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Crystallite size effect on the conductivity of the ultradisperse ceramics of SnO_2 and In_2O_3

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Electronic and protonic contributions to the conductivity of ultradisperse SnO_2 and In_2O_3 ceramics with a grain size of 3–40 nm have been studied by DC measurements and impedance spectroscopy.

Nanocrystalline metal oxides are used for the production of functional materials for electrochemical devices, gas sensors, solar cells and optoelectronic transducers.[1–4] These materials are usually electronic and, in some cases, ionic or mixed electronic-ionic conductors. For example, SnO_2 ceramics has the electronic type of conductivity, while hydrated tin dioxide has high protonic conductivity.[5] The relation between the conductivity components varies with the degree of hydratation[5] and depends on the crystallite size.[6] The latter factor is of great importance for ceramics with a nanometer-scaled grain size. This work was

Table 1 Characteristics of the samples and impedance spectra parameters at T = 25 °C.

Oxide	T_{anneal}/°C	d/nm	l/mm	R_{DC}/kOhm	R_b/kOhm	C_b/pF	R_c/Ohm	C_c/nF	W_a/Ohm s$^{-1/2}$
SnO_2	Dry gel	—	2.4	5880	0.54	—[a]	71	9	2.2×10^5
	300	3	1.4	1670	1.85	57	90	43	5.9×10^3
	300	3	2.3	2500	3.55	30	100	40	4.2×10^3
	500	9	2.2	1540	14.0	—[a]	3.1×10^4	0.05	—[a]
	700	22	2.2	200	13.0	—[a]	9.4×10^4	0.03	—[a]
	1000	35	2.0	15.4	1.10	180	—[a]	—[a]	—[a]
	Merck	43	2.0	0.185	0.22	780	—[a]	—[a]	—[a]
In_2O_3	300	15	2.2	14.8	2.40	50	250	60	6.7×10^2
	500	18	2.0	3.6	2.55	70	60	70	—[a]
	700	28	1.6	0.1	90	560	—[a]	—[a]	—[a]

[a] The element is not observed at the impedance spectra.

aimed to establish a correlation between the mean crystallite size and the ionic and electronic contributions to the conductivity.

Nanocrystalline samples of In_2O_3 and SnO_2 were synthesised by the precipitation of α-stannic acid and indium hydroxide gels from aqueous solutions of $SnCl_4$ and $In(NO_3)_3$, respectively, followed by drying at 100 °C. The powders of the hydrated oxides were annealed in air at T_{anneal} = 300–1000 °C for 24 h to obtain nanocrystalline systems with various grain sizes.[7] The average crystallite size d is estimated from the broadening of reflections in X-ray patterns according to the Debye–Scherrer equation (Table 1). Commercial SnO_2 (Merck) with a crystallite size of 43 nm was also used. The ceramic samples for electric measurements were pressed at 100 MPa into tablets 8 mm in diameter and thickness l = 1.4–2.4 mm. Golden contacts were deposited on the opposite planes of the tablets by vacuum evaporation.

Electrophysical measurements were performed in a cell with pressure contacts at T = 25 and 300 °C. Before the measurements at room temperature (25 °C), the samples were kept in a dry argon atmosphere for 24 h. The measurements at 300 °C were performed in dry oxygen. A Solartron 1255 impedance spectrometer integrated with a Solartron 1287 potentiostate was used to perform AC experiments. The amplitude of the reference signal was chosen in the interval 10–100 mV, the reference frequency was varied within 1–10^6 Hz. The frequency dependence of the complex impedance $Z = Z' - jZ''$ was analysed with use of the ZView2.3 software (Scribner Associates). The error of approximation parameters was about 1%. The resistance R_{DC} corresponding to the electronic component of conductivity was measured at a fixed voltage of 0.1–1 V by the polarization cell method.[5] The ionic (proton) component of the conductivity was estimated as difference between the total conductivity calculated from impedance data and the electronic component obtained from DC measurements. The contact resistance was determined from impedance hodograph in the case of AC measurements and from the data obtained for samples with different thickness in the case of DC measurements. The contact resistance value has always been substracted at the calculation of the ceramics conductivity components.

A typical view of the impedance spectra (Z' *versus* Z'' taken at room temperature) is shown in Figure 1. The appropriate equivalent circuit is given in the insert. It includes two RC circuits (high frequency R_b, C_b and low frequency one R_c, C_c) and the Warburg element $Z = (1 - j)W_a\varpi^{-1/2}$. The parameters corresponding to the equivalent circuit approximation for the samples with different crystallite sizes are given in Table 1.

The high frequency RC circuit seems to be relative to the samples volume, the low frequency circuit may belong to the contacts. This consideration is supported by the following experimental fact. Variation of the sample thickness results in modification of the high frequency circuit parameters, while the parameters of the low frequency circuit stay nearly invariable. The Warburg element corresponds to the proton diffusion. W_a value reduces and finally disappears as the T_{anneal} increases. It means that at room temperature the protonic component dominates in hydrated oxides and nanoscaled ceramics annealed at the lowest temperature. The increase of the annealing temperature results in reduction of the ionic contribution to the conductivity. The hodograph modification correlates with the estimations of the protonic (σ_i) and electronic (σ_e) contributions to the conductivity. Calculations of σ_e and σ_i values were made under the assumption that the resistance of the high frequency circuit is relative to the summary effect of eletronic and protonic conductivities. The results of the calculation are presented in Figure 2. The ionic contribution does not exceed 1% of the total conductivity if the annealing temperature is higher than 700 °C for the SnO_2 ceramics or higher than 300 °C for the In_2O_3 ceramics. At these temperatures, the Warburg element is not observed at the impedance hodographs. One more argument, pointing that the hydrated water is lost during the crystallization anneal gives thermogravimetric analysis. The electron component of the conductivity successively rises with the annealing temperature.

Impedance spectra taken at a higher temperature (300 °C) appear to be single half circles shifted along the axis of Z' (Figure 3). The equivalent circuit includes RC circuit (R_b, C_b) connected in series with a resistance R_c. The element responsible for proton diffusion was not observed. This fact may be associated with the absence of a protonic component of the conductivity at T = 300 °C. Therefore, the RC circuit appears to be relative to electronic transport only. The R_c value stays constant under the exposure in oxygen while the resistance of

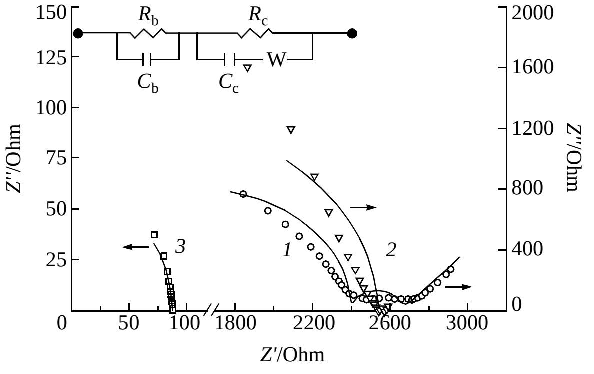

Figure 1 Impedance spectra of the In_2O_3 samples taken in dry argon at T = 25 °C: (*1*) T_{anneal} = 300 °C, (*2*) 500 °C, (*3*) 700 °C. Lines refer to calculated data.

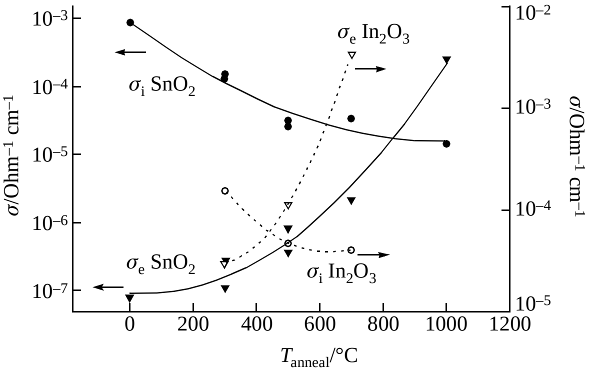

Figure 2 The dependence of the electronic (σ_e) and ionic (protonic) (σ_i) components of the conductivity on the annealing temperature of SnO_2 and In_2O_3 ceramics. T = 25 °C.

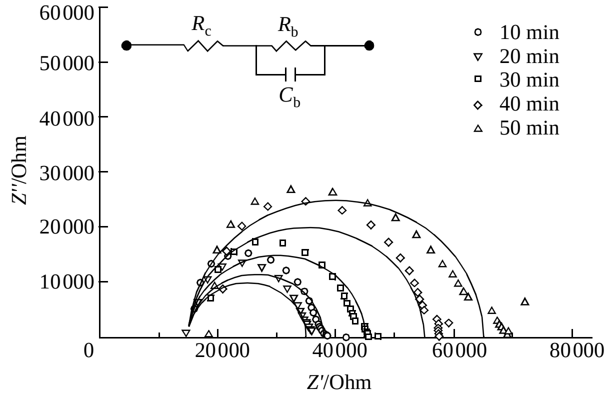

Figure 3 The typical impedance spectra of the samples at T = 300 °C in dry oxygen in view of SnO_2 ceramics annealed at 700 °C. Different symbols correspond to various exposures to an oxygen atmosphere. Lines indicate the results of the calculation.

the RC circuit rises. The resistance increase may be attributed to oxygen chemisorption or/and the reduction of the oxygen vacancy concentration in the bulk of ceramic grains. It has been suggested that R_b corresponds to the samples bulk and R_c is the contact resistance. Nevertheless, an alternative interpretation cannot be excluded: R_b is determined by the resistance of grain boundaries and R_c corresponds to the bulk resistance of the grains.

The dependence of the electronic conductivity on the crystallite size is shown in Figure 4. The data at T = 300 °C were taken after a preliminary exposure of the samples in dry oxygen for 1 h. In the case of the SnO_2 ceramics, the conductivity rises by two orders of magnitude as the crystallite size changes from 20 to 40 nm. In the interval of the crystallite sizes from 3 to 20 nm, a small change in the conductivity is observed. This may be related to the formation of a depletion layer, whose length is comparable with the crystallite size. Thus, the crystallite size becomes smaller than the Debye length. According to published data,[8–10] the depletion layer length varied within 3–20 nm for polycrystalline SnO_2 samples in the temperature range 25–400 °C. This value correlates with the results of this work. For In_2O_3 ceramics, only a monotonous conductivity variation region has been observed. It means that for the investigated range of the crystallite size the Debye length is less than the average grain size.

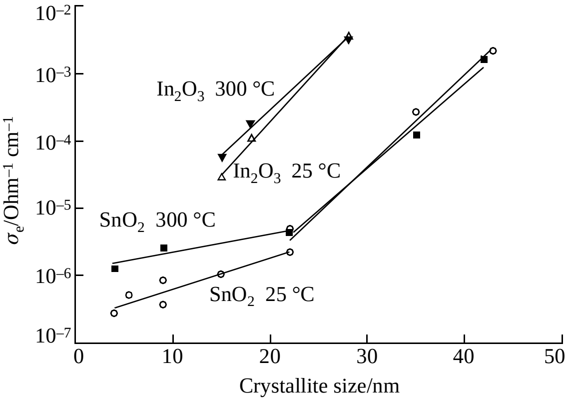

Figure 4 Dependence of the electron conductivity σ_e on the crystallite size d for SnO_2 and In_2O_3 ceramics at T = 25 °C and 300 °C.

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