BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48 (1), 144—146 (1975)

Electrical Properties of TeO_2.[1] I.

Kazuo Doi, Tomoaki Sasaki, and Kenzo Hijikata

Institute of Inorganic Chemistry, Department of Chemistry, Nihon University, 3-25-40
Sakurajosui, Setagaya-ku Tokyo 156

(Received December 15, 1973)

The electrical conductivity σ of polycrystalline tellurium dioxide (paratellurite; purity: 6-nine) was measured as a function of the oxygen partial pressure (1—760 mmHg) at temperatures between 475 and 550 °C. The relations between the experimental values of log σ and $1/T$ were well represented by straight lines, giving the apparent activation energy of about 1.36 eV. The oxygen-pressure dependence of the isothermal conductivity was well expressed by the $\sigma \propto P_{O_2}{}^{1/6}$ relation; this may be interpreted by assuming that electron holes with fully-ionized oxygen interstitials predominantly act as charge carriers. The p-type behavior in the conduction process was also confirmed by thermal emf measurements.

There have been a few papers on the piezoelectric,[2] elastic and photoelastic[3] characteristics of tellurium dioxide. There have not, however, been any reports on the electrical conductivity as a function of the oxygen partial pressure or on whether the predominant semiconductivity is of the p- or n-type in tellurium dioxide. Therefore, the aim of this investigation was to observe the temperature and oxygen-pressure dependences of the electrical conductivity for highly pure polycrystalline paratellurite, and, on the basis of these, to obtain some information on the defect type of paratellurite, which had not yet been elucidated.

Experimental

Specimens. Highly pure powders of paratellurite were prepared from 6-nine tellurium metal (Osaka Asahi Metal Co., Ltd.). The white precipitate which was obtained by dissolving the tellurium metal into dilute pure nitric acid (Super Special Grade: Wako Pure Chemical Industries, Ltd.), was filtered, washed fully with distilled water, and dried in a vacuum at 80 °C. The dried powders were heated to 400 °C for 1 hr in a Pt-crucible to drive off the residual nitric acid. The X-ray diffraction patterns of the resulting powders indicated a well-crystallized structure of paratellurite. Pellets (10 mm in diameter and 3 mm thick) were made by compacting the powders at 2 ton/cm^2 and by then sintering the compacts for 150 hr at 630 °C in the Pt-crucible in air. The densities of the sintered disks were approximately 64% of the theoretical yield.

The impurities of the specimens before and after the conductivity measurements were found to be Mg and Cu by means of emission spectrographic analysis,[4] and no other elements were detected. Chemical analysis indicated Mg: 0.5 ppm and Cu: 0.0 ppm. The specimens before and after the measurements were both estimated to be 6-nine purity.

Measurements. The electrical conductivity was measured by a two-terminal method in a comparatively low temperature range so as to be able to neglect the influence of the evaporation of tellurium dioxide on the measurements.

A detailed schematic diagram of the apparatus for electrical conductivity measurements has been presented elsewhere.[5] Two thermocouples (0.3 mmϕ Pt–Pt13%Rh) were welded to each electrode of a platinum plate. The platinum arms of the thermocouples were used to measure the AC and DC conductivities and the Seebeck effect.

The various partial pressures of oxygen were provided by oxygen-nitrogen tank mixtures (dew points: -50 °C).

The specimen temperature was controlled within ± 0.15 °C by regulating the SCR power supply. The AC conductivity was taken by means of a bridge (Type TR-1C: Ando Electric Co., Ltd.), applying selected frequencies in the range of 0.03—3 kHz to the specimens in all runs, while the DC conductivity was determined on an electrometer (Type TR-8651: Takeda Electric Co., Ltd.). The equilibrium value between the specimen conductivity and the oxygen partial pressure in the surrounding atmosphere was determined after the specimen resistance had been stabilized for 2 hr; this value remained constant for 30 hr or more.

The conductivity values were obtained with a good reproducibility in all the cases tried.

Results

The DC conductivity data nearly coincided with those at 30 Hz, as is shown in Fig. 1. The measured conductivity value was reproducible for both increasing and decreasing temperatures and for the ambient oxygen partial pressures.

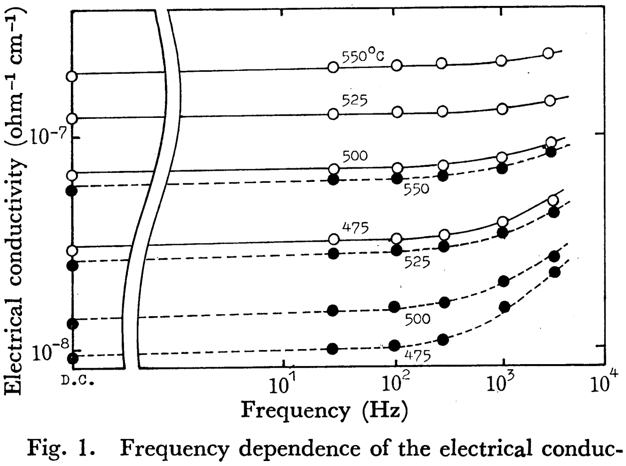

Fig. 1. Frequency dependence of the electrical conductivity TeO_2.

—○—○—: the values measured under oxygen gas (760 mmHg)

—●—●—: the values under nitrogen gas (760 mmHg)

Plots of log σ *vs.* $1/T$ at various oxygen partial pressures are shown in Fig. 2. In the temperature range examined, the plots were well represented by a straight line at each oxygen pressure. From these results, the apparent activation energy for the electrical conductivity of the paratellurite was calculated as about 1.36 eV in all the atmospheres tested. The oxygen

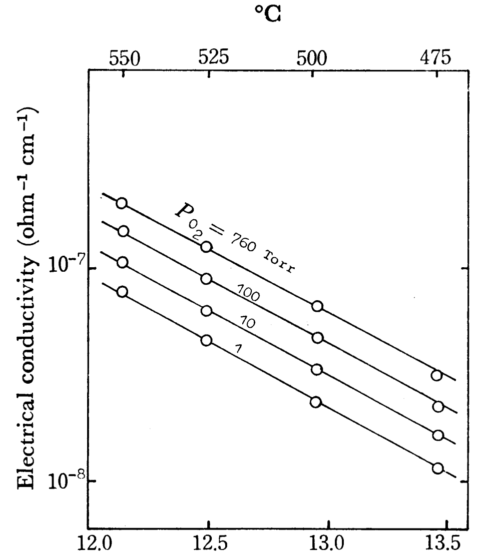

Fig. 2. The electrical conductivity of TeO_2 (at 30 Hz) *vs.* the reciprocal of absolute temperature. $P_{O_2}+P_{N_2}=760$ mmHg

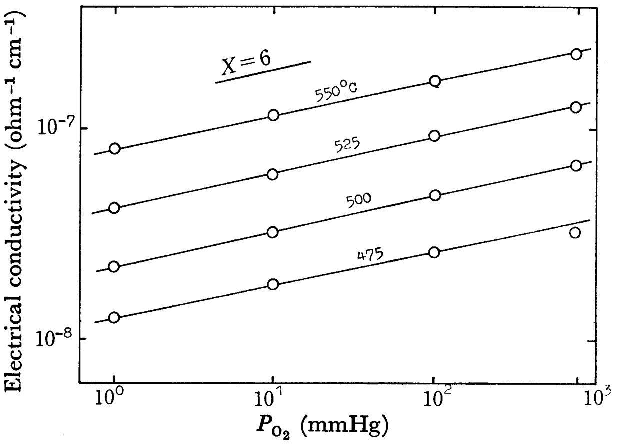

Fig. 3. The relation between the electrical conductivity of TeO_2 (at 30 Hz) and the oxygen partial pressure. X is defined in the conductivity expression $\sigma \propto P_{O_2}{}^{1/X}$.

partial pressure dependence of the electrical conductivity for the polycrystalline paratellurite is indicated in Fig. 3.

As may be seen, the electrical conductivity increased with an increase in the oxygen partial pressure in the surrounding atmosphere; therefore, it seems that the semiconductive nature of paratellurite is the p-type under the present experimental conditions. The p-type character of paratellurite was also confirmed from the sign of the Seebeck voltages under the temperatures examined.

The linear relationship of the conductivity isotherm can be written as $\sigma=K\cdot P_{O_2}{}^{1/X}$, with $X=6$.

Discussion

It could be assumed that the contamination of the specimen by its surroundings and the evaporation of the specimen were negligible in the present investigation, because a linear relationship between log σ and $1/T$ was obtained with a good reproducibility for both increasing and decreasing temperatures under ambient oxygen partial pressures, as may be seen in Fig. 2.

The coincidence of the DC conductivity data with those of AC (at 30 Hz) indicated that the predominant semiconduction for the paratellurite is electronic rather than ionic for the oxygen partial pressure and temperature range examined.

Considering the purity of the specimen used in this study, it may be assumed that the influence of the impurities on the pressure dependence of the conductivity is negligible.

The electrical conductivity increased with an increase in the oxygen partial pressure at each temperature, and the electrical conductivity was expressed as a function of the oxygen partial pressure by the relation: $\sigma=K\cdot P_{O_2}{}^{1/6}$.

If this character were intrinsic behavior, it could be determined by applying the Baumbach-Wagner law[6] whether the predominant defect is cation vacancies or anion interstitials resulting from the deviation of stoichiometry.

1) Cation-vacancy Model.

$$O_2(\text{gas}) \rightleftharpoons 2O(\text{lattice}) + \text{Te}_v{}^{+m} + m\oplus \qquad (1)$$

where $\text{Te}_v{}^{+m}$ is the cation vacancy and $\oplus$, the electron hole, and where the degree of ionization, m, takes integral values up to 4.

Then, $$K'\cdot P_{O_2} = [\text{Te}_v{}^{+m}][\oplus]^m \quad m = 1, 2, 3, 4. \qquad (2)$$

Here, K' is an equilibrium constant and the square brackets indicate the concentration. If the electroneutrality condition can be simplified as $m[\text{Te}_v{}^{+m}]=[\oplus]$,

then, $$\sigma = [\oplus] \propto P_{O_2}^{1/m+1}. \qquad (3)$$

Therefore, the cation-vacancy models have oxygen-pressure dependences of 1/2, 1/3, 1/4, and 1/5 ($m=$ 1, 2, 3, 4).

2) Anion-interstitial Model.

$$1/2O_2(\text{gas}) \rightleftharpoons O_{\text{int}}^{-n} + n\oplus \qquad (4)$$

where O_{int}^{-n} is the oxygen interstitials; the degree of ionization, n, may be 1 or 2. Applying the mass action law,

$$K''\cdot P_{O_2}^{1/2} = [O_{\text{int}}^{-n}][\oplus]^n \qquad (5)$$

If the electroneutrality condition is now shown as:

$$n[O_{\text{int}}^{-n}][\oplus], \text{ then } [\oplus] \propto P_{O_2}^{1/2(n+1)} \qquad (6)$$

Thus, the oxygen-interstitial model has a pressure dependence of 1/4 or 1/6 ($n=1$, 2).

The slope, 1/6 ($X=6$), corresponded to the predominance of doubly-ionized oxygen interstitials, with electron holes as the charge carriers, as has been described above.

This suggests that oxygen atoms (ions) from oxygen gas in the surrounding atmosphere dissolve into the crystal of paratellurite. The crystal structure of paratellurite has been studied by several authors.[7,8] Lindqvist[9] suggested that paratellurite is four-fold coordinated by a polyhedron, being a somewhat distorted trigonal bipyramid with bond distances of

Te–O_{eq}=1.90±0.02 Å and Te–O_{ax}=2.08±0.02 Å, and lacking one atom in the equatorial position.

Therefore, it can be inferred that the oxygen atoms (ions) predominantly penetrate into these lacking sites in the crystal of paratellurite.

The authors wish to thank Dr. Hajime Kishi, Mr. Ko Yokomizo, and Mr. Takeo Hirasawa, Mitsubishi Central Research Institute, Mitsubishi Metal Corp., Oomiya, Japan, for their spectrographic and chemical analyses.

References

1) Reported at the Fall Meeting of the Japan Society of Powder Metallurgy, Osaka, Japan. Nov. 17 (1972).
2) G. Arlt and H. Schweppe, *Solid State Comm.*, **6**, 783 (1968).
3) N. Uchida and Y. Ohmachi, *J. Appl. Phys.*, **40**, 4692 (1969).
4) Jarrell-Ash Co., emission spectrograph with a diffraction grating, Ebert-mount 3.4 m.
5) J. Hattori, T. Sasaki, and K. Hijikata, *Jap. Soc. Powder Metall.*, **19**, 90 (1972).
6) H. H. Baumbach and C. Wagner, *Z. Phys. Chem.*, **B22**, 199 (1933).
7) J. Zemann, *Z. Krist.*, **127**, 319 (1968).
8) J. Leciejewicz, *ibid.*, **116**, 345 (1961).
9) O. Lindqvist, *Acta Chem. Scand.*, **22**, 977 (1968).