# SOME ELECTRICAL AND ELECTROCHEMICAL PROPERTIES OF SINTERED ZINC OXIDE WITH METAL EXCESS

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Abstract: Samples of zinc oxide with metal excess ZnO+xZn are made by sintering. The electrical dc and ac conductivity is measured in the temperature range from 300 K to 800 K and in the frequency range from 50 Hz to 500 kHz for three different x values. The activation energies and preexponential factors are estimated and the possible conductivity mechanism is suggested. The current-voltage characteristics measured in a reaction proceeding at ZnO+xZn electrode provide evidence of its electrochemical behaviour.

## 1. Introduction

Composits, metal oxides with metal excess, exhibit properties significantly different in many aspects than pure metal oxides (1,2). Therefore it was of interest to investigate the behaviour of zinc oxide with metal excess ZnO+xZn. This paper is a preliminary report on our study of some electrical and electrochemical properties of sintered disordered ZnO+xZn composits. It is known that ZnO crystals are able to capture a reasonable fraction of solar spectrum. As it is experimentally determined that composits ZnO+xZn have smaller energy gap than ZnO, conditions for solar energy converting electrolytic cells are being sought through a research carried out into the electrochemical behaviour of ZnO+xZn / electrolyte system.

## 2. Experimental

The specimens were made by mixing zinc oxide and zinc powder in certain proportions. The mixtures were molded into the disks 12 mm in diameter and 2-3 mm long. The samples were sintered at different temperatures from 700 K to 1000 K in argon atmosphere for two hours. The best results were obtained when sintering process was performed at 800 K.

The electrical property measurements were carried out in an alumina tube furnace, where the specimens were held between platinum electrodes with platinum lead wires. The dc conducti-

vity measurements were made by Keitley electrometer 610 C in its resistance mode. At the same time the measurements of the temperature dependence of the ac conductivity in the range from 50 Hz to 500 kHz were conveniently made using Hewlett-Packard impedance meter model 4800 A.

Electrochemical measurements were made in a fairly standard cell containing a working electrode ZnO+xZn, a saturated calomel electrode and a coiled platinum wire electrode. Current - voltage characteristics were measured by Wenking potentiostat model 70 HV1. The supporting electrolyte was borate buffered to pH=8.9 to which redox couple $Fe(CN)_6^{4-/3-}$ or $Ce(SO_4)_2$ was added.

## 3. Results and discussion

Fig.1 shows the typical temperature dependence of dc and ac conductivity for three specimens ZnO+xZn.

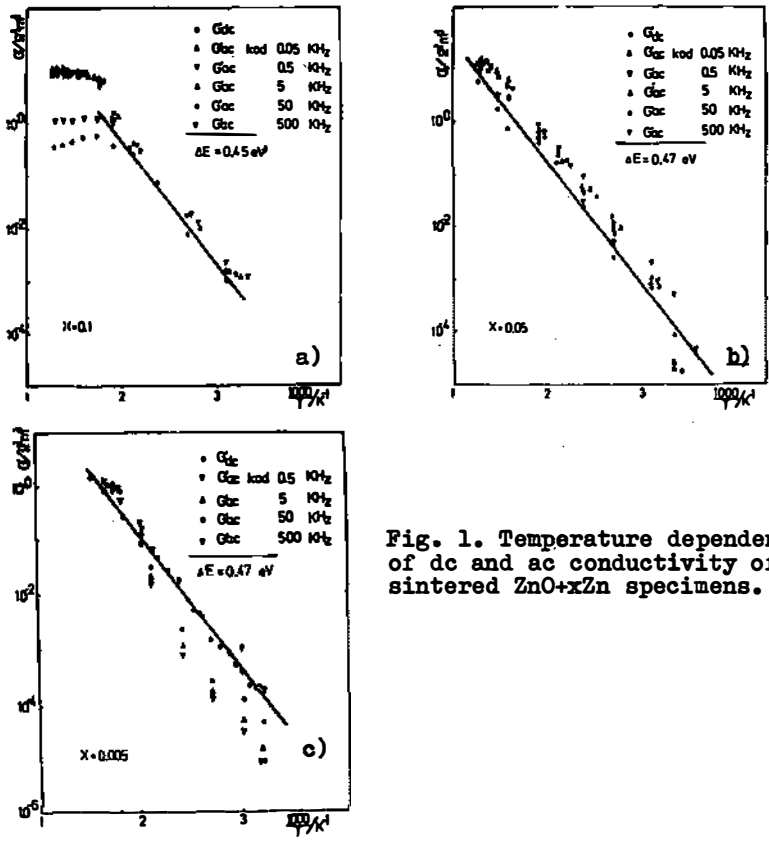


Fig. 1. Temperature dependence of dc and ac conductivity of sintered ZnO+xZn specimens.

The dc conductivity has activated character

$$\sigma_{dc} = C \exp(-\frac{\Delta E}{kT}) \qquad (1)$$

with $\Delta E$=0.45 eV and C of the order of $10^4$ ohm$^{-1}$m$^{-1}$.

The frequency independent ac conductivity with the same activation energy prevails at temperatures above 400 K. The magnitude of preexponential factor suggests that the conduction process in disordered sintered ZnO+xZn is by the charge carriers with an energy exceeding a corresponding "percolation" level (3). Our experiments show that the addition of zinc lowers the energy gap in comparison with $E_g$ (3.2 eV) in ZnO crystals. This is in agreement with similar observation concerning energy gap in $Al_2O_3$+xAl (1).

The influence of metal excess (x-value) on conductivity exists, but it is not very pronounced. As determinations of x values have been done only before sintering process, we would not discuss this problem. If specimens are heated above 800 K the dc and ac conductivity for ZnO+xZn with higher metal excess is lowered as a result of sublimation of excess zinc.

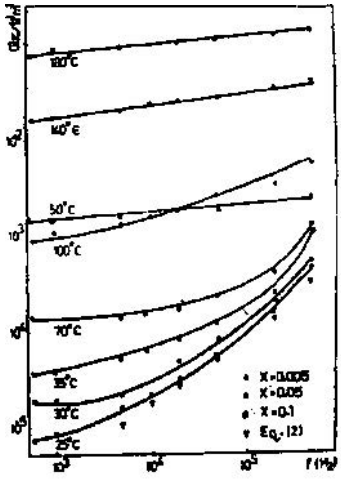


Fig.2.

The ac conductivity of ZnO+xZn specimens over a wide frequency range at different temperatures.

Fig.2 shows the conductive properties of ZnO+xZn as a function of frequency at different temperatures. Above $10^4$ Hz and at low temperatures $\sigma_{ac}$ exhibits dependence on conductivity as $\omega^s$ with $0.7 < s < 1.0$ for specimens with x=0.005 and 0.05, while such behaviour is not observed for specimen with x=0.1. For example it is possible to fit the lowest experimental curve in Fig.2 to the data obtained from the relation

$$\sigma_{ac} = \text{cons.}\ \omega^s \qquad (2)$$

with s=0.8. This may be taken as evidence that in these specimens $\sigma_{ac}$ is caused by a kind of hopping conduction.

It is known that polycrystalline materials can be operated in regenerative electrolytic solar cells at substantial fractions of the respectable energy conversion efficiency of single crystal electrodes to even more economic methods of manifacrure (4). As our interest has been directed towards photoelectrochemical processes applicable for solar energy conversion , the electrochemical investigation of ZnO+xZn electrode has been first done and results are now briefly presented. Among many variables that affect the rate of hole transport only the influence of redox couple and its concentration on j(U) characteristics is studied.

Fig.3 and 4, chosen as examples among electrochemical measurements on ZnO+xZn electrode, show the essential properties of the j(U) characteristics in comparison with j(U) curves of Pt electrode. The appearance of limiting currents in the anodic potential range, without respect to electrolytes, is obvious,

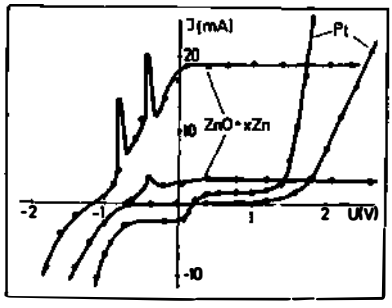


Fig.3. The current density - potential curves in buffered borate solution of pH=8.9 (- • -) and after the addition of 0.05 N redox couple $K_3Fe(CN)_6/K_4Fe(CN)_6$ (- o -).

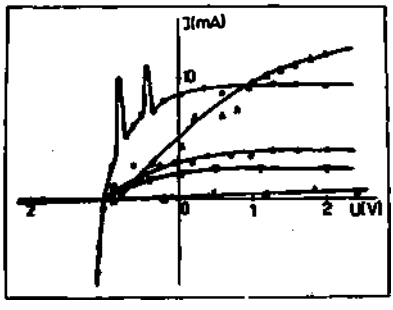


Fig.4. The current density - potential curves in water solutions at various concentrations of added $Ce(SO_4)_2$ :
- ▲ - no $Ce(SO_4)_2$ present
- ▼ - 0.0025 N $Ce(SO_4)_2$
- o - 0.005 N $Ce(SO_4)_2$
- • - 0.025 N $Ce(SO_4)_2$
- Δ - 0.25 N $Ce(SO_4)_2$

what confirms our supposition that reasons for their existence lie in solid phase. Although mechanisms of electron transfer through particular electron transfer channels at disordered oxide - electrolyte interphase can be very complex (5), the essential analogy between the shape of j(U) characteristics in Fig.3 and 4 and those obtained on crystalline n-type semiconductors (6) indicates that electron reactions include electron transfer via valence band. The increase of the limiting currents caused by increasing the $Ce^{3+/4+}$ redox couple concentration, whose aqueous redox potential is lower than redox potential of $Fe(CN)_6^{4-/3-}$ couple (7), suggests that anodic charge process is probably Red + $p^+ \rightleftarrows$ Ox.

The holes arriving at the surface may oxidize the electrode itself (8). Such a reaction competes with the desired oxidation of the redox couple in solution and destroys the electrode. The experimental fact that ZnO+xZn electrode during the experiments behaves reversible and remains stable indicates that rates of oxidation od the dissolved redox couple greatly exceeds the rate of oxidation of ZnO+0.5Zn electrode.

It could be noticed that our understanding of electrochemical processes remains incomplete. Therefore addition research in electrical and electrochemical behaviour of ZnO+xZn composits is needed and should provide more information on electron transfer through interphase preceeding and forming the basis for further photoelectrochemical and photochemical investigation and its practical application.

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