

# Electrical Conductivity of Composite Solid Electrolytes Copper(I) Bromide-Titanium Dioxide

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**Abstract.** Electrical properties of two-phase mixtures of copper(I) bromide with titanium dioxide are investigated by impedance spectroscopy coupled with X-ray diffraction and scanning electron microscopy. An increase of conductivity of more than an order of magnitude with respect to pure copper(I) bromide is detected in the extrinsic domain. The results can be interpreted in the framework of the brick-layer space charge model. The importance of OH groups on the surface of titania particles as preferred sites for internal adsorption of copper ions is confirmed. A maximum effect on conductivity is revealed for about 15 mol% of second phase and related to the microstructure of the composites.

**Keywords:** ionic conductors, electrical properties, interfaces, point defects, space charges, impedance

## 1. Introduction

The elaboration of composites gives a supplementary degree of freedom for the development of advanced materials with tailored properties. In the domain of electroceramics, the main interest is the improvement of electrical and mechanical properties. The electrical properties of “physical” composites, i.e. two-phase mixtures without strong interactions at the phase boundaries, have been discussed recently from a theoretical point of view [1]. The so-called “lower bound” of conductivity corresponds to serial arrangement of the two phases and the so-called “upper bound” to a parallel layered structure. The true conductivity of the composite, which presents a complex superposition of parallel and serial pathways, is between these limits.

A different behavior must be expected if important grain or phase boundary effects are present. In that case, conductivity can be strongly increased especially if parallel contributions are important. In the case of solid ionic conductors, the large increase of conductivity at low temperatures, experimentally observed for numerous two-phase mixtures, was successfully interpreted by the space charge layer theory using a simple brick layer model of the

composites [2,3]. In this approach, the non-homogeneous distribution of point defects near interfaces at equilibrium is taken into account. Ionic defect profiles are particularly important if internal adsorption phenomena of mobile ions on the surface of second phase particles are possible. Using a brick layer model, the total conductivity  $\sigma_m$  of the composites can be calculated in good agreement with the experiment in spite of the numerous simplifications. In a pseudo-parallel geometry, the main equation is

$$\sigma_m = (1 - \varphi_A)\sigma + 3\beta\varphi_A/r_A(2\varepsilon\varepsilon_0 RTN_v/V)^{0.5}u_v \quad (1)$$

In this relation,  $\varphi_A$  and  $r_A$  are the volume fraction and the radius of second phase particles,  $\varepsilon \cdot \varepsilon_0$  the absolute permittivity,  $\sigma$  the conductivity and  $V$  the molar volume of the ionic conductor;  $u_v$  and  $N_v$  are the mobility and the molar fraction of the dominant charge carriers, assumed to be metal vacancies. A maximum enrichment of metal vacancies in the first layer adjacent to the surface of the second phase, i.e. a molar fraction  $N_v \approx 1$ , is assumed [2]. For a network of highly conductive “parallel” paths, the loss factor  $\beta$ , which takes into account that perpendicular pathways are not effective for conduction, lies between 0.2 and 0.7 and is, in a first approximation, set to 0.5 [2].

In recent papers, we presented electrical properties of composites of copper(I) bromide with alumina [4,5]. The enhanced electrical conductivities could be successfully interpreted by the space charge layer theory. In this work, we continue the study of composites of copper(I) bromide, using titanium dioxide as a second phase. In order to further clarify the mechanisms of conductivity enhancement and more generally the interfacial chemistry in composite materials, we used titanium dioxide calcined at two very different temperatures and for which analytical data and important physicochemical parameters were previously determined.

## 2. Experimental

Composite materials were prepared from pure copper(I) bromide (99.999%, Aldrich) and titanium dioxide supplied by Bayer. Two different titania samples, both obtained by the sulfate process [6], but with calcination at 300 or 1100°C respectively, were used. Chemical analysis of the two samples was comparable; main impurities (ppm) are: Na 1300, Si 385, P 270, S 200, Nb 68, Mg 21, Al 13, V 9, Fe 8, Pb 5, all other elements were below 5 ppm. The specific surface area of titanium dioxide particles (Table 1) was determined by the BET technique [7]. The gravimetric loss on ignition at 1000°C during 1 h (Table 1) was interesting to quantify volatile components, especially physisorbed or chemisorbed water.

The X-ray diffraction pattern of the product calcined at 300°C corresponded to pure metastable anatase; at 1100°C, it was totally transformed into the thermodynamically stable rutile phase. Mean grain diameters  $d$  of the products (Table 1) were determined from the width  $\varepsilon$  of the X-ray diffraction peaks using Scherrer's equation  $d = \lambda / (\varepsilon \cos \vartheta)$ , where  $\lambda$  is the

Table 1. Physical parameters of titanium dioxide samples calcined at two different temperatures ( $d_{\text{XRD}}$ : mean grain size from X-ray diffraction,  $A_{\text{BET}}$ : specific surface area from adsorption measurements according to BET technique,  $\Delta m$ : mass loss on ignition at 1000°C during 1h)

$T$ °C	Phase	$d_{\text{XRD}}$ nm	$A_{\text{BET}}$ $\text{m}^2 \text{g}^{-1}$	$\Delta m$ %
300	anatase	40	115	2.15
1100	rutile	(110)	1	0.02

wavelength of the radiation ( $\text{CuK}\alpha$ ) and  $\vartheta$  the Bragg angle. It was also confirmed that no phase transformation of anatase into rutile and no chemical reactions occurred during the impedance measurements.

The composite pellets were elaborated by a classical three-step procedure:

1. grinding of the pure powders in an agate mortar,
2. compression under 4000 bar at room temperature,
3. annealing at 350°C to eliminate transient defects produced by the preparation.

The density of the pellets was determined from sample dimensions and mass. The microstructure of the composites was investigated by optical and scanning electron microscopy after chemical etching with a methanol solution of HCl and deposition of a conducting carbon film.

Electrical impedance was measured between 25 and 350°C under an atmosphere of pure argon. An electrochemical impedance analyzer (EG&G, M6310) was used with an a.c. amplitude of 5 mV at frequencies between  $10^{-1}$  and  $10^5$  Hz. The measurement cell and details on the method of operation were previously described [8,9].

## 3. Results

A typical impedance spectrum is shown in Fig. 1. In this so-called "Nyquist plot", the imaginary part of impedance is plotted versus its real part. Frequency (indicated in logarithmic units on Fig. 1) increases from the right to the left. Parallel circuits of a resistance and a more or less distributed capacitance give a more or less ideal semi-circle, which intersection with the real axis permits to determine simply the resistance values. The electrical resistance is mainly determined by the short-circuiting "par-

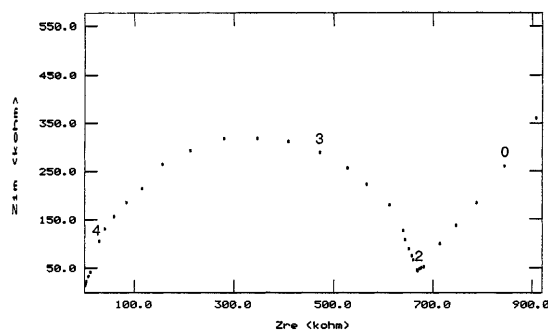


Fig. 1 impedance spectrum of a  $\text{CuBr-TiO}_2$  (15.6 mol%) composite at 19°C.

allel" pathways [10]. The corresponding constant-phase angle element is a nearly pure capacitance ( $n > 0.90$ ), slightly higher than the ideal geometrical value ( $\approx 10^{-11}$  F/cm). Arrhenius plots of conductivity are shown in Fig. 2: one directly notes an important increase of conductivity for composites prepared with titanium dioxide calcined at 300°C. On the other hand, no significant variation of conductivity is observed if titanium dioxide calcined at 1100°C is used for preparation. Activation energies are  $(100 \pm 10)$  kJ/mol in the high temperature region, slightly less than  $(45 \pm 5)$  kJ/mol in the low temperature domain. Finally, the low frequency response is a complex superposition of different contributions: impedance of the interface Cu-CuBr, blocking of current by "perpendicular" interfaces, current constrictions... It will not be discussed further.

The microstructure of composites with different molar fractions of titanium dioxide is presented in Fig. 3a and 3b. Densities of the composite samples are reported in Table 2. Porosity is relatively low for this type of material; some pores can be seen on the electron micrographs. The mean grain diameter of

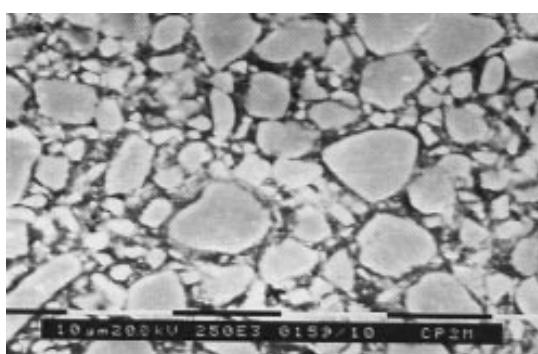
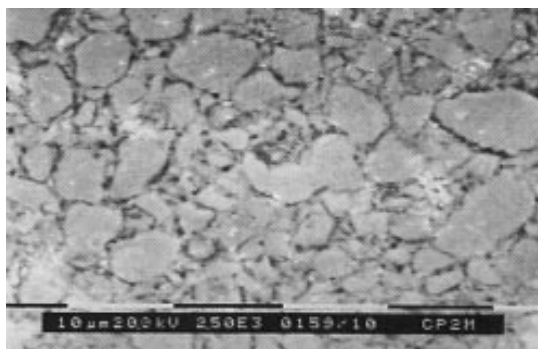


Fig. 3 electron micrographs of composite samples with a) 15.6 mol% b) 21.5 mol%  $\text{TiO}_2$ .

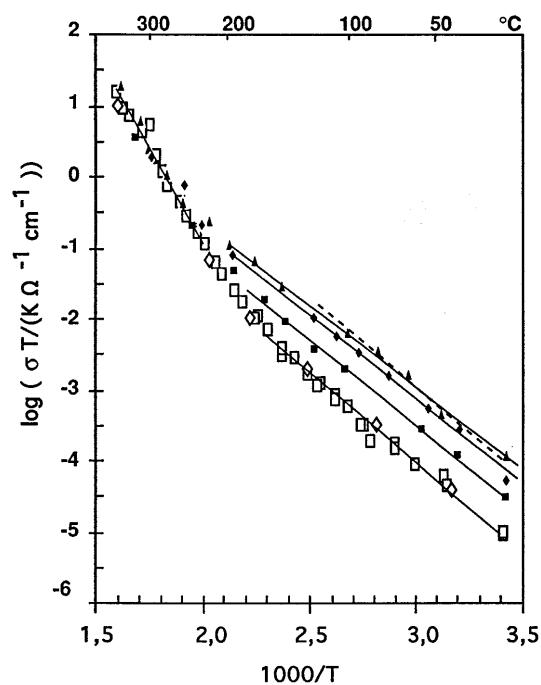


Fig. 2 Arrhenius plots of electrical conductivity: pure CuBr  $\square$ , composites prepared with 1.  $\text{TiO}_2$  calcined at 1100°C  $\diamond$ , 2.  $\text{TiO}_2$  calcined at 300°C  $\blacksquare$ ,  $\blacktriangle$ ,  $\blacklozenge$  6.7 mol%, 15.6 mol%, 21.5 mol%. Dotted line: space charge layer theory for 15.6 mol%.

Table 2. Composition and density of CuBr- $\text{TiO}_2$  two-phase mixtures

$x(\text{TiO}_2)$ mol%	$\phi(\text{TiO}_2)$ vol%	phase	exp. density $\text{g cm}^{-3}$	exp./theor. density (%)
6.7	4.8	anatase	4.99	97.8
15.6	11.1	anatase	4.79	94.9
19.8	14.7	rutile	4.77	94.9
21.5	16.0	anatase	4.73	94.4

copper(I) bromide is about 5  $\mu\text{m}$ . Titanium dioxide particles are surrounding grains of solid ionic conductor.

#### 4. Discussion

The first interesting point to note is the important difference between composite samples prepared with titania calcined at high (1100°C) or low (300°C) temperatures. With the high temperature product no significant change of conductivity compared with polycrystalline copper(I) bromide is found, whereas

with the low temperature titania distinctly higher conductivities are observed. The largest increase (more than one order of magnitude) is obtained for about 15 mol% of second phase. Addition of more titania leads to a depression of conductivity. This result can be correlated with the microstructure of the samples as shown on the electron micrographs (Fig. 3). The maximum of conductivity corresponds to a situation where grains of ionic conductor are completely enveloped by thin layers of titanium dioxide particles of about 200 nm thickness. At higher titania contents, thicker layers are formed by agglomeration and blocking effects occur, which can be unambiguously detected by depression of conductivity.

Equation (1) derived from space charge layer theory can be used to calculate the conductivity of the composite with maximum enhancement (15.6 mol%). We introduce the previously determined temperature dependence of the mobility  $u_V$  of copper vacancies [4] and the mean grain size derived from X-ray diffraction (Table 1). Grain diameters calculated from BET specific surface area under assumption of spherical grains differ by a factor of about 3, probably because the particles are porous, agglomerate and exhibit a distribution of grain sizes. Calculated conductivity values are superimposed on the experimental results in Fig. 2 (dotted line). The agreement is relatively satisfactory, emphasizing that the main features of two-phase mixtures are correctly described.

Concerning the origin of the conductance enhancement, different possibilities can be discussed.

First, a relation with the structure of the second phase (anatase or rutile) is unlikely, because the crystallographic difference between anatase and rutile is small. Pores can have two opposite effects: increase of conductivity by accelerated diffusion on internal pore surfaces and decrease of conductivity by current constriction. The latter effect is generally more important and porous samples are normally less conductive. In our case, the porosity of the samples is comparable and no correlation between conductance and porosity can be established.

An effect of impurities introduced by the second phase must also be discussed. The important difference between composites prepared with two different titanium dioxide samples is an argument against this hypothesis, because both products have identical chemical analysis. It is thus very unlikely that the conductance effect is due to "homogeneous" doping by impurities.

Actually, the surface chemistry of the second phase is of central importance. Although majority protonic conduction can be excluded (this would imply a notable change of activation energy), hydroxide groups [11] are a preferred site for internal adsorption of mobile cations, in our case  $\text{Cu}^+$  ions, on the nucleophilic surface of oxides. It is probable that the titanium dioxide sample calcined at 1100°C presents less OH groups than the product calcined at 300°C. The experimental mass loss of titania samples on ignition at 1000°C (Table 1), which is essentially due to loss of physisorbed and chemisorbed water, seems to confirm this conclusion, but the different specific surface area must also be considered. However, our conclusion is also in accordance with previous work by Maier [12], who found a similar difference for composites prepared with  $\gamma$ - or  $\alpha$ -alumina, which contain different amounts of OH groups.

A possible effect of structural defects near the phase boundaries copper halide-oxide must finally be considered. Dislocations or mechanical stresses may be present near interfaces in composites, especially if the samples are heated because thermomechanical stresses can then occur (difference in thermal expansion coefficient). Non-equilibrium defects can modify the space charge layers and electrical conductivity. Recently, Jiang and Wagner [13] presented a model in which the formation of an amorphous interlayer at the interface  $\text{CuCl-Al}_2\text{O}_3$  is postulated. Definitive conclusions on "new" conduction mechanisms can not be drawn; however, the good accordance of activation energies for composites with that of bulk  $\text{CuBr}$  is an argument for the space charge layer model, because in this equilibrium model the standard thermodynamic data of defects should be the same throughout bulk and space charge layers, without presence of a new phase (in that case a "new" conduction mechanism would be active and thus activation energies should be modified). Unfortunately, high resolution electron microscopy which is the technique most likely able to confirm or invalidate this conclusion is difficult to perform on our system, because copper(I) halides are very sensitive to all types of radiation.

## 5. Conclusion

The study of two-phase mixtures  $\text{CuBr-TiO}_2$  confirms the important enhancement of electrical conductivity

reported for other systems. Space charge layer theory is able to interpret the results. The importance of the surface groups of the second phase is emphasized. Further work on composites with titania of different grain sizes and modified surfaces is currently in progress.

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