JOURNAL OF APPLIED ELECTROCHEMISTRY 15 (1985) 737–744

Effect of an organic additive on the impedance of cadmium in alkaline solution

M. Z. A. MUNSHI,* A. C. C. TSEUNG
Department of Chemistry, The City University, Northampton Square, London EC1, UK

J. PARKER
Marathon Alcad Limited, P.O. Box 4, Union Street, Redditch, Worcestershire, UK

J. L. DAWSON
Corrosion and Protection Centre, University of Manchester Institute of Science and Technology, Manchester, UK

Received 12 July 1984; revised 12 October 1984

The a.c. impedance of a planar cadmium electrode in KOH solution was measured over the active and passive region using a potentiostatic technique. Different concentrations of polyvinyl alcohol (PVA) were subsequently introduced into the alkaline solution and the impedance remeasured. It was found that the addition of PVA markedly increased the double layer capacity of the electrode and decreased electrolyte resistance, R_{sol}. The impedance spectra in the presence of PVA were analysed in terms of an equivalent circuit involving the series combination of two double layer capacitances and a resistance proportional to the conductivity of the electrolyte.

1. Introduction

Organic materials are used in the cadmium negative electrode of a Ni–Cd battery to prevent crystal growth, thus retaining capacity. Though much of the experimental work on crystal growth at negative plates has been done with sintered plates the results also apply to any system in which cadmium is in contact with alkaline solution. In general the beneficial additives are those that reduce the size of crystals formed on the cadmium electrode thus providing larger area for the reaction. Very little information is available concerning the use of organic additives to control the morphology of the cadmium electrode.

Vasueva-Rao *et al.* [1] found that the discharge efficiency of a sintered-plate cadmium electrode is improved when quaternary ammonium compounds such as acetyltrimethylammonium halides are added to the active material during impregnation. The result was based on the smaller size of the active material present in the plate.

Gossenberger [2] evaluated the behaviour of various cellulose and starch derivatives on the capacity of the cadmium electrode and suggested that growth of the cadmium metal was inhibited by the additives. Kantner *et al.* [3] impregnated positive and negative plates with acetate salt and claimed it improved charge retention. The function of the additives is thought to be to act as agents for the preservation of negative capacity throughout cell life. Other additive materials have been suggested in the literature but there is no detailed long-term experience. The choice of such a material would be made easier if the operating principles of additives were understood. Such principles would probably apply to all aqueous electrolyte

---

* *Present address*: Department of Metallurgy and Material Science, McMaster University, Hamilton, Ontario, Canada L8S 4L7.

0021–891X/85 $03.00 + .12

cell negatives and would probably be related to those of crystal growth.

Both the active and passive regions of a negative cadmium electrode have been studied extensively using potentiostatic and galvanostatic measurements [4–11]. However, the use of a.c. impedance analysis to assess the beneficial effect of additives on the cadmium electrode in alkaline solution have eluded many researchers. The aim of the present work was to evaluate such an effect in the active-dissolution and passive regions using PVA as the expander. The technique was found to be a quick and efficient means for organic additive assessment.

2. Experimental details

Impedance measurements were made on a planar cadmium disc electrode, 0.283 cm^2, cut from a rod supplies by BDH (99.9% pure) and set in an Araldite holder. A conventional 3-electrode cell was used with a calomel reference and a large Ni counter electrode. The solution used was 5 M KOH made up from Aristar pellets and deionized water. All solutions were deoxygenated with nitrogen and the experiment was conducted at room temperature.

Prior to the experiment the electrode was polished mechanically with 4/0 emery paper wetted with methanol, cleaned with methanol and water and then polished with diamond paste until a mirror-like finish was obtained. Subsequent polishings were carried out on a rotating buff and the electrode was finally cleaned with methanol and then deionized water before being immersed into the KOH solution and held at the various potentials at which the impedance measurements were made.

The apparatus used was a Solatron 1170 Transfer Function Analyser (TFA) consisting essentially of a programmable generator that provided the perturbing sinusoidal signal, a correlator to analyse the response of the system and a display of the results. The TFA had the advantage of rejecting all harmonics present in the output of the system thus minimizing the effect of random noise. The generator was programmed to sweep through a large frequency range from 9.999 kHz to 10.0 mHz. The TFA generated small sinewave voltage perturbations of known frequencies and the input/output of the electrochemical cell was then correlated and presented in terms of phase shift and modulus of impedance. The results were first obtained as data lists of frequency, phase shift in degrees and modulus of impedance which were then presented as complex plane plots of real (R_s) and imaginary $-(\omega C_s)^{-1}$ impedance in the normal manner using a PVD-11/10 computer system and plotted on a X–Y recorder (Rikadenki).

The time required for the TFA to make a single measurement is equal to the period of the signal (i.e. 1 s at 1 Hz) and this becomes a major contribution to the total experimental time at low frequencies. Automated impedance measurements were carried out under potentiostatic conditions using a ministat supplied by Thompson and Associates.

The cell impedance was measured as recommended by Sluyters [12]. The a.c. current through the experimental cell was monitored in the usual way, as a voltage drop across a resistor in the potentiostat output (auxillary electrode) lead. The a.c. voltage across the cell was measured directly between the working and the auxillary electrode. The ratio of the cell voltage to the cell current gave the cell impedance and since the impedance of the auxillary electrode/electrolyte interface was made negligibly small it was in effect the impedance of the working electrode/electrolyte interface that was measured. It should be noted that this arrangement eliminated the effects of phase shift occurring within the potentiostat itself. The potentiostat, however, still had a sufficient bandwidth so that true potentiostatic control of the electrode interface was maintained even at high frequencies.

A d.c. bias was applied to the system using the d.c. source provided by the 1170 TFA. A Fenlow Electronics digital multimeter was used to measure the applied d.c. potential and a Keithley 610^c electrometer was used to monitor the voltage drop across the counter resistor and hence the current through the cell.

The steady-state current/voltage curve for cadmium dissolution in 5 M KOH represents an active region at potentials cathodic to -1050 mV at which there is a sharp discontinuity to a passive region due to film formation

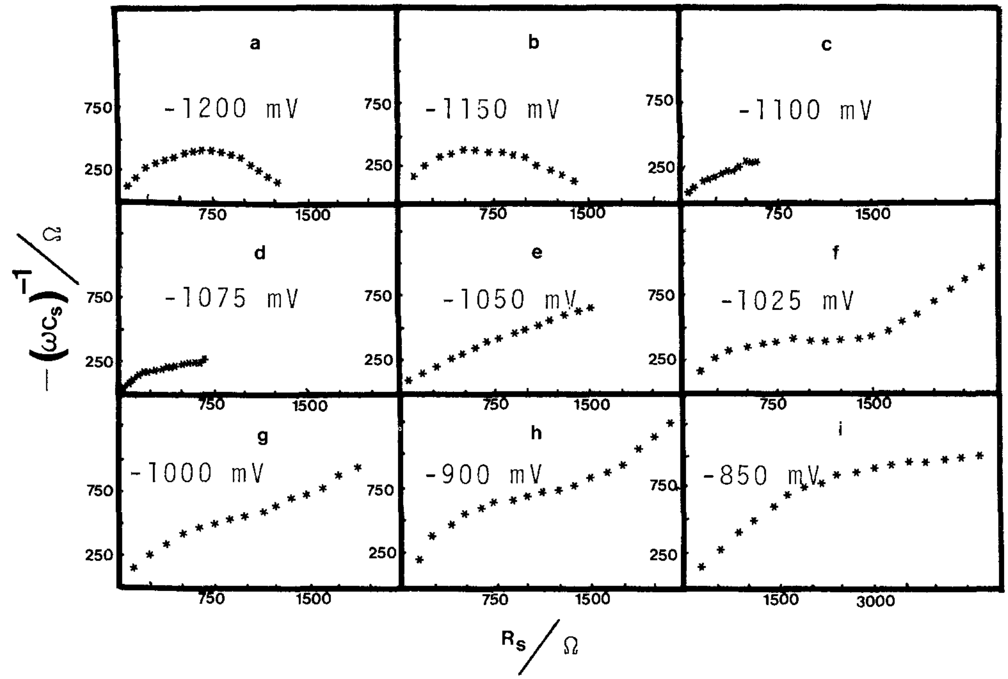

Fig. 1. Complex plane impedance diagrams for planar Cd in 600 ml KOH only.

[13]. The open-circuit voltage occurs at −1090 mV.

Automated impedance measurements were carried out in deoxygenated 5 M KOH solutions on planar electrodes in both the active and passive region from −1200 mV to −850 mV vs calomel reference electrode. Since PVA is only sparingly soluble in KOH solution (soluble concentration in 5 M KOH is 2×10^{-4}m), three separate portions of a saturated solution (3 ml, 5 ml and 10 ml) wre added to 600 ml of 5 M KOH to study the effect of varying concentration on the faradaic impedance of cadmium. (3 ml of a saturated solution in 600 ml KOH $\equiv 10^{-6}$M.)

3. Results and discussion

Figs. 1a–i shows the complex plane impedance plots obtained for a planar cadmium electrode in KOH solution only, in both the active and passive regions. At potentials cathodic to Open Circuit Voltage the impedance plots can be fitted to a semicircle whereas at potentials positive to −1050 mV, i.e. after passivation, the impedance plots correspond to a semicircle at high frequencies and to a straight line of slope unity at low frequencies.

Thus the shapes of the first and second spectrum obtained at potentials negative to the rest potential (−1090 mV) are simply large semicircles. As at these potentials the current due to the faradaic reaction is small, these are analysed in terms of a combination of double layer capacitance and charge transfer resistance. The charge transfer resistance, however, will be large under these conditions.

As the potential is increased these quantities become smaller and the distinct semicircle character disappears or is slightly distorted (−1100 mV). At −1075 mV the shape of the impedance spectrum changes from a semicircle to a semicircle with a Warburg character. However, an enlarged complex impedance plot at this potential (Fig. 2) shows that another phenomenon might also be occurring. The sudden change up to the potential where passivation occurs must be due to OH^- adsorption prior to film formation. This seems to be confirmed since the possibility of a second semicircle appears to be inherent in the complex plot. The adsorption of OH^- on the planar cadmium has also been shown by Armstrong and Edmondson [14].

At −1050 mV (Fig. 1e), the impedance plot

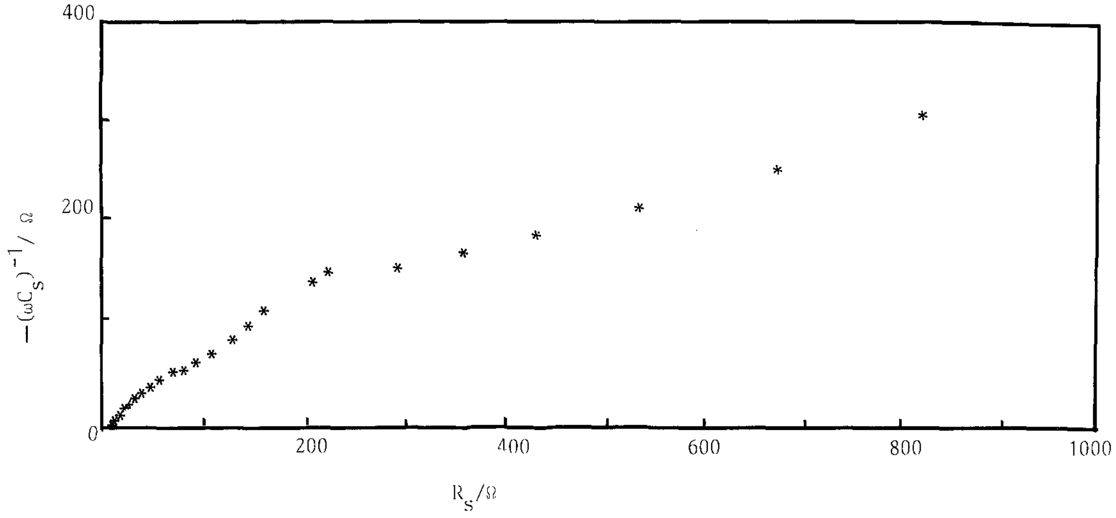

Fig. 2. Complex plane impedance diagram for planar Cd electrode in deoxygenated 5 M KOH at a potential of − 1075 mV vs calomel.

begins to form a definite shape again but this time it was necessary to include in the analysis a Warburg diffusion to allow for diffusion of species in the film present on the surface.

As over the whole potential range positive to the rest potential the cadmium electrode is covered with hydroxide layers due to passivation; this and subsequent spectra (Fig. 1f–i) can be interpreted in terms of a variation in the stoichiometry of the film with potential. As the region in which the current does not vary with potential is reached, diffusion begins to take part in the reversible dissolution process and the circuit is, in the simplest case, a Warburg impedance in parallel with the double layer capacity, C_{dl}.

The introduction of various concentrations of PVA to the electrolyte produces a change in the complex plane impedance plots. However, the addition of 3 ml of a saturated solution of PVA to the electrolyte causes very little or no difference to the impedance spectra (Fig. 3a–i) and semicircles with resistance R_p in parallel with the double layer capacity C_{dl} are observed in the active region. In the passive region reversible dissolution gives rise to an additional Warburg impedance. The absence of a possible second semicircle could not be explained (at ∼ − 1075 mV), but the semicircle that was obtained appeared to be flat at the top and the Warburg diffusion tended towards 22.5° initially and then rising to one of unit slope (Fig. 4). This was probably due to a combined interaction of charge transfer and adsorption effects.

The complex plane impedance plots obtained when 5 ml of the PVA solution were added to the electrolyte showed very interesting results (Fig. 5a–i). In the active region the impedance spectra were semicircles as in the case when there was no additive present. At about − 1075 mV (Fig. 6) the complex plane plot again appeared to give a second semicircle. This start of the second semicircle was clearly distinguished from any Warburg behaviour in that the line was greater than 45° (Fig. 6e). This prominent feature can only be attributed to the PVA being strongly adsorbed on the surface of the cadmium electrode. This can also be interpreted in terms of an equivalent circuit involving the series combination of two double layer capacitances and a resistance proportional to the conductivity of the electrolyte. At potentials more positive than − 1025 mV the familiar shapes of a semicircle followed by Warburg impedance begin to occur. The capacity currents in this set of experiments are much higher than in the case without PVA.

As the PVA concentration is increased to 10 ml, very similar shapes in the impedance spectra are obtained (Fig. 7a–h) and match closely to those from 3 ml PVA and those without PVA. Thus, a concentration of 5 ml of a saturated

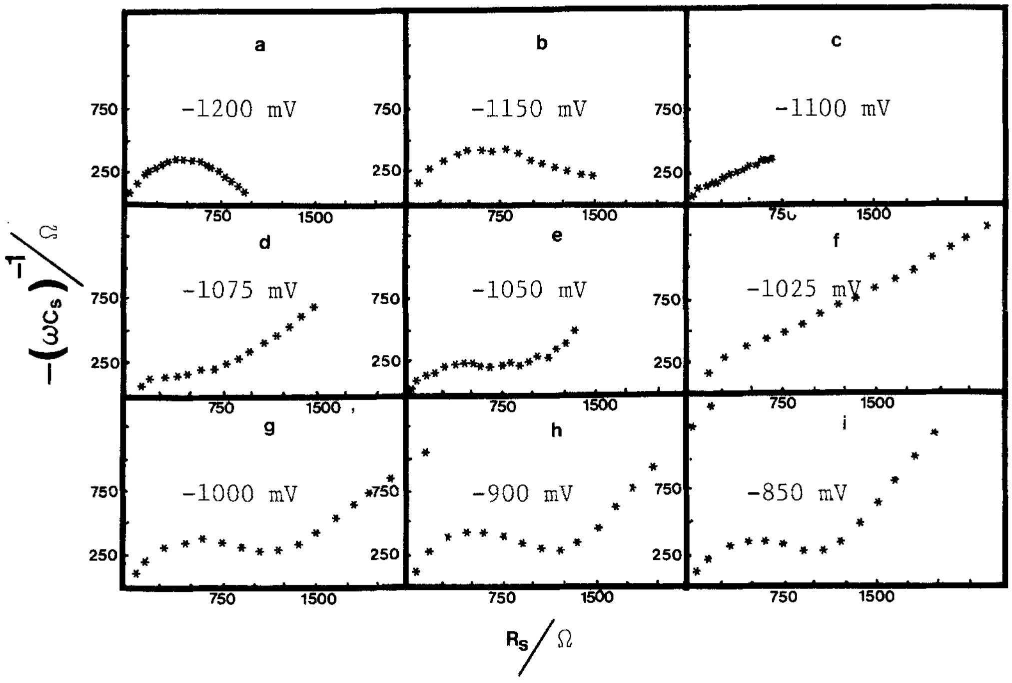

Fig. 3. Complex plane impedance diagrams for planar Cd in 600 ml KOH + 3 ml PVA.

solution of PVA in 600 ml of KOH electrolyte appears to give the optimum result in terms of adsorption phenomena. This is expected, however, since it is universally known that too much organic additive is detrimental to any electrochemical system and too little is insufficient for any effect to be observed.

The interface of cadmium in alkaline solution in the presence of PVA can also be depicted as consisting of two regions; one the double layer of cadmium and the other of PVA. Both these regions may be considered as being a network of resistors and capacitors in parallel with each other. The values of these resistances and capaci-

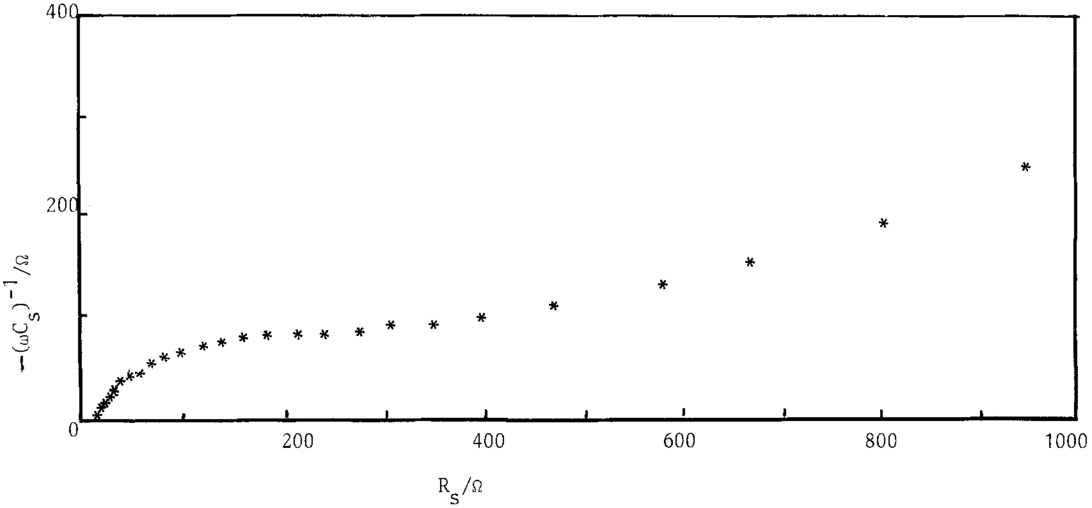

Fig. 4. Complex plane impedance diagram for planar Cd electrode in deoxygenated 5 M KOH + 3 ml saturated PVA at a potential of −1075 mV vs calomel.

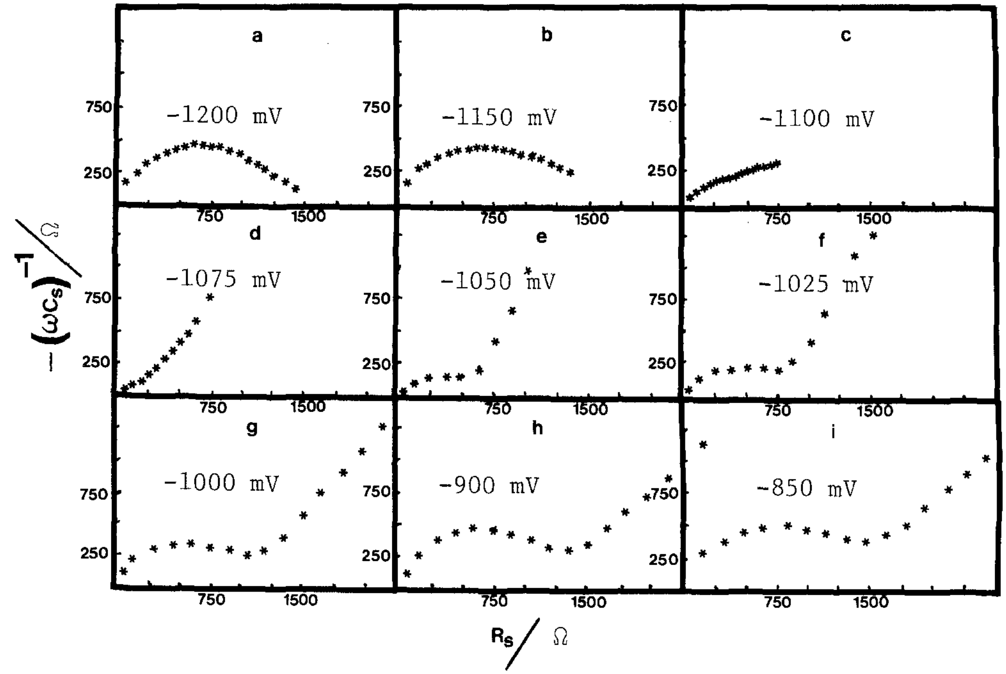

Fig. 5. Complex plane impedance diagrams for planar Cd in 600 ml KOH + 5 ml PVA.

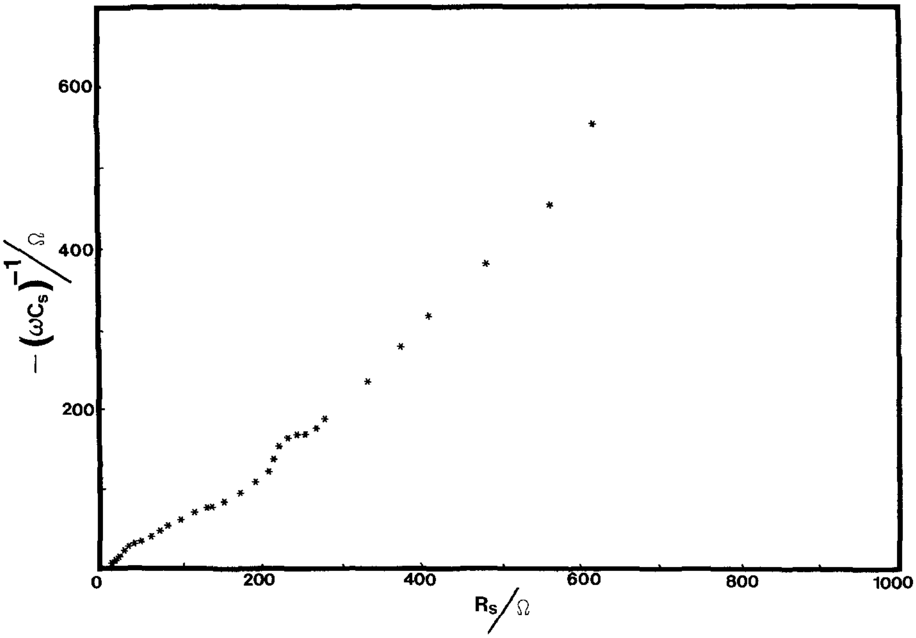

Fig. 6. Complex plane impedance diagram for planar Cd electrode in deoxygenated 5 M KOH + 5 ml saturated PVA at a potential of −1075 mV vs calomel.

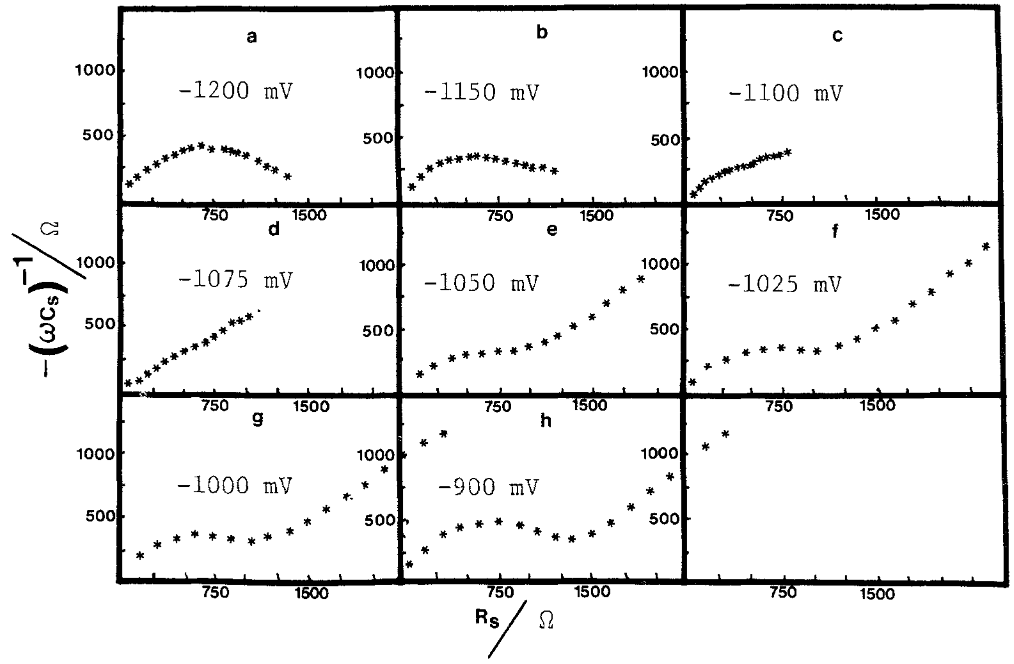

Fig. 7. Complex plane impedance diagrams for planar Cd in 600 ml KOH + 10 ml PVA.

tances are likely to be greatly different between the two regions. Two separate and identifiable sets of impedance data are thus expected, giving rise to two semicircles. In our experiment using 5 ml PVA a second very large semicircle was apparent due mainly to the PVA layer adsorbed on the cadmium surface.

The double layer capacities were computed from the impedance data and the potential dependence of the double layer capacity is shown in Fig. 8. It is seen that the increase in C_{dl} with variable concentrations of PVA agree well with the results of the complex plane plots obtained above. The sharp increase in C_{dl} up to the potential where passivation occurs must be due to OH^- adsorption prior to film formation and in the presence of additives the increase in C_{dl} is primarily due to PVA adsorption. Thus the action of PVA is confirmed to be one of adsorption on the surface of the cadmium electrode at the potential where passivation takes place.

The introduction of PVA to the electrolyte complicates matters as this increases the number of possible mobile species at the film/solution interface to three along with OH^- and $Cd(OH)_4^{2-}$ ions. It is difficult to determine any changes occurring in the mechanism of the cadmium electrode in the presence of this additive.

In alkaline solution PVA behaves as an anionic species [15]. Therefore, due to a decrease in R_{sol} and an increase in the double layer capacity of the film/solution interface, it is more likely that the presence of PVA will only enhance the dissolution/precipitation mechanism by increasing the anionic atmosphere surrounding the cadmium ions. This would lead to a transfer of these cadmium ions to interstitial sites giving rise to a build-up of cadmium ions in those sites and hence an increase in the concentration/potential gradient. These ions would then move via defects or vacancies to the film/solution interface to form cadmium hydroxide. The model proposed here appears to satisfy the impedance data.

4. Summary

The impedance of a planar cadmium electrode in 5 M KOH solution was measured over a range of potential in the active dissolution/passive region. The addition of PVA to the electrolyte caused a dramatic change in the impedance spec-

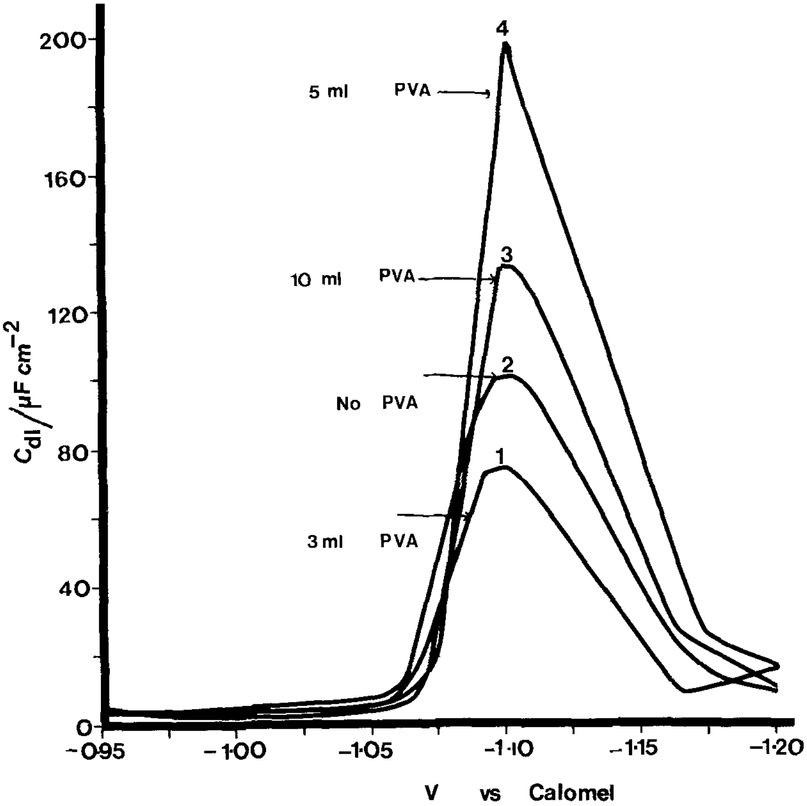

Fig. 8. Plot of C_{dl} against V in the active and passive regions.

tra giving rise to a relatively higher capacity current and double layer capacity of the electrode. The overall effect was the adsorption of PVA on the surface of the cadmium electrode enhancing the active dissolution/precipitation mechanism.

Acknowledgements

This work was supported by the Science Research Council (UK) and Marathon Alcad Limited. The excellent technical assistance of K. Haladky is gratefully acknowledged.

References

[1] P. V. Vasueva-Rao, T. Vasanthi and H. U. K. Udupa, *J. Power Sources* **1** (1976–77) 81.
[2] H. F. Gossenberger, PhD thesis, Polytechnic Institute of Brooklyn (1959).
[3] E. Kantner, R. Tarantino, P. Ritterman and R. C. Shzir, Technical Report ‡AF/AFL-TR-66-77 (September 1966).
[4] R. D. Armstrong, K. Edmondson and G. D. West, 'Electrochemistry', Vol. 4, Chemical Society, London, (1974) pp. 18–32.
[5] Y. Okinaka, *J. Electrochem. Soc.* **117** (1970) 289.
[6] A. K. N. Reddy, *ibid.* **117** (1970) 217.
[7] G. T. Croft, *ibid.* **106** (1959) 278.
[8] G. T. Croft and D. Tuomi, *ibid.* **108** (1961) 915.
[9] B. Behr and J. Taraszewska, *J. Electroanal. Chem.* **19** (1968) 373.
[10] M. Fleischmann, K. S. Rajagopalan and H. R. Thirsk, *Trans. Faraday Soc.* **59** (1963) 741.
[11] H. Y. Kang, *J. Electrochem. Soc.* **118** (1971) 462.
[12] J. H. Sluyters, *Rec. Trav. chim.* **79** (1960) 1092.
[13] R. D. Armstrong and G. D. West, *J. Electroanal. Chem. Interfacial Electrochem.* **30** (1971) 385.
[14] R. D. Armstrong and K. Edmondson, *J. Electroanal. Chem.* **53** (1974) 371.
[15] M. Z. A. Munshi, PhD thesis, The City University, London (1981).