Journal of the European Ceramic Society 21 (2001) 1759–1762

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Determination of the local electrical properties in ceramic materials gained by microcontact impedance spectroscopy

A. Sever Škapin [a,b,*], S. Pejovnik [a,c], J. Jamnik [a]

[a] National Institute of Chemistry, Hajdrihova 19, Ljubljana, Slovenia
[b] Slovenian National Building and Civil Engineering Institute, Dimičeva 12, Ljubljana, Slovenia
[c] Faculty of Chemistry and Chemical Technology, University of Ljubljana, Aškrčeva 5, Ljubljana, Slovenia

Received 4 September 2000; received in revised form 23 October 2000; accepted 21 December 2000

Abstract

We used microcontact impedance spectroscopy with spatial resolution of about few micrometers to study the influence of microstructure on electrical conductivity of two selected ceramic materials: (I) polycrystalline AgBr with highly conductive grain boundaries and well-known bulk properties and (II) $LiMn_2O_4$–carbon black composite which is of technological importance for lithium rechargeable batteries. In the quantitative study of AgBr polycrystals we could easily separate grain conductivity from grain boundary conductance. We found that the grain conductivity followed the behavior of single crystals, while the grain boundary conductance exhibited single activation energy in the whole temperature range studied. Comparing the results obtained by micro-impedance spectroscopy with conventional impedance spectroscopy, we showed that the brick layer model relates accurately the local electrical properties to the overall sample's conductance. In the study of $LiMn_2O_4$–carbon black composite we showed that if the carbon black coating was prepared by controlled deposition from dispersion, the electronic conductivity was higher than that of the conventional composites prepared by mixing. Microcontact impedance spectroscopy shows that in the former case the distribution of the interfacial conductances (carbon black) is much narrower which explains the percolation threshold observed already at very low carbon black fractions. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Electrical conductivity; Halides; Impedance; Interfaces

1. Introduction

Electrical conductance of ceramic materials is often controlled by internal interfaces. In the simplest case (isotropic situation), these are either highly conductive or blocking. Using impedance spectroscopy,[1] blocking interfaces are relatively easy to detect: those interfaces, which appear in series with the bulk, yield an additional semicircle in the impedance plot. Highly conductive boundaries, on the other hand, represent additional current pathways being parallel to the bulk. In this case, using impedance spectroscopy solely, one cannot separate the boundary conductance from the bulk one.[1] To distinguish between these, probing of electrical conductivity with spatial resolution is needed. Several techniques are available at present. If ionic conductivity is under focus, tracer diffusion with SIMS can be used.[2] Regardless of the type of charge carriers, spatial resolution in thin films can be achieved by penetration impedance spectroscopy.[3] Here, the portion of the film probed depends on the frequency of the excitation signal. Spatial resolution is also achieved with microelectrodes. Since the electrical current density in the proximity of the "point" electrode is much higher than in the rest of the sample (it decreases with the distance from the electrode squared), only the resistivity within the proximity region determines the measured resistance,[4] R. If the sample is electrically homogeneous with conductivity σ, and the contact is hemispherical with diameter d, then $R = (\pi d \sigma)^{-1}$. We assume, in addition, that the sample is large when compared to d. Please note, that in such cases the distance between the micro- and the counter-electrode and the size of the counter electrode does not affect the measured resistance at all. Interesting situation arises if the sample is electrically inhomogeneous. Then, the measured resistance will vary with the electrode position. If

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* Corresponding author. Tel.: +386-01-4760-319; fax: +386-01-4259-244.

E-mail address: andrijana.sever@ki.si (A. Sever Škapin).

PII: S0955-2219(01)00110-8

the resistivity variations are not abrupt (resistivity does not change significantly along the distance *d*), the above Newman's formula[4] is still a good approximation. Under such circumstances the technique has a long tradition for characterization of heterogeneously doped semiconductors. Blocking grain boundaries in semiconductors (ZnO) have been investigated as well.[5] As far as the breakthrough voltage is concerned, the technique is straightforward. Calculation of the effective grain boundary resistivity, on the other hand, is much more difficult and uncertain, as finite element simulations showed.

In ionic and mixed conductors electrical transport is accompanied by the mass transport. To avoid morphological changes at the electrodes, impedance spectroscopy is used in combination with microelectrodes. Such microcontact impedance spectroscopy has been used for studies of blocking grain boundaries in Fe-doped $SrTiO_3$ polycrystals.[6] Highly conductive grain boundaries in AgCl polycrystals have been studied at room[7] and, also, at elevated temperatures.[8] In this paper we report on investigation of highly conductive grain boundaries in AgBr and on studies of conductivity percolation in composite materials for lithium batteries.

2. Grain boundary conductance in AgBr

It is well known that the effective conductivity of polycrystalline AgBr exceeds the conductivity of AgBr single crystals for up to one order of magnitude. Microcontact impedance spectroscopy allows for measurements of grain conductivity and grain boundary conductance (sheet conductance) independently. The polyctystals of AgBr were prepared according to the route described in Ref. 8. We choose this material for our model studies since the bulk properties of AgBr are well investigated[9] and since the material is relatively soft. The latter property allows for a pristine contact between the microelectrode and the sample, achieved simply by pressing the electrode on the top of the sample (see Fig. 1a, electrode imprints are visible as black spots). Resistances measured in cases in which the microelectrode was positioned on the top of a grain yield, according to Newman's equation, directly the grain conductivity σ_{bulk} (the contact diameter, $d \approx$ 2–5 μm, was estimated by means of optical microscope). The grain boundary conductance, Y_{gb}, is calculated from the measured resistance obtained with the microelectrode positioned on the top of a grain boundary. Since *d* is much greater than the grain boundary thickness, only sheet conductance is obtained (effective grain boundary conductivity times effective grain boundary thickness). In this case the Newman's equation does not hold since the sample's conductivity under the microcontact changes "abruptly" (on our scale). Thus the calculation (see Ref. 8 for details) was based on finite element simulations, as described by Fleig and Maier.[7] Fig. 1(b) and (c) shows the distribution of grain conductivities obtained at 30 different grains and the distribution of grain boundary conductances obtained at 33-grain boundaries, respectively. While the distribution of σ_{bulk} is relatively narrow, the grain boundary conductance spans over a broader range. Actually, this is expected since the grain boundary properties are influenced by several parameters (grain orientation, impurity segregation), which appear in addition to the bulk ones. On the other hand, in calculations of Y_{gb} more assumptions are made and the error is definitely much larger when compared to σ_{bulk}.

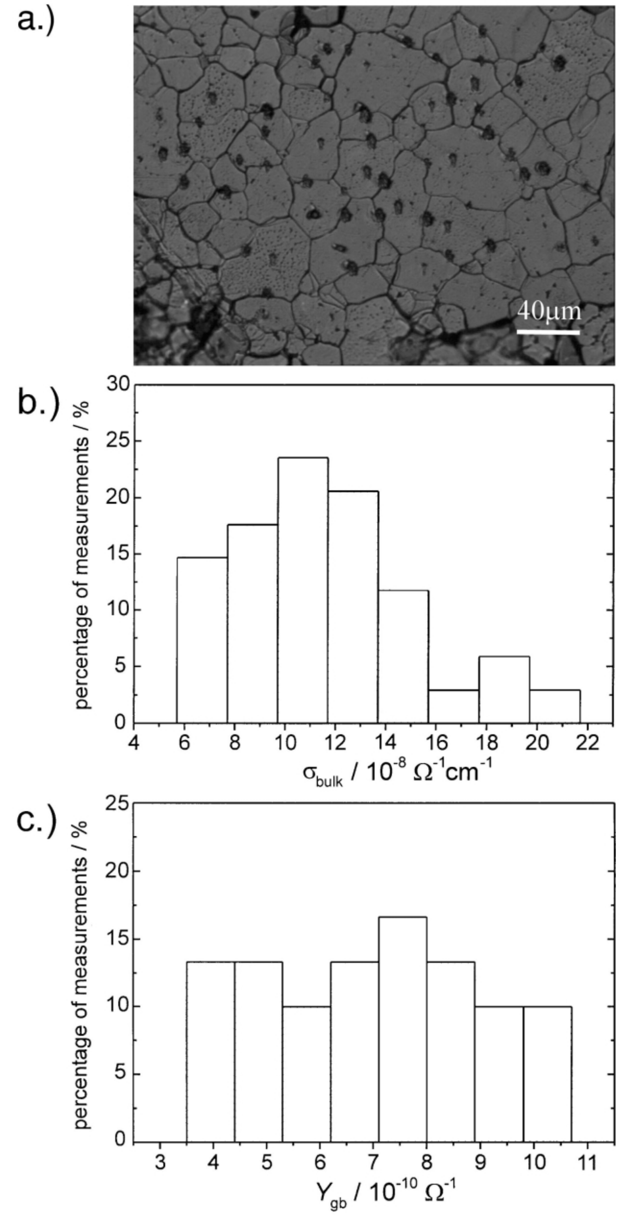

Fig. 1. (a) Micrograph of polished and etched AgBr pellet. Black spots indicate the electrode imprints. Distribution of σ_{bulk} obtained from measurements on grains is shown in (b) and the distribution of Y_{gb} calculated from the resistances probed at different grain boundaries is displayed in (c).

Fig. 2 shows the temperature dependence of conductivities. Filled circles refer to σ_{bulk}, while open circles correspond to Y_{gb}. From Fig. 2a we see that the average grain conductivity is about one order of magnitude lower than the effective conductivity of the polycrystal (solid line, obtained conventionally). On the other hand, it is still higher than the conductivity of an undoped single crystal (dashed line)[9]. Probably the purity of the single crystal exceeds that of the polycrystal grains. Additional reason might be a non-negligible surface conductivity, which is not considered by Newman's equation. Independent measurements of grain and grain boundary conductance allow for an elegant verification of the brick layer model.[1] This model, which assumes that cube-shaped grains are packed together with a translational symmetry, is the basic model used in impedance spectroscopy, but very difficult to verify conventionally. Fig. 2b compares the effective conductivity of the polycrystal, as predicted from the measured σ_{bulk} and Y_{gb} according to the brick layer model (open squares) and the effective conductivity of the polycrystal measured conventionally. The agreement is not as good as in the case of AgCl,[7,8] but, taking into account the larger measuring error in the case of AgBr, still convincing.

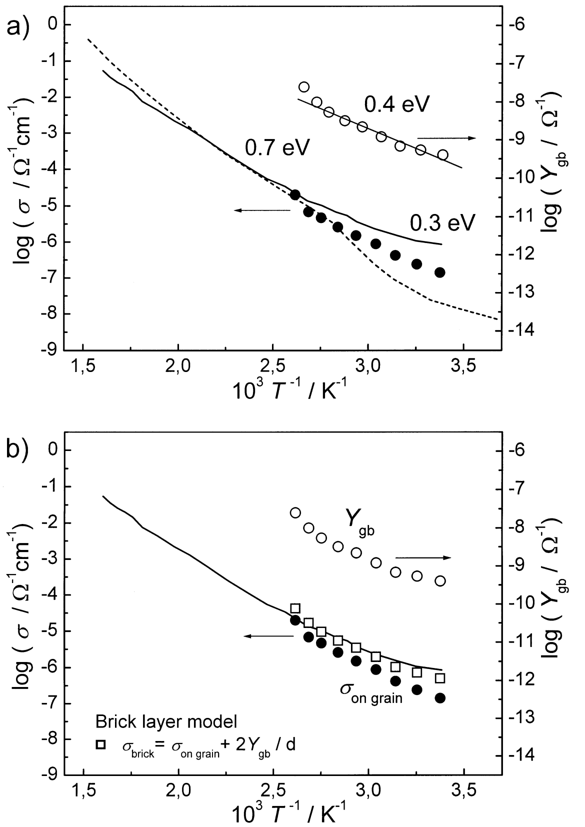

Fig. 2. Arrhenius plots of conductivity data. (a) Comparison of σ_{bulk} (filled circles) and Y_{gb} (open circles) obtained by microcontact impedance spectroscopy of a polycrystal with its macroscopic conductivity (solid line) and the conductivity of a single crystal (dashed line).[9] Numbers denote the activation energies. (b) Verification of the brick layer model.

3. Determination of conductivity of $LiMn_2O_4$–carbon black–binder composites

$LiMn_2O_4$ is a mixed conducting material used for cathodes in Li rechargeable batteries. In order to increase the electronic conductivity of the electrode, carbon black is added during the preparation. We report here on investigations of electronic conductivity in such composites. $LiMn_2O_4$–carbon black–binder composite materials were prepared according to 2 different procedures. In the first (conventional) procedure, $LiMn_2O_4$ spherical particles with an average radius of 45 μm were simply mixed with a known quantity of carbon black (average diameter 0.5 μm) and with 10 wt.% of PTFE binder and pressed into pellets. In the second procedure, invented in our laboratory, $LiMn_2O_4$ particles were first coated by carbon black and then pressed into pellets.

Average electronic conductivity of pellets (Fig. 4a) was determined by conventional impedance measurements. In the whole range of carbon black content studied (0–10 wt.%), average conductivity of the novel type of composites is better than that of the conventional ones. In other words, the percolation threshold of the novel composite appears at significantly lower carbon black content. We assumed that the reason for that

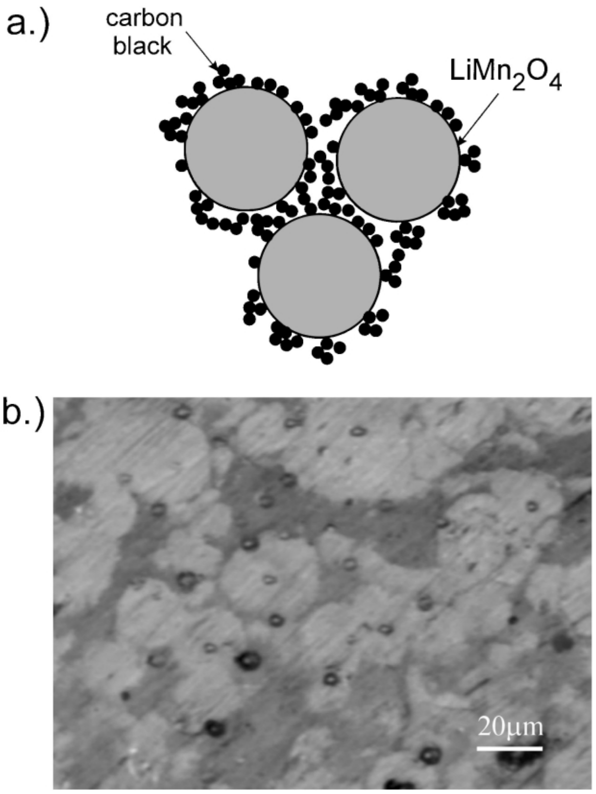

Fig. 3. (a) Sketch of $LiMn_2O_4$–carbon black composite. (b) Micrograph of the grinded composite. Black spots denote the microelectrode imprints.

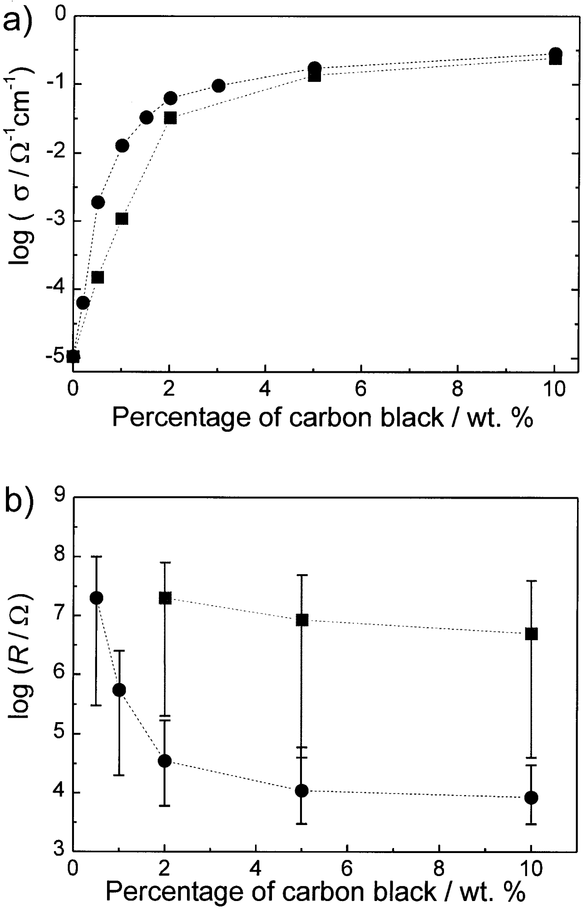

Fig. 4. (a) Macroscopic electronic conductivity of the composite as a function of carbon black content. Symbols refer to materials prepared according to novel (circles) and conventional (squares) preparation routes. Dashed lines serve as eye-guide only. (b) Resistances measured by microcontact impedance spectroscopy. Microelectrode was located at points as shown exemplarily in Fig. 3b. For each carbon black content several measurements were made. Circles and squares denote mean values; bars indicate the spans of the distributions.

was in the more uniform distribution of carbon black particles in the new composite. We checked the assumption by microcontact impedance spectroscopy. We probed the resistance locally around the $LiMnO_2$ particles (Fig. 3b), i.e. in regions, which are supposed to act as highly conductive pathways.

Results are shown in Fig. 4b. For each carbon black content a distribution of resistances was obtained. Mean values are shown by symbols, the span of the distributions is indicated by bars.

From Fig. 4b it is evident that the mean resistance along the highly conductive pathways in the new composite (circles) is much lower than in the conventional material (squares) for all fractions of carbon black. Moreover, the resistance distribution is significantly narrower (shorter bars) in the new composites. This explains straightforwardly the observed differences in percolation thresholds for both composites. Obviously, using our preparation method, carbon black does not tend to agglomerate but rather forms continuous pathways.

4. Conclusions

We showed that microcontact impedance spectroscopy is a suitable method to determine local electrical conductivity of heterogeneous materials. Two selected materials were studied:

1. Polycrystalline AgBr.
    - The resistances measured at grain boundaries were one order of magnitude lower than the resistances detected on grains (room temperature).
    - The grain conductivity corresponds to single crystal values.
    - It was confirmed that the brick layer model describes accurately the polycrystal conductivity.
2. $LiMn_2O_4$–carbon black composites.
    - We were able to trace local resistances along highly conductive pathways in two differently prepared materials and thus explained the different percolation thresholds observed conventionally.

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