

The behaviour of carboxy methyl cellulose at the planar Cd/Cd(OH)₂ electrode interface

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The anodic oxidation of cadmium in alkaline solution was investigated using cyclic voltammetry and A.C. impedance techniques. Addition of carboxy methyl cellulose (CMC) to the electrolyte produced a marked increase in the area available for the reaction. Impedance measurements indicated a decrease in the charge transfer resistance and an increase in the double layer capacity in the presence of CMC.

Key words: Cadmium electrode, addition of CMC, cyclic voltammetry, impedance studies

INTRODUCTION

Earlier studies indicate that various cellulose and starch derivatives have a marked effect on the capacity of the cadmium electrode and reduce the fall in capacity on cycling [1]. Recently, the effect of ethyl cellulose [2] and that of polyvinyl alcohol [3] on cadmium electrode has been studied and recommended. This paper examines the behaviour of CMC using cyclic voltammetry and a.c. impedance techniques.

EXPERIMENTAL

The area of the cadmium was 0.2 cm². All measurements were made in a 3-electrode cell with a large Ni foil counter electrode and an Hg/HgO reference electrode. The solutions used throughout were 5M KOH and deoxygenated with N₂ before use.

Cyclic voltammetry measurements were carried out using a Wenking Potentiostat in conjunction with a voltage scan generator and an x-y-t chart recorder.

Impedance measurements were made using PAR Model 173 A.C. Impedance system at frequencies from 100 kHz to 50 mHz and the applied signal amplitude was 10 mV.

RESULTS AND DISCUSSION

Cyclic voltammetry studies

In the absence of CMC (Fig. 1) normal behaviour is exhibited i.e. the dissolution of cadmium as Cd(OH)₃⁻ ion or Cd(OH)₄²⁻ ion species followed by reprecipitation or multilayer formation. The formation of multilayer results in the passivation of the electrode surface at -860 mV vs Hg/HgO electrode. The addition of CMC to the electrolyte (Fig. 2) causes a marked change in the polarization curve.

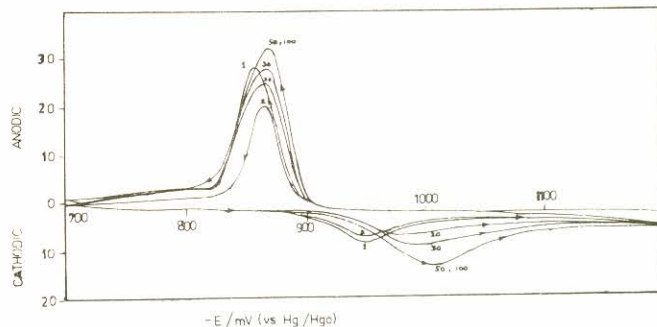


Fig. 1: Cyclic potential sweeps of planar cadmium in 5M KOH between -1200 mV and -700 mV; sweep speed: 20 mV sec⁻¹

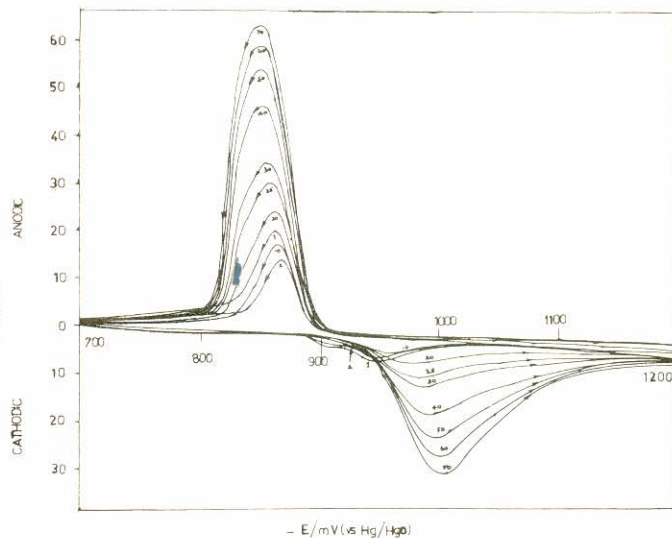


Fig. 2: Cyclic potential sweeps of planar cadmium in 5M KOH containing CMC between -1200 mV and -700 mV; sweep speed: 20 mV sec⁻¹

In the oxidative process, a greater amount of charge is required to passivate the electrode surface.

It was anticipated in the present work that the adsorption of CMC on cadmium hydroxide crystallites may retard the crystal growth by a protective colloid action of CMC.

Impedance studies

The decrease in the charge-transfer resistance is interpreted as due to an increase in the active surface area from the action of CMC (Fig. 3). In the active dissolution region (−880 mV) the double layer capacities with and without CMC, computed from the maximum of the semicircle where $C_{dl} = 1/R_{ct}\omega$ are $48.2 \mu\text{F}\cdot\text{cm}^{-2}$ and $21.2 \mu\text{F}\cdot\text{cm}^{-2}$ respectively. The effect appears to be more pronounced when CMC is present.

CONCLUSION

The results indicate that CMC in the electrolyte hinders the Cd(OH)₂ film formation and enhances the overall dissolution rate of metallic cadmium.

REFERENCES

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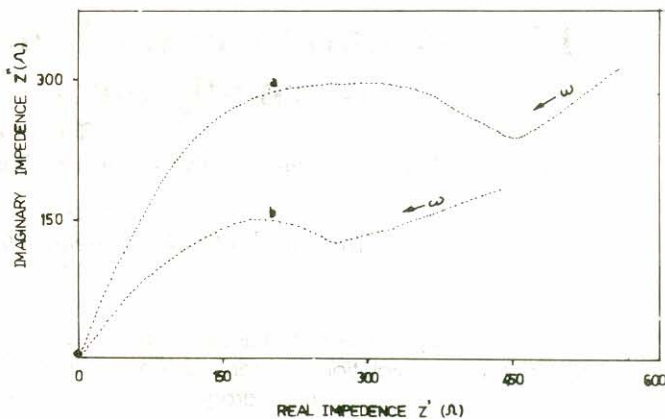


Fig. 3: Complex impedance plots of planar cadmium at −880 mV (a) in KOH solution (b) in KOH solution containing CMC

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