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Effect of pH on the formation–dissolution processes of anodic films on bismuth

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Interrupted polarization measurements indicate that among Na_2SO_4, buffer (pH 7) and NaOH, the most passivating anodic film is formed on bismuth in the buffer solution. Under open-circuit conditions, film growth occurs on the metal surface in buffer solutions of pH 1.81 to 11.25. The rate of growth increases with decrease in pH. The passive metal undergoes dissolution in buffer solutions according to a zero-order mechanism; the most effective pH values for film dissolution lie between 8 and 10. The results indicate the simultaneous importance of the anion type and pH of the electrolyte in determining anodic film stability.

1. Introduction

The formation of anodic films on bismuth is favoured in both aqueous alkaline, neutral and acidic [1–6] as well as in non-aqueous electrolytes [7, 8]. The anodic films on bismuth grow at the lowest field strengths compared with all typical valve metals [9–12], these films exhibiting interesting electrochemical and photoelectrochemical properties [13, 14], which qualifies bismith to occupy a particular place among valve metals. Hence, bismuth is not classified usually as a typical valve metal [15].

The anodic oxide grown on bismuth metal was shown to be formed of a thin adherent film covered by an amorphous, more defective film [16, 17]. The pH of the electrolyte affects to a great extent the morphology of the continuous adherent layer; a value of 7.6 was reported for the isoelectric point of the oxide [18]. This agrees with reports on the variation in the nature of the film with pH of the electrolyte [19] and the difference in behaviour under anodic polarization observed when the concentration of H_2SO_4 electrolyte is above or below 0.5 N [20].

The formation of anodic oxide bismuth films in aqueous solutions at pH 5 to 14 has been reported [18]; however, the effect of the pH of the medium on the rate of formation and dissolution of the oxide has not been considered before. In this study, we report the effect of pH on the growth and dissolution of anodic oxide films and under open-circuit conditions.

2. Experimental details

The impedance measurements technique and electrolytic cell were the same as reported previously [21]. The measured series capacitance, C_s, and resistance, R_s, of the impedance of the bismuth electrode were traced at 1 kHz. Potentials were recorded against a saturated calomel electrode (SCE) using a valve voltmeter (Electronic Instruments Ltd, UK), then referred to normal calomel electrode (NCE). The process of oxide building was followed by repeated interruption of the applied current ($20\,\mu A\,cm^{-2}$) after each 5 min polarization. The open-circuit potential, C_s and R_s were then traced for 20 min after each polarization interval. The open-circuit behaviour of the metal and the oxide layer formed at a current density of $0.5\,mA\,cm^{-2}$ in 0.05 M Na_2SO_4 on bismuth, were studied by following the potential E_h, C_s and R_s as a function of time at $30 \pm 0.5^\circ C$ for 3 h.

The bismuth electrode was made by fixing a 99.99% Bi rod (Johnson and Matthey, UK) of $0.196\,cm^2$ cross-sectional area in a glass tube with an adhesive resin. The electrode was mechanically polished with successive treatments by finer grades of metallurgical papers and finally with fine tissue paper. Solutions were prepared from Analar grade (B.D.H.) reagents and triply distilled water. A solution of 0.2 N NaOH was used in adjusting the pH of a mixture of 0.04 M solutions of each of acetic, boric and phosphoric acids, which constitute the universal buffer.

3. Results and discussion

To distinguish between the effect of pH and anion type which were both reported to affect the growth of the anodic film [15, 20], interrupted polarization at a constant current density of $20\,\mu A\,cm^{-2}$ was carried out. The electrode capacitance was traced at the end of each 5 min polarization interval for a duration of 20 min at 1 kHz. Taking C_s^{-1} as a relative measure of film thickness [22], the results in Fig. 1 for 0.05 N Na_2SO_4 (pH 6.7), universal buffer of pH 7 and 0.1 N NaOH at pH 13, show the variation of film thickness for the different polarization intervals. While a linear rise in potential was observed, a continuous variation in C_s for each cycle was recorded, this attained an almost constant value when the arrest potential corresponding to oxygen evolution was reached. The plots show that the recorded electrode capacitance at the end of each polarization stage remains almost constant over the 20 min interruption period. In all cases increase in C_s^{-1} for each successive polarization stage is in favour of continuous oxide growth. The variation in the relative oxide thickness after each

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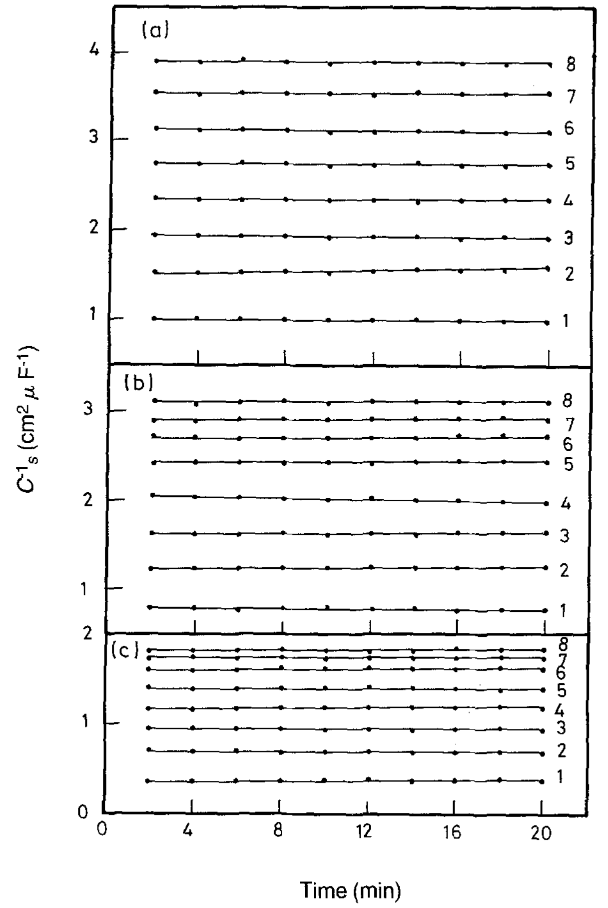

Figure 1 Variation of open-circuit reciprocal capacitance after equal anodic polarization intervals. (a) 0.05 N Na_2SO_4, (b) buffer pH 7, (c) 0.1 N NaOH; (numbers refer to sequence of polarization intervals).

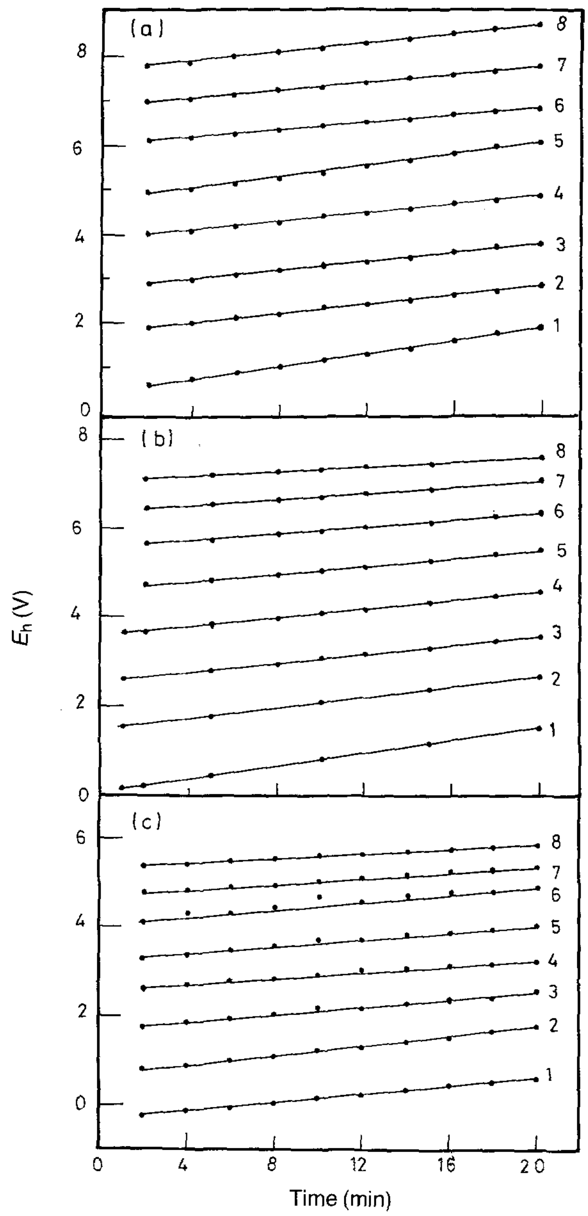

Figure 2 Variation of open-circuit potential with successive accumulation of oxide layer during interruption. (a) 0.05 N Na_2SO_4, (b) buffer pH 7, (c) 0.1 N NaOH.

polarization interval is dependent on the medium. Comparison of C_s^{-1} values for the solution of pH 6.7 and 7 after identical polarization intervals reveals a difference which may probably be attributed to the difference in passivating properties of the anions, rather than to a difference of pH.

However, the measured capacitance does not give a reliable measure of film thickness, a better discrimination between the passivating powers of these media may be obtained by considering the results of interrupted polarization measurements.

Fig. 2 shows the variation in potential during the 20 min interruption interval in the three media studied. In all cases the linear increase of potential is slightly higher at the early interruption periods for identical media. The differential unitary formation rate, R_d, calculated from $(\Delta E/\Delta t)_i \times 1/i$ is more exact than the integral unitary formation rate calculated from the linear part of the charging curves. Average R_d values were found to decrease from a value of 4.75 (pH 7) to 2.65 (pH 6.7) to 2.13 (pH 13) which thus parallels roughly the passivating power of these media. The quite close values obtained for R_d in pH 6.7 and 13 may indicate the importance of anion type over pH in determining the passivating properties of the medium.

It has been explained that the rate of increase of open circuit potential with oxide accumulation is greater in a more passivating medium [23]. These are highest in both pH 7 and 6.7, the lower value in pH 13 accords with the lower R_d value in this medium indicating its relatively weaker passivating property.

Assuming a 100% efficiency during the formation of anodic films the quantity of electricity consumed, Q (μC cm^{-2}), was calculated from

$$Q = \frac{60\Delta E}{R_d}$$

where 60 is the units conversion factor and ΔE(V) is the potential difference over which anodic film formation takes place. Q decreased from 175 (pH 13) to 163 (pH 6.7) to 93 (pH 7) and is directly related to the film thickness, d(nm), by the relation $d = 10^9 QM/4F\varrho$, where M is the molecular weight of the species formed by anodic oxidation and ϱ is its density. The value of d is dependent on the values of both M and ϱ so that Q cannot be taken as a criterion of film thickness except when M and ϱ are constant, i.e. the same oxide species is formed. However, it may be inferred that a thinner film is produced in the buffer of pH 7, indicating that the thinnest film is produced in the most

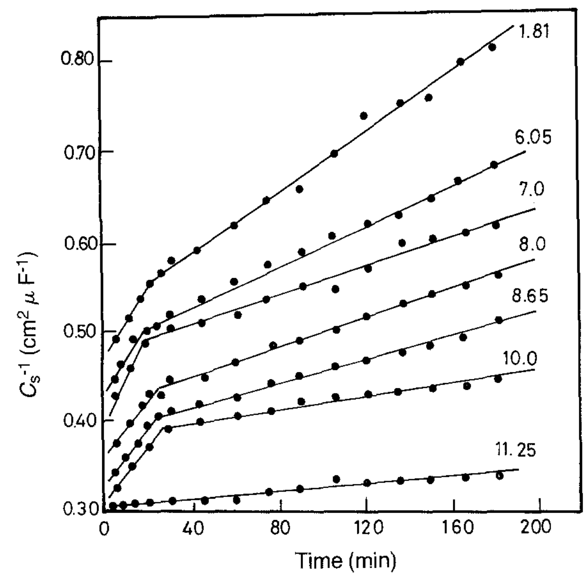

Figure 3 Dependence of the reciprocal capacitance on pH for a mechanically polished bismuth electrode under open-circuit conditions.

passivating medium as evinced by the value of Q which is lowest in this medium. This is supported by the results discussed earlier and accords with reports that the rate of oxide formation is maximum in Na_2SO_4 and decreases in alkaline solutions [15].

The results indicate the importance of anion type on the growth of the anodic film. To clarify the effect of pH only on the behaviour of the metal under open-circuit conditions the anion type was kept constant by employing the universal buffer of different pH. This buffer includes the borate and phosphate anions which are reported to be suitable for oxide growth on bismuth [18]. The effect of pH on film thickening on the metal is remarkable, Fig. 3. In alkaline electrolyte of pH 11.25 slow film thickening is observed. The decrease of pH to 10 reveals a different phenomenon. Film growth occurs at a considerable rate as manifested by the increase in slope of the relation up to $\simeq 30$ min, the inflection observed which is followed by a linear relation possessing a lower slope is probably related to the beginning of nucleation of a second layer at a slower rate of thickening. It has been reported that the anodic film on bismuth is formed of a very rough layer with an underlying thin barrier layer of interlocking plaques, and that the continued thickening of the film occurs by a dissolution–precipitation mechanism [24]. The present results indicate that a similar process occurs. The lower rate of thickening is probably related to the growth of the inner layer through the defects present in the outer rough layer.

It is clear that the rates of thickening around the isoelectric point, reported to be 7.6 [18], are more or less the same. At much higher and lower pH values, the rates decrease and increase, respectively. It has been observed that the film forms at low pH values in a manner different than at high pH values [18]; in the present case the increased rate of thickening in acid medium may be attributed to the possibility of proton incorporation within the anodic film, reported to be extremely defective [13].

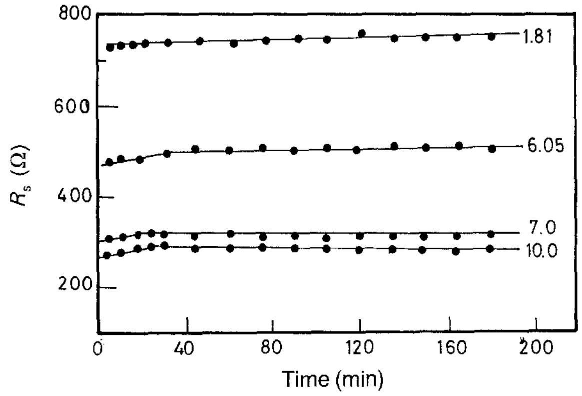

Figure 4 Variation of the resistance with pH for the bismuth electrode.

Although the resistance is a less sensitive index than capacitance for film growth or dissolution [22], the results of R_s measurements against time at different pH values (Fig. 4) reflect the general picture of C_s measurements.

The ennobling of potential with time (Fig. 5) supports film thickening. The inflections in the figure are observed to occur at nearly the same time intervals as in Figs 3 and 4. The existence of two linear relations favours the idea of formation of a double layer film, which has been reported during the formation of anodic films [16, 17, 24]. A difference in the physical properties of each of these layers may be assumed on the grounds of a difference in the rates of thickening at the same pH. For different pH values there is a possibility that the chemical nature of the films may also differ. It has been established that the film grown in Na_2SO_4 is formed of Bi_2O_3 [16], while there is speculation on that formed in NaOH [17]. The results indicate that under open-circuit conditions a decrease in pH enhances film thickening.

To investigate the effect of pH on the passive metal, an anodic oxide was formed in 0.05 N Na_2SO_4 at a current density of 0.5 mA cm^{-2} up to 50 V, then the electrode was transferred to the dissolution medium consisting of a universal buffer of definite pH. The results of impedance measurements under open-circuit conditions are shown in Figs 6 and 7. As mentioned above there is evidence that the anodic oxide on bismuth consists of a thin barrier layer

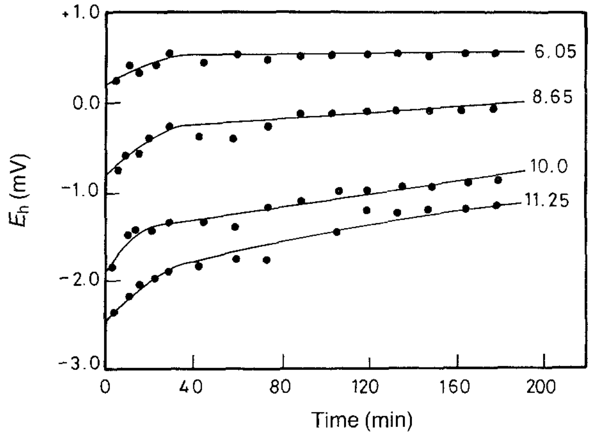

Figure 5 Relation between open-circuit potential of the bismuth electrode and time at different pH values.

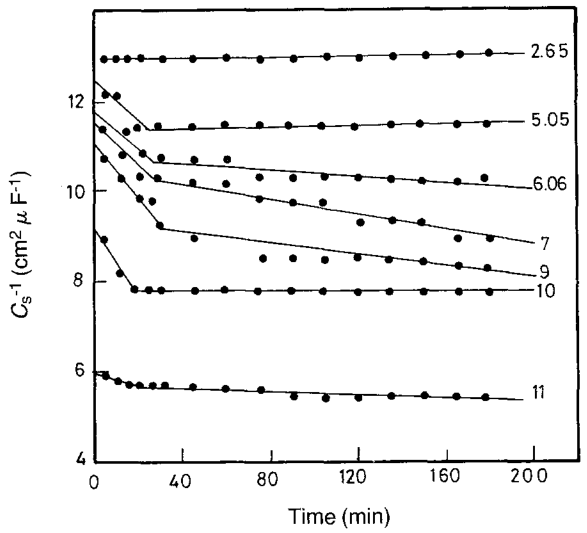

Figure 6 Variation of reciprocal capacitance with pH during dissolution of the anodic film on bismuth.

covered by a thicker defective one [16, 17, 24]. The dissolution of the outer layer is greatly affected by pH 10 to 5.05, especially between 9 and 6.06, as manifested by the increase in the rate of lowering in C_s^{-1} (Fig. 6). At pH 11, the rate of decrease in C_s^{-1} is very limited while at pH 2.65 it does not apparently affect the anodic oxide.

The same sequence is also observed for the dissolution of the inner layer. However, the rate of dissolution is somewhat lower as compared to that of the outer layer at the same pH. This is expected, in view of the more defective nature of the outer layer [16, 17, 24]. The dissolution of the anodic oxide is due to the presence of a non-stoichiometric layer at the film–metal interface, having a large number of trapping states which are in electronic equilibrium with the metal [13]. The results indicate that the dissolution follows a zero-order equation of the form

$$-\mathrm{d}C_s^{-1}/\mathrm{d}t = k$$

where $-\mathrm{d}C_s^{-1}/\mathrm{d}t$ is the rate of dissolution, and k is the dissolution constant (cm$^2\mu$F^{-1}min^{-1}). Values of k_1 and k_2, the rates of dissolution of the outer and inner layers, respectively, are listed in Table I.

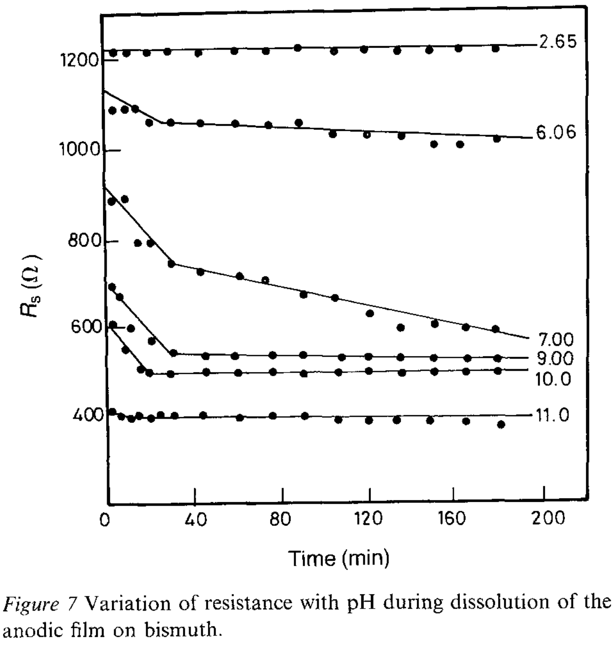

Figure 7 Variation of resistance with pH during dissolution of the anodic film on bismuth.

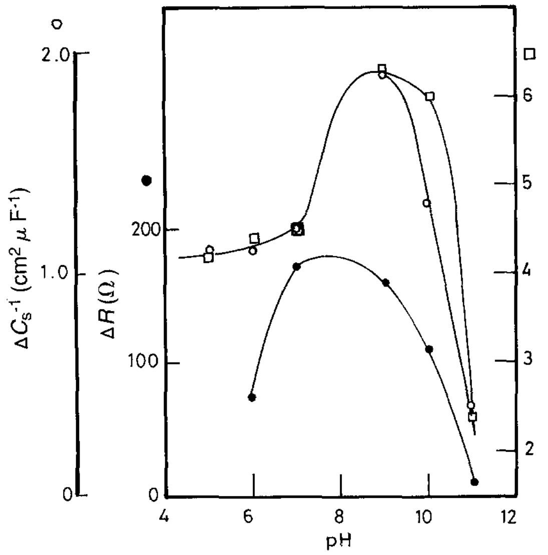

Figure 8 Dependence of lowering in R_s, decrease in C_s^{-1} and dissolution rate constant for the outer layer, on pH.

The rate of dissolution of the anodic oxide formed in Na_2SO_4 and dissolving in buffers of different pH follows the order: near neutral > pH 11 > 2.65. This is the reverse sequence of the magnitude of charge transfer resistance in different pH values [25]. It has been shown that during the growth of the anodic oxide on bismuth the rate-controlling process is either electron transfer or surface diffusion [24]. It seems that during dissolution of the anodic film the rate-controlling step is the charge transfer process.

Fig. 7 indicates clearly a decrease in R_s which is associated with film dissolution. The greatest decrease occurs at pH 7, indicating greater solubility of the oxide at such a pH. The rate of decrease in R_s increases in both directions of increasing and decreasing pH. No apparent change is observed in R_s at pH 11 and 2.65. Fig. 8 shows that the maximum decrease in film thickness occurs at pH 8 to 10, hence the maximum

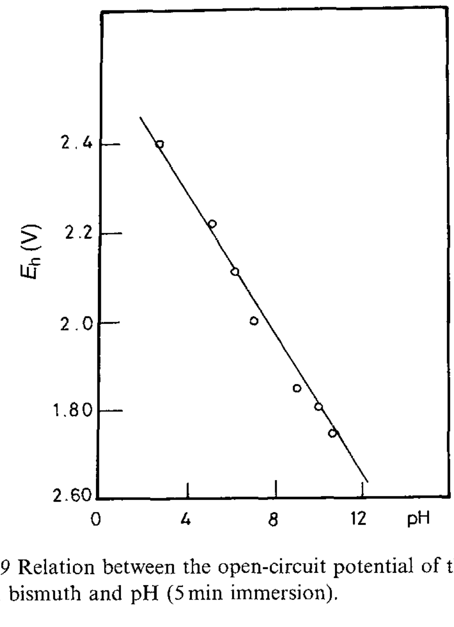

Figure 9 Relation between the open-circuit potential of the anodic film on bismuth and pH (5 min immersion).

TABLE I Rates of dissolution as function of pH

	pH						
	2.65	5.05	6.06	7.0	9.0	10.0	11.0
$10^2 k_1$ ($\mathrm{cm^2 \mu F^{-1} min^{-1}}$)	–	4.2	4.4	4.5	6.3	6.0	2.3
$10^3 k_2$($\mathrm{cm^2 \mu F^{-1} min^{-1}}$)	–	–	5.0	10.0	6.0	–	

rate of dissolution (here plotted for the outer layer which is more sensitive) also occurs at the same pH interval. The highest decrease in R_s during dissolution of the outer layer is somewhat shifted to lower pH values; however, R_s does not follow C_s strictly and is not as sensitive as it.

The relation plotted in Fig. 9 represents the variation in open-circuit potential with the pH of the universal buffer. For all pH values, except 2.65, the variation of E_h with time was towards less positive values. The values plotted in the figure are those recorded after 5 min immersion in the dissolution medium. The slope of the relation is 88 m V/pH. For increasing immersion times the slope of the linear relation was observed to decrease. Thus, it may be inferred that the oxide-coated bismuth electrode cannot be employed as a pH indicator electrode. A previous study has shown that the variation of the open-circuit potential of the metal with pH was smaller than the value expected for a reversible electrode employed in pH indication [19].

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