Mobility of Electronic Charge Carriers in Titanium Dioxide

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The present work reports the mobility of electronic charge carriers for well-defined TiO_2. The mobility terms were determined by using the electrical conductivity for high-purity TiO_2, including both single-crystal and polycrystalline specimens. The concentrations of electronic charge carriers were derived from defect disorder diagrams. The determined data indicate that the transport of electrons and holes occurs according to the band model and the hopping model, respectively. The differences in the electrical conductivity data between the single-crystal and polycrystalline specimens are considered within two scenarios: (1) The difference is due to the mobility terms. This scenario indicates that (i) the mobility of electrons for polycrystalline specimens is larger than that for the single crystal, and (ii) the mobility of electron holes for polycrystalline specimens is smaller than that for the single crystal. (2) The effect is due to the concentration terms. The analysis of data according to this scenario indicates that the concentration of electrons in the n-type regime for polycrystalline specimen is larger than that in the TiO_2 single crystal. The mobility and the concentration data are considered in terms of the effect of grain boundaries on the charge transport in polycrystalline TiO_2. The obtained data indicate that the charge transport in polycrystalline specimens may be modified in a controlled manner by grain boundary engineering.

Introduction

The properties of nonstoichiometric oxides, such as TiO_2, are closely related to their defect disorder. Therefore, defect-related properties, such as electrical properties, may be changed in a controlled manner by the modification of the defect disorder.

The measurements of the electrical conductivity have been commonly applied in the assessment of electrical properties, and the related defect disorder, of nonstoichiometric oxides.[1] It has been shown, knowledge of the defect disorder is essential for correct understanding of chemical properties of oxides and their reactivity. Therefore, defect chemistry may be used as a tool in addressing the challenges in the development of oxide materials with enhanced properties.

The electrical conductivity data of metal oxides may be used for the assessment of defect disorder only when they are determined at elevated temperatures, which correspond to the gas/solid equilibrium, in the gas phase of controlled oxygen activity. These data are frequently reported in terms of the effect of oxygen activity on electrical conductivity. It is known, however, that the physical meaning of the electrical conductivity data is complex and its assessment requires knowledge of both the concentration and the mobility terms. Unfortunately, the data on the mobility of electronic charge carriers are mainly reported at room temperature. On the other hand, little is known about the charge transport at elevated temperatures. TiO_2 is not an exception.

Interest in studies of the electrical properties of TiO_2 arises from its increasing importance as a photosensitive oxide semiconductor, which have potential applications as photocatalysts for water purification[2–4] and photoelectrodes for water splitting.[5–7] Its functional properties are closely related to defect disorder.[8]

Correct assessment of the electrical conductivity data in terms of defect disorder and defect-related properties requires knowledge of the mobility data for electronic charge carriers at elevated temperatures (during processing or subsequent annealing), when the specimen is in the gas/solid equilibrium.[1] The determination of these terms for TiO_2 is the aim of the present work.

Independently, there is an increasingly urgent need to assess the effect of grain boundaries on the charge transport in polycrystalline specimens. Therefore, the aim of the present work is to address this issue by the determination the mobility of electrons and holes for both TiO_2 single-crystal and polycrystalline TiO_2 of the same impurity level.

Definition of Terms and the Postulation of the Problem. Electrical conductivity is the product of the concentration and the mobility terms:

$$\sigma = e(n\mu_n + p\mu_p) \qquad (1)$$

where e is elementary charge, n and p denote the concentrations of electrons and electron holes, respectively, and μ_n and μ_p are the respective mobility terms. Therefore, the determination of the mobility term from the electrical conductivity data requires knowledge of the concentration term. These may be determined from the recently derived defect disorder diagrams for TiO_2.[9]

The recent studies of the authors on defect chemistry of TiO_2 have led to the derivation of defect disorder diagrams representing the formation of point defects in the lattice of TiO_2, including ionic defects, such as oxygen vacancies, titanium vacancies, and titanium interstitials, and electronic defects (electrons and electron holes).[9–11] Figure 1 represents a defect disorder diagram of TiO_2 at 1073 K for an arbitrary concentration of donors and acceptors, involved in the quantity A, which is defined as follows:

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$$A = 4[V_{Ti}''''] + [A'] - [D^\bullet] \tag{2}$$

where square brackets denote the concentrations, V_{Ti}'''' denotes tetravalent titanium vacancies, and A' and $D^\bullet$ denote singly ionized acceptors and donors, respectively. As seen, the diagram allows the determination of the concentration of both electrons (n) and electron holes (p).

The concentration of electronic charge carriers depends on temperature, oxygen activity, and concentration of aliovalent ions, which may be expressed by the effective concentration of acceptors, defined by eq 2.

1. Effect of Temperature. The effect of temperature on the concentration of electronic charge carriers may be considered in terms of several processes, including (i) the formation of ionic defects, (ii) ionization of the ionic defects, and (iii) ionization over the band gap.[1]

2. Effect of Oxygen Activity. The effect of $p(O_2)$ on the concentration of electronic charge carriers depends on defect disorder. Within the n–p transition regime, both charge carriers are present at comparable concentrations. Therefore, both charge carriers should be taken into account:[10,11]

$$n = n_0 p(O_2)^{-\frac{1}{4}}$$

$$p = p_0 p(O_2)^{\frac{1}{4}} \tag{3}$$

where n_0 and p_0 denote the concentration terms in standard conditions. However, in strongly reduced conditions, the concentration of electrons, which are then the predominant carriers, assumes the following dependence:[10,11]

$$n = n_0 p(O_2)^{-\frac{1}{6}} \tag{4}$$

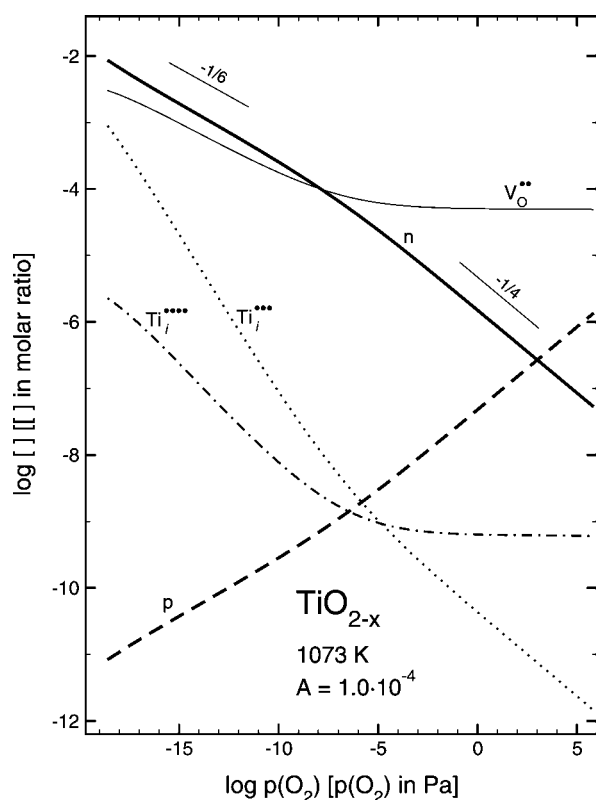***3. Effect of Aliovalent Ions.*** The effect of these ions on the concentration of electronic charge carriers may be described by a complex relationship, involving $p(O_2)$, equilibrium constants, and the effective concentration of acceptors as parameters:[9]

$$n^5 + An^4 - K_i n^3 - 2K_1 p(O_2)^{-\frac{1}{2}} n^2 - 3K_2 p(O_2)^{-1} n -$$
$$4K_3 p(O_2)^{-1} = 0 \tag{5}$$

where K_1, K_2, and K_3 are the equilibrium constants of the formation of ionic defects, including doubly ionized oxygen vacancies, trivalent titanium interstitials, and tetravalent titanium interstitials, respectively, and K_i is the intrinsic electronic equilibrium constant:

$$K_i = np \tag{6}$$

The experimental part of the present work will be preceded by a brief overview of the literature reports on electrical conductivity of TiO_2.

Brief Overview of the Literature. The electrical properties of TiO_2 have been mainly considered in terms of n-type properties. Consequently, the mobility data have been reported mainly for electrons. Recent studies have shown, however, that TiO_2 is an amphoteric semiconductor that exhibits n-type and p-type properties at low and high oxygen partial pressures, respectively.[10,11] Consequently, the electrical conductivity data must be considered in terms of both electrons and electron holes.

There is no agreement concerning the electrical conductivity data for TiO_2, which have been reported in the literature. A substantial scatter of the electrical conductivity data, which have been reported for undoped (but not pure) TiO_2, concerns both absolute values and their temperature dependence.[10,12–19] This scatter is representative of the complication in the determination of well-defined data on electrical properties at elevated temperatures. This effect indicates the following: (1) The charge transport in TiO_2, and the related electrical conductivity, should be considered in terms of both intrinsic properties, such as nonstoichiometry and the related defect disorder, and extrinsic properties, such as the content of impurities. (2) There is a need for the determination of well-defined electrical conductivity data for TiO_2 of high purity, which is equilibrated in the gas phase of controlled oxygen activity.

The reported mobility terms for TiO_2 are shown in Figure 2. These data were determined either by the studies of electrical conductivity,[13–15,20,21] of thermogravimetry,[22–24] or the measurements of the Hall effect.[15,20] The data reported by the authors[22] were determined using a number of the electrical conductivity data reported in the literature.[13–21] As seen, the data exhibit a substantial discrepancy in their absolute values and also in their temperature dependence. Consequently, there is no agreement between these data.

Blumenthal et al.[13] have evaluated the mobility terms using their own data of the effect of $p(O_2)$ on electrical conductivity and the thermogravimetric data of Kofstad[23] and Moser et al.[24] The earlier involved both the concentration and the mobility terms. The latter are determined by the concentration of ionic defects, which may be used for the evaluation of the concentration of electronic defects. The effect of $p(O_2)$ on the thermogravimetric data of Kofstad at $p(O_2) = \sim 10^{-7}$ Pa (1350–1500 K) was considered in terms of doubly ionized oxygen vacancies as the predominant defects. These data resulted in the mobility of electrons to be independent of temperature. On the other hand, the data of Moser et al.[24] determined at $p(O_2) = \sim 10^{-7}$ Pa (1373–1573 K) were considered in terms of trivalent titanium interstitials. These data resulted in the mobility of electrons that exhibits a negative temperature coefficient.

Figure 1. Defect disorder diagram for TiO_2 at 1073 K.[9]
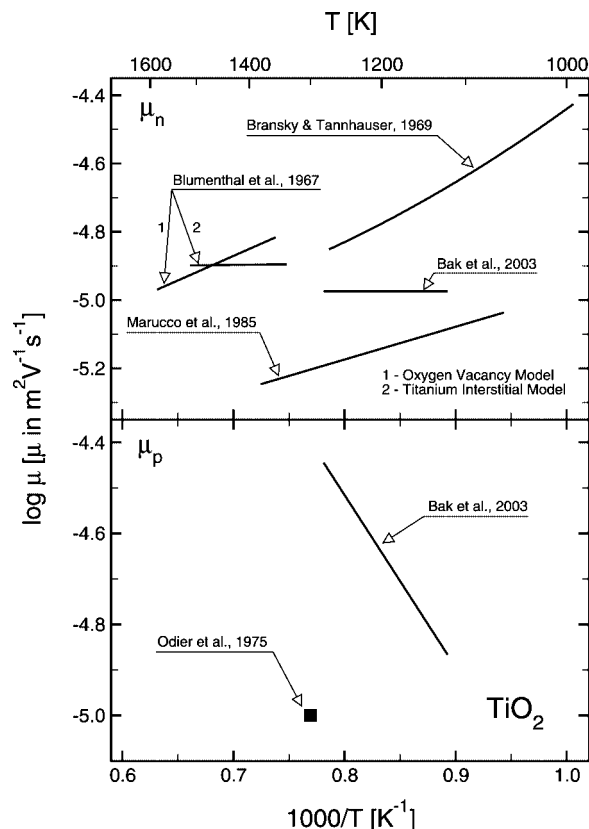
Figure 2. Arrhenius plots of the literature data on the mobility of electrons (upper part) and electron holes (lower part) in TiO$_2$ as a function of the reciprocal of temperature in the range 1000−1600 K.[13,15,20–22]

A similar experimental approach was applied by Marucco et al.[21] They determined the mobility term from the data of electrical conductivity and thermogravimetry (1073−1373 K). In the determination of the concentration of electronic charge

carriers (electrons), they assumed that the charge neutrality involves both tetravalent titanium interstitials and doubly ionized oxygen vacancies.

As seen in Figure 2, the mobility terms reported by Blumenthal et al.[13] (resulting in two sets of data) and Marucco et al.[21] are different. The difference is expected to be due to the fact that in all three cases the charge neutrality conditions assumed for the determination of the concentration of electrons were different.

Bransky and Tannhauser[20] have determined the mobility of electrons for TiO$_2$ single crystal using the measurements of Hall effect within a wide temperature range (573−1523 K). Oxygen activity in this study was imposed by the CO/CO$_2$ mixture. The Hall mobility was found to decrease with temperature and be independent of p(O$_2$).

Based on the Hall effect method, Odier et al.[15] have determined that the mobility of electron holes of undoped TiO$_2$ at 1300 K is 0.1 cm^2 V $^{-1}$ s $^{-1}$. Both Bransky and Tannhauser[20] and Marucco et al.[21] reported that the mobility of electronic charge carriers is independent of p(O$_2$).

The reported data on the effect of temperature on the mobility terms suggest that the transport of electrons and electron holes in the TiO$_2$ lattice occurs according to different mechanisms: (1) *Electrons.* While the scatter between the reported absolute values of the mobility terms is substantial, all data exhibit either no temperature dependence or a negative temperature dependence.[21] Although the reported data are consistent with the band transport mechanism, the substantial scatter indicates the need to verify these data. (2) *Electron Holes.* According to the only data on the effect of temperature on the mobility of electron holes, which were reported by Bak et al.,[22] their transport occurs according to the hopping model. These data, however, require verification.

The mobility terms determined in the present work will be based on well-defined electrical conductivity data for high-purity TiO$_2$, including both single-crystal and polycrystalline specimens. These data will also be used to assess the effect of grain
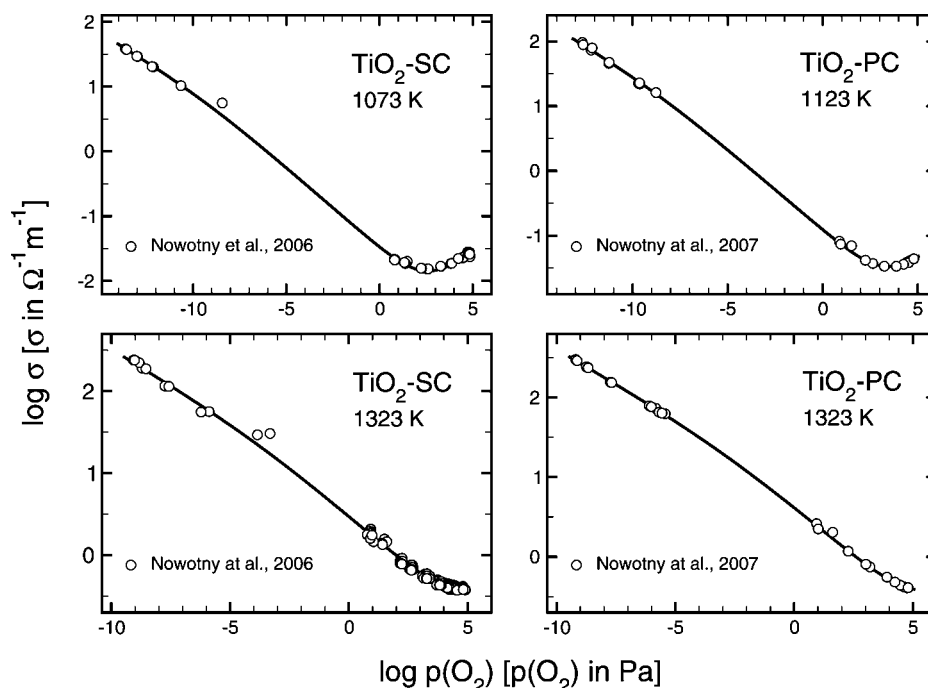
Figure 3. Effect of oxygen activity on the electrical conductivity of TiO$_2$. Points correspond to the experimental data for high-purity TiO$_2$ (single crystal, SC;[10] polycrystal, PC),[11] and the continuous lines correspond to the fitted theoretical dependence determined by eq 1.

boundaries on the charge transport in TiO$_2$. The data on the concentration terms that are required to solve eq 1 will be determined from eq 5 by using the equilibrium constants reported elsewhere.[9]

The present work will also determine the mobility terms from the electrical conductivity data reported by Balachandran and Eror.[12]

Experimental Section

The electrical conductivity was determined for high-purity TiO$_2$ single crystal by using the high-temperature Seebeck probe.[10] The content of acceptor-type impurities was limited to 32 ppm (Cu, 5 ppm; Ni, 5 ppm; Fe, 2 ppm; Ag, 5 ppm; Si, 10 ppm; Mg, 5 ppm). Required oxygen activity, p(O$_2$), was imposed by either an argon–oxygen mixture (high oxygen activity) or the mixture of hydrogen and water vapor (low oxygen activity). The details of the measurement procedure and the equipment were reported elsewhere.[10] The obtained data representing the effect of oxygen activity on the electrical conductivity of TiO$_2$ single crystal (TiO$_2$ -SC) in the temperature range 1073–1323 K[10] have been considered as well defined for the following reasons: (1) The evidence has been reported that these data were measured in the equilibrium in the gas phase of controlled oxygen activity. (2) The specimen was of high purity.

The polycrystalline specimens of undoped TiO$_2$ were prepared from titanium isopropoxide, Ti[(CH$_2$)$_2$CH$_2$OH]$_4$, of spectral purity. The concentration of acceptor-type impurities was limited to 34 ppm. The density of the specimen sintered at 1423 K for 12 h was 95.5% of the theoretical density. The average grain size was 2 μm.[11] Assuming, as the first approximation, that grains are cubes in shape and their surface layer 10 nm thick can be considered as part of a grain boundary, then ~3% of the volume of a polycrystalline specimen are grain boundaries.

The effect of oxygen activity on the electrical conductivity of polycrystalline TiO$_2$ (TiO$_2$-PC) was determined in the temperature range 1073–1323 K.[11] While the absolute values of these data are different from those for TiO$_2$-SC, the electrical conductivity data have also been considered as well defined for the same reasons as outlined above (high purity, controlled oxygen activity, gas/solid equilibrium).

The electrical conductivity data of Balachandran and Eror[12] were reported for polycrystalline TiO$_2$ (TiO$_2$-BE) obtained from tetraisopropyl titanate solution. Balachandran and Eror did not report the content of the impurities in their specimen; however, their electrical conductivity data were measured over a wide range of temperatures (1123–1323 K) and oxygen partial pressures (10^{-15} Pa < p(O$_2$) < 10^5 Pa).[12]

Discussion

Mobility Terms. The aim of the present work is the determination of the mobility terms for electrons and electron holes for TiO$_2$ from eq 1 by using the electrical conductivity data determined experimentally.[10–12] The related concentration terms were derived from defect disorder diagrams reported elsewhere.[9]

The mobility determination is based on the assumption that the electrical conductivity depends on the concentration of electronic charge carriers (electrons and holes), and, consequently, the ionic component of the electrical conductivity may be ignored.

The mobility terms were determined as parameters of a fitting procedure according to Nedler–Mead simplex algorithm[25] by minimizing the following summation:

$$\sum_j [(\sigma_{th,j} - \sigma_j)w_j]^2 \tag{7}$$

where σ_{th} is defined as a theoretical electrical conductivity expressed by eq 1, σ_j are the experimental values of electrical conductivity, and w_j are the standard weighting factors, which are defined as follows:[26]

$$w_j = \frac{1}{\sigma_j} \tag{8}$$

The determined mobility terms are involved in σ_{th}. The concentrations of electrons and electron holes in eq 1, corresponding to each experimental point σ_j, were obtained by solving eqs 5 and 6. The fitting procedure aimed at achieving the simplex size below a preselected value, which in our case was 10^{-8}.

The theoretical relation for the electrical conductivity, expressed by eq 1, is fitted numerically to the empirical data, σ_j, for TiO$_2$-SC in the range 1073–1323 K. The fitting procedure used the mobility terms as parameters. The effect of oxygen activity on the electrical conductivity of TiO$_2$ at two extreme temperatures (1073 and 1323 K) for high-purity TiO$_2$ single crystal is shown by the data points in Figure 3, where the continuous line corresponds to the theoretical dependence determined by eq 1. The obtained parameters μ_n and μ_p are plotted in Figure 4. These data may be represented by the following forms:

$$\mu_n(TiO_2 - SC) = (6.7 \pm 0.3) \times 10^{-6} \, (m^2 \, V^{-1} \, s^{-1})$$

$$\mu_p(TiO_2 - SC) = (1.5 \pm 0.7) \times 10^{-1} \times$$
$$\exp\left(-\frac{94 \pm 4(kJ/mol)}{RT}\right)(m^2 \, V^{-1} \, s^{-1}) \tag{9}$$

In analogy, the effect of oxygen activity on the electrical conductivity of TiO$_2$ at two extreme temperatures (1123 and 1323 K) for high-purity polycrystalline TiO$_2$[11] is shown by the data points in Figure 3 (the continuous line corresponds to the theoretical dependence determined by eq 1). The obtained parameters μ_n and μ_p are plotted in Figure 4. These data may be represented by the following forms:

$$\mu_n(TiO_2 - PC) = (9.0 \pm 1.3) \times 10^{-6} \, (m^2 \, V^{-1} \, s^{-1})$$

$$\mu_p(TiO_2 - PC) = (3.9 \pm 10.1) \times 10^{-2} \times$$
$$\exp\left(-\frac{84 \pm 13(kJ/mol)}{RT}\right)(m^2 \, V^{-1} \, s^{-1}) \tag{10}$$

As seen, the charge transport mechanism for both electrons and electron holes is the same for both TiO$_2$-SC and TiO$_2$-PC. Moreover, the absolute values of the mobility are similar.

Figure 5 shows the results of the fittings for the data of Balachandran and Eror at two extreme temperatures, 1123 and 1323 K. Again, a good fit has been achieved. The determined mobility data, compared to those for the TiO$_2$-PC specimen, are shown in Figure 6. These data may be represented by the following expressions:

$$\mu_n(TiO_2 - BE) = (1.6 \pm 0.2) \times 10^{-6} \times$$
$$\exp\left(\frac{15 \pm 1(kJ/mol)}{RT}\right)(m^2 \, V^{-1} \, s^{-1})$$

$$\mu_p(TiO_2 - BE) = (3.0 \pm 4.6) \times 10^{-2} \times$$
$$\exp\left(-\frac{94 \pm 9(kJ/mol)}{RT}\right)(m^2 \, V^{-1} \, s^{-1}) \tag{11}$$

As seen, in this case the mobility of electrons depends slightly on temperature ($E_\mu = -15$ kJ/mol), although their absolute
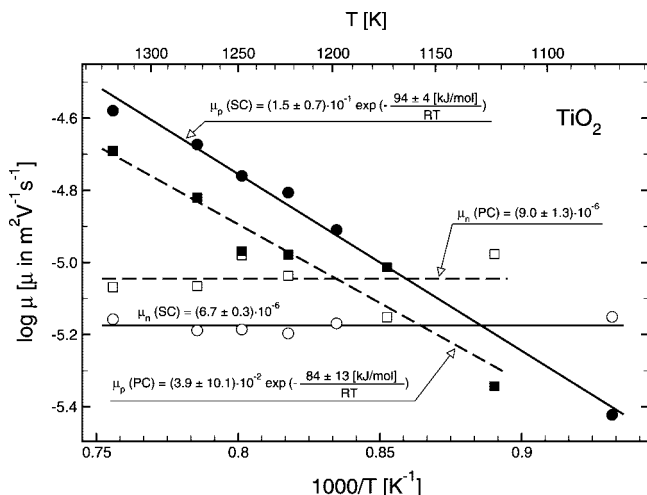
Figure 4. Arrhenius plots of the mobility terms for high-purity TiO$_2$, including single-crystal (SC) and polycrystalline (PC) specimens.
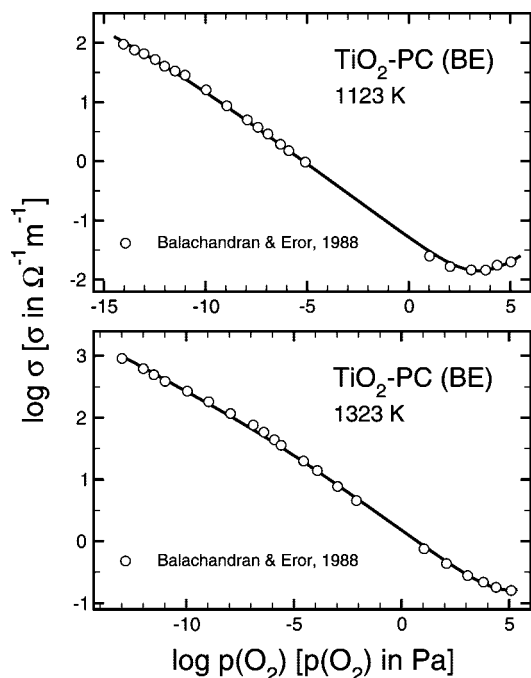

Figure 5. Effect of oxygen activity on the electrical conductivity of TiO$_2$ according to Balachandran and Eror.. Points correspond to the experimental data, and the continuous lines correspond to the theoretical dependence determined by eq 1.
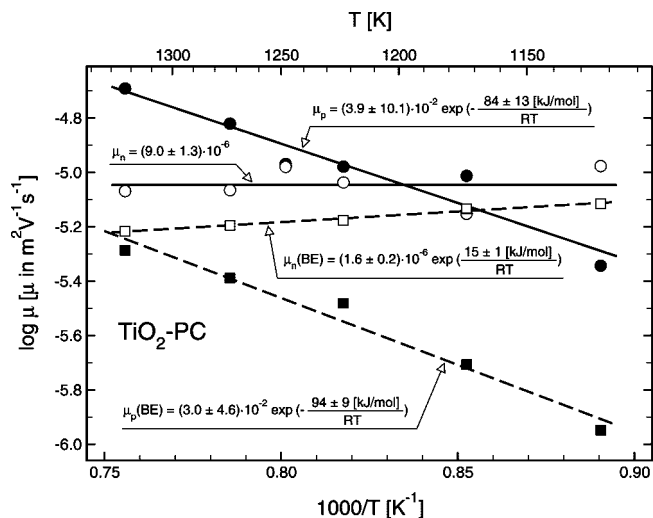

Figure 6. Arrhenius plots of the mobility terms determined in the present work for high-purity polycrystalline TiO$_2$ (PC) and the polycrystalline TiO$_2$ specimen studied by Balachandran et al.[12] (BE).
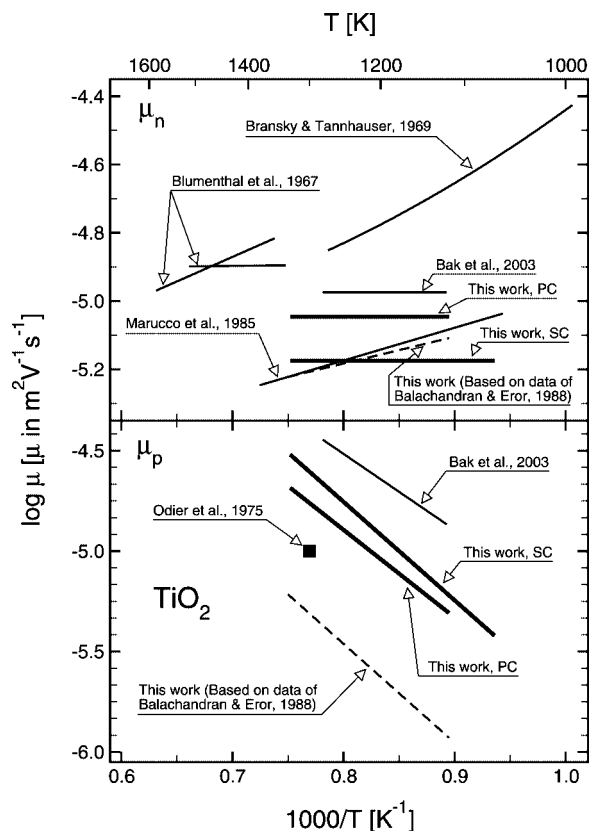

Figure 7. Arrhenius plots of the mobility of electrons (upper part) and electron holes (lower part) in TiO$_2$ as a function of the reciprocal of temperature in the range 1000−1600 K for the specimens studied in the present work along those reported in the literature.[12,13,15,20–22]

values are similar to those for the TiO$_2$-SC. The temperature dependence for the mobility of electron holes is similar to those for the TiO$_2$-SC (E_μ = 94 kJ/mol).

Figure 7 represents the mobility data determined in the present work along the data reported in the literature. These data allow the following conclusions to be made: (1) The determined mobility data for both TiO$_2$-SC and TiO$_2$-PC are consistent. (2) The mobility terms for electrons, which are independent of temperature, are consistent with the transport mechnism according to the band model. While the mobility terms determined from the electrical conductivity data of Balanchandran and Eror (TiO$_2$-BE)[12] exhibit a slight temperature dependence, their absolute values are similar to those of the high purity TiO$_2$-SC specimens. (3) The mobility terms for electron holes exhibit a temperature dependence (84 kJ/mol < E_μ < 94 kJ/mol), which is consistent with the hopping charge transport model.

Effect of Grain Boundaries. The effect of p(O$_2$) on electrical conductivity for both SC-TiO$_2$ and PC-TiO$_2$ at 1223, 1273 and 1323 K is shown in Figure 8.[27] As can be seen, the following characteristic features may be distinguished: (1) The isobaric values of the electrical conductivity data in the n-type regime, p(O$_2$) < 10^3 Pa, are larger for PC-TiO$_2$ by ~0.1 order of magnitude. This effect indicates that the PC-TiO$_2$ in the n-type regime exhibits higher conduction than the SC-TiO$_2$. This effect is reversed at high p(O$_2$) when the slope of log σ versus log
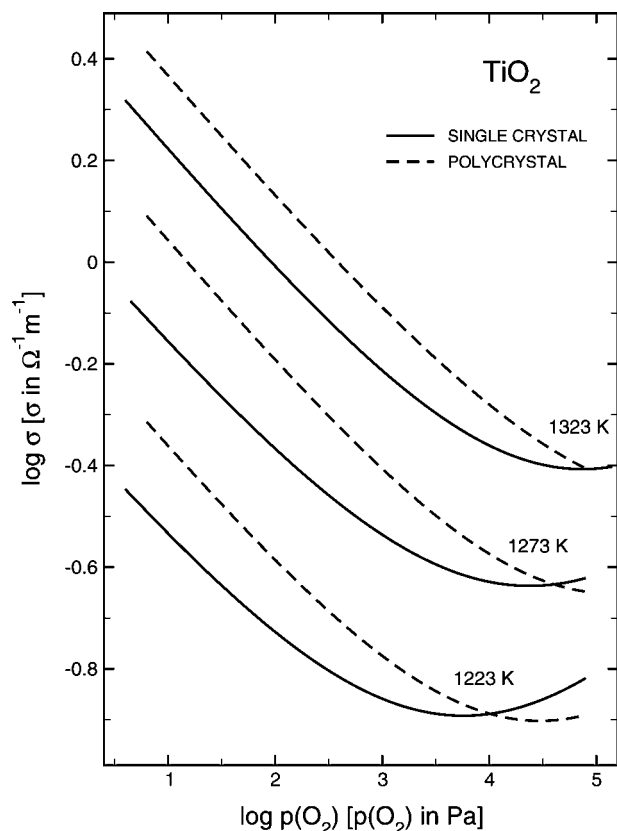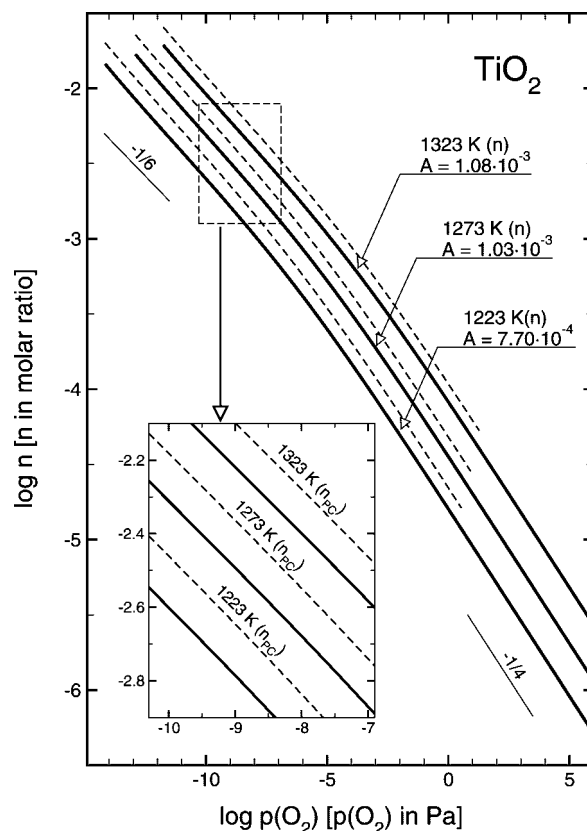
Figure 8. Effect of oxygen activity on the electrical conductivity of high-purity TiO$_2$, including TiO$_2$-PC[11] and TiO$_2$-SC[10] in the range 1223−1323 K.[27]

Figure 9. Effect of oxygen activity on the concentration of electrons for both TiO$_2$-PC and TiO$_2$-SC in the range 1223−1323 K.

p(O$_2$) becomes positive. (2) The SC-TiO$_2$ exhibits the minimums of the electrical conductivity data at the p(O$_2$) that are substantially lower that those for PC-TiO$_2$ by ∼1 order of magnitude.

These data indicate that the PC-TiO$_2$ in the n-type regime exhibits either higher concentration of electrons, relative to SC-TiO$_2$, or larger mobility term. Alternatively, in the p-type regime, the PC-TiO$_2$ exhibits either lower concentration of holes or their mobility is smaller. The procedure applied above for the determination of the mobility data for both TiO$_2$-SC and TiO$_2$-PC specimens was based on the assumption that the difference between the two sets of data are determined by the mobility terms. The purpose of the present section is to consider the electrical conductivity data based on the following assumptions: (1) The mobility terms expressed by eqs 9 and 10 are the same for both TiO$_2$-SC and TiO$_2$-PC. (2) The differences between the electrical conductivity data for TiO$_2$-SC and TiO$_2$-PC are due to the concentration terms. The differences between these concentration terms, derived from the two sets of the electrical conductivity data in the n-type regime, are shown in Figure 9. In other words, Figure 9 represents the concentrations of electrons for the bulk phase (solid lines) and for the polycrystalline material, including both the bulk phase component and the grain boundary component (dashed lines).

As seen in Figure 9, the concentrations of electrons for TiO$_2$-PC are slightly elevated. This effect may be considered in terms of the elevated concentration of electrons at grain boundaries. It may also be considered in terms of low dimensional interface structures, which are formed as a result of segregation. It has been shown that such structures have entirely different properties than the bulk phase.[28]

Conclusions

The mobility data determined in the present work indicate that the charge transport for electrons and electrons holes occurs according to the band model and the hopping model, respectively. These mobility data may be considered as well defined for the following reasons: (1) The mobility data were determined from the experimental data of the electrical conductivity, which were measured for high-purity specimens. (2) The electrical conductivity data used in the present work were measured in the gas/solid equilibrium in the gas phase of controlled oxygen activity with a high precision and they exhibit a good reproducibility. (3) The mobility terms determined in the present work are consistent with the observed n-p transition.

The obtained mobility data pave the way for quantitative interpretation of the electrical conductivity data of TiO$_2$. These data are essential for using the electrical conductivity measurements to assess the chemistry, reactivity, and related charge transfer of this important oxide material.

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