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Electronic and Ionic Conductivity of TiO_2 Single Crystal Within the n–p Transition Range

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Abstract: The electrical conductivity of TiO_2 single crystal (rutile) was determined within the n–p transition regime in the temperature range 985–1387 K and $p(O_2)$ 1–10^5 Pa. The determined values of the $p(O_2)$ exponent differ from those predicted by defect disorder models (in both n- and p-type regimes), which were derived assuming validity of ionic charge compensation. This difference allows the evaluation of the ionic conductivity. The ionic component thus determined within the n–p transition regime exhibits an activation energy of $E_a = 158\,kJ\,mol^{-1}$. It was found that the ionic transfer number for undoped TiO_2 at the n–p transition is approximately 0.5. The electronic conductivity component was used to determine the width of the forbidden gap of TiO_2 ($E_g = 2.86\,eV$). © 1998 Elsevier Science Limited and Techna S.r.l.

1 INTRODUCTION

Literature reports on the electrical properties of TiO_2 involve speculation and conflicting conclusions concerning the ionic conductivity contribution to the overall conductivity process in this compound.[1–7]

It has been generally assumed that the electrical properties of TiO_2 are determined by electronic conduction while the ionic component assumes negligibly small values. So far, however, this assumption has not been verified by direct measurement of the ionic conductivity component.

Popov *et al.*[1] reported that, below 1000°C, undoped TiO_2 is mainly an ionic semiconductor with an activation energy of 0.55–0.75 eV along the c-axis and 2 eV along the a-axis. On the other hand, Cronemeyer[2] argued that the electrical conductivity is determined by the transport of electronic charge carriers while the contribution of the ionic component is negligible. Also, Baumard and Tani[3] claimed that the contribution of the ionic component at 1273 K is limited to 0.1% of the total conductivity value. Carpentier *et al.*[4–6] concluded that TiO_2 at 1273 K under $p(O_2) = 10^5$ Pa exhibits mixed conductivity with the ionic component smaller than 5%. Finally, Singheiser and Auer[7] reported that the ionic component plays a significant role in conduction in reduced TiO_2 (10^{-14}–10^{-19} Pa) at 1125–1255 K; however, they did not specify the absolute value of this component.

As seen, the available reports represent a variety of conflicting views on the transport mechanism in TiO_2, which so far remains unresolved.

The purpose of the present work was to evaluate the ionic conductivity component in undoped TiO_2 at elevated temperatures using an indirect approach. In the present study, the possible defect disorder models of TiO_2 will be considered. The defect disorder models, based on both ionic and electronic charge compensations, will then be

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verified against electrical conductivity and thermopower data in the n–p transition regime, in which the ionic conductivity component assumes its highest value.

2 DEFECT DISORDER MODELS

2.1 General

Most of the experimental data on defect-related properties of TiO_2 are reported for the n-type regime. So far, little is known of the electrical properties of rutile within the p– and the n–p transition regimes.

In preceding paper,[8] semiconducting properties of TiO_2 in terms of possible defect disorder models constructed in both n- and p-type regimes were considered. It was concluded that, in the vicinity of the n–p transition regime, the defect structure should be considered to involve the presence of several defects at comparable concentrations, such as Ti interstitials and Ti vacancies as well as acceptor-type impurities.

In the present work, the electronic properties of TiO_2 within a narrow regime corresponding to the n–p transition range, in which the ionic conductivity component may have the most substantial effect on the conduction process, will be considered.

2.2 Schottky-type defect disorder

At high temperatures and low $p(O_2)$, rutile exhibits n-type conductivity which may be related to defects forming donors, such as oxygen vacancies and Ti interstitials. In the first case, the defects are formed according to the following reaction:[8–10]

$$O_O \rightleftharpoons 1/2O_2 + V_O^{\cdot\cdot} + 2e' \qquad (1)$$

where $V_O^{\cdot\cdot}$ is a doubly ionised oxygen vacancy. Reaction (1) may be termed a quasi-Schottky-type reaction. In this case, the correct formula for rutile is TiO_{2-y}. Then:

$$y = [V_O^{\cdot\cdot}] \qquad (2)$$

where the brackets denote concentration.
The equilibrium constant of eqn (1) is:

$$K_V = [V_O^{\cdot\cdot}][e']^2 p(O_2)^{1/2} \qquad (3)$$

The formation of oxygen vacancies may also be considered a Schottky-type defect disorder involving the formation of vacancies in both cation and oxygen sublattices:[11,12]

$$nil \rightleftharpoons V_{Ti}'''' + 2V_O^{\cdot\cdot} \qquad (4)$$

The equilibrium constant of reaction (4) is:

$$K_S = [V_O^{\cdot\cdot}]^2[V_{Ti}''''] \qquad (5)$$

Assuming charge neutrality:

$$[V_O^{\cdot\cdot}] = 2[V_{Ti}''''] = (2K_S)^{1/3} \qquad (6)$$

The concentration of electrons may be expressed as:

$$[e'] = K_V^{1/2}(2K_S)^{-1/3}p(O_2)^{-1/4} \qquad (7)$$

2.3 Frenkel-type defect disorder

The formation of Ti interstitials[13,14] may be expressed by the following equilibrium:

$$Ti_{Ti} + 2O_O \rightleftharpoons Ti_i^{+4} + O_2 + 4e' \qquad (8)$$

Reaction (8) may be termed a quasi-Frenkel-type reaction. Then, the correct formula for rutile, involving an excess of Ti, is $Ti_{1+x}O_2$, where:

$$x = [Ti_i^{+3}] + [Ti_i^{+4}] \qquad (9)$$

The equilibrium constant of reaction (8) is:

$$K_I = [Ti_i^{+4}][e']^4 \; p(O_2)^{1/2} \qquad (10)$$

The formation of Frenkel-type defect disorder may be expressed by the following equilibrium:

$$Ti_{Ti} \rightleftharpoons Ti_i^{+4} + V_{Ti}'''' \qquad (11)$$

for which the equilibrium constant is:

$$K_F \rightleftharpoons [Ti_i^{+4}][V_{Ti}''''] \qquad (12)$$

Assuming that:

$$[Ti_i^{+4}] = [V_{Ti}''''] = (K_F)^{1/2} \qquad (13)$$

the following is obtained:

$$[e'] = (K_I)^{1/4}(K_F)^{-1/8}p(O_2)^{-1/4} \qquad (14)$$

2.4 The extrinsic model

The extrinsic model[10] assumes that the predominant donor-type defects are either oxygen vacancies or Ti interstitials which are compensated by acceptor-type impurities, A'. Two types of disorder models based on extrinsic compensation, such as extrinsic-Schottky-type disorder and extrinsic-Frenkel-type disorder, may be considered.

2.4.1 Extrinsic-Schottky-type disorder

Charge neutrality of this disorder requires that:

$$[A'] = 2[V_O^{\cdot\cdot}] \tag{15}$$

Then combining eqns (3) and 15, the following is obtained:

$$[e'] = \{2K_V/[A']\}^{1/2} p(O_2)^{-1/4} \tag{16}$$

2.4.2 Extrinsic-Frenkel-type disorder

The charge neutrality condition of the extrinsic-Frenkel-type disorder requires that:

$$[A'] = 4[Ti_i^{+4}] \tag{17}$$

The combination of eqns (10) and (17) results in the following expression:

$$[e'] = \{4K_I/[A']\}^{1/4} p(O_2)^{-1/4} \tag{18}$$

2.5 Summary

According to literature reports both oxygen vacancies and Ti interstitials are present at comparable concentrations.[13–17] Accordingly, the correct formula for reduced rutile is $Ti_{1+x}O_{2-y}$ rather than TiO_{2-y}. It was shown that the valency of Ti interstitials and oxygen vacancies is four and two, respectively.[8]

It would be expected that the predominant defects in the n-type regime are Ti interstitials and oxygen vacancies while Schottky-type disorder is predominant in the p-type regime.[8,18,19]

All four defect disorders considered above result in the same type of $p(O_2)$ dependence for the concentration of electrons:

$$[e'] = const\ p(O_2)^{-1/4} \tag{19}$$

Assuming that:

$$K_i = [e'][h^{\cdot}] \tag{20}$$

the concentration of electron holes assumes the following dependence:

$$[h^{\cdot}] = const\ p(O_2)^{1/4} \tag{21}$$

Therefore, assuming that the mobility terms are independent of $p(O_2)$, one may expect that changes in the electrical conductivity of undoped TiO_2 within n- and p-type regimes should exhibit $p(O_2)$ exponents equal to 1/4 and −1/4, respectively. The deviation from this dependence, derived from defect disorder models ignoring ionic conductivity, may be considered in terms of an ionic conductivity component.

Below, the electrical properties of TiO_2 within the n–p transition range in terms of the theoretical models described above, will be analysed.

3 EXPERIMENTAL

TiO_2 single crystal was grown by the Verneuil method. A slab (10×3.5×3.5 mm) was oriented in such a way that the c-axis was parallel to the slab's length (10 mm). Spectral analysis revealed presence of Fe and Si at the level of 20 and 30 ppm, respectively.

The dc conductivity was determined along the [001] crystallographic direction using the four-probe method. Thermopower was determined against Pt[8,19] from the Seebeck voltage within 6–10 temperature gradients. Both electrical resistivity and thermopower were determined simultaneously within the temperature range 985–1387 K and oxygen partial pressure 1–10^5 Pa. The experimental set-up for the measurement of both thermopower and the electrical conductivity has been described previously.[20]

The experimental procedure involved determination of the electrical conductivity and thermopower of the TiO_2 crystal in equilibrium with the gas phase. The equilibration experiments involved isothermal changes of $p(O_2)$, imposed by an argon/oxygen mixture flowing, with the flow rate 300 ml min^{-1}, over the TiO_2 specimen, and then monitoring the changes in electrical properties with time. It was assumed that the crystal reached the equilibrium state after both electrical conductivity and thermopower had reached constant values. The equilibration time was approximately 30 min at 985 K and decreased to several minutes at 1387 K.

4 RESULTS

Figures 1 and 2 show the isothermal dependencies of the electrical conductivity as functions of oxygen partial pressure at 985–1387 K. A minimum in the electrical conductivity vs $p(O_2)$ was observed at 1166 K and below this temperature. With increasing

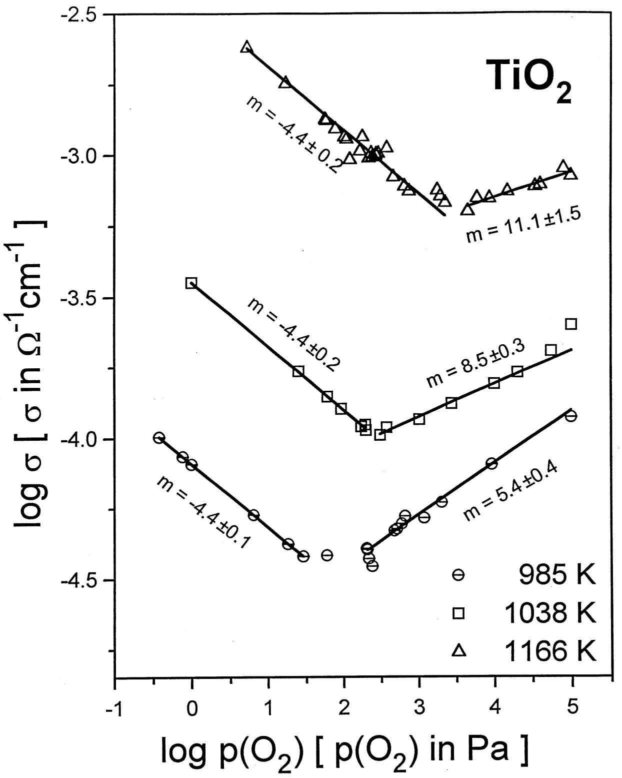

Fig. 1. Logarithm of the electrical conductivity of undoped TiO_2 single crystal vs logarithm of the oxygen partial pressure at 985, 1038 and 1166 K (the straight lines indicate the regimes for which the slope, m, was determined).

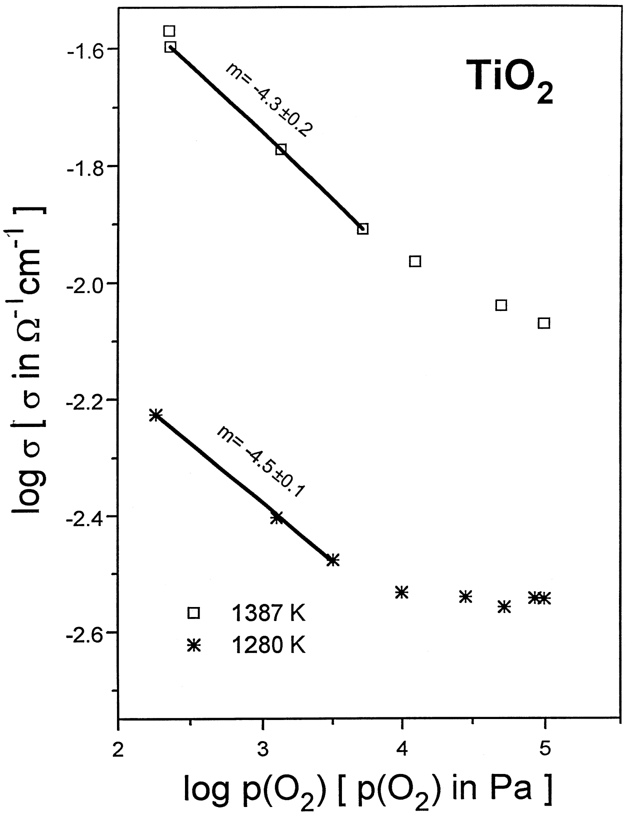

Fig. 2. Logarithm of the electrical conductivity for undoped TiO_2 single crystal vs logarithm of the oxygen partial pressure at 1280 and 1387 K (the straight lines indicate the regimes for which the slope, m, was determined).

temperature, the minimum was shifted towards higher p(O_2).

As seen from Fig. 3, showing both thermopower and conductivity vs p(O_2) at 1038 K, there was good agreement between the p(O_2) value corresponding to the minimum of the electrical conductivity and that corresponding to the zero value of thermopower. This agreement was also observed at 985 and 1166 K.

5 DISCUSSION

5.1 Verification of the defect models

In verification of the defect models derived above, it is assumed that the mobilities of the electronic charge carriers are independent of the equilibrium p(O_2) and, therefore, of nonstoichiometry. Then the conductivity components related to electrons and electron holes may be expressed by the respective formulae:

$$\sigma_e = \sigma_e^o p(O_2)^{-1/4} \tag{22}$$

$$\sigma_h = \sigma_h^o p(O_2)^{1/4} \tag{23}$$

where the superscript “o” denotes the conductivity terms, which are independent of p(O_2).

As seen in Fig. 1, the electrical conductivity exhibits a clear minimum which, assuming equality of the mobility terms, corresponds to the n–p transition. The p(O_2) corresponding to the transition increases from approximately 10^2 Pa at 985 K to approximately 10^4 Pa at 1166 K. At temperatures 1280 and 1387 K the n–p transition is shifted to higher p(O_2) which corresponds to about 5×10^4 and 10^5 Pa, respectively.

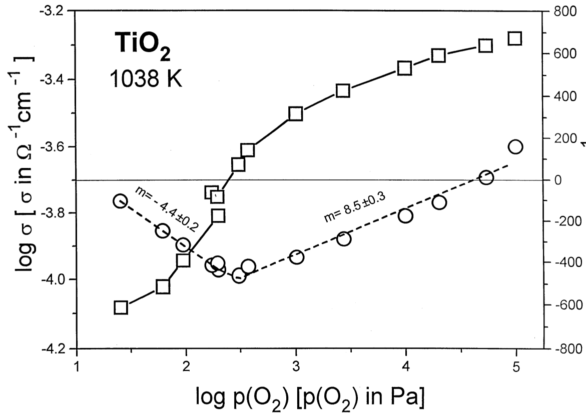

Fig. 3. Thermopower and logarithm of the electrical conductivity for undoped TiO_2 single crystal vs logarithm of the oxygen partial pressure at 1038 K.

The slope of the log σ vs log $p(O_2)$ dependence in Figs 1–3 was determined within the range in which the experimental data showed a linear dependence. For n-type regime, this slope remained between $-1/4.4$ and $-1/4.3$ while, for the p-type regime, it varied between $1/5.6$ and $1/9.7$. As seen, the experimental values of the $p(O_2)$ exponent at all temperatures (Figs 1–3) differ essentially from that expected by the defect disorder models, which were derived assuming that the ionic conductivity is negligible. Assuming that the departure of the obtained experimental data from the derived defect disorder model is caused by an ionic conductivity component, σ_{ion}, the expression for σ assumes the following form:

$$\sigma_{tot} = \sigma_e + \sigma_h + \sigma_{ion} \tag{24}$$

Therefore:

$$\sigma_{tot} = \sigma_e^o p(O_2)^{-1/4} + \sigma_h^o p(O_2)^{1/4} + \sigma_{ion}^o \tag{25}$$

Figures 4 and 5 illustrate the experimental conductivity as a function of $p(O_2)^{-1/4}$ and $p(O_2)^{1/4}$ at 985 and 1387 K, respectively. It is seen that there is good agreement between the experimental data and the $p(O_2)^{-1/4}$ dependence in the n-type regime. Similar agreement is observed between the conductivity data and the $p(O_2)^{1/4}$ dependence in the p-type regime. This agreement confirms the validity of eqn (25), where the slopes of the linear dependencies correspond to the conductivity components σ_o^e and σ_o^h for n-type and p-type regimes, respectively, which are independent of $p(O_2)$.

It is also interesting that both linear dependencies of σ vs $p(O_2)^{1/4}$ and σ vs $p(O_2)^{-1/4}$ intersect at the same value of the ordinate axis, which assumes a positive value. This indicates that the determined experimental data result in the ionic component in eqn (25), which is the same for both n- and p-type regimes. As seen in Fig. 4, there is excellent agreement between the ionic component value determined this way for the n-type regime on one side and the p-type regime on the other side. This ionic conductivity component, σ_{ion}^o, is independent of $p(O_2)$.

The Arrhenius plot of the ionic component, σ_{ion}^o, is shown in Fig. 6. The determined activation energy ($E_a = 158\,kJ\,mol^{-1}$) corresponds to the mobility of ionic defects, such as oxygen vacancies or Ti interstitials.

Figure 7 illustrates the conductivity components of eqn (25) at 1166 K as a function of log $p(O_2)$ within the n–p transition range. The ionic component was determined according to the procedure

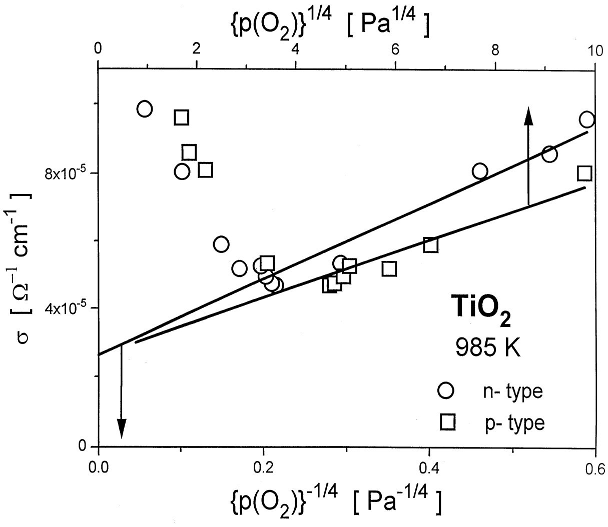

Fig. 4. The electrical conductivity of undoped TiO_2 as a function of $p(O_2)^{-1/4}$ and $p(O_2)^{1/4}$ at 985 K.

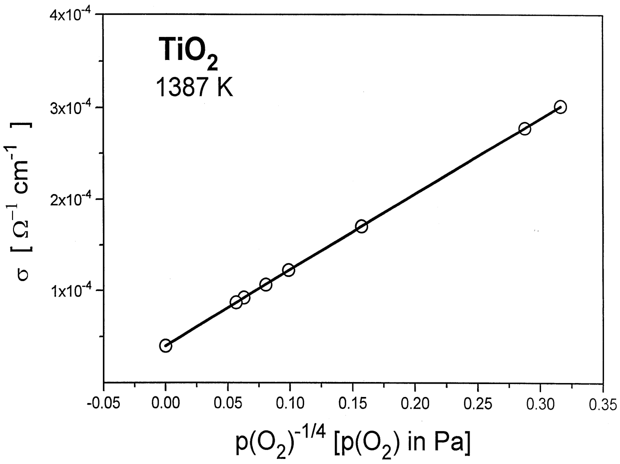

Fig. 5. The electrical conductivity of undoped TiO_2 as a function of $p(O_2)^{-1/4}$ in the p-type regime at 1387 K.

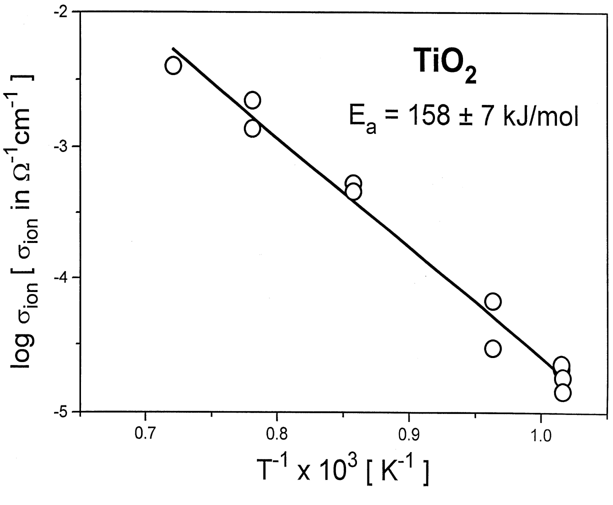

Fig. 6. Arrhenius-type plot of the ionic components of the electrical conductivity of undoped TiO_2.

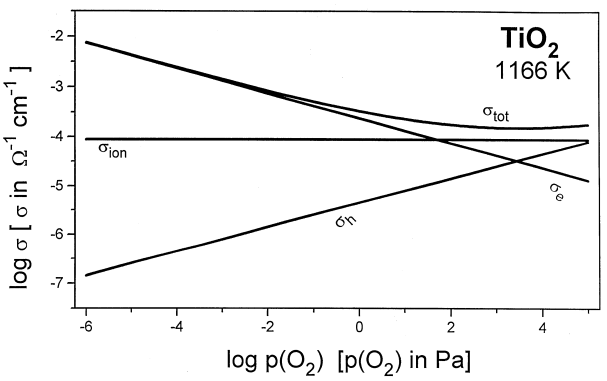

Fig. 7. The components σ_{ion}, σ_e and σ_h of the electrical conductivity (eqn (25)) for undoped TiO$_2$ single crystal vs logarithm of the oxygen partial pressure at 1166 K.

described above while both σ_e and σ_h were evaluated from eqn (25) by fitting its respective components.

Figure 8 shows the transport numbers of both electronic and ionic defects as a function of equilibrium p(O$_2$) determined from the values taken from Fig. 7. It is seen, in a wide range of p(O$_2$) within the n–p transition range, that the σ_{ion} component assumes a substantial value that cannot be ignored. The ionic component assumes negligible values for very reduced or highly oxidised specimens.

A minimum value of the electrical conductivity has been generally assumed to be determined by the intrinsic electronic transition and is used in the determination of the forbidden gap. This assumption is correct when the conductivity is determined by electronic charge carriers and the ionic conductivity component can be ignored. Figure 9 shows an Arrhenius plot of the minimum value of σ, σ_{min}, using both the total conductivity component, σ_{tot}, and the electronic conductivity component ($\sigma_e + e_h$). As seen there is a difference in the activation energies determined from these two values. The value of the forbidden gap, E_g, determined from the electronic component is 2.86 ± 0.16 eV while the apparent value of the forbidden gap resulting from the overall conductivity value, E^*_g, is elevated to 3.08 ± 0.06 eV.

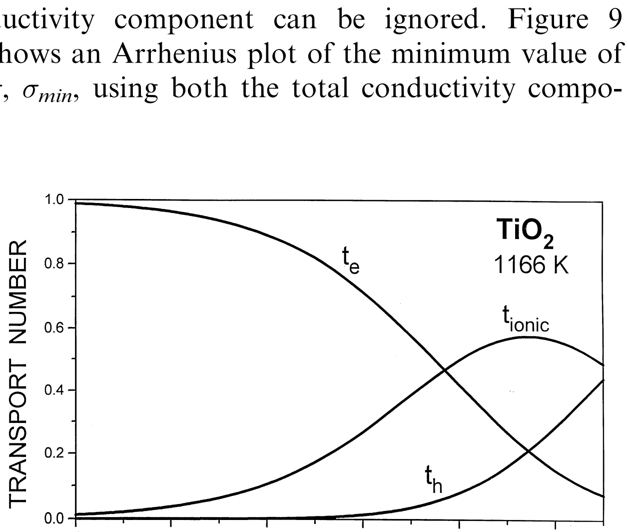

Fig. 8. Transport numbers of different charge carriers in TiO$_2$ as a function of the logarithm of the oxygen partial pressure at 1166 K.

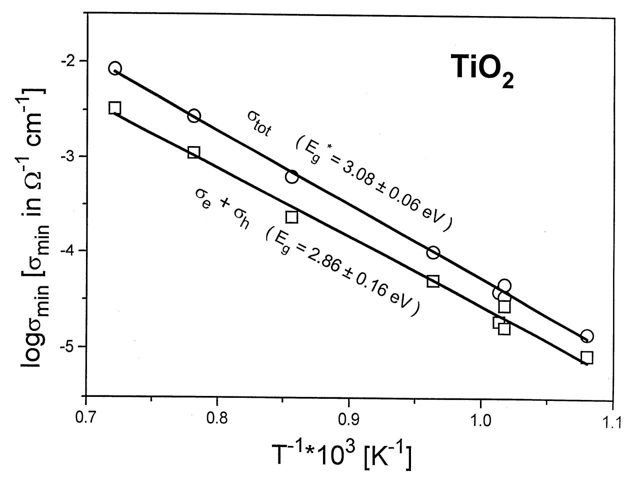

Fig. 9. Arrhenius plot of the logarithm of the minimum of the electrical conductivity determined from the total conductivity, σ_{tot}, and from the electronic component, $\sigma_e + \sigma_h$.

It is appropriate to comment briefly on the possible effect of minority charge carriers on the observed p(O$_2$) exponent within the n–p transition range, which is illustrated in Fig. 10. Namely, line 1 in Fig. 10 shows schematically the dependence of the electrical conductivity within a wide range of p(O$_2$) in both n- and p-type regimes.[8] As seen, the p(O$_2$) exponent assumes −1/6 and 1/5 for extremely reduced conditions (n-type regime) and

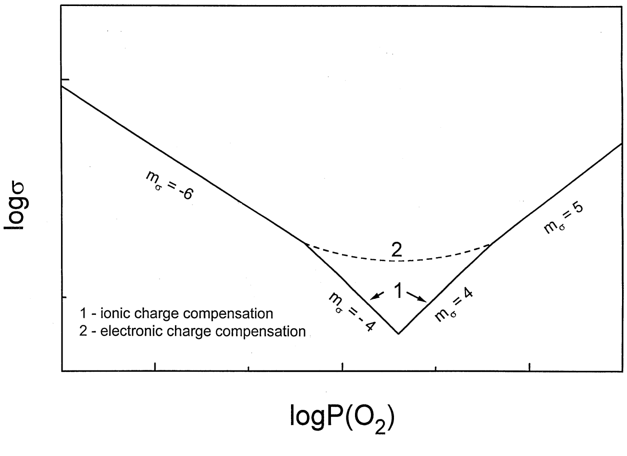

Fig. 10. Schematic illustration of log σ (where σ denotes the electronic conductivity component) vs log p(O$_2$) for TiO$_2$ within the n–p transition regime: (1) expected according to the defect models derived in the present work and (2) assuming contribution from both electronic charge carriers.

extremely oxidised conditions (p-type regime), respectively.[8] However, in the vicinity of the n–p transition, the exponent assumes $-1/4$ and $1/4$. Line 2 in Fig. 10 illustrates the $p(O_2)$ dependence that could be expected as a result of the effect of electronic charge carriers assuming minority charge carriers play an important role in conduction in both regimes. Concordantly, it may concluded that the experimental data reported in the present work, which are in agreement with the dependence illustrated by line 1, indicate that the electrical conductivity vs $p(O_2)$ dependence within the n–p transition range is determined by the effect of ionic conductivity rather than by minority charge carriers.

6 SUMMARY AND CONCLUSIONS

It was shown that the electrical properties of TiO_2 may be explained using any of four competitive defect models. All these models, derived using ionic compensation, result in the $p(O_2)$ exponents being equal to $-1/4$ and $1/4$ for n- and p-type regimes, respectively. It was also shown that the electrical conductivity data within the n–p transition range confirm the validity of ionic compensation. The discrepancy between the absolute values of the observed $p(O_2)$ exponent and those predicted by the proposed defect disorder models was used to determine the ionic conductivity component at the n–p transition point. Thus, the determined value of the ionic transfer number is equal to approximately 0.6. The activation energy of this determined ionic component is $158\,\mathrm{kJ\,mol^{-1}}$. Thus the determined electronic conductivity component at the n–p transition results in a width of the forbidden gap equal to 2.86 eV.

It is believed that this procedure allows evaluation of the ionic conductivity component indirectly but with good precision. It is felt, however, that the determined values require verification by direct experimental observation, e.g. by conductivity measurement when the electronic conductivity is blocked or by the determination of the Nernst voltage.

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