

# Defect Engineering of Titanium Dioxide

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## Abstract

The present work reports the measurements of defect-related properties, such as electrical properties, may be used for "in situ" monitoring of TiO<sub>2</sub>-based oxide semiconductors during processing at elevated temperatures and also during cooling. It is shown that such "in situ" monitoring of defect-related properties allows to conduct the process in a controlled manner. The data obtained during the "in situ" monitoring may be used for instantaneous modification of processing conditions, such as temperature, oxygen activity, the time of annealing and cooling rate, in order to achieve the desired properties. The procedure of "in situ" monitoring is represented by the experimental data of the electrical conductivity and thermoelectric power during oxidation and reduction at 1198 K. The effect of oxygen activity on the electrical conductivity for pure and Nb-doped TiO<sub>2</sub> is considered in terms of defect disorder.

## INTRODUCTION

A wide range of approaches have been reported to process photosensitive oxide materials with controlled properties that are desired for specific applications, including photocatalysts for water purification and photoelectrodes for water splitting [1-15]. These applications require the materials with specific properties that allow to absorb solar energy and to convert it into other types of energy. While titanium dioxide, TiO<sub>2</sub>, has been commonly considered as the best candidate as a photosensitive material [1], more research is needed in order to enhanced its photosensitivity.

The photosensitivity of commercially available TiO<sub>2</sub> is limited due to its relatively large band gap (3 eV). Consequently, the amount of the absorbed solar energy spectrum is very small (~5 %). Therefore, a wide range of procedures have been applied in order to reduce its band gap, including the incorporation of aliovalent ions, resulting in the formation of solid solutions. The most spectacular effects have been reported by Wilke and Brauer [16] and Khan et al [17], including:

- 1) Wilke and Brauer [16] have shown that the incorporation of Cr and Mo into TiO<sub>2</sub> leads to the reduction of the band gap to 2 eV and 2.8 eV, respectively.
- 2) Khan et al. [17] reported that the incorporation of carbon in the TiO<sub>2</sub>, by heating in a natural gas flame, results in a decrease of the band gap to 2.32 eV.

The recent studies of the authors have shown that functional properties of TiO<sub>2</sub>, including the photoelectrochemical properties, are closely related to its defect disorder [18]. Therefore, defect chemistry may be used for the modification of the functional properties in a controlled manner. The purpose of the present work is to consider the "in situ" monitoring of defect-related properties for engineering a TiO<sub>2</sub>-based photosensitive oxide semiconductors with enhanced properties. It will be shown that the measurements of both electrical conductivity and thermoelectric power may be used for "in situ" monitoring semiconducting properties during processing at elevated temperatures.

## RESEARCH STRATEGY

The commonly applied research strategy to process TiO<sub>2</sub> with controlled functional properties consists in the processing of TiO<sub>2</sub> solid solutions or composites at elevated temperatures, cooling down the systems to room temperature and then testing the performance-related properties [1,3,8-15]. This "trial and error" strategy applied in the processing of TiO<sub>2</sub>-based systems with enhanced photosensitivity as it is shown in Fig 1.

The testing includes the functional properties, such as:

- 1) The determination of the efficiency of the conversion of solar energy into chemical energy, for example by using the current vs. voltage characteristics for a photoelectrochemical cell, or
- 2) The determination of photo-catalytic activity.

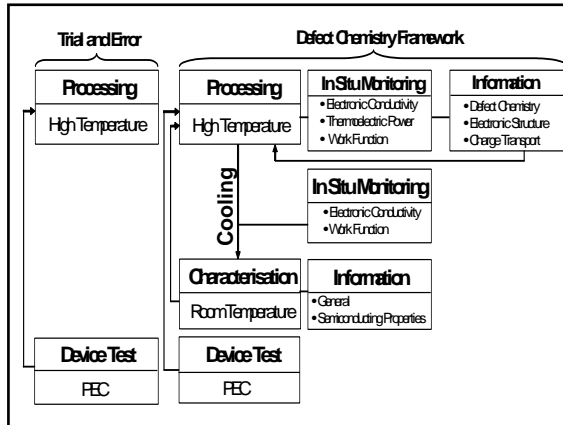


Fig. 1: The representation of the research strategy based on the "trial and error" and the "in situ" monitoring of defect-related properties at elevated temperatures and in the gas phase of controlled oxygen activity

The main disadvantage of the "trial and error" approach is a substantial time gap between the processing, usually taking place at elevated temperatures, and the testing of the performance-related properties, the latter taking place at usually at room temperature. Specifically, the time delays resulting from the cooling down the system, the testing for the performance, and the reimposition of the elevated temperature required for the process, are substantial, leading, in consequence, to a very long and complex cycle of the investigations.

The additional disadvantage of the "trial and error" is that it does not allow for an "inspection" into the kinetics of the reactions during processing, such as solid-state or gas/solid reactions. In other words, a substantial number of the "trial and error" cycles is required in order to assess the kinetics at elevated temperatures through testing taking place at room temperature. Another complication is the establishment of the optimal oxygen activity in the gas phase on the performance.

A substantial reduction of the time gap between the processing and the final performance test may be achieved through "in situ" monitoring of the functional properties of  $\text{TiO}_2$ , such as electrical properties.

This kind of inspection of the processing allows the following:

- 1) Intervention in the process, while the specimen is still in the reaction chamber at elevated temperatures, through e.g. the variation of processing conditions, such as the gas phase composition and temperature,
- 2) Interception of the process at the stage when optimal properties have been achieved.

Therefore, the "in situ" monitoring allows to achieve optimal properties at a minimum of time delay. The inspection may be achieved through "in situ" monitoring of several defect-sensitive properties, including the electrical conductivity and thermoelectric power.

## EXPERIMENTAL

The polycrystalline specimens of undoped  $\text{TiO}_2$  were prepared from high purity (99.999%) Ti-isopropoxide  $[\text{Ti}\{(\text{CH}_2)_2\text{CH}_2\text{OH}\}_4]$ . The powder of Nb-doped  $\text{TiO}_2$  was prepared by precipitation of two solutions involving: (a) high purity titanium isopropoxide and (b) high purity  $\text{NbCl}_5$ . The powder was cold pressed (200 MPa) into 15 mm diameter pellets and then sintered at 1423 K for 12 h. The total concentration of acceptor-type cation impurities and anions was 33.9 ppm and 20 ppm, respectively. The XRD data have shown that the specimens were of the rutile polymorph. The specimen exhibits high density and the grain size in 10 - 20  $\mu\text{m}$ .

Both thermoelectric power and electrical conductivity were determined using high temperature Seebeck probe, which is shown in Fig 2 [ ]. Thermoelectric power was measured along the temperature difference of two different polarities,  $\Delta T$  and  $-\Delta T$ . The thermoelectric power, obtained at 20-40 different temperature gradients in the range 0 - 5 K, was determined from the slope of approximately 20-30 independent measurements of thermovoltage which was plotted vs. the temperature gradient (Fig 3). The standard deviation of the individual determinations of thermoelectric power remained within  $\nabla 1\%$ .

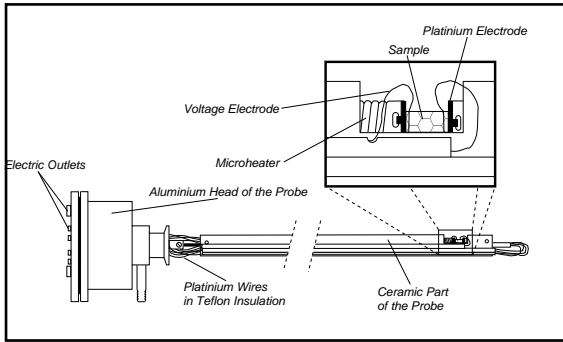


Fig. 2: The high temperature Seebeck probe for the measurements of the electrical conductivity and thermoelectric power [ ]

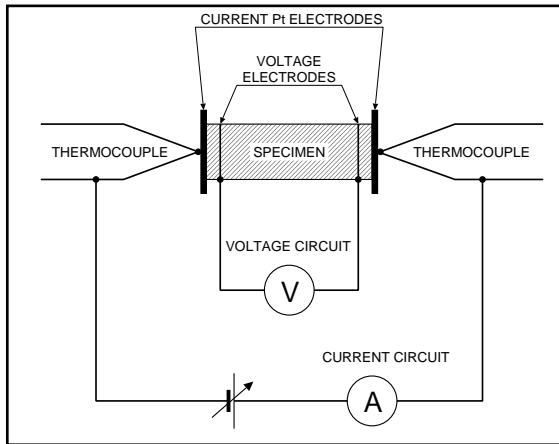


Fig. 3: The experimental plot of thermovoltage,  $\Delta V$ , along the temperature gradient for  $\text{TiO}_2$  at 1223 K at  $p(\text{O}_2) = 7.3 \text{ kPa}$

Electrical conductivity was determined using the four probe method. The probe involved the sample holder located in alumina tube in which the gas phase of controlled composition was imposed and the probe's head equipped with electrical outlets of the electrical leads for the probes and thermocouples. The sample holder included the electrodes and thermocouples for simultaneous determination of electrical conductivity and thermopower. The external (current) probes were formed of Pt plates attached to both sides of the slabs of rectangular-shaped specimen. A spring mechanism, located outside the high temperature zone, was used to maintain good galvanic contact between the Pt electrodes and the specimen. Voltage electrodes were formed of two Pt wires wrapped around the specimen and welded to the Pt connecting wires. The distance between these electrodes was 6.6 mm. Details of the procedure are reported before [19].

Required oxygen activity in the reaction chamber was imposed by an argon-oxygen mixture, of appropriate composition, flowing through the reaction chamber with a constant flow rate (100 ml/min). Zirconia electrochemical sensor was applied for the determination of oxygen activity which remained between 10 Pa (Ar) and 72 kPa

(pure oxygen). The experiments in which oxygen activity was increased and decreased are termed oxidation and reduction experiments, respectively. The oxidation and reduction runs were determined at several  $p(\text{O}_2)$  intervals within the above  $p(\text{O}_2)$  range.

The standard monitoring sheets for the measurements of both electrical conductivity and thermoelectric power during oxidation and reduction experiments at 1198 K are shown in Figs

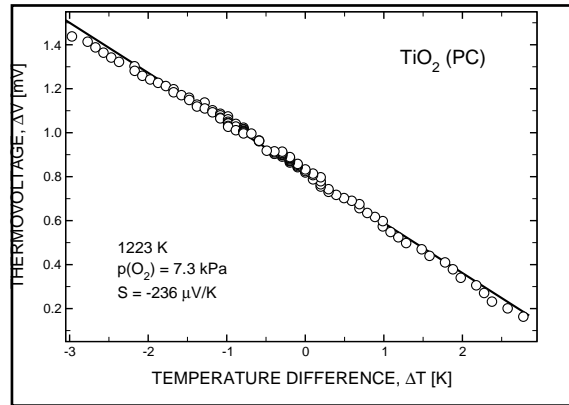


Fig. 4: The changes of thermoelectric power ( $S$ ), electrical conductivity ( $\sigma$ ), and oxygen activity,  $p(\text{O}_2)$ , during oxidation experiments at 1198 K

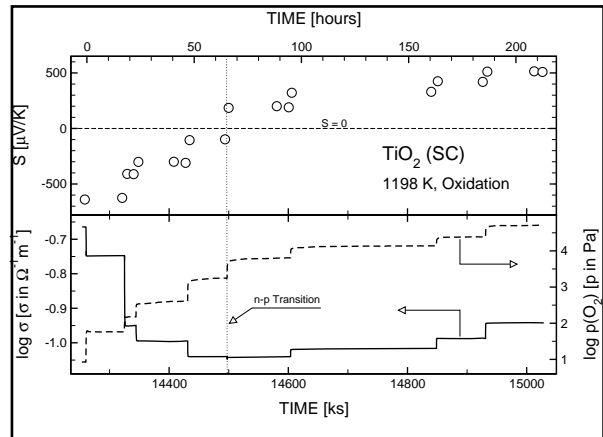


Fig. 5: The changes of thermoelectric power ( $S$ ), electrical conductivity ( $\sigma$ ), and oxygen activity,  $p(\text{O}_2)$ , during reduction experiments at 1198 K

As seen in Fig 4, the increase of  $p(\text{O}_2)$  results in an increase of thermoelectric power (determined in certain time intervals) and a decrease of the electrical conductivity (measured continuously). These data indicate that the  $\text{TiO}_2$  specimen at low oxygen activity is an n-type semiconductor and after oxidation becomes a p-type semiconductor [at  $p(\text{O}_2) = 75 \text{ kPa}$   $S=450 \text{ μV/K}$ ]. As also seen, the electrical conductivity assumes a minimum at the  $p(\text{O}_2)$ , which corresponds to  $S=0$ .

As seen in Fig 5, the decrease of  $p(O_2)$  during reduction results in an decrease of thermoelectric power and an increase of the electrical conductivity. These data indicate that reduction results in the conversion of p-type  $TiO_2$  to n-type  $TiO_2$ .

**RESULTS AND DISCUSSION**

The effect of oxygen activity on the electrical conductivity of both undoped and Nb-doped  $TiO_2$  in the range 1073 K - 1273 K is shown in Fig 6. These data may be considered in terms of defect disorder based on the exponent related to the slope of the following dependence [20]:

$$\frac{1}{m_\sigma} = \frac{\log \sigma}{\log p(O_2)} \quad (1)$$

where the exponent of the  $\log \sigma$  vs.  $\log p(O_2)$  dependence,  $1/m_\sigma$ , may be related to defect disorder. The data in Fig 6 allow to establish the following effects:

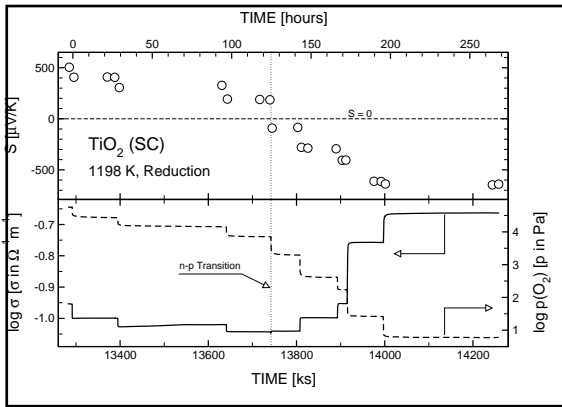


Fig. 6: Effect of oxygen activity on isothermal changes of the electrical conductivity for both undoped and Nb-doped  $TiO_2$  in the range 1073 K - 1273 K

**Undoped  $TiO_2$**

- 1) The exponent in strongly reductive conditions is  $-1/6$ . This exponent is consistent with the defect disorder, in which the predominant defects are doubly ionised oxygen vacancies that are compensated by electrons [19,20].
- 2) The exponent in oxidation conditions is  $-1/4$ . As seen, it has a tendency to decrease to zero and ultimately to assume a positive value. The exponent  $-1/4$  is consistent with the defect disorder of n-type  $TiO_2$ , in which the predominant defects are doubly ionised oxygen vacancies that are compensated Ti vacancies [21]. The minimum of the electrical conductivity is consistent with the n-p transition. The exponent  $1/4$  is consistent

with the defect disorder of p-type  $TiO_2$ , in which the predominant defects are doubly ionised oxygen vacancies that are compensated Ti vacancies [21].

**Nb-Doped  $TiO_2$**

- 1) As seen, the electrical conductivity in strongly reductive conditions is practically independent of  $p(O_2)$ . This behaviour is consistent with the defect disorder, in which the predominant defects are Nb ions in the Ti lattice sites that are compensated by electrons.
- 2) The exponent in oxidation conditions is  $-1/4$ . As seen, it has a tendency to decrease to zero and ultimately to assume a positive value. The exponent  $-1/4$  is consistent with the defect disorder of n-type  $TiO_2$ , in which the predominant defects are doubly ionised oxygen vacancies that are compensated Ti vacancies [21].

The effect of cooling on the electrical conductivity for both undoped and Nb-doped  $TiO_2$  in strongly reduced conditions from 1273 K to 300 K is shown in Fig 7. As seen, the cooling results in a complex temperature dependence of the electrical conductivity, which exhibits different activation energy values at high and lower temperatures.

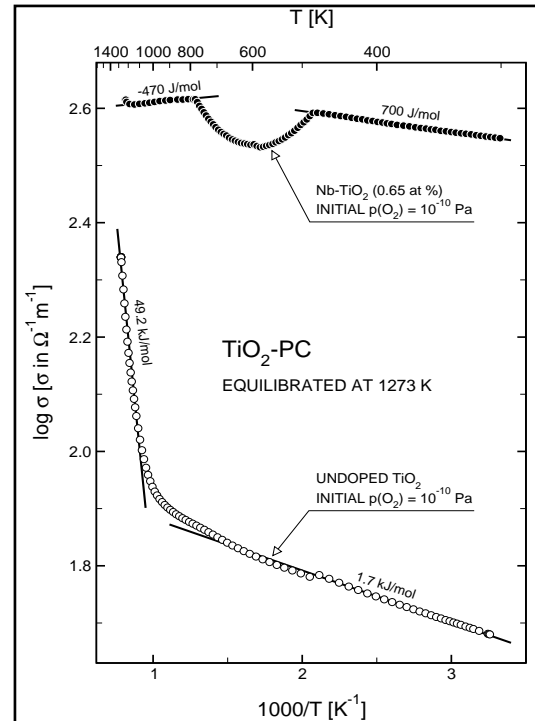


Fig. 7: The Arrhenius-type plot of the electrical conductivity for both undoped and Nb-doped  $TiO_2$  during cooling at  $p(O_2)=10^{10}$  Pa

**Undoped TiO<sub>2</sub>**

- 1) In the range 1273 K - 1000 K:  $E_{\sigma}=49.2$  kJ/mol
- 2) Below 1000 K:  $E_{\sigma}=1.7$  kJ/mol

The activation energy of the electrical conductivity for nonstoichiometric oxides, such as TiO<sub>2</sub>, has a complex physical meaning. At elevated temperatures, the activation energy term includes the term related to a change of the concentration of ionic defects and the term related to the mobility of electronic charge carriers [20]:

$$E_{\sigma} = \frac{2}{m_{\sigma}} \Delta H_f + \Delta H_m \quad (2)$$

where  $\Delta H_f$  is the activation enthalpy of the formation of defects, and  $\Delta H_m$  is the activation enthalpy of the mobility of charge carriers. These two terms are related to the activation energy above 1000 K when the change of temperature. However, the changes of temperature below 1000 K is determined by the mobility term ( $\Delta H_m = 1.7$  kJ/mol). Therefore, the determined  $\Delta H_f = 142.5$  kJ/mol.

**Nb-Doped TiO<sub>2</sub>**

- 1) In the range 1273 K - 800 K:  $E_{\sigma} = -470$  J/mol
- 2) In the range 800 - 500 K: variable temperature dependence  
Below 500 K:  $E_{\sigma}=700$  J/mol

In this case the concentration of ionic defect is determined by the content of Nb in the entire temperature range. Therefore, the activation energy should be considered in terms of  $\Delta H_m$ . Consequently:

- 1) The negative value of the mobility term in the range 1273 K - 800 K,  $\Delta H_m = -470$  J/mol, indicates that the charge is transported according to a quasi-metallic mechanism. This information is consistent with the mobility of electronic reported for Nb-doped TiO<sub>2</sub> [22].
- 2) The variable temperature dependence in the range 800 - 500 K indicates that the charge transport exhibits a complex dependence.
- 3) The activation energy term below 500 K is consistent with semiconducting charge transport ( $\Delta H_m = 700$  J/mol). As seen, the activation energy of the mobility term in this regime is lower than that for undoped TiO<sub>2</sub>.

**CONCLUSIONS**

The present work reports "in situ" monitoring of defect-related properties of TiO<sub>2</sub>, including electrical conductivity and thermoelectric power in order to assess its semiconducting properties during processing at elevated temperatures and also during cooling. The "in situ" monitoring is shown by the experimental data of the electrical conductivity and thermoelectric power during oxidation and reduction at 1198 K for both pure and Nb-doped TiO<sub>2</sub>.

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