percolation model similar to that studied earlier for dispersed ionic conductors [10]. In this model, the size of dispersed particles is considered explicitly and the conductivity is estimated by means of the effective medium approximation (EMA), yielding an analytical expression for $\sigma_{\text{dc}}(p)$. Denoting by $P_0(p)$, $P_A(p)$, and $P_B(p)$, the concentrations of the insulator, the highly conducting diphas boundaries, and the ionic conductor, respectively, $\sigma_{\text{dc}}(p)$ is given within EMA by

$$\sigma_{\text{dc}}(p) = \sigma_B \frac{1}{z - 2} \times [-A + (A^2 + 2\tau[z - 2 - zP_0])^{1/2}], \quad (1)$$

where $A = \tau(1 - zP_A/2) + (1 - zP_B/2)$, z is a parameter determining the percolation threshold p_c at which $\sigma_{\text{dc}} = 0$, and $\tau = \sigma_A/\sigma_B$ is the enhancement factor, defined as the ratio between the conductivities of the highly conducting interface and of pure Li_2O , respectively. It is natural to assume, as suggested by the experiments, that both σ_A and σ_B are thermally activated, i.e., $\sigma_A = \sigma_A^{(0)} \exp(-\beta E_A)$ and $\sigma_B = \sigma_B^{(0)} \exp(-\beta E_B)$, where E_A and E_B denote the corresponding activation energies.

In the present model, the concentrations of the three components are given by $P_0(p) = p$, $P_B(p) = (1 - p)^\eta$, and $P_A(p) = 1 - p - P_B(p)$, with

$$\eta = \frac{R + \lambda}{R}, \quad (2)$$

where R is the radius of the particles ($R \approx 10$ nm for the nanoparticles and $R \approx 5 \mu\text{m}$ for the microparticles) and λ is typically between 0.5 and 1 nm [2]. According to Eq. (1), the percolation threshold for the disruption of conducting paths, p_c , is given by $p_c = (z - 2)/z$. Thus, from our previous discussion, we expect that for nanocrystalline samples, $p_c \approx 0.97$, obtaining $z_{\text{nano}} = 59$, while in the microcrystalline case $p_c \approx 0.70$ and $z_{\text{micro}} = 7$.

The remaining parameters, except for the value of the interface conductivity $\sigma_A^{(0)}$, can be easily estimated from the measurements of σ_{dc} for pure Li_2O , yielding $E_B \approx 1$ eV and $\sigma_B^{(0)} = 1.5 \times 10^4$ S/cm. Further, we assume that $E_A = 1$ eV, as suggested by the Arrhenius behavior of $\sigma_{\text{dc}}(p)$, and take $R = 10$ nm for the nanoparticles, $R = 5 \mu\text{m}$ for the microparticles, and $\lambda = 1$ nm for the width of the highly conducting region.

The theoretical results, obtained for the reasonable choice $\sigma_A^{(0)} = 1.5 \times 10^6$ S/cm, are displayed in Fig. 3, where they are compared with the experimental data at the three different temperatures considered. The agreement between experimental and theoretical results is remarkably good in view of the simplicity of the model employed. The choice of $\sigma_A^{(0)}$ depends on the value for E_A . For slightly smaller values of E_A , considerably smaller values of $\sigma_A^{(0)}/\sigma_B^{(0)}$ (e.g., $\sigma_A^{(0)}/\sigma_B^{(0)} \approx 10$ for $E_A = 0.9$ eV) are needed to obtain similarly good agreement with the experimental data.

In summary, we have presented measurements of the ionic conductivity of micro- and nanocrystalline $\text{Li}_2\text{O}:\text{B}_2\text{O}_3$ composites. We found that the ionic conductivity depends drastically on the grain size of both components. For microcrystalline samples, the conductivity decreases monotonically with the B_2O_3 content, while for the nanocrystalline samples, the conductivity shows a maximum at about 50% of B_2O_3 content. In both cases, the conductivity seems to vanish above certain

thresholds. We can explain this striking behavior by a percolation model that takes into account the different sizes of the grains and the enhanced conductivity at the interface between conducting and insulating components. We expect that similar effects will show up also in other two-component composites suggesting a rather generic behavior for this type of heterogeneous materials.

We are grateful to the Deutsche Forschungsgemeinschaft for financial support.

-
- [1] H. Gleiter, *Prog. Mater. Science* **33**, 223 (1989).
 - [2] R. W. Siegel, *Encycl. Appl. Phys.* **11**, 173 (1994).
 - [3] W. Puin and P. Heitjans, *Nanostruct. Mater.* **6**, 885 (1995).
 - [4] C. C. Liang, *J. Electrochem. Soc.* **120**, 1289 (1973).
 - [5] J. Maier, *Ber. Bunsen-Ges. Phys. Chem.* **88**, 1057 (1984).
 - [6] N. J. Dudney, *Annu. Rev. Mater. Sci.* **19**, 103 (1989).
 - [7] J. Maier, *Prog. Solid State Chem.* **23**, 171 (1995).
 - [8] A. Bunde, W. Dieterich, and H. E. Roman, *Phys. Rev. Lett.* **55**, 5 (1985).
 - [9] H. E. Roman, A. Bunde, and W. Dieterich, *Phys. Rev. B* **34**, 3439 (1986).
 - [10] H. E. Roman, *J. Phys. Condensed Matter* **2**, 3909 (1990).
 - [11] D. Bork and P. Heitjans, *J. Phys. Chem. B* **102**, 7303 (1998).
 - [12] P. Heitjans and A. Schirmer, in *Diffusion in Condensed Matter*, edited by J. Kärger, P. Heitjans, and R. Haberlandt (Vieweg, Braunschweig/Wiesbaden, 1998).
 - [13] The volume fraction p is simply related to the insulator content x by $p = \alpha x / (\alpha x - x + 1)$, where $\alpha = V_{\text{mol}}(\text{B}_2\text{O}_3) / V_{\text{mol}}(\text{Li}_2\text{O}) \approx 1.91$ is the ratio between the mole volumes.
 - [14] This is in contrast to, e.g., CaF_2 , where the increased density of grain boundaries leads to an enhanced conductivity for nanocrystalline material.
 - [15] A. Bunde and S. Havlin, in *Fractals and Disordered Systems*, edited by A. Bunde and S. Havlin (Springer, Berlin, 1996).