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Effect of humidity on the conduction processes of Li_3VO_4

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Abstract Polycrystalline Li_3VO_4 was prepared by solid-state reaction method at 950 °C for 5 h. The X-ray diffraction pattern of the material shows the formation of single phase orthorhombic βII-type structure with no impurities. TGA measurements reveal 1.0 wt% loss in the temperature range between 25 and 120 °C attributed to humidity desorption. Impedance spectroscopy measurements were carried out on pellets of polycrystalline Li_3VO_4 at temperatures from 25 to 500 °C at 25 °C steps. An anomalous behavior of the conductivity attributed to the presence of water in the temperature range between 25 and 120 °C is observed. The activation energy values of the conduction process within the grains (bulk conductivity) and across grain boundaries were found to be 1.00 and 0.87 eV, respectively.

Introduction

The increase of demand for high energy density batteries used in applications, ranging from cellular phones and other electronic devices to electric vehicles, has caused considerable research activity to materials that could be used as lithium insertion cathodes and metallic anodes. In the category of $LiMVO_4$ materials, where M = Cu, Ni, Co, Zn, Cd, Mg, Be, and Li, much attention has been paid to $LiNiVO_4$ and $LiCoVO_4$ that have an inverse spinel structure and can be reversibly lithiated [1]. $LiNiVO_4$ is the first material with inverse spinel structure that has been patented as a potential cathode material for rechargeable lithium cells [1, 2]. $LiCuVO_4$ shows good reversibility and can be also used in rechargeable lithium batteries [1, 3, 4]. Considerable interest has been shown in systems based on Li_3VO_4 [5]. Li_3VO_4 has a versatile host structure and can form non-stoichiometric materials by doping with different cations such as Ge^{4+}, Si^{4+}, etc. [5, 6]. Song et al. [7] have shown that Li_3VO_4 synthesized by citrated sol–gel method has a greater ionic conductivity than that synthesized by solid-state reaction but they provide conductivity data only from measurements at 15 and 600 °C. As they report in [7], it has been confirmed by a DC polarization method at relatively low temperatures (<600 °C) that its electric conduction is almost purely ionic. Transport and structural properties of pure and Cr doped Li_3VO_4 have been studied in [8] for temperatures above 300 °C. A study of the phase diagram and of the ionic conductivity of the Li_2SO_4–Li_3VO_4 system has been reported in [9] but the authors give conductivity values only at 300, 500, 600, and 700 °C. Impedance spectroscopy measurements on a Li_3VO_4 single crystal have been reported in [10] but they are limited in the temperature interval 330–480 °C. Recently, we have reported an impedance analysis study of $LiCuVO_4$ [11] and of $LiNiVO_4$, $LiCoVO_4$ [12]. In the case of $LiNiVO_4$ and $LiCoVO_4$, we have shown that a reversible water absorption–desorption mechanism, in the temperature range between 25 and 150 °C is responsible for an anomalous behavior of the ionic conductivity, in this temperature range for this class of materials. We have also shown that the amount and the rate of water absorption and desorption depends on microstructure, i.e., grain size, and on air

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exposure conditions. In this article, we present the study of the conduction processes of polycrystalline Li_3VO_4 in the whole temperature range from 25 to 500 °C by means of impedance spectroscopy. It is shown that, similarly to $LiNiVO_4$ and $LiCoVO_4$, humidity strongly affects the electric behavior of Li_3VO_4 in the temperature range between room temperature and 120 °C. As far as we know, impedance studies on polycrystalline Li_3VO_4 in such a temperature range and especially the effect of humidity on its conductivity at relative low temperatures is reported for the first time.

Experimental

Li_3VO_4 was prepared by high temperature solid-state reaction [7]:

$$3Li_2CO_3 + V_2O_5 \xrightarrow{950\,^{\circ}C,\,5\,h} 2Li_3VO_4 + 3CO_2.$$

The prepared material was chemically characterized by electron microprobe (EDAX). Its morphology was studied using photographs taken by Scanning Electron Microscopy (SEM). The structure was confirmed by X-ray powder diffraction (XRD) using $CuK\alpha_1$ radiation. Thermogravimetric (TG/DTA) measurements were carried out with SETARAM SETSYS TG/DTA equipment. Impedance data were collected on cylindrical pellets ($\sim$16 mm in diameter with a thickness of 2 mm) obtained by applying pressure of 5 ton/cm^2 for 30 s in a 16 mm die. The density of the samples reached 81% of the crystallographic density. The electrodes were nickel plates. The impedance data were collected by using a HIOKI 3532-50 impedance analyzer over the frequency range from 42 Hz to 1 MHz. All measurements were carried out while applying a constant voltage of 200 mV, at which it was proved that the samples presented linear behavior in the temperature range studied. Impedance measurements were taken at frequencies from 50 Hz, 100 Hz, 1 KHz, 10 KHz, 100 KHz, and 1 MHz as the pellet was heated up to 500 °C at a rate of 50 °C/h and then cooled down to room temperature in order to check the reproducibility of the measurements and hysteresis phenomena. Finally, the impedance of the samples was measured at 100 different frequency values, logarithmically distributed in the range from 42 to 10^6 Hz, at temperatures from 25 to 500 °C, in 25 °C steps in air atmosphere. A constant pressure was applied on the electrode–sample system during the measurements. Stabilization time before each data acquisition was 1 h and the temperature variation during the measurement, at each specific temperature level, was less than 1 °C. The temperature was controlled by a Eurotherm 818P temperature controller.

Results and discussion

From electron microprobe (EDAX) a ratio of 1:4 was found for the vanadium and oxygen atoms as predicted by the chemical formula Li_3VO_4. However, the amount of Li was not measured because of its small atomic number. In Fig. 1 a SEM photograph is given showing the presence of polycrystalline powder with particles' size ranging from 5 to 50 μm. The XRD pattern of the prepared powder is given in Fig. 2. No additional lines that could be assigned to the presence of impurities were found. The XRD pattern confirms the presence of single phase orthorhombic βII-type structure (PDF #38-1247; SG $Pnm2_1$).

In Fig. 3 $\log(\sigma)$ vs. $\log(f)$ plots at different temperatures are shown. At each temperature level there is a frequency above which the conductivity is an almost linear function of frequency, which qualitatively means that it can be

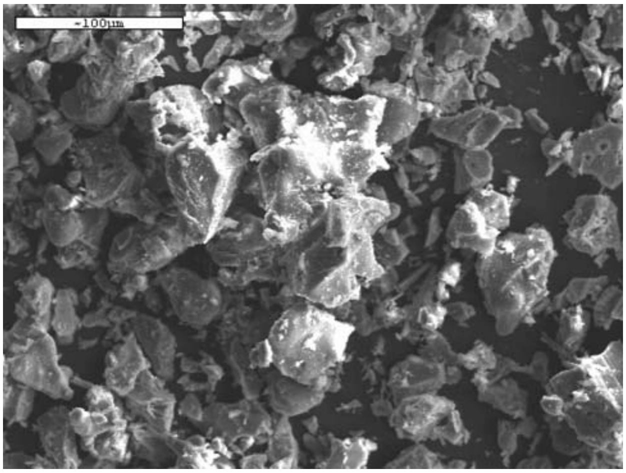

Fig. 1 SEM photograph of Li_3VO_4

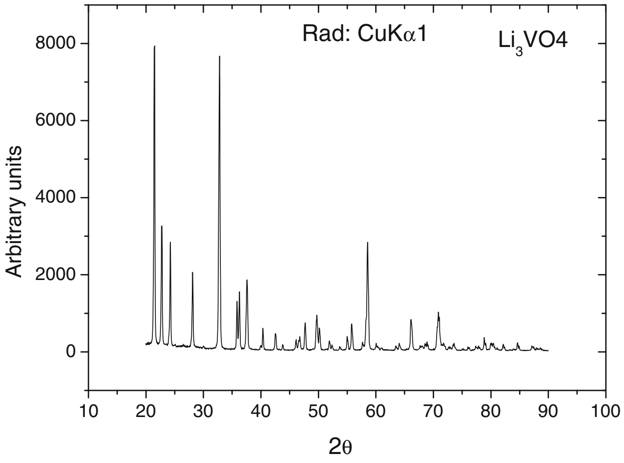

Fig. 2 XRD pattern of Li_3VO_4

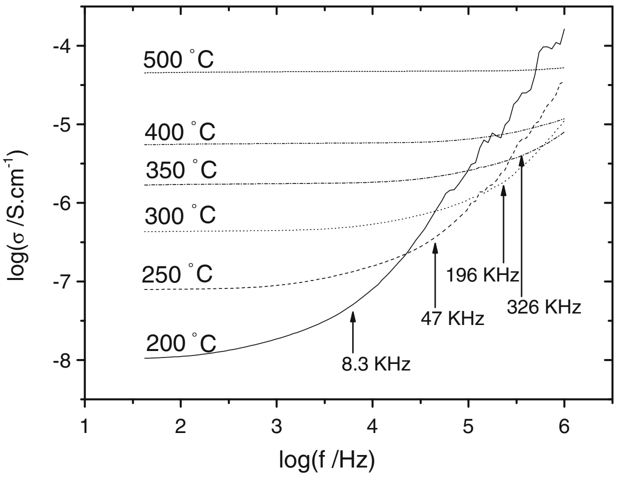

Fig. 3 Log–log plot of the real part of specific conductivity versus frequency at different temperature levels

represented by a power law expression $\sigma(f) = Af^s$, $0 < s < 1$ [13]. The hopping frequency, f_p, as arrowed in Fig. 3 corresponds to the frequency at which the conductivity dispersion commences. Selected impedance measurements taken at 30, 100, 200, 300, 400, and 500 °C are shown in Fig. 4 as an example. Using the EQUIVCRT.PAS program [14] the results of the impedance measurements were fitted and the equivalent circuits were drawn at each temperature, from room temperature to 500 °C, in 25 °C steps. Typical equivalent circuits and fitting results are given in Fig. 4. The equivalent circuit used to fit the impedance plots consists of in series (*R*//*Q*) elements, together with a capacitance of geometric origin and a *Q* element which is related to diffusion phenomena as described below. *Q* is the symbol for the constant phase elements. Every Voigt element (*R*//*Q*) of the equivalent circuit corresponds to a conductivity process. Not all processes were simultaneously present at all temperatures in the available frequency range used for the measurements (see Fig. 4). The double layer capacitance, C_{dl}, between the nickel plates and the material was calculated to be in the order of 8×10^{-13} F/cm in all the temperature range. The element, Q_{dl}, that appears in series at the fit circuits above 325 °C could be attributed to either a blocking electrode which is rather rough or to a non-blocking electrode which is smooth and exhibiting a Warburg impedance due to the slow diffusion of a reactant species to the interface [13]. Since the nickel electrodes that were used are blocking to Li^+ ions, the element Q_{dl}, could be attributed to the roughness of the interface between the electrodes and the material. One of the major causes of this 'Warburg element like behavior' is that different parts of the interface have different bulk resistance pathways to them, in some cases causing transmission-like behavior. However, since the frequency limit of our device at the low frequency region is 42 Hz, in the impedance plots of Fig. 4 only the start of a semi-circle is shown at the low frequency region. For the assignment of the different conductivity processes we followed the procedure we have applied in the case of $LiNiVO_4$ and $LiCoVO_4$ described in [12]. Using time constant arguments [15], one *RQ* circuit was assigned to bulk conductivity, σ_b, a second *RQ* circuit to across grain boundary impedance, σ_{gb}, and a third *RQ* circuit which exists at temperatures below 175 °C was assigned to along grain boundary impedance, σ_{agb}, Fig. 4. A distinguish between across grain boundary impedance and along grain boundary impedance has been used in other studies [16]. The latter presents the smallest time constant value revealing a fast process. As it is shown in Fig. 4, the factor *n* in the (*rQ*) elements of bulk and across grain boundary conductivity is close to 1 almost in the whole temperature range, representing a Constant Phase Element (CPE) with strongly capacitive behavior.

In Fig. 5 conductivities σ_b, σ_{gb}, and σ_{agb} versus temperature, calculated from the measurements as the pellet was heated up to 500 °C and then cooled down to room temperature, are shown. As the material is heated up to about 120 °C there is a reversible dramatic change in conductivity in the case of bulk, σ_b, and grain boundaries conductivity, σ_{gb}, phenomenon that is not consistent with the temperature dependence of ionic conductivity. Such a behavior has been observed in the conductivity of $LiNiVO_4$ and $LiCoVO_4$ too [12]. In those materials it has been shown that this phenomenon is explained by the presence of reversible water absorption–desorption mechanism, in the temperature range between 25 and 150 °C which is responsible for this anomalous behavior [12]. Regarding Li_3VO_4, the TG/DTA measurements showed a weight loss of about 1.0 wt%, in the temperature range from 25 to 120 °C, Fig. 6. As in the case of $LiNiVO_4$ and $LiCoVO_4$, this weight loss is attributed to a loss of absorbed humidity. A slight weight loss of 0.1% in the range from 200 to 500 °C probably reflects the loss of some small amount of intercalated water. It is characteristic that, as it is shown in Fig. 5, the change in conductivity is larger in the case of the grain boundary conductivity, σ_{gb}, which shows a decrease of four orders of magnitude. This is attributed to the fact that the absorbed water forms a humidity film surrounding the grains, strongly affecting the grain boundary conductivity. As it is noticed in [8] by Massarotti et al., the room temperature, σ value ($1.71 \times 10^{-5}\ \Omega\ cm^{-1}$) for Li_3VO_4 from solid-state synthesis [7] is surprisingly high for the insulating βII phase. According to their results, a significantly low σ value (at least six orders of magnitude) should be expected at room temperature. We believe that the value reported in [7] as well as the high σ values found in our study in the temperature interval 25–120 °C, Fig. 5, reflect the effect of humidity resulting to the dramatic

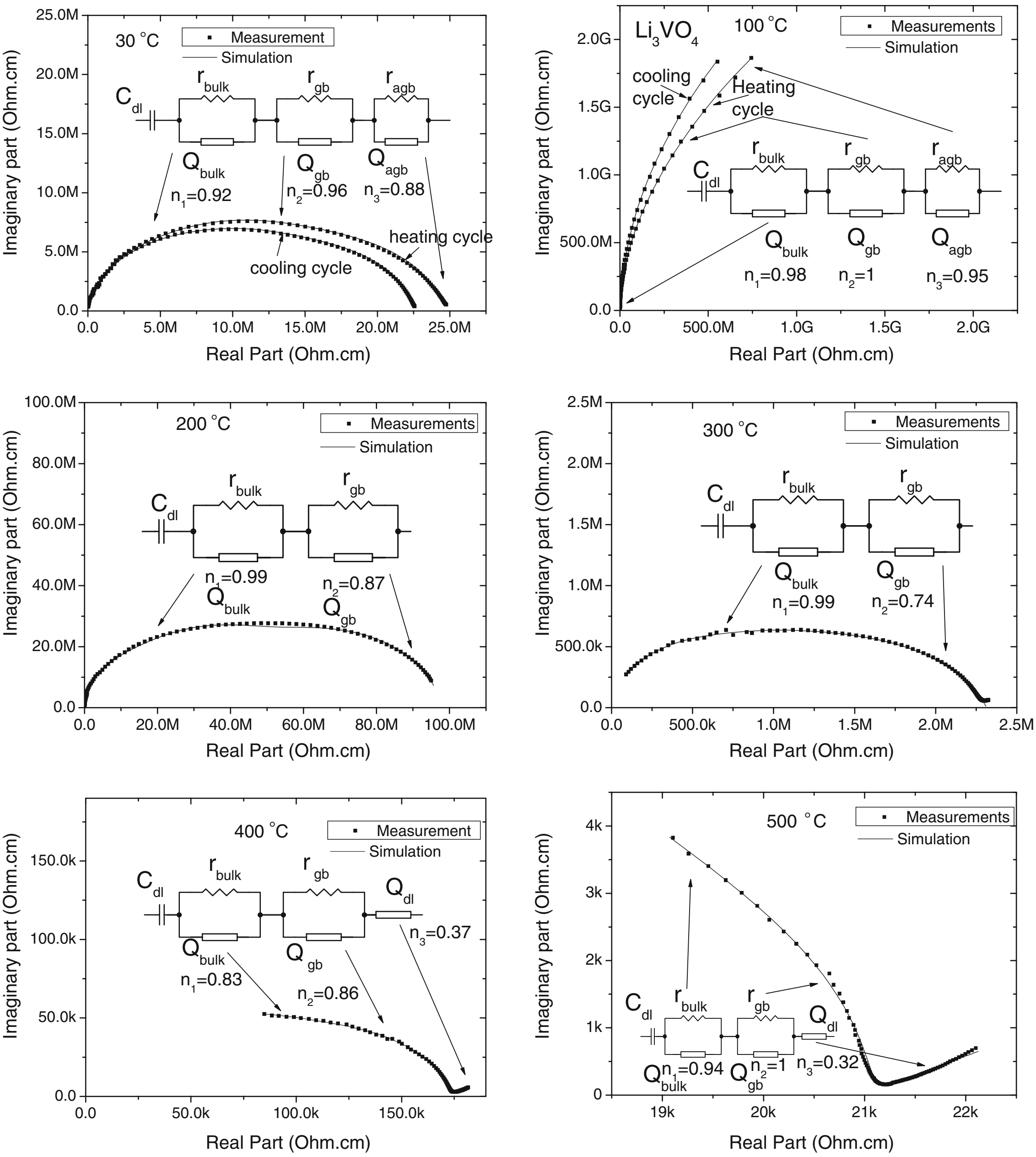

Fig. 4 Impedance spectra of Li_3VO_4 at 30, 100, 200, 300, 400, and 500 °C; equivalent circuits drawn at each of these temperatures and fitting results

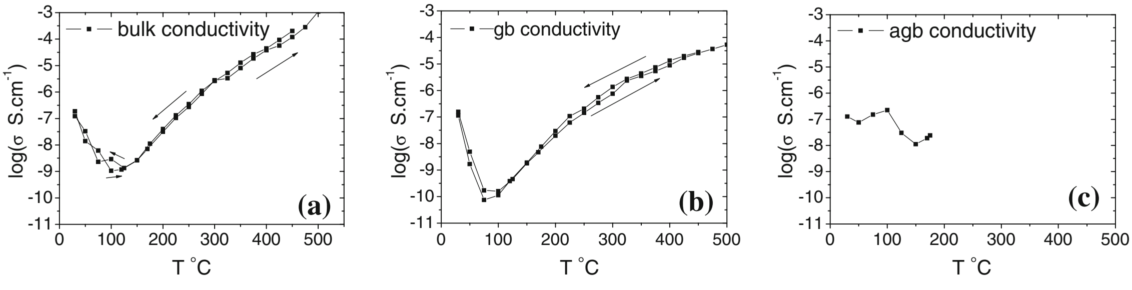

Fig. 5 Specific conductivity vs temperature plots for Li_3VO_4: **a** bulk; **b** across grain boundary, and **c** along grain boundary conductivity

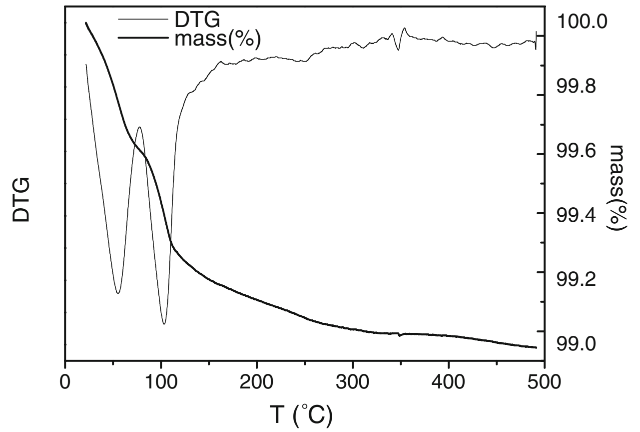

Fig. 6 Mass loss (TG/%) and derivative mass loss (DTG) measurements of Li_3VO_4

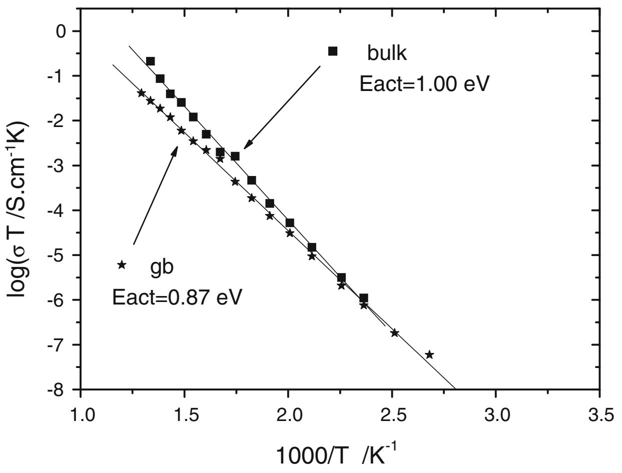

Fig. 7 Arrhenius plots of Li_3VO_4 conduction processes and their calculated activation energy values

enhancement of conductivity. It is characteristic that an extrapolation of the high temperature part of logσ vs. T bulk conductivity plot, Fig. 5a, predicts room temperature conductivity 3–4 orders of magnitude lower, as expected in [8]. The change of conductivity depends on the amount of absorbed humidity. In the case of $LiNiVO_4$ and $LiCoVO_4$ the weight loss was 0.8 and 0.5 wt% and the conductivity enhancement 2–3 and 1–2 orders of magnitude, respectively [12]. On the other hand, as it is mentioned above, 1.0 wt% loss in Li_3VO_4 results in a difference of 3–4 orders of magnitude. We believe that the third process shown in Fig. 5c is strongly related to the weight loss and uptake observed in the TG measurements and reflects a conduction mechanism along the grain boundaries due to water absorbed and desorbed during the heating and the cooling cycle at low temperatures. Our conductivity values at higher temperatures are in good agreement with the available literature values [7–10] for this temperature interval, 300–500 °C.

Seemingly, in Fig. 5 there is perfect reversibility but in fact some hysteresis between the heating and the cooling cycles is present which cannot be seen due to the use of logarithmic scale. Hysteresis can be evidenced in the impedance measurements at 30 and 100 °C during the heating and the cooling cycle shown in Fig. 4. A smaller hysteresis loop is present also at the other temperatures of Fig. 4, for which only the cooling cycle is shown. Regarding the reversibility of the dependence of the conductivity from the temperature we believe that reflects a reversible cycle of humidity absorption/desorption. In our impedance measurements we used slow cooling rate (50 °C/h) and the sample remained 1 h at each temperature before recording the measurement. Since the measurements were carried out in air there is time for the system to reabsorb even a slight amount of atmospheric humidity, which is adequate to dramatically change its conductivity. Such a process is not prevented by the presence of the electrodes since they cover only the pellet's flat surfaces. The reversible character of humidity absorption/desorption has been proven by means of cumulative TGA measurements in the case of the related $LiNiVO_4$ and $LiCoVO_4$ compounds [12].

In Fig. 7 the Arrhenius plots of the Li_3VO_4 bulk and grain boundary conduction processes have been drawn for the temperature range from 140 to 500 °C. Their linear behavior reveals conductivity processes that follow the Arrhenius expression, $\sigma = A\exp(-\Delta H_m/RT)$. As shown in Fig. 7, the bulk activation energy was calculated to be 1.00 eV and the across grain boundaries activation energy was calculated to be 0.87 eV in good agreement with previously reported values for Li_3VO_4 [7–10]. We believe that this agreement, as well as the agreement of our high temperature conductivity values with those of sintered samples [7–9] and single crystal samples [10], strengthens the validity of our equivalent circuit and the reliability of our results, despite the fact that we used pressed polycrystalline samples with 81% of the crystallographic density.

Conclusions

The conduction mechanisms involved in the electrical behavior of polycrystalline Li_3VO_4 and especially the effect of humidity were studied. The real part of the specific conductivity increases with frequency at any given temperature but at 500 °C it is the same in the whole frequency range of measurements from 42 Hz to 1 MHz. Three conductivity processes were identified, bulk, σ_b, across grain boundary, σ_{gb}, and along grain boundaries, σ_{agb}, (at low temperatures) attributed to water absorption.

Bulk and grain boundary conductivities were found to show a significant reversible change in the temperature interval 25–120 °C. This dramatic change is attributed to humidity absorption–desorption mechanism. This mechanism explains the surprisingly high room temperature conductivity values for the insulating βII phase. From the Arrhenius plots the activation energy of the bulk conductivity was calculated to be 1.00 eV and the activation energy of the across the grain boundaries conductivity was calculated to be 0.87 eV.

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