Monatshefte für Chemie 122, 1019 – 1027 (1991)

Monatshefte für Chemie
Chemical Monthly

Electrochemical Behaviour of an Indium Electrode in Concentrated KOH Solutions at Different Temperatures

A. El Sayed[1,*], **S. S. Abd El Rehim**[2], and **H. Mansour**[3]

[1] Department of Chemistry, Faculty of Science, Sohag University, Sohag, Egypt
[2] Department of Chemistry, Faculty of Science, Ain Shams University, Kairo, Egypt
[3] Department of Chemistry, Faculty of Science, Qena University, Egypt

Summary. The electrochemical behaviour of pure indium in KOH solutions (1–4 *M*) was studied at different temperatures (25–70°C) by potentiostatic techniques. Two anodic peaks corresponding to the formation of $In(OH)_3$ and In_2O_3 were observed. The heights of the two peaks increased with the increase of alkali concentration. An increase of temperature increased the peak currents and shifted their corresponding potentials to more negative values. The variation of the peak currents and peak potentials with scan rate suggested that the anodic dissolution of indium was a diffusion controlled process. In cyclic voltammetry, the reverse scan consistently showed one peak which was attributed to the reduction of anodic oxidation products into indium. X-ray diffraction analysis confirmed the presence of $In(OH)_3$ at the first anodic peak, $In(OH)_3$ and In_2O_3 at the second anodic peak and In_2O_3 in the permanent passive region.

Keywords. Potentiostatic electrochemical behaviour; Indium electrode, alkaline solutions.

Zum elektrochemischen Verhalten einer Indium-Elektrode in konzentrierter Kalilauge bei verschiedenen Temperaturen

Zusammenfassung. Es wurde das Verhalten von reinem Indium in 1 – 4 *M* KOH-Lösungen bei Temperaturen zwischen 25 und 70 °C mittels potentiostatischer Methoden untersucht. Zwei anodische Peaks, entsprechend der Bildung von $In(OH)_3$ und In_2O_3, traten auf. Die Höhe der beiden Peaks wurde mit zunehmender Alkalikonzentration gesteigert. Eine Temperaturerhöhung verstärkte die Peakströme und verschob die entsprechenden Potentiale zu negativeren Werten. Die Abhängigkeit der Peakströme und Peakpotentiale von der Scangeschwindigkeit legte den Schluß nahe, daß die anodische Lösung von Indium in einem diffusionskontrollierten Prozeß stattfindet. Bei der cyclischen Voltammetrie zeigte der reverse Scan einheitlich einen Peak, der der Reduktion der anodischen Oxidationsprodukte zu Indium zugeschrieben wurde. Röntgendiffraktionsanalyse bestätigte die Präsenz von $In(OH)_3$ beim ersten anodischen Peak, $In(OH)_3$ beim zweiten Peak und In_2O_3 im permanent passiven Bereich.

Introduction

Although little work has been done to investigate the electrochemical behaviour of indium potentiostatically in alkaline solutions, many works have focused attention on the electrochemical behaviour of indium and indium amalgam in alkaline solutions using galvanostatic techniques [1–8]. Fizullin et al. [7] showed that the anodic polarization of indium in KOH solutions occurred in three stages including the process of oxygen evolution. The first stage was the dissolution of indium into the solution of alkali as In(I), which as a result of a disproportional reaction was oxidized to In(III). Both in the first and in the second stage of anodic polarization $In(OH)_3$ was formed on the electrode surface. Filippova et al. [9] and Lewis et al. [10] doubt the results of Fizullin et al. According to their opinions, the main dissolution product at low current densities is $In(OH)_3$. Salem and Ismail [11] demonstrated that in the anodic polarization of indium in NaOH solutions two anodic processes took place before oxygen evolution. In the first stage, anodic dissolution occurs with the formation of indate (InO_2^-) ions. After the saturation of the anodic film with these ions, the anodic potential increases to more positive values and the second stage of oxidation starts with the deposition of $In(OH)_3$ on the electrode surface.

On the other hand, Clicksman et al. [3] and Boswell [12] showed that the metal oxidized to give a layer of In_2O_3 or $In(OH)_3$, and current densities of more than $1\,mA\,cm^{-2}$ can be drawn through this oxide. Similar results have been reported by Popova and Simonova [4].

The aim of the present work is to shed more light on the anodic behaviour of indium electrodes in KOH solutions (1–4 *M*) and to investigate the influence of temperature (25–70°C) on this behaviour by means of potentiostatic techniques.

Experimental

Solutions containing 1, 2, 3, and 4 *M* KOH were prepared from reagent grade chemicals and bidistilled water.

Specpure indium rod (99.999%, Gold Label) was embedded in araldite and prepared as a disk electrode with a surface area of $0.196\,cm^2$. Each electrode was polished with No. 600 emery papers and degreased in ethanol and washed in running doubly distilled water, before being inserted in the polarization cell. The counter electrode was a platinum sheet of $1\,cm^2$. A saturated calomel electrode (SCE) was used as the reference electrode. To avoid contamination, the reference electrode was connected to the working electrode through a bridge filled with the solution under test, the tip of the bridge being pressed against the electrode. The cell used has been described previously [13].

Potentiostatic polarization was achieved by means of a wenking ST 72 (Gerhard Bank Elektroniks). The potential was moved from open circuit potential ($E_{eq.}$) to a positive direction by manually changing the potentiometer stepwise to a constant steady state current density as recorded 1 min later. The rate of scan range was 5 to 100 mV/min in steps. Cyclic voltammetry experiments were achieved by a Potentiostat/Galvanostat Model 273 supplied from GαEG company (princeton applied research); two types of ohmic resistance (positive feed back and current interrupt) and a Model RE 00 89 x-y recorder were used. The scan rate used in this technique was $20\,mV\,sec^{-1}$. Before each polarization experiment, the specimens were cleaned cathodically in the same electrolyte (at about $-2000\,mV$ for 5 min) with vigorous H_2 evolution to remove any surface contamination and air formed oxide.

Each run was performed with a freshly prepared solution and a newly polished set of electrodes. Measurements were performed at different temperatures. Most of the experiments were repeated at least twice, the reproducibility was found to be satisfactory.

X-ray was carried out using a Jeol-Model JSC-60 PA diffractometer (35 KV, 15 mA). The specimens were potentiostatically polarized from the quasi-steady state corrosion potential to a chosen potential and maintained therefore 30 min in the test solution, withdrawn, cleaned with bidistilled water and examined.

Results

Potentiostatic Anodic Polarization Curves

The potentiostatic current-potential (i/E) curves for indium anode in 1, 2, 3, and 4 M KOH solutions are given in Figs. 1–4 under the influence of increasing temperature (25 – 170°C). Each experiment was started from the quasi-steady state corrosion potential up to +400 mV with the scan rate 20 mV min^{-1}. The anodic potential scan exhibits an active to passive transition. Two anodic peaks I and II are observed in the active region of the curves. The second anodic peak II shows at its descending portion a shoulder III before the occurrence of permanent passivity. It is evident from these figures that the peak currents of the anodic peaks increase

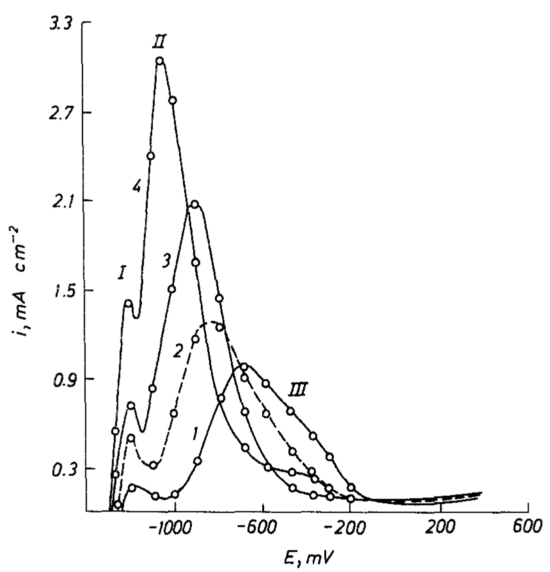


Fig. 1. Effects of temperature on potentiostatic anodic polarization curves for an In electrode in 1 M KOH (scan rate, 20 mV min^{-1}) at *1:* 25°, *2:* 40°, *3:* 55°, and *4:* 70°C

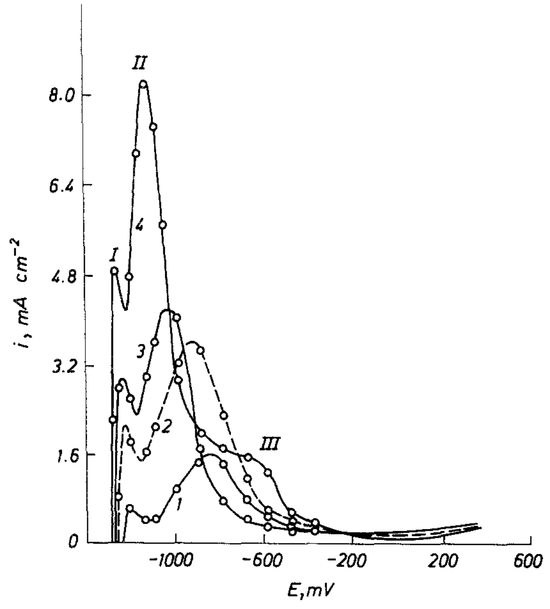


Fig. 2. Effects of temperature on potentiostatic anodic polarization curves for an In electrode in 2 M KOH (scan rate, 20 mV min^{-1}) at *1:* 25°, *2:* 40°, *3:* 55°, and *4:* 70°C

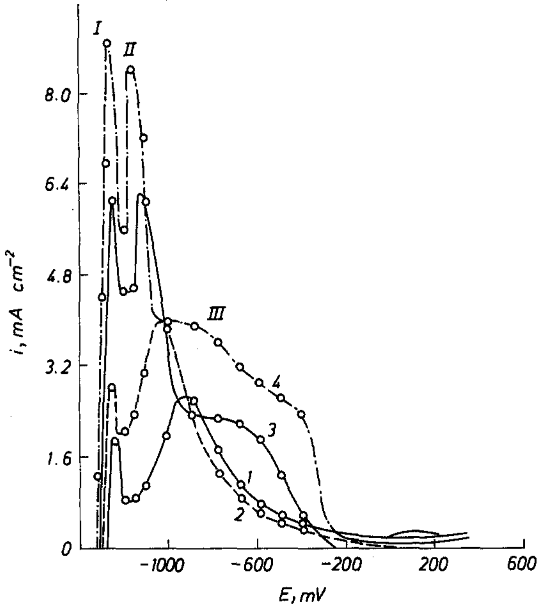


Fig. 3. Effects of temperature on potentiostatic anodic polarization curves for an In electrode in 3 *M* KOH (scan rate, 20 mV min^{-1}) at *1:* 25°, *2:* 40°, *3:* 55°, and *4:* 70°C

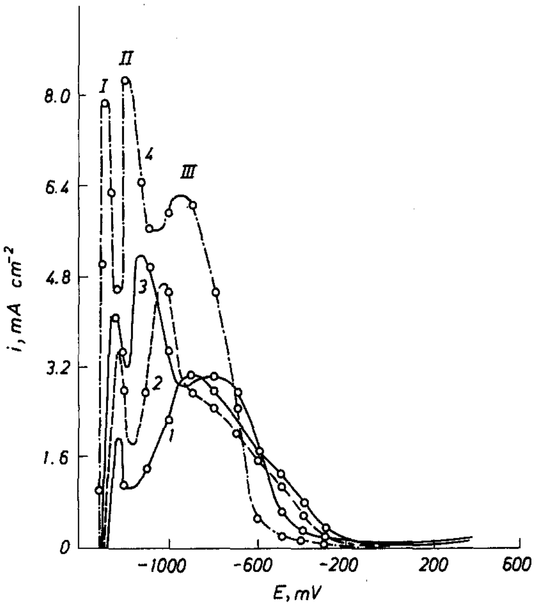


Fig. 4. Effects of temperature on potentiostatic anodic polarization curves for an In electrode in 4 *M* KOH (scan rate, 20 mV min^{-1}) at *1:* 25°, *2:* 40°, *3:* 55°, and *4:* 70°C

and in the same time their corresponding potentials shift to more negative values with increase of electrolytic concentration and temperature. The influence of temperature is more remarkable for peak I than for peak II, specially at higher concentrations. The anodic peak II consumes larger quantities of charge than that required for the first anodic peak I. The data reveal also that the variation of solution concentration or temperature has no significant effect on the current passing through the permanent passive region.

Some experiments were performed to illustrate the influence of scan rat (5–100 mV min^{-1}) on the anodic behaviour of indium in 1 *M* KOH at 25°C. The data

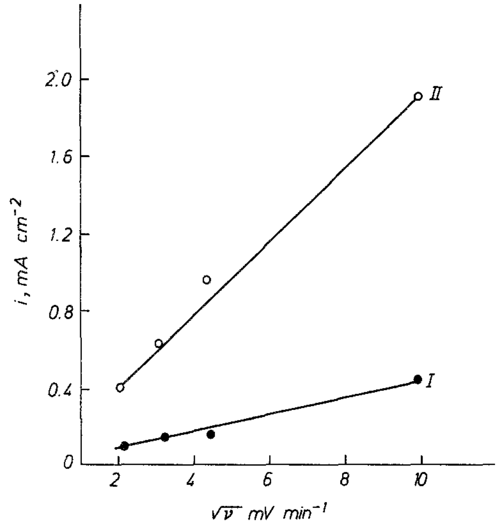


Fig. 5. Plots of peak current i_p for the anodic peaks I and II vs. $v^{1/2}$ for an In electrode in 1 *M* KOH at 25°C

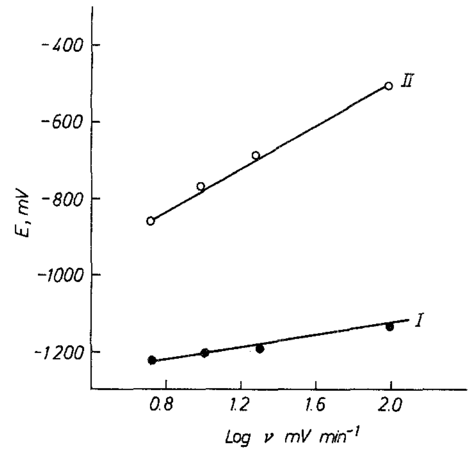


Fig. 6. Plots of peak potential E_p for the anodic peaks I and II vs. log v for an In electrode in 1 *M* KOH at 25°C

display that the heights of the anodic peaks i_p increases linearly with the squar root of v (Fig. 5) and their corresponding peak potentials E_p increase linearly with log v (Fig. 6).

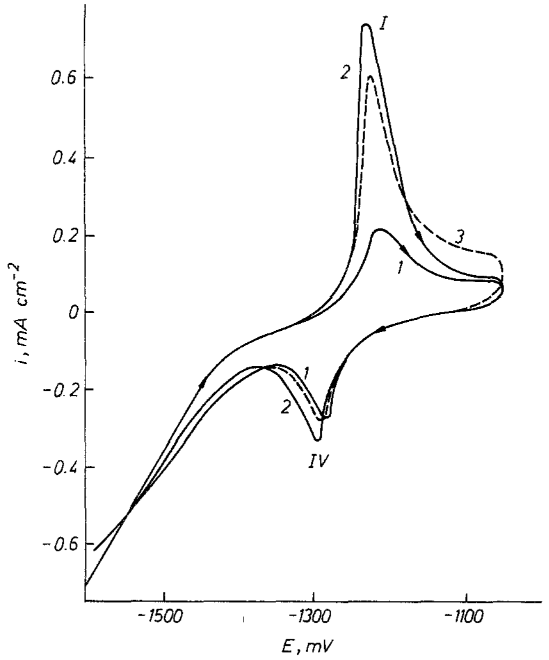


Fig. 7. Cyclic voltammogram for an In electrode, scan rate = 20 mV s^{-1} between − 1 600 and − 1 050 mV; *1:* in 1 *M* KOH at 25°C, *2:* in 3 *M* KOH at 25°C, and *3:* in 1 *M* KOH at 70°C

Cyclic Voltammetry

Cyclic voltammetric polarization curves for an indium electrode in 1 *M* KOH at 25°C (cycle 1), in 3 *M* KOH at 25°C (cycle 2) and in 1 *M* KOH at 70°C (cycle 3) at a scan rate of 20 mV s^{-1} are given in Fig. 7. The forward scan was started from − 1 600 mV and terminated at − 1 050 mV (at the end of peak I). The reverse scan reveals one cathodic peak (peak IV) around − 1 290 mV. After this peak the cathodic current increases to the hydrogen evolution reaction. Fig. 8 shows the cyclic voltammogram of indium in 1 *M* KOH at 25°C and a scan rate of 20 mV s^{-1} where the forward scan was started from − 1 600 mV and terminated at + 100 mV. The reverse scan reveals also one cathodic peak IV at − 1 370 mV. An increase of scan number increases the charge under all peaks continuously while the peak potentials remain nearly constant.

X-Ray Diffraction

X-ray diffraction analysis of the oxidation products formed on the surface of the indium anode polarized potentiostatically in 1 *M* and 3 *M* KOH solutions at 25 and 70°C were performed. Three specific polarization potentials were chosen for the study which represented the different characteristic regions of the potentiostatic curve. These potentials were as follows: (a) at the E_p corresponding to peak I, (b) at the E_p corresponding to peak II, (c) at a potential of + 100 mV which is in the permanent passive region. In all these cases spectra of the specimen polarized in peak I indicate the presence of In and $In(OH)_3$ while those of the specimen polarized in peak II confirm the existence of In, $In(OH)_3$, and In_2O_3. At a passivity potential + 100 mV only In and In_2O_3 are observed. Some of these data are given in Fig. 9.

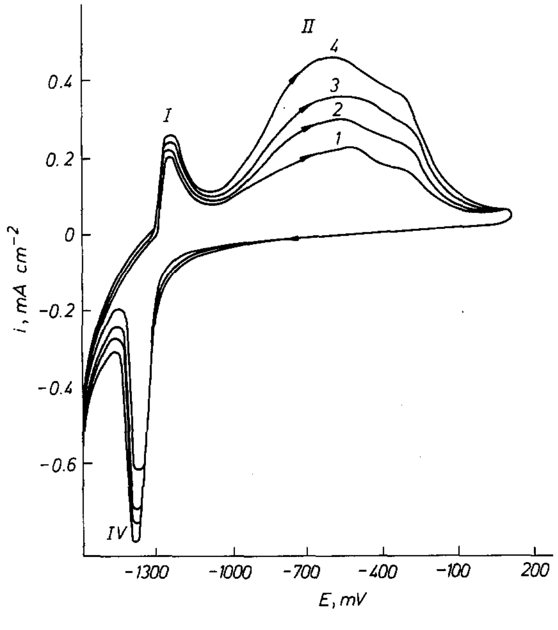
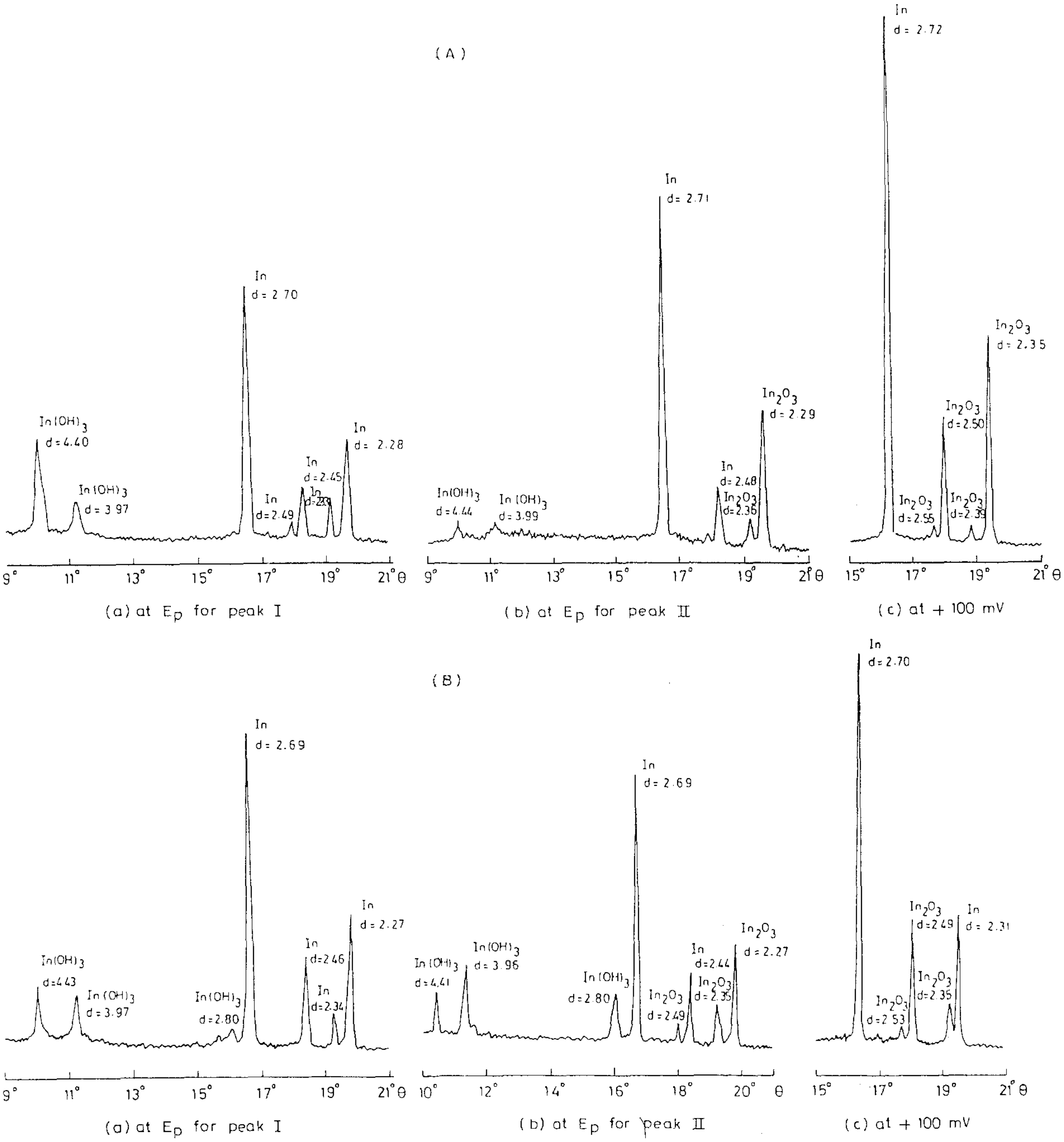


Fig. 8. Repetitive cyclic voltammogram for an In electrode in 1 *M* KOH at 25°C, scan rate = 20 mV s^{-1}, between − 1 600 and + 100 mV; *1:* first cycle, *2:* second cycle, *3:* third cycle, and *4:* forth cycle



(a) at E_p for peak I (b) at E_p for peak II (c) at + 100 mV

(a) at E_p for peak I (b) at E_p for peak II (c) at + 100 mV

Fig. 9. X-ray diffraction patterns for specimen polarized at a scan rate of 20 mV min^{-1}, **A** in 1 *M* KOH at 25°C and **B** in 3 *M* KOH at 70°C

Discussion

The present X-ray diffraction method has identified the anodic film formed as $In(OH)_3$ and In_2O_3 under varying conditions. Comparing the potentiostatic anodic peak potential with thermodynamic data (though dangerous), can be used to check the suggested anodic oxidation mechanism in the light of equilibrium potentials of varying systems. Equilibrium potentials of the system $In/In(OH)_3$ at different KOH concentrations have been calculated using the following equation at 25°C [14]:

$$E = E^0 - 0.0591 \log [OH^-].$$

The value of E^0 has been calculated from the free energy data taken from Latimer's monograph [15] according to the following reaction:

$$In + 30H^- = In(OH)_3 + 3e^-.$$

The calculated equilibrium potential of the system $In/In(OH)_3$ (−1240 mV vs. SCE) compare very satisfactory with the present experimental values of peak I (ca. −1180 mV vs. SCE in 1 *M* KOH at 25°C). Therefore one can conclude that the anodic process in the potential range of peak I may be due to dissolution of indium and formation of a porous layer of $In(OH)_3$. This process may start as a surface reaction at the monolayer level with the simultaneous trend to decrease in *pH* at the interface, namely a *pH* gradient through the anodically formed layer. According to the literature [6, 16, 17] this reaction can be considered the sum of three consecutive one-charge processes:

$$In + OH^- = In(OH)_{ads} + e^-,$$

$$In(OH)_{ads} + OH^- = In(OH)_{2ads} + e^-,$$

$$In(OH)_{2ads} + OH^- = In(OH)_3 + e^-.$$

On the other hand, peak II can be attributed to the formation of In_2O_3 since X-ray diffraction analysis indicated that in this potential range the oxide is involved beside the existence of $In(OH)_3$. The value of the peak potential E_p for peak II in 4 *M* KOH at 25°C is −980 mV vs. SCE compared with the equilibrium indium and its oxide at *pH* 14. Pourbaix [18] has calculated the equilibrium potential to be −1257 mV vs. SCE for anhydrous In_2O_3. However, it is possible that the increase in the anodic potential leads to the direct oxidation of the metal at the base of the pores to indium oxide according to the reaction

$$2In + 6OH^- = In_2O_3 + 3H_2O + 6e^-.$$

However, at this stage it is difficult to offer a satisfactory explanation for the occurrence of shoulder III. It is seen that this shoulder becomes more prominent with an increase in temperature and/or concentration. Therefore, its occurrence probably can be explained in terms of competition between anodic film formation and its chemical dissolution. It seems posible that, when the surface of the anode is completely covered with a barrier oxide and compact film, the current drops to a very small value indicating the onset of permanent passivation.

It is probable that the anodic dissolution of indium in the alkali solutions depends upon the diffusion of OH^- through the anodic layer. This should be directly proportional to the electrolyte concentration and temperature. Therefore, the increase in the peak currents with increase of the temperature and concentration could be ascribed to the effect of these two variables on the rate of both diffusion and chemical dissolution. Furthermore, the rise in the anodic peak currents depending on the square root of v (Fig. 5) can be intterpreted in terms of a diffusion controlled process occurring through the anodic layer. The dependence of the peak potentials on log ν (Fig. 6) can also principally be caused by a local change in *pH* which in turn is also ν dependent.

Figs. 7 and 8 outline cyclic voltammetric curves for indium electrodes at different conditions. Comparing the data of these two figures with those of Figs. 1–4 indicates that the form of the anodic polarization depends to some extent on the starting potential. Fig. 8 shows that the oxidation peaks I and II result into the same oxidation state since they show as one cathodic peak [19]. Therefore, at more positive potentials (+100 mV vs. SCE) more cathodic potential is required to reduce the corrosion products. On the other hand, when the forward scan was started from −1 600 mV and terminated at −1 050 mV (Fig. 7) the reverse scan reveals one cathodic peak (IV). It is clear from cycle 1 in Fig. 7 that the height of current peak I (oxidation process) is approximately equal to the height of current peak IV (reduction process). This indicates that the oxidation products are quantitatively reduced to metallic indium.

The results obtained in 3 *M* KOH (Fig. 7, cycle 2) and at 70°C (Fig. 7, cycle 3) show that the charge under the anodic peak I (Q_a) is greater than that for the cathodic peak IV (Q_c) suggesting that chemical dissolution of hydroxide can take place under the prevailing conditions. On repetitive cycling the heights of the different peaks increase with increasing the number of cycles. This influence can be due to an activation porocess of the electrode by cycling polarization. These data suggest also that the anodic and cathodic reactions are conjugated.

References

[1] Pointelli R., Poli G. (1950) Compt. Rend. Reunion: 136
[2] McElroy A. D., Kleinberg J., Davison A. W. (1952) J. Am. Chem. Soc. **74**: 736
[3] Glicksman R., Morehouse C. K. (1957) J. Electrochem. Soc. **104**: 589
[4] Popova T. I., Simonova N. A. (1963) Izvest. Akad. Nauk. S.S.S.R. Ser. Khim: 1187
[5] Amirkhanova N. A., Fizullin F. F. (1964) Electrolitov. Kazan Sbornik: 98
[6] Visco R. E. (1965) J. Electrochem. Soc. **112**: 932
[7] Fizullin F. F., Amirkhanova N. A. (1965) Sbornick Aspirant-skikh Rabot, Kazansk Gas. Univ: 162
[8] Murtazaer A. M., Nikol Skaya K. Ya. (1964) Dokl. Akad. Nauk. Uzbek S.S.S.R. **21**: 31
[9] Filippova L. I., Kuzmin L. L. (1969) Izv. Vyssh. Ucheb. Zaved. Khim. Technol. **12**: 1199
[10] Lewis R. W., Partridge H. H. (1960) Proc. Second Int. Symp. on Batteries, Cournemouth, p. 2
[11] Salem T. M., Ismail A. A. (1970) J. Chem. Soc. (A): 2415
[12] Boswell T. L. (1958) J. Electrochem. Soc. **105**: 289
[13] Abd El Rehim S. S., Abd El Haleem S. M., Abd El Wahab S. M., Shalaby M. Sh. (1983) Surf. Technol. **19**: 261
[14] Shams El-Din A. M., Abd El Wahab F. M. (1964) Electrochim. Acta **9**: 883
[15] Latimer W. M. (1953) Oxidation Potentials, Prentice-Hall, New York
[16] Budov G. M., Losev V. V. (1959) Dokl. Akad. Nauk. S.S.S.R. **129**: 6
[17] Armstrong R. D., Suttie A. B., Thirsk H. R. (1968) Electrochim. Acta **13**: 1
[18] Pourbaix M. (1966) Atlas of Electrochemical Equilibria in Aqueous Solutions. Pergamon Press, Oxford, p. 436
[19] El-Tantawy Y. A., Al-Kharafi F. M. (1982) Electrochim. Acta **27**: 691

Received May 2, 1990. Revised April 6, 1991. Accepted May 13, 1991