JOURNAL OF SOLID STATE CHEMISTRY 3, 125–130 (1971)

Study of Noise Associated with Oxidation Reactions at the Illuminated Single Crystal Zinc Oxide Anode

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Received, July 13, 1970

The number of correlated electrons involved in the charge transfer step during anodic oxidation of various reactants at the illuminated ZnO electrode was determined by noise measurements. This number was found to be equal to unity in the case of anodic dissolution of ZnO and of oxidation of I^-. For the anodic oxidation of aliphatic alcohols, which is known to occur by a current multiplication mechanism, the hole capture and electron injection steps were shown to be correlated. Basing upon the noise measurements, the lifetime and surface concentration of the intermediate radicals, formed during the alcohol oxidation, are discussed.

1. Introduction

It has been demonstrated by Tyagai and Lukyanchikova (*1–5*) that electrochemical noise measurements can be used to determine the number of electrons participating in the slow step of an electrode reaction. As well as metal (Pt) (*1*, *2*), a semiconductor (CdS) (*3–5*) was used as electrode material by these authors. From their measurements of the electrochemical noise associated with the cathodic reduction of the I_3^- ion on the CdS surface (*3*, *4*), it appeared that one electron only participates in the slow step, the overall reaction involving two electrons. This result was explained by assuming a fast preadsorption and dissociation of the iodine molecule at the CdS surface, the slow step of the reaction then being the transfer of one electron from the conduction band of CdS to each of the surface iodine atoms. The same authors have also studied (*5*) the noise associated with the anodic dissolution of CdS under band-gap illumination, a reaction involving valence band holes. Also in this case, they found a value of one for the shot noise coefficient γ which is given by

$$\gamma = \frac{\overline{(\delta i)^2}}{2eJ(\Delta f)}. \qquad (1)$$

In this formula $\overline{(\delta i)^2}$ represents the mean squared fluctuation of the current in the frequency interval Δf and J is the dc current through the system. In the case of photochemical noise, the value of γ is, under certain conditions, related to the phenomenon of current multiplication. From γ, it is possible to calculate the number m of consecutive one-equivalent electrochemical reaction steps which are to be considered as being correlated. Two consecutive reaction steps are observed as being correlated if the lifetime of the intermediate product is smaller than the time interval used in measuring the deviations from the mean value of the current.

Tyagai and Lukyanchikova concluded that no current multiplication occurs during the anodic photodissolution of CdS, i.e., that the hole capture process is not accompanied by injection of electrons into the conduction band of the semiconductor. It is our belief however that a value of $\gamma = 1$ does not exclude the possibility of current multiplication; it could be that the hole capture step and the consecutive electron injection step are not correlated, which would imply that the intermediate species formed after capture of one hole has a relatively large lifetime (see discussion). However, in all cases of semiconductors with a band-gap larger than 1 eV in which the contribution of holes to the anodic dissolution has been determined, this contribution has been found to be close to unity (*6*).

In a previous paper (*7*), we reported our results concerning the first part of a study on electrochemical noise phenomena at the ZnO/electrolyte interface. This system was chosen mainly because of its stability, and also because of the relatively large amount of data available on its electrochemical behavior [for a review, see e.g., (*8*)]. The reaction studied in (*7*) was the cathodic reduction of $Fe(CN)_6^{3-}$ where a value of $\gamma = 1$ was to be normally expected. It was found, that the presence of surface states at the interface complicated the noise results considerably.

This paper includes the results we obtained in the second part of our investigation on electrochemical noise at the ZnO/electrolyte interface. Here, anodic oxidation reactions taking place under band-gap illumination in the limiting current region are concerned. Three types of reactions have been studied. The first one is the anodic dissolution of ZnO, for which there are good reasons to believe that valence band holes only are involved. One argument is that a quantum efficiency of one has been observed for this reaction (*9*). Another argument follows from the observation of the current multiplication phenomenon, which will be discussed below. The latter argument also holds in the case of the oxidation of I^-, which is the second reaction studied in this work. These two reactions have been mainly selected in order to check whether the same kind of complications arise as encountered in the cathodic measurements. Since this appeared not to be the case (see results), we then proceeded with the study of a third reaction type, namely the anodic oxidation of aliphatic alcohols, during which current multiplication has been found (*10*). We will briefly recall the experimental facts which have led to the proposed mechanism of this reaction type.

In darkness, the current density at the ZnO anode is very low (usually a few nA/cm^2), in an indifferent electrolyte solution as well as in the solutions of most reducing agents, some reactants with high reducing power excepted (*11*). Apparently, electron transfer from reactants in solution to the conduction band of ZnO is uncommon.

When the ZnO anode in contact with an indifferent electrolyte is illuminated with light of energy larger than the band-gap, an anodic current J_0 is measured, which, from a certain anodic voltage on, tends to saturation. In the saturation region, J_0 is proportional to the light intensity. The reaction involved here has been shown to be the anodic photodissolution of ZnO (*9, 12, 13*). The same current is observed, at constant light intensity, in the presence of all one-equivalent and many two- or multiequivalent reducing agents (an example is I^-). Obviously, valence band holes are needed for all these reactions, and the rate-determining step is the supply of holes at the interface.

With some two- or multiequivalent reducing agents present in solution, an anodic current $J > J_0$ was found at constant light intensity. This effect was first observed with formate ion (*14*), and was further found (*10*) to occur with several reactants such as primary and secondary aliphatic alcohols. The mechanism suggested (*14*) is one, in which the reactant A captures a hole to form a radical-type species $A^{+\cdot}$ which has an electron energy level nearby or above the bottom of the conduction band, and is thus able to inject an electron in this band. This process is expressed in the surface reactions

$$A + p \rightarrow A^{+\cdot} \tag{2}$$

$$A^{+\cdot} \rightarrow A^{2+} + e \tag{3}$$

where p is a valence band hole and e a conduction band electron. For instance, if A stands for 2-propanol, the symbol A^{2+} represents the reaction products acetone + $2H^+$. The nature of the radical is unknown; it has been suggested that it could be the hydrogen atom (*10*).

In principle, the multiplication factor M, given by

$$M = \frac{J}{J_0} \tag{4}$$

should be equal to 2. In favorable cases, values of M near 2 have been observed. This proves that the anodic dissolution reaction, giving rise to the current J_0, involves very little or no multiplication. In other cases, such as in this work, $1 < M < 2$, which could be due to the competition for holes by the anodic dissolution reaction. False observation of J_0 due to current multiplication during anodic dissolution is unlikely in such case, since J_0 does not decrease upon addition of I^- to the solution of indifferent electrolyte. That I^- does get oxidized by holes is shown by the decrease of the current J, which was originally measured in the presence of alcohol, when I^- is subsequently added. This effect is ascribed to a competition of both reactants for holes (*10*).

The multiplication effect, originally observed in the cases mentioned above, was also found with formaldehyde at the CdS anode (*15*). The counterpart of this oxidative current multiplication has been found for the cathodic reduction of $S_2O_8^{2-}$ and H_2O_2 at illuminated p-GaP (*16*) and of Br_2 at illuminated p-GaAs (*15*).

The main objective of the noise measurements during the anodic oxidation of alcohols was to investigate, whether the two reaction steps, represented by the Eqs. (2) and (3), are correlated or not. This could allow us to get some information about the lifetime of the radical intermediate.

2. Experimental

The apparatus consisted of an electrochemical cell, an electrical measuring circuit and a light source. The cell contained a ZnO single-crystal electrode, a Pt electrode and an aqueous electrolyte, and was equipped with a window through which the illumination of the ZnO electrode occurred. Zinc oxide single-crystals with a specific conductivity of the order of 1 Ω^{-1} cm^{-1} were purchased from Minnesota Mining and Manufacturing Company. They were in the form of hexagonal wafers cut perpendicular to the *c*-axis, with dimensions of about 5 mm diameter and 1 mm thickness. In all experiments, the $(000\bar{1})$ face was exposed to the electrolyte. Etching and identification of this face occurred by a short immersion in concentrated HCl solution, while subsequent chemical polishing involved a 2-h treatment in 85% H_3PO_4. Ohmic contact was made with the (0001) face by means of an In–Hg alloy. An insulating paint was used to separate the electrolyte from the back contact and to mask part of the $(000\bar{1})$ face, since a small surface area was favorable for noise measurements. Three crystals *A*, *B*, and *C* were used, with a surface area in contact with the solution of 3.5, 1.5, and 3 mm^2, respectively. The composition of the electrolyte solutions is given in the results. All chemicals were reagent grade. Before each measurement, high purity nitrogen was bubbled through the solutions in order to remove dissolved O_2, since oxygen has been shown (*10*, *14*) to lower the current multiplication effect. All measurements were made at room temperature.

A battery was included in the electrical circuit in order to apply a voltage between the ZnO and Pt electrodes. In all experiments, the voltage of the ZnO was +2.4 V versus Pt. The electrical circuit allowed the measurement of the cell current (by means of a Hewlett Packard 425A dc microvolt-ammeter), of the impedance between both electrodes (by means of an Electro Scientific Industries capacitance bridge 277 and ac generator-detector 861 A), and of the noise. For the noise measurements, a resistance *R* was inserted into the circuit so that the impedance over which the noise voltage was measured consisted of a parallel connection of the impedance *Z* of the cell and the resistance *R* in series with the battery used for the dc current *J*. The resistance *R* was taken sufficiently large (10^6 Ω) in order to have a noise voltage largely due to the cell. After being amplified by an ultra-low noise Keithley model 103 amplifier (10^7 Ω, 20 pF imput impedance in normal position), the noise voltage was inserted into a General Radio 1900 A wave-analyser with frequency range from 20–55000 cps. The bandwidth Δf was 10 cps in all experiments. The 1 mA dc output of the wave analyser was connected to a pen recorder. An integrating circuit with a time constant of 3 min was however inserted between wave analyser and recorder to eliminate fast fluctuations of the signal. The experimental set-up for the noise measurements is given in Fig. 1.

For the illumination of the cell, an incandescent lamp was used. No optical filters were needed as no difference for the shot noise coefficient was observed between monochromatic and white light illumination.

3. Results

3.1. Anodic Dissolution of ZnO

In general, noise measurements during anodic dissolution of ZnO were hampered by a lack of stability of the system. Nevertheless, we have been able to make a few measurements on crystal *B*. The aqueous electrolyte contained 1 *M* KCl and 0.1 *M* $Na_2B_4O_7$. The photocurrent was 0.15 μA. Values of $\gamma = 1.21$, 1.27, and 1.24 were found at frequencies of 1048, 2078, and 4015 cps, respectively.

3.2. Anodic Oxidation of I^-

In this case, the stability of the system is satisfactory. Table I shows the results of 21 measurements, made on three crystals at different values of the frequency and of the pH. In all cases, the aqueous solutions were 1 *M* in KCl and 0.1 *M* in KI. The solutions were brought to the pH values of approximately 9, 12, and 13 by adding 0.1 *M* $Na_2B_4O_7$, 0.01 *M* KOH, and 0.1 *M* KOH, respectively. The

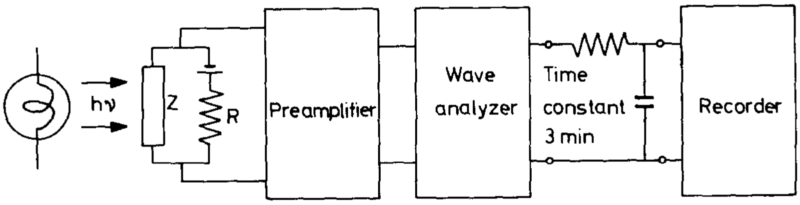

FIG. 1. Experimental set up for noise measurements.

TABLE I

Crystal	pH	f(cps)	No. of Experiments	γ
A	12	133	2	1.16
		222	2	1.05
		374	2	1.03
		521	2	1.06
		1048	2	1.08
	13	521	1	1.06
B	9	222	1	1.18
		521	1	1.13
		1048	2	1.05
		2078	1	1.11
		4015	1	1.28
		6015	1	1.15
C	13	133	1	1.14
		222	2	1.01

values of the photocurrent were 0.55 μA with crystal A, 0.22 μA with crystal B and 0.125 μA with crystal C. In case a measurement was made in duplicate, the average value of γ is listed in the table. From the data of Table I, an average value of $\gamma = 1.09$ is calculated, the mean deviation being 0.06. No noticeable influence of any of the parameters under investigation (i.e., the frequency) is observed.

3.3 Anodic Oxidation of Alcohols

In Table II are listed the results of 20 noise measurements made at different values of the frequency during the anodic oxidation of three alcohols, namely, methanol, ethanol, and 2-propanol.

TABLE II

Reactant	f(cps)	No. of Experiments	M	γ	m
CH_3OH	133	1	1.57	1.82	2.26
	222	1	1.61	1.85	2.24
	374	1	1.54	1.66	1.88
C_2H_5OH	133	4	1.55	1.83	2.34
	222	4	1.57	1.66	1.82
	374	2	1.55	1.68	1.92
	521	3	1.56	1.79	2.20
	1048	1	1.56	1.80	2.23
$(CH_3)_2CHOH$	133	1	1.70	1.94	2.28
	222	1	1.70	1.74	1.80
	374	1	1.66	1.91	2.29

The experiments were made on crystal C. The electrolyte was an aqueous solution of 1 M KCl, 0.1 M KOH, and 1 M of the alcohol under investigation. The photocurrent J was in all experiments in the range of 0.2 μA. The multiplication factor M was obtained by dividing J by the photocurrent J_0 measured with an electrolyte containing iodide. For the results obtained in identical circumstances, averages have been made (the number of experiments is indicated in the table).

The results clearly demonstrate that γ is considerably larger than one in all cases. The last column of Table II contains m, the number of correlated electrons involved in the alcohol oxidation, as calculated from each experiment. In the discussion, the basis of this calculation will be exposed. Over the 20 experiments made, an average value of $m = 2.10$ is found, with a mean deviation of 0.20.

4. Discussion

In order to calculate the shot noise coefficient γ, the impedance Z of the cell and the rms noise voltage across the parallel connection of Z and the resistance R was measured. With the rms noise voltage

$$\sqrt{\overline{(\delta V_{tot})^2}},$$

there corresponds a noise current generator

$$\sqrt{\overline{(\delta i_{tot})^2}}$$

given by

$$\overline{(\delta i_{tot})^2} = |Z^{-1} + R^{-1}|^2 \overline{(\delta V_{tot})^2}. \qquad (5)$$

This noise current generator can be separated into a noise current generator

$$\sqrt{\overline{(\delta i_R)^2}} = \left(4kT\frac{\Delta f}{R}\right)^{1/2}$$

for the thermal noise of the resistor R and a second noise current generator

$$\sqrt{\overline{(\delta i)^2}}$$

for the cell. The value of $\overline{(\delta i)^2}$ inserted into Eq. (1), gives the shot noise coefficient if the current J is only due to the photochemical reaction under investigation. In the dark however a small dc current, at least two orders of magnitude smaller than the photoelectrochemical current, is observed. The nature of the reactions involved is not known with certainty. Williams (*17*) ascribes the dark current to the dissolution of excess zinc. In the circumstances of our experiments however, the dark current is too high to be accounted for completely by this effect. In case the process observed in darkness also exists under illumination, its contribution to the total current J will be small. Its contribution to the impedance Z of the cell, on the other hand, may be important. This follows from the fact that the experiments are performed under conditions of current saturation. In this case the resistance R_p, in an equivalent parallel circuit of the impedance of the photochemical reactions, is very large at low frequencies and $Z = \infty$ for $f = 0$ in a first approximation. The small current of unknown origin however is not necessarily saturated, and the corresponding R_p may be smaller than the parallel resistance for the photochemical reaction. This fact does not constitute a difficulty for the interpretation of γ as a parameter of the photoelectrochemical reaction. The impedance is a rather complex function of the frequency and could not be ascribed, as in the case of cathodic reduction (*18*), to a parallel connection of space charge capacitance, reaction resistance, and a series circuit due to surface states. As the upward band bending is now relatively large, the surface states are probably empty and do not affect the impedance. One of the reasons why the impedance is a complicated function of frequency may be the change of the space charge capacitance by the trapping of holes during illumination of the cell.

The observed photoelectrochemical noise originates from several sources. First, the noise of the light source, which will contribute to the noise of the photoelectrochemical diode. A second source may be the drift or the diffusion of the holes to the surface. The reaction at the interface involving holes also constitutes a noise source. In the case of current multiplication, one has to consider the noise due to the injection of the electrons from the radicals into the conduction band. Finally, there is additional noise because a hole may be used in competing reactions giving different numbers of electrons in the external circuit.

The noise sources due to the reaction can be neglected since the current increases linearly with the light intensity and is equal for anodic dissolution of ZnO and anodic oxidation of I^-. This means that each hole reaching the surface is immediately used in the reaction and therefore the noise of this process is negligibly small. In the case of anodic oxidation of alcohols where the possibility of the competing anodic oxidation of ZnO still exists, one expects again that all holes at the surface are used in the reaction.

The linear dependence of the current upon light intensity and the current saturation does not distinguish between the cases where the effect of the drift or the diffusion of the holes to the surface can be neglected or not. If this drift or diffusion can be neglected, a current of holes with noise originating from the photon current arrives at the surface. In the opposite case the noise from the light source can be neglected, but the noise from the drift or the diffusion has to be considered. In the latter case, a Poisson distribution for the holes arriving at the surface is expected.

Tyagai and Lukyanchikova (*5*) have calculated the noise power for a system with current multiplication. They considered the case where the rate of the process is controlled by the optical generation of free holes, and they included in their derivation the fluctuations of the light intensity, of the quantum yield and of the current multiplication factor M. They assumed two competing processes which give, respectively, n and m elementary charges in the external circuit, and introduced the probability β that one hole is used in the reaction with n electrons. Following their argumentations, we obtained the Eqs. (6) and (7) for the shot noise coefficient γ and the multiplication factor M

$$\gamma = M + \frac{\beta(1-\beta)(n-m)^2}{M}, \tag{6}$$

where

$$M = \beta n + (1-\beta)m \tag{7}$$

These Eqs. are also valid for the case where the drift or diffusion of holes to the surface has to be considered.

Tyagai and Lukyanchikova give for γ the same expression except that the exponent 2 is missing. Experimentally they found $\gamma = 1$ for the oxidation of CdS and they concluded from Eqs. (6) and (7) that there is no multiplication of the anodic current. However, they implicitely assumed in these calculations that the n (or m) elementary charges were correlated. If the $n + m$ transitions are uncorrelated, one always expects to have $\gamma = 1$. This case implies the existence of important amounts of intermediate products. The currents corresponding to the different partial reactions fluctuate independently if the observation time for the noise current is small compared to the lifetime of the species involved Experimentally, the observation time Δt is equal to $\frac{1}{2}B$, where B is the bandwidth of the preamplifier. If however any other physical process occurs in the system with a time constant larger than $\frac{1}{2}B$, this process determines the observation time. Such a process may be, for example, the trapping of electrons in the bulk of the semiconductor. If the observation time is larger than the lifetime of an intermediate product, then the corresponding transitions have to be considered as being correlated, and as a result $\gamma > 1$. A shot noise coefficient $\gamma = 1$ however, does not allow one to conclude that there is no multiplication.

In the case of the anodic dissolution of ZnO, values of $\gamma \cong 1.25$ were found. It should be remarked that the experiment was characterized by instabilities in the current. Some additional noise source, due to phenomena occurring only during dissolution of the crystal, could lead to values of $\gamma > 1$.

For the oxidation of I^-, γ was found to be near unity. The system was much more stable in this case. The same stability was shown by the alcohol systems. As in the latter case current multiplication occurs, and γ is considerably larger than one, Eqs. (6) and (7) allow calculation of the number of electrons that can be considered as being correlated. By elimination of β from Eqs. (6) and (7), one obtains

$$m = \frac{M(\gamma - n)}{(M - n)}. \tag{8}$$

There is at least one competing reaction without current multiplication, namely the anodic dissolution of ZnO; therefore we put $n = 1$. If there is more than one reaction with $n = 1$, Eq. (8) still holds, since in the theoretical derivation only the probability β that a hole is used in a reaction yielding one electron in the external circuit is introduced. By application of Eq. (8), $m \cong 2$ is found for the oxidation of alcohols (see results, Table II). This shows that the hole capture and electron injection steps are correlated, and that

$$\Delta t > \tau_{A^+\cdot}. \tag{9}$$

Here, $\tau_{A^+\cdot}$ is the lifetime of the intermediate radical $A^+\cdot$.

The value of the shot noise coefficient given above is that for the low frequency range, where the noise spectrum is constant. At higher frequencies, γ will decrease and will approach zero at sufficiently high frequency. The frequency f where γ starts to decrease will be given by

$$2\pi f \Delta t = 1. \tag{10}$$

In our experiments, no decrease of γ has been observed for frequencies up to 1000 cps. This result allows us to calculate an upper limit for the lifetime of the intermediate radical. Using Eqs. (9) and (10), one finds $\tau_{A^+\cdot} < 1.6 \times 10^{-4}$ sec. From this result, an upper limit for the surface concentration of radicals $[A^+\cdot]_s$ in the circumstances of the experiment can be calculated. The current density I due to the decomposition of the radicals is given by

$$I = e\frac{[A^+\cdot]_s}{\tau_{A^+\cdot}}. \tag{11}$$

Inserting into Eq. (11) an experimental value of $I \cong 2.4 \times 10^{-6}$ A/cm² ($J \cong 2 \times 10^{-7}$ A, surface area $\cong 3$ mm², $M \cong 1.6$) it is found that $[A^+\cdot]_s < 2.4 \times 10^9/\text{cm}^2$.

Acknowledgment

The authors wish to thank Prof. Dr. W. Dekeyser for his continuous interest in this work.

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