

## THE BEHAVIOUR OF POLYVINYL ALCOHOL AT THE PLANAR Cd/Cd(OH)<sub>2</sub> ELECTRODE INTERFACE

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### Summary

The anodic oxidation of Cd in alkaline solution was investigated using potentiostatic pulse and a.c. impedance techniques. In the active dissolution region, the slope of the  $\eta$ -log  $i$  curve was close to the "Nernstian" Tafel slope of 30 mV/decade. Addition of an organic additive, polyvinyl alcohol (PVA), to the electrolyte caused a marked change in the Tafel slope corresponding to a 2e consecutive electron transfer reaction. Impedance measurement indicated a decrease in the charge transfer resistance in the presence of PVA. The results indicate that expanders such as PVA modify the anodic oxidation mechanism of Cd in alkaline solution.

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### 1. Introduction

Sintered-plate nickel-cadmium cells which have been stored for a few years undergo electrolyte leakage during charging due to premature hydrogen evolution from the electrode [1]. Scanning electron microscopy has been used to detect crystal growth of cadmium hydroxide negative active material which may have resulted in a decrease in the active surface area and thus of charging capacity. Differences in the crystal structure of a new cell and an aged cell have been quite marked. Here recrystallization occurred at the cadmium negative electrode such that the submicron particles of Cd(OH)<sub>2</sub> in a fresh cell have enlarged to become rhombic crystals of greater than 10  $\mu$ m size in the stored defective cell.

Further studies concerning the aging of cadmium have been conducted by Papazova *et al.* [2] in silver-cadmium cells. After one year's storage at room temperature, the metallic cadmium particles increased in size by at

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least an order of magnitude, from  $10^{-5}$  -  $10^{-4}$  cm to  $10^{-3}$  cm. It was claimed that the same relative increase in size could be induced after only six months' storage at 50 °C.

Performance improvement of the cadmium electrode has been obtained by introducing inorganic oxides such as  $\text{Fe}_2\text{O}_3$ , NiO,  $\text{TiO}_2$  or organic materials such as polyvinyl alcohol (PVA), cellacol, terephthalic acid into the cell. Such additives are beneficial if they reduce the size of crystals formed, thereby providing a large area for the reaction. The effect of additives controlling the morphology of the cadmium electrode is well documented [3 - 6]. However, very little is known about the behaviour of the electrode processes concerning these additives. Though much of the experimental work on crystal growth has been done using sintered negative plates, these results also apply to pocket plates or any system in which cadmium is in contact with an alkaline solution.

Galvanostatic and potentiostatic techniques have already been used by many researchers on the cadmium electrode [7 - 14], but not in the presence of organic additives. This paper examines the behaviour of a planar Cd electrode in the active dissolution region in the presence and absence of an organic additive, *viz.*, PVA using potential step and a.c. impedance techniques.

## 2. Experimental

The cadmium used in this investigation was a disc electrode, area 0.283 cm<sup>2</sup>, cut from a rod supplied by BDH (99.9% pure). It was set in an Araldite holder. Measurements were made in a conventional, enclosed 3-electrode cell using an Hg/HgO reference electrode and a large Ni foil counter electrode. The solution used throughout was 5 M KOH, prepared from Aristar potassium hydroxide pellets and deionised-distilled water. All solutions were deoxygenated with  $\text{N}_2$  before use. The experiment was conducted at room temperature.

Prior to the experiment, the electrode was mechanically polished with 4/0 emery paper wetted with methanol, cleaned with methanol and water, and then polished with 1  $\mu\text{m}$ -size diamond paste. Subsequent polishing was carried out on a buff (particle size 1  $\mu\text{m}$ ) and then by rinsing with methanol and water before final immersion in the working solution.

A Wenking type potentiostat was used (10 V-3 A) in conjunction with a waveform generator (Chemical Electronics, type O1), a transient recorder (Data Lab, DL901) and an x-y-t chart recorder (Bryans, 2900).

The electrode was allowed to equilibrate in the alkaline solution for 15 - 30 min until a steady, open-circuit potential was reached ( $-0.925$  V *versus* Hg/HgO reference electrode). The cathodic voltage was set at this value potentiostatically and small voltage pulses of 5 mV (100 ms) in magnitude were applied to the electrode after each polishing. PVA is only sparingly soluble in KOH solution and once the initial experiment had terminat-

ed, a 5 ml aliquot of a saturated solution of PVA was added to 600 ml of KOH to study its effect ( $1.67 \times 10^{-6}$  M).

Impedance measurements were made at a series of anodic overpotentials in order to determine the variation in the charge transfer resistance. The measurements were repeated with PVA added to the electrolyte. The apparatus used was a Solartron 1170 Transfer Function Analyser consisting essentially of a programmable generator providing the perturbing sinusoidal signal and a correlator to analyse the response of the system and display the result. The frequency sweep was made between 10.0 mHz and 9.999 kHz. The TFA generates small sinewave voltage perturbations of known frequencies, and the input/output of the electrochemical cell was then correlated and presented as complex plane plots of real and imaginary impedance in the normal manner using a PDP 11/10 computer system and plotted on an X-Y recorder (Rikadenki).

The cell impedance was measured as recommended by Sluyters [15]. The a.c. current through the cell was monitored as a voltage drop across a resistor in the potentiostatic output lead. The a.c. voltage across the cell was measured directly between the working and the auxiliary electrode. The ratio of the cell voltage to the cell current gave the cell impedance. Since the impedance of the auxiliary electrode/electrolyte interface can be made negligibly small, it is, in effect, the impedance of the working electrode/electrolyte interface that is measured.

### 3. Results and discussion

#### *Potential step studies*

Since the potential is pulsed for a very short time interval, very little of the reactant is consumed; thus mass transfer effects are negligible. Therefore, the  $i-\eta$  relationship is governed solely by the charge transfer (neglecting ohmic drop and double layer charging effects). Mass transfer effects become more significant as the reaction time increases, and after an infinite time steady state values are attained. The electrode behaves as a "leaky" condenser and at the instant of applying the potential, a very small, but finite, time is required to charge the electrode. Thus, due to the double layer charging effect, it is not possible to take measurements at exactly zero time. This time depends on the capacity of the electrode double layer and, consequently, on the electrode surface area.

In order to avoid mass transfer effects, it is important to determine the time interval at which current readings are taken. Ideally, the current should be measured immediately after the double layer charging of the electrode is complete. Unfortunately, in the case of cadmium, the double layer charging time could not be measured as the electrode was active at all potentials (*i.e.*, no non-faradaic region). The experimental current is measured after the double layer charging time, and a simple calculation allows a reasonable value to be worked out for this time and, hence, to avoid this effect.

In general, the capacity,  $C$ , of a planar electrode is about  $20 \mu\text{F cm}^{-2}$  for most metals (not allowing for surface roughness) [16]. When surface roughness is taken into account, the capacity  $C$  is given by  $Q_s = CV = it$  where  $Q_s$  is the charge on the electrode surface,  $V$  is the magnitude of the voltage pulse,  $i$  is the current and  $t$ , the double layer charging time. Since the current is not constant at any potential,  $Q_s = \int i dt$ . Therefore, using the minimum current measured and the maximum overpotential, and assuming a surface roughness of 3 for cadmium, the maximum charging time is calculated to be about 2.8 ms. Therefore, the currents in our study were measured after this time. It should be noted that this is an approximate value and the charging time could vary somewhat with potential.

Potentiostatic pulse measurements were made by stepping from a potential in the open-circuit voltage (OCV) region, to one in the active dissolution region and observing the transient current. The response consisted of a rapidly rising and falling current, reaching a minimum (after about 400 ms) and then, at higher anodic potentials, rising and eventually falling again.

Figure 1 illustrates a typical  $i$  versus  $t^{1/2}$  plot of pulses taken in the anodic region from OCV of  $-0.925$  V (versus Hg/HgO reference electrode) of cadmium in alkaline solution in the absence of PVA. Figure 2(a) shows the corresponding plot of  $\log i_{(t=0)}$  versus  $\eta$ .

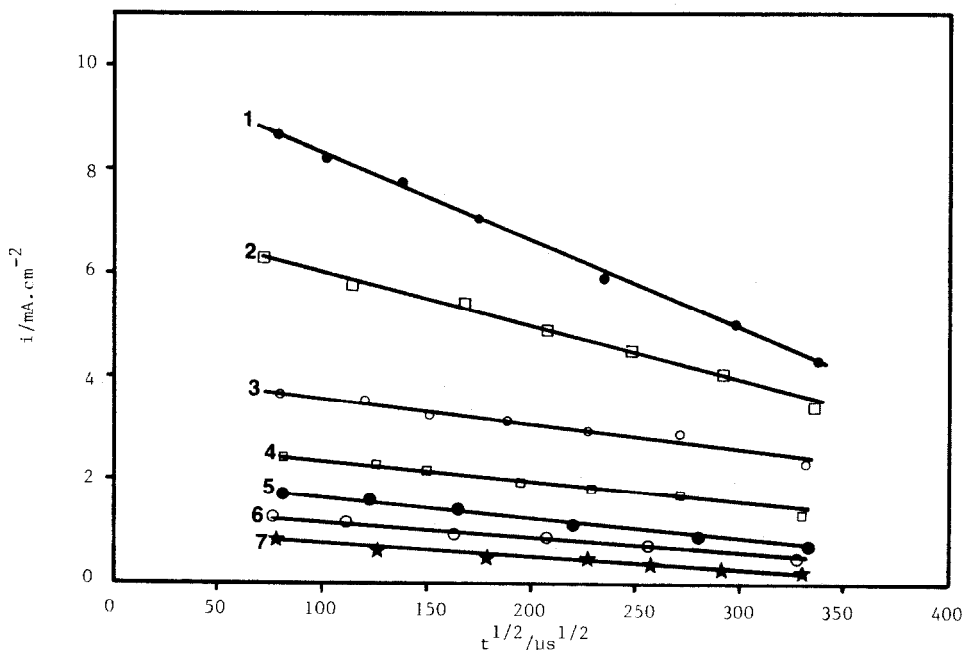


Fig. 1. Typical  $i$  vs.  $t^{1/2}$  plots for Cd electrode in KOH solution only. 1,  $-875$  mV; 2,  $-880$  mV; 3,  $-890$  mV; 4,  $-895$  mV; 5,  $-900$  mV; 6,  $-905$  mV; 7,  $-910$  mV.

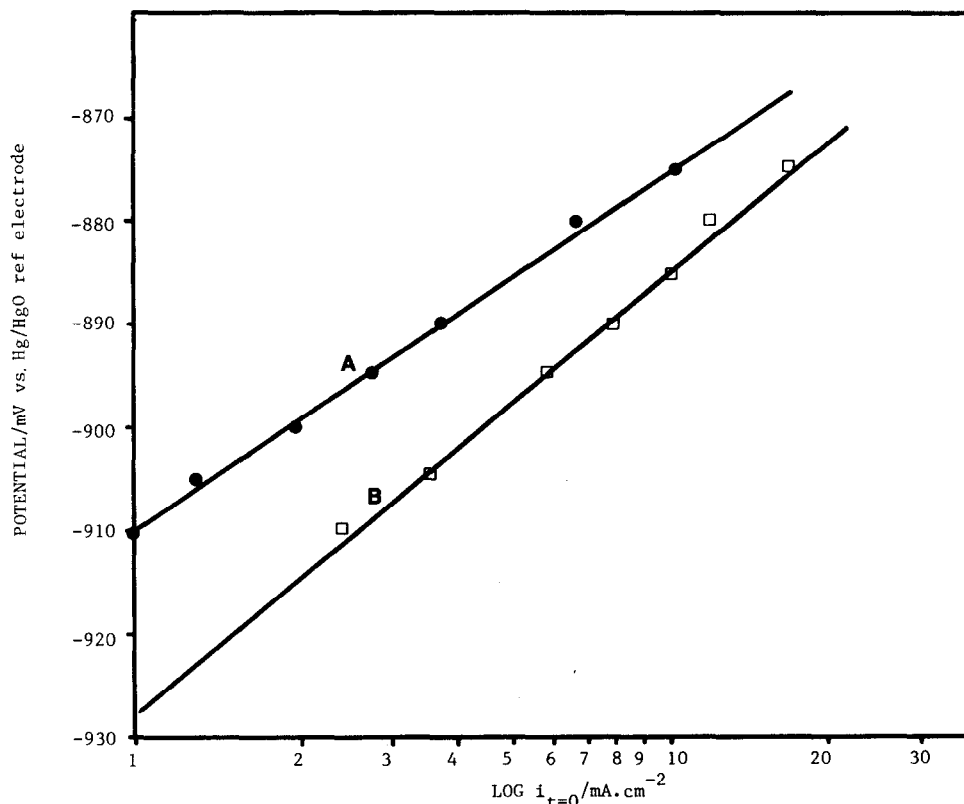


Fig. 2. Semi-logarithmic plot of  $i_{t=0}$  vs. potential for Cd electrode in (A) KOH solution; (B) KOH solution containing PVA.

A slope of  $34 \pm 3$  mV/decade is obtained corresponding closely to the 30 mV/decade for a "Nernstian"  $2e$  reversible electron transfer reaction. The correlation coefficient is 0.980. This reaction is consistent with the dissolution mechanism:



and in excellent agreement with previous work [7, 14, 17].

Figure 3 illustrates a typical  $i$  versus  $t^{1/2}$  plot in which PVA has been added to the KOH electrolyte, and Fig. 2(b) is the corresponding plot of  $\log i_{(t=0)}$  versus  $\eta$ . A slope of  $43 \pm 3$  mV/decade is obtained, indicating a change in the mechanism of the electrochemical reaction. A "Nernstian" Tafel slope of 40 mV/decade is generally obtained for a reaction involving two consecutive electron transfers; the first one, reversible and the second, rate determining [17], e.g.,



On the other hand, surface processes caused by the adsorption of PVA onto the Cd/Cd(OH)<sub>2</sub> layer might also yield the same Tafel slope. The differences

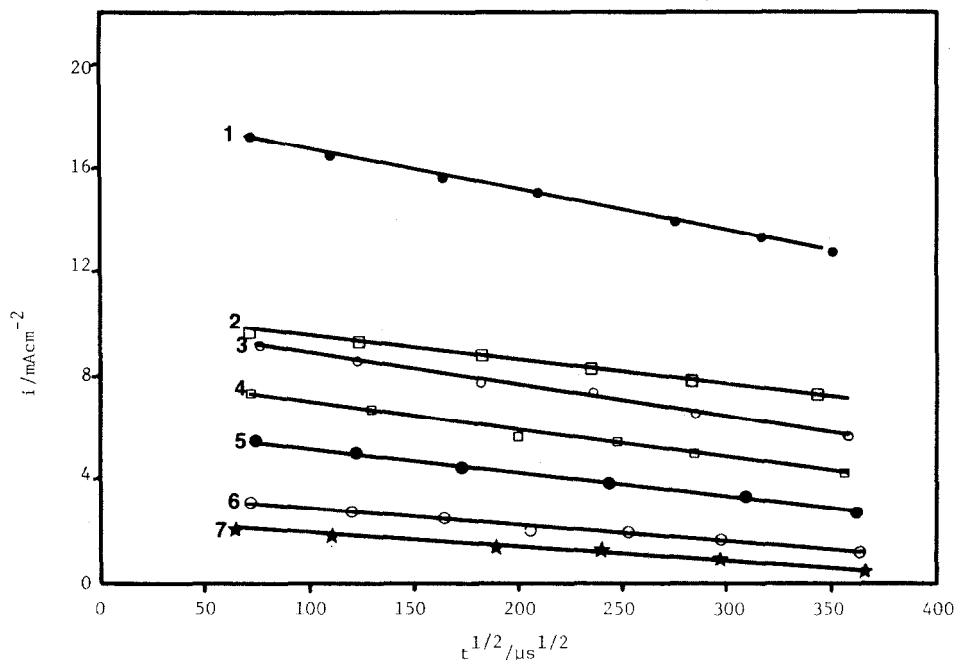


Fig. 3. Typical  $i$  vs.  $t^{1/2}$  plots for Cd electrode in KOH solution containing PVA. 1,  $-875$  mV; 2,  $-880$  mV; 3,  $-885$  mV; 4,  $-890$  mV; 5,  $-895$  mV; 6,  $-905$  mV; 7,  $-910$  mV.

in the behaviour could be accounted for in several important respects. The initial rise and fall of the transients (not shown) are more enhanced in the presence of PVA (although qualitatively they are similar). This indicates a greater surface area accompanying a greater double layer charge when the potential is stepped. The charge transfer current is also greater when PVA is added to the electrolyte (Figs. 1 and 3). When the double layer effects have subsided, the current again rises, which is characteristic of an electrocrystallization process [18]. This rise in current as shown in a previous publication is considerably delayed when PVA is present. Nonetheless, it is difficult to deduce from the above experimental evidence that the change in the reaction mechanism and the change in the surface area are two unrelated, independent phenomena. However, recent studies [18] have shown that PVA contributes significantly to an increase in the available active surface area by modifying the two-dimensional film growth of  $\text{Cd}(\text{OH})_2$ , and this may be a direct consequence of the mechanism change in the electron transfer reaction.

#### Impedance studies

The impedance of the cadmium electrode in KOH solution was analysed using the complex plane plot or Nyquist diagram. Figure 4 shows the complex plane impedance plot obtained for a planar cadmium electrode in KOH solution at a series of anodic overpotentials. It is seen that well-

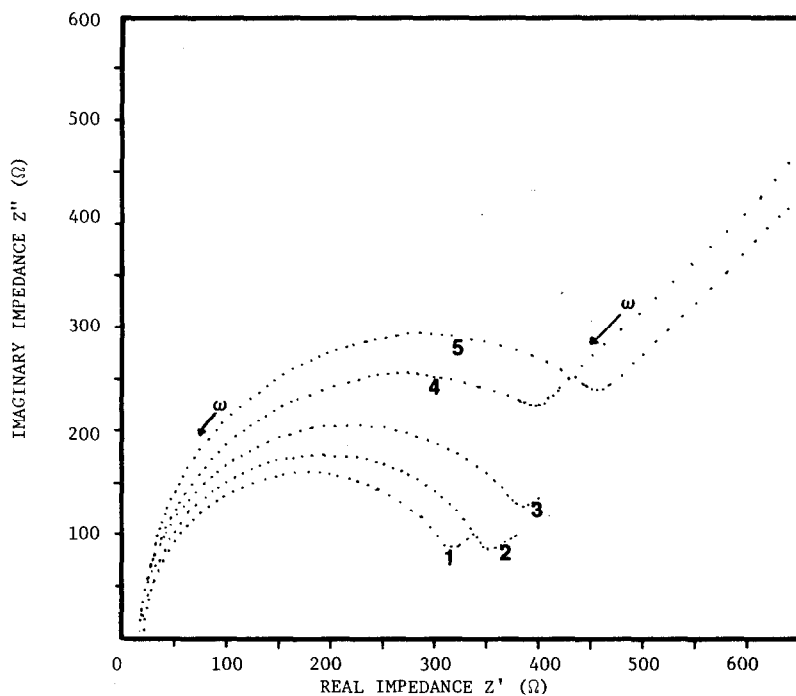


Fig. 4. Complex plane plots of Cd electrode in KOH solution only as a function of overpotential. 1,  $-910$  mV; 2,  $-905$  mV; 3,  $-895$  mV; 4,  $-890$  mV; 5,  $-880$  mV.

defined semi-circles are obtained with the charge transfer resistance increasing with the overpotential. The interphasial response to this signal can be compared to the components of an equivalent circuit containing a charge transfer resistance and a double layer capacitance in parallel and connected in series with a solution resistance. As the overpotential is increased ( $-890$  mV), the shape of the impedance spectrum changes from a semi-circle to a semi-circle with a Warburg character, indicating that diffusion of the soluble species plays a dominant role in the reaction mechanism.

The addition of PVA to the electrolyte produces a change in the complex plane impedance plots (Fig. 5). In addition to the semi-circle, there was a distinct Warburg diffusion at all anodic potentials. The semi-circles that were obtained appeared to be flat at the top and the Warburg diffusion tended towards  $22.5^\circ$  initially and then rose to one of unit slope. This was probably due to a combined interaction of charge transfer and adsorption effect caused by the changes taking place at the Cd/Cd(OH)<sub>2</sub> interface resulting from the PVA addition. Besides the additional Warburg impedance, there was a marked decrease in the charge transfer resistance. This was interpreted as due to an increase in the active surface area from the action of PVA. The double layer capacities were computed from the maximum of the semi-circle where  $C_{dl} = 1/R_{ct}\omega$ . Figure 6 shows the variation in the double layer capacity with overpotential in the presence and absence of the ex-

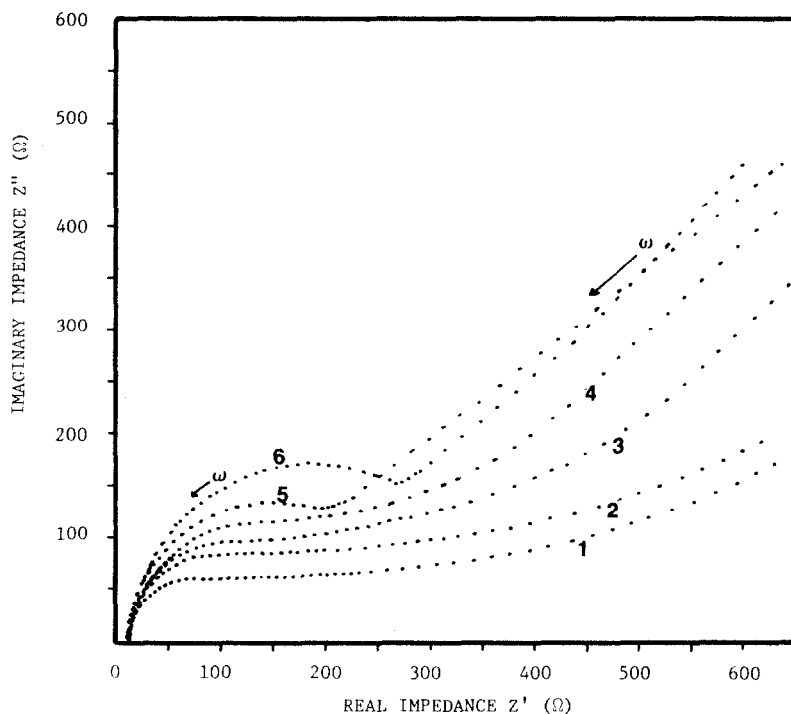


Fig. 5. Complex plane plots of Cd electrode in KOH solution containing PVA as a function of overpotential. 1,  $-910$  mV; 2,  $-905$  mV; 3,  $-895$  mV; 4,  $-890$  mV; 5,  $-880$  mV; 6,  $-875$  mV.

pander. The effect appears to be more pronounced when PVA is present. This has been explained as being due to PVA adsorption on the surface of the electrode facilitating electron transfer reaction [19]. The overall effect is to enhance the dissolution of cadmium and hinder the film formation, thereby leading to higher currents and, consequently, large electrochemically-active surface areas. This would, in turn, allow greater utilization of the electrode and, hence, performance.

#### 4. Conclusion

The anodic oxidation of cadmium in KOH solution has been studied in the presence of a PVA expander. Potential step investigation indicates that there is a change in the reaction mechanism as a result of PVA addition to the electrolyte, and this is caused by a change in the active surface area. Impedance measurements indicate a decrease in the charge transfer resistance and an increase in the double layer capacity when PVA is present. All this further confirms that PVA in the electrolyte hinders the  $\text{Cd}(\text{OH})_2$  film formation and enhances the overall dissolution rate of metallic cadmium.



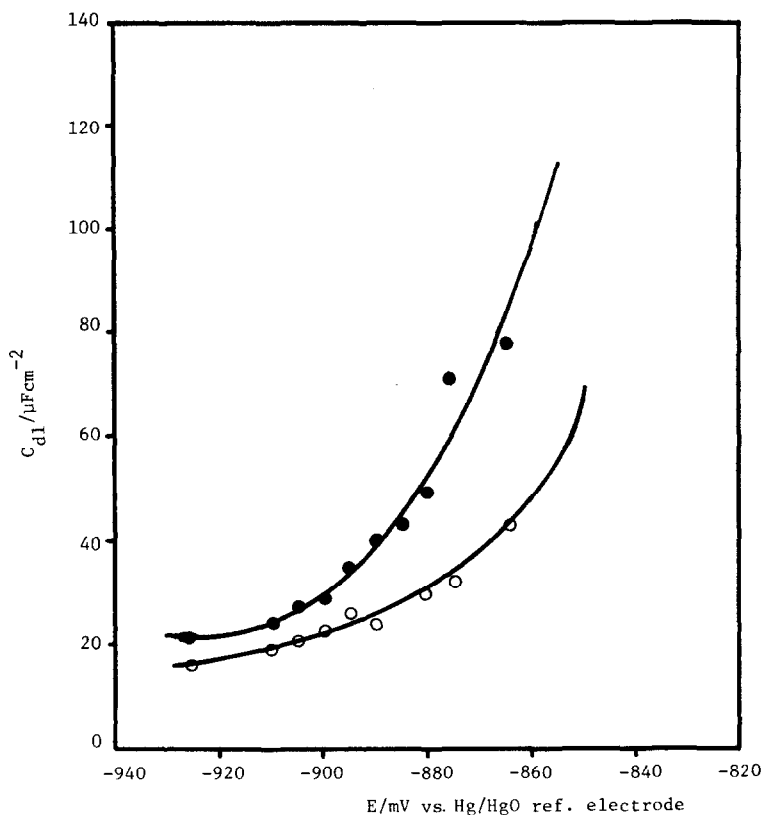


Fig. 6. Plot of  $C_{dl}$  against  $E$  in the active region for:  $\circ$ , Cd in KOH solution only;  $\bullet$ , Cd in KOH containing PVA.

### Acknowledgements

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### List of symbols

$C$	Capacity of an electrode
$i$	Current density
$F$	Faraday
$\eta$	Overpotential
$C_{dl}$	Double layer capacity
$R_{ct}$	Charge transfer resistance
$\omega$	Angular frequency
$Q_s$	Charge on electrode surface

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