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*The anodic behaviour of zinc in KOH solution. V: Galvanostatic polarization with an interruption**

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Galvanostatic polarization experiments, in which the current flow is interrupted and re-established, show that the process of passivation is controlled by the transport of mass in the solution phase.

Introduction

The dissolution of Zn anodes in aqueous alkali

$$\mathrm{Zn} + 4\mathrm{OH}^- \rightarrow \mathrm{Zn(OH)}_4^{2-} + 2e \qquad (1)$$

has been the subject of many investigations reported in the literature [1]. The mechanism of the active-passive transition for the Zn/OH$^-$ system has also been extensively investigated [1, 2]. Passivation of the Zn occurs when the electrode is no longer oxidized to Zn(II) and the potential rises to that required for the o.e.r. It is generally agreed that the formation of a layer of ZnO or $\mathrm{Zn(OH)_2}$ occurs at the instant of the active-passive transition. Two possibilities exist for the formation of the film (*a*) *precipitation*, in which the passivating layer is formed by precipitation from the electrolyte layers immediately surrounding the electrode and (*b*) *direct*, in which the passivating layer is formed directly on the surface as a solid phase. It has been intuitively accepted, if not always stated explicitly, that the composition of the electrolyte in the vicinity of the anode is the factor determining the onset of film formation by either (*a*) or (*b*). The passivity which may ultimately be attained by zinc in alkali is then formally similar to 'cover passivity' as discussed by Müller [3] who distinguished between this and 'chemical passivity' where a higher valency metal compound is formed at the electrode surface.

The identity of the process of film growth ((*a*) or (*b*)) under galvanostatic conditions in general does not alter the kinetics of the attainment of the passive state since as soon as the electrolyte conditions at the electrode are 'critical', passivation occurs and the potential rises. It has been shown theoretically [4, 5] that if diffusion is the only mode of mass transport then

$$it^{\frac{1}{2}} = k \qquad (2)$$

where t is the time to passivation from initially closing the circuit at a current density i; k is a constant for a given set of composition and temperature conditions. Equation (2) has been thoroughly justified experimentally under conditions where diffusion is the only significant mode of mass transport [6]. When diffusion is the major mode of mass transport but some other minor modes (e.g. convection) are present a limiting current i_1, is observed [7] (i must be replaced by (i-i_1) in Equation (2)).

Equations of the form (2) can fit data due to controlling mechanisms other than diffusion in solution as, for example, if the transition between the active dissolution and the passive electrode state occurs at a definite potential and the products of polarization in the active region remain (either (*a*) completely or (*b*) partly) as an insoluble film at the electrode surface [8]. The

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purpose of this note is to present data which satisfactorily precludes these other possibilities.

The experimental situation

The quantitative treatment of a completely diffusion controlled system to the point of passivation in two distinct steps each separated from the other by an open circuit period has already been given [9]. Assuming semi-linear infinite diffusion it was shown that for the case of an electrode which became passive due to the Müller mechanism:

$$i_2\sqrt{t_3}+i_1\left[\sqrt{t_1+t_2+t_3}-\sqrt{t_2+t_3}\right]=k' \tag{3}$$

where i_1 is the initial current flowing for time t_1, followed by an open circuit period for time t_2, and finally polarized at i_2 until passivation occurs after a time, t_3. It is clear that (3) reduces to (1) when t_2 and t_3 are zero; k' in Equation (3) is equal in magnitude to k in Equation (2) ($= \frac{1}{2}ZFC^*\sqrt{D\pi}$, where D is the diffusion coefficient of the electrode product and C^* is the concentration of electrode product required to bring about passivation).‡

Experimental

The experimental arrangement in which horizontal sheet anodes orientated with the bulk of the solution vertically above so that convection is effectively suppressed (at least in the experimental time range) has been described [10]. Zinc sheet (99·95%) was degreased (CCl_4) and etched (~2 mol l^{-1} H_2SO_4) immediately before the electrolyte was introduced into the cell. Cell electrolytes were prepared from AR grade KOH and doubly distilled water.

Passivation experiments were made both with and without an open circuit period interposed in the active dissolution region. From uninterrupted polarization data i-$t^{-\frac{1}{2}}$ curves were drawn all of which were straight lines and extrapolated through the origin; the slope of these lines k, was measured geometrically. From

Table 1

1 mol l^{-1} KOH		*electrode area = 1·76 cm^2 k = 0·12*			
i_1	i_2	t_1	t_2	t_3	k'
0·015	0·020	30	45	85	0·11
0·020	0·025	30	32	53	0·12
0·025	0·030	15	45	34	0·11
0·015	0·025	30	45	55	0·12
2 mol l^{-1} KOH		*electrode area = 1 cm^2 k = 0·38*			
i_1	i_2	t_1	t_2	t_3	k'
0·04	0·045	60	30	41·5	0·41
0·042	0·048	40	30	35	0·38
0·045	0·042	30	30	45·5	0·35
0·056	0·045	15	30	63	0·40
0·056	0·051	20	40	40·5	0·40
4 mol l^{-1} KOH		*electrode area = 1·76 cm^2 k = 0·95*			
i_1	i_2	t_1	t_2	t_3	k'
0·075	0·18	180	30	56	1·07
0·10	0·14	120	22	77	0·97
0·20	0·30	30	20	18	0·97
0·25	0·33	20	20	16	0·96
5 mol l^{-1} KOH		*electrode area = 1 cm^2 k = 1·16*			
i_1	i_2	t_1	t_2	t_3	k'
0·083	0·088	60	30	158	1·28
0·088	0·094	60	30	117	1·22
0·088	0·099	60	30	99	1·14
0·094	0·099	60	30	88	1·16
0·099	0·105	60	30	92·5	1·25
7 mol l^{-1} KOH		*electrode area = 1 cm^2 k = 1·35*			
i_1	i_2	t_1	t_2	t_3	k'
0·075	0·75	304	300	39·5	1·27
0·130	0·13	133	300	54·0	1·26
0·30	0·30	14·5	300	14	1·39
10 mol l^{-1} KOH		*electrode area 1·81 cm^2 k = 1·32*			
i_1	i_2	t_1	t_2	t_3	k'
0·20	0·20	60	60	95	1·32
0·20	0·20	60	90	64	1·13
0·20	0·20	30	60	95	1·20
0·20	0·20	90	60	72	1·32
0·20	0·30	30	60	45	1·26
0·30	0·20	30	60	36	1·23
14 mol l^{-1} KOH		*electrode area 1·77 cm^2 k = 1·1*			
i_1	i_2	t_1	t_2	t_3	k'
0·15	0·20	30	60	82·5	1·13
0·20	0·15	30	30	98	0·98
0·20	0·25	30	30	45	1·13
0·25	0·10	20	50	452	1·26

Notes

(*i*) Units i_1 i_2: A; t_1, t_2, t_3: s; k, k': $Acm^{-2}\,s^{\frac{1}{2}}$

(*ii*) All measurements were made at 23°C.

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‡ At the point of passivation a very considerable degree of supersaturation occurs; consequently it is not possible to assess the relative significance of the variables C* and D as [KOH] increases [11].

interrupted polarization data k' was calculated numerically. The results are shown in Table 1.

Discussion

The values of k are in good agreement with previously reported data [6]. The agreement between k and k' is very satisfactory, particularly since the experiments deal with solid metal systems.

It can be concluded that mass transport in solution is the controlling process for the passivation of *smooth* electrodes in KOH solution (this conclusion does not necessarily apply to microporous electrode systems [8]).

Acknowledgment

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