Aust. J. Chem., 1976, **29**, 1099–100

The Non-Stoichiometry and Electrical Conductivity of Pink Zinc Oxide

Victor J. Norman

Australian Defence Scientific Service, Department of Defence,
Materials Research Laboratories, P.O. Box 1935, Adelaide, S.A. 5001.

Abstract

The electrical conductivities of samples of pink zinc oxide made by two different processes, and that of the white zinc oxide from which they were prepared, are shown to be proportional to their non-stoichiometry provided that the concentration of chemisorbed oxygen is expressed as a function of the surface area of the zinc oxide.

Introduction

In a previous paper[1] it was shown that the amount of reactive oxygen (expressed in ppm by weight) chemisorbed on pink zinc oxide prepared by the ammonium carbamate process[1,2] was more than 20 times greater than that chemisorbed on the white zinc oxide from which it was prepared. On the other hand, the photoconductivity/dark conductivity ratio of the pink zinc oxide was not markedly higher than that of the white zinc oxide, and this did not reflect the increase that might be expected to result from the increased oxygen chemisorption.

This apparent discrepancy may be explained by observing that the specific surface area of pink zinc oxide prepared by heating white zinc oxide with ammonium carbamate was nearly an order greater than that of the white zinc oxide, so that any direct correlation between the electrical properties and non-stoichiometry of these two samples should not be expected if the concentration of the chemisorbed species (which is situated exclusively on the surface) is expressed in ppm by weight, or in ion m^{-3}.

Ehret and Greenstone[3] have reported that their method of preparation (heating with ammonium nitrate to about 300°C) produced a pink zinc oxide having a larger particle size than that of the white zinc oxide from which it was prepared. It was decided, therefore, to examine pink zinc oxide prepared by Ehret and Greenstone's method,[3] in conjunction with that made by the carbamate process,[1] with a view to correlating electrical properties with non-stoichiometry, when the chemisorbed reactive oxygen is expressed as a function of the surface area, rather than as a function of the mass of the zinc oxide.

Results and Discussion

The mechanism for dissolution of nitrogen in zinc oxide tentatively proposed by Hoeffgen and Hauffe[2] involves the consumption of free electrons with the simul-

[1] Norman, V. J., *Aust. J. Chem.*, 1975, **28**, 229.
[2] Hoeffgen, D., and Hauffe, K., *Phys. Status Solidi A*, 1970, **3**, 185.
[3] Ehret, W., and Greenstone, A., *J. Am. Chem. Soc.*, 1943, **65**, 872.

taneous production of interstitial zinc ions (Zn^+). However, Zn^+ ions associated with an equivalent electron deficiency cannot be determined by the chemical method,[4] and can only be estimated indirectly from the amount of chemisorbed reactive oxygen with which the Zn^+ ions are associated.

The maximum chemisorption of reactive oxygen[5] on the pink zinc oxide prepared by the method of Ehret and Greenstone[3] was 10 ppm by weight ($2 \cdot 1 \times 10^{24}$ ion m^{-3}), and was recorded on the sample in the 'as prepared' condition. Exposure to atmospheric air at 23°C and 50% relative humidity for periods up to 50 days resulted in a progressive lowering of the reactive oxygen content. This is in marked contrast to the behaviour[1] of pink zinc oxide prepared by the carbamate process, and suggests that, at the higher temperature of Ehret and Greenstone's method of preparation, the species of oxygen initially chemisorbed is the reactive variety (O^-).

The results of examination of, (*a*) pink zinc oxide prepared by the method of Ehret and Greenstone,[3] (*b*) pink zinc oxide prepared by the carbamate process[1] and (*c*) high-purity white zinc oxide from which the pink zinc oxides were prepared, are shown in Table 1. Reactive oxygen was determined by the chemical method,[5] and the results expressed both as a concentration of the zinc oxide surface area, and as a concentration of the mass of the zinc oxide. Specific surface areas were determined by electron microscopy and dye adsorption, and conductivity measurements were made in dry oxygen by the method of Nobbs.[6] The reproducibility of the conductivity measurements was estimated to be ±20%.

Table 1. Non-stoichiometry and conductivity of three samples of zinc oxide

Parameter	Sample (*a*)	Sample (*b*)	Sample (*c*)
Specific surface area (m^2 kg^{-1})	$1 \cdot 6 \times 10^3$	$4 \cdot 4 \times 10^4$	$4 \cdot 8 \times 10^3$
Chemisorbed oxygen (ion m^{-3}) (*A*)	$2 \cdot 1 \times 10^{24}$	$1 \cdot 1 \times 10^{25}$	$3 \cdot 7 \times 10^{23}$
(ion m^{-2}) (*B*)	$2 \cdot 3 \times 10^{17}$	$4 \cdot 5 \times 10^{16}$	$1 \cdot 4 \times 10^{16}$
Dark conductivity k_d (S m^{-1})	$2 \cdot 9 \times 10^{-13}$	$2 \cdot 9 \times 10^{-14}$	$2 \cdot 2 \times 10^{-12}$
Photoconductivity k_p (S m^{-1})	$1 \cdot 1 \times 10^{-8}$	$2 \cdot 4 \times 10^{-10}$	$6 \cdot 9 \times 10^{-9}$
Ratio k_p/k_d (*C*)	$3 \cdot 8 \times 10^4$	$8 \cdot 3 \times 10^3$	$3 \cdot 2 \times 10^3$
Ratio B/C	$6 \cdot 1 \times 10^{12}$	$5 \cdot 4 \times 10^{12}$	$4 \cdot 4 \times 10^{12}$
Ratio A/C	$0 \cdot 55 \times 10^{20}$	$13 \cdot 0 \times 10^{20}$	$1 \cdot 2 \times 10^{20}$

Reference to the final two lines of Table 1 shows that the photoconductivity/dark conductivity ratio is, to within the limits of reproducibility of conductivity measurements, proportional to the amount of oxygen chemisorbed on the surface of the zinc oxide, but that this relationship is not apparent when the concentration of the non-stoichiometric species is expressed as a function of the mass of the zinc oxide. Non-stoichiometry should therefore, when it is employed to predict electrical properties and electrographic behaviour, be expressed as excess zinc or chemisorbed oxygen ions per unit area of the zinc oxide surface.

Manuscript received 2 December 1975

[4] Norman, V. J., *Analyst (London)*, 1964, **89**, 261.
[5] Norman, V. J., *Aust. J. Chem.*, 1966, **19**, 1133.
[6] Nobbs, J. Mck., *J. Phys. Chem. Solids*, 1967, **28**, 205.