

EFFECT OF IRON ADDITION TO THE CADMIUM ELECTRODE

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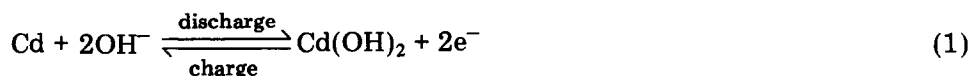
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Summary

A study is made of the high- and low-rate performance characteristics of a cadmium electrode with different percentages of iron added during impregnation. It is found that a cadmium electrode containing 20 wt.% Fe gives better capacity output at both rates of discharge. Cycling voltammetry measurements indicate an increase in the effective area available for the reaction in the presence of 20 wt.% Fe.

Introduction

The reaction mechanism at the cadmium electrode is generally recognised as



The understanding of the mechanism of anodic oxidation of cadmium in alkaline solution is of practical importance with respect to nickel/cadmium batteries. It has been argued that the oxidation of cadmium proceeds via two radically different mechanisms: (i) dissolution-precipitation; (ii) solid-state reaction. Some investigations [1, 2] support the dissolution-precipitation mechanism that finally goes over to soluble $\text{Cd}(\text{OH})_4^{2-}$, whereas others [3, 4] suggest a CdO layer. The reaction mechanism is believed, however, to be that given in eqn. (1).

The cyclic charge/discharge behaviour of sintered plate and planar cadmium electrodes has been studied [5] using galvanostatic and potentiostatic sweep techniques. Performance improvement of the cadmium electrode is obtained by introducing inorganic oxides such as Fe_2O_3 , NiO, TiO_2 , or organic materials such as poly(vinyl alcohol) (PVA), cellacol or

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terephthalic acid into the cell. Such additives are beneficial if they reduce the size of the crystals formed, thereby providing a larger area for the reaction. The effect of additives controlling the morphology of the cadmium electrode is well documented [6 - 9]. Recently, the behaviour of poly(vinyl alcohol) at the planar Cd/Cd(OH)₂ electrode interface has been studied [10].

The present work was undertaken to study the effect of iron on the sintered cadmium electrode of vented-type nickel/cadmium batteries. It should be remembered that iron causes a detrimental effect in sealed types [11].

Experimental

Charge/discharge tests

The experimental cell comprised one negative plate and two positive plates in order to study the characteristics of the negative plate, *i.e.*, the negative plate limits the capacity. The plates were prepared by sintering carbonyl nickel powder (type 255) in an inert atmosphere on a punched, nickel-plated, mild-steel grid of dimension 7.5 cm × 6 cm. The thickness of the plates was 0.8 ± 0.05 mm and the porosity of the sintered plaque prior to forming was between 70 and 75%.

The impregnating solution was prepared from AR grade nickel nitrate for the positive, and cadmium nitrate for the negative. A vacuum impregnation method, generally used for preparing the plates, was also adopted in this investigation. The plaques were immersed in a mixture of cadmium nitrate and ferric nitrate solution, mixed at different percentages and impregnated in the vacuum. The plaques were then formed electrolytically in a solution of 20% sodium hydroxide. After forming, the plates were washed free of nitrate and dried. This cycle of impregnation and forming was repeated until the plaques were impregnated with the desired weight of active material.

The plates were assembled into cells, with two positive plates and nylon cloth as separator. 30% wt./vol. potassium hydroxide (AR) was used as the electrolyte. Potentials were reported against an Hg/HgO/30% KOH reference electrode. The cells were cycled for three conditioning cycles to arrive at the practical capacity, designated as *C*. The electrodes were charged at 0.1 *C* rate for 14 h. The charged electrodes were then discharged at five different rates, *viz.*, 0.1 *C*, 0.2 *C*, 1 *C*, 3 *C* and 5 *C*. The negative plate was considered to have discharged when it reached a potential of -0.75 V at low rates and -0.6 V at high rates with respect to the reference electrode.

Voltammetric measurements

The electrodes were made from nickel sinter impregnated with either cadmium nitrate alone or with cadmium nitrate with different percentages of ferric nitrate. The cadmium used in this investigation was a porous electrode of area 2 cm² cut from a plate similar to that described above. For compari-

son, a cadmium disc electrode of 99.9% purity (0.65 cm^2) was set in an Araldite holder.

Measurements were made in a conventional, enclosed three-electrode cell using an Hg/HgO reference electrode and a large platinum-foil counter electrode. The solution used throughout was 30% (wt./vol.) KOH and the experiment was conducted at room temperature.

A Wenking potentiostat (model ST 72 3A) was used in conjunction with a voltage scan generator (Wenking model VSG 72) and an X-Y-t chart recorder (Rikadenki).

Results and discussion

Charge/discharge studies

The performance of the negative plates at different rates (after 10 cycles) is shown in Figs. 1 - 5. The potential values are plotted against time of discharge. The capacity output (%) of the plates as a function of iron content at different rates of discharge is given in Fig. 6. The capacity output of the plates containing iron passes through a maximum at an iron content of 20 wt.%. The capacity decrease for 30 wt.% Fe and 40 wt.% Fe is especially noticeable at high rates of discharge. The data of Fig. 6 reveal that the coefficient of utilisation of the cadmium alone is normal and is higher for iron-containing electrodes. It follows from Figs. 1 - 5 that the open-circuit potential of iron-containing plates before discharge is 10 - 35 mV less than that for a cadmium electrode without additive. The lowest observed value of 875 mV (Figs. 1 and 2) is obtained with a cadmium electrode containing 20 wt.% Fe which shows, at the same time, the best capacity performance (Fig. 6).

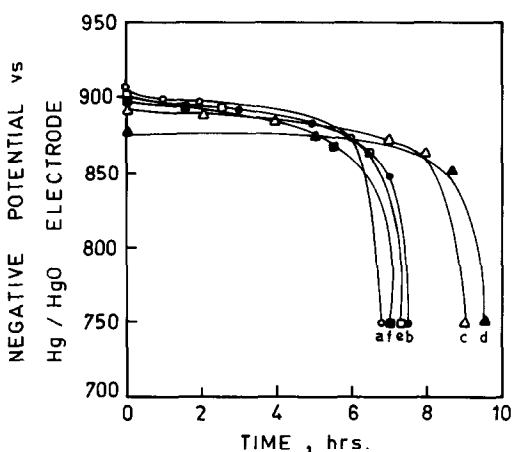


Fig. 1. Discharge curve of Cd electrode at 0.1 C rate with iron additions: (a) 0 wt.%; (b) 5 wt.%; (c) 10 wt.%; (d) 20 wt.%; (e) 30 wt.%; (f) 40 wt.%.

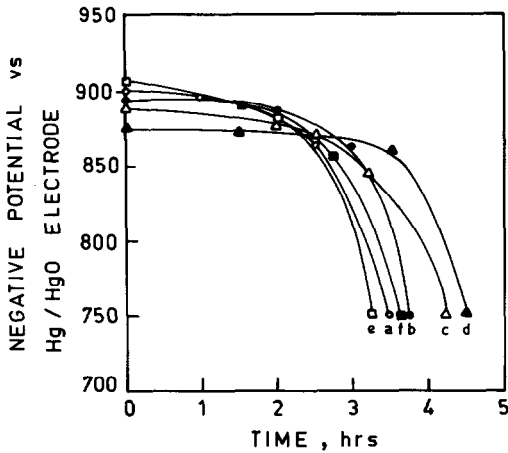


Fig. 2. Discharge curve of Cd electrode at 0.2 C rate with iron additions: (a) 0 wt.%; (b) 5 wt.%; (c) 10 wt.%; (d) 20 wt.%; (e) 30 wt.%; (f) 40 wt.%.

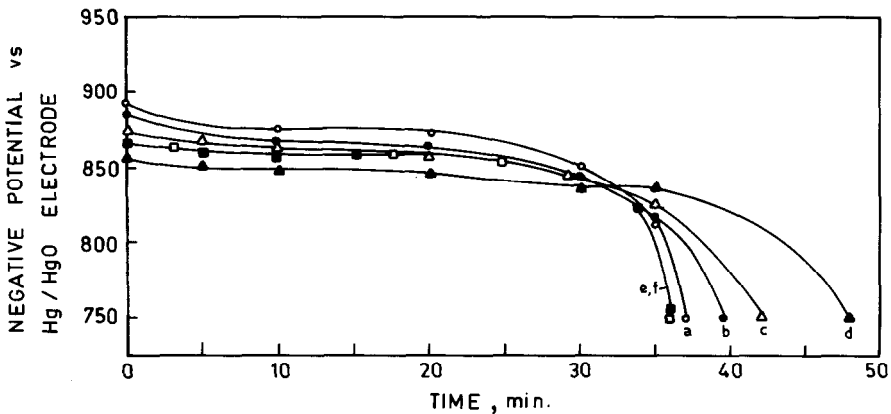


Fig. 3. Discharge curve of Cd electrode at 1 C rate with iron additions: (a) 0 wt.%; (b) 5 wt.%; (c) 10 wt.%; (d) 20 wt.%; (e) 30 wt.%; (f) 40 wt.%.

The charging characteristics of cadmium electrodes containing iron (Fig. 7) show that the charging potential lies between -800 mV and -930 mV, and that the end-of-charge potential is between -975 mV and -1075 mV, which is the charging potential range for a cadmium electrode. It can be concluded, therefore, that iron is not taking part in the reaction but provides an increase in the active surface area. At high percentages of iron, the capacity decreases due to a corresponding decrease in the amount of cadmium available for reaction.

Voltammetric studies

Cyclic voltammograms for a planar cadmium electrode are presented in Fig. 8. Passivation occurs at -860 mV and good evidence for the presence of

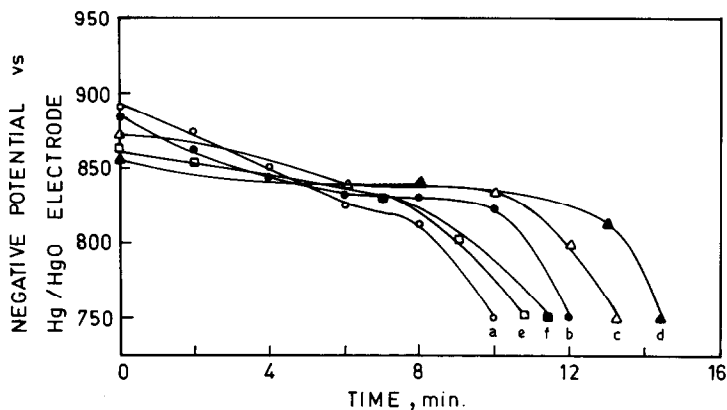


Fig. 4. Discharge curve of Cd electrode at 3 C rate with iron additions: (a) 0 wt.%, (b) 5 wt.%; (c) 10 wt.%; (d) 20 wt.%; (e) 30 wt.%; (f) 40 wt.%.

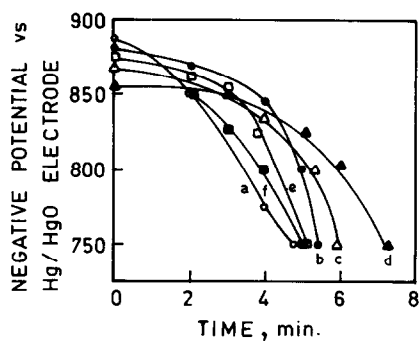


Fig. 5. Discharge curve of Cd electrode at 5 C rate with iron additions: (a) 0 wt.%; (b) 5 wt.%; (c) 10 wt.%; (d) 20 wt.%; (e) 30 wt.%; (f) 40 wt.%.

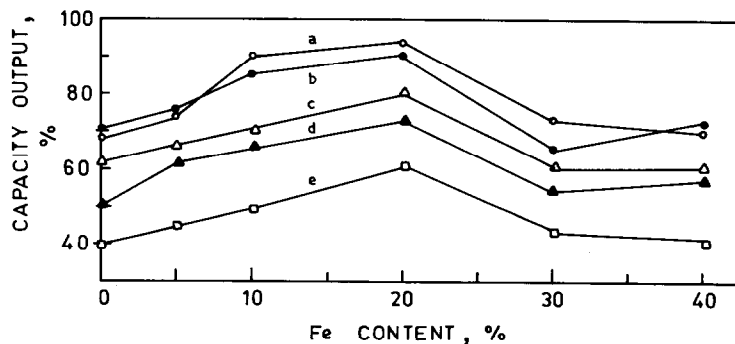


Fig. 6. Capacity output of Cd electrode vs. iron content at: (a) 0.1 C; (b) 0.2 C; (c) 1 C; (d) 3 C; (e) 5 C.

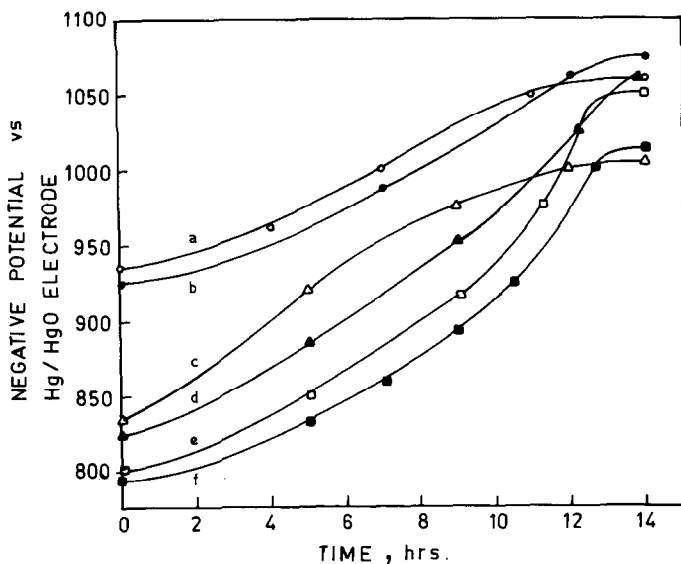


Fig. 7. Charging characteristics of Cd electrode with iron additions: (a) 0 wt.%; (b) 5 wt.%; (c) 10 wt.%; (d) 20 wt.%; (e) 30 wt.%; (f) 40 wt.%.

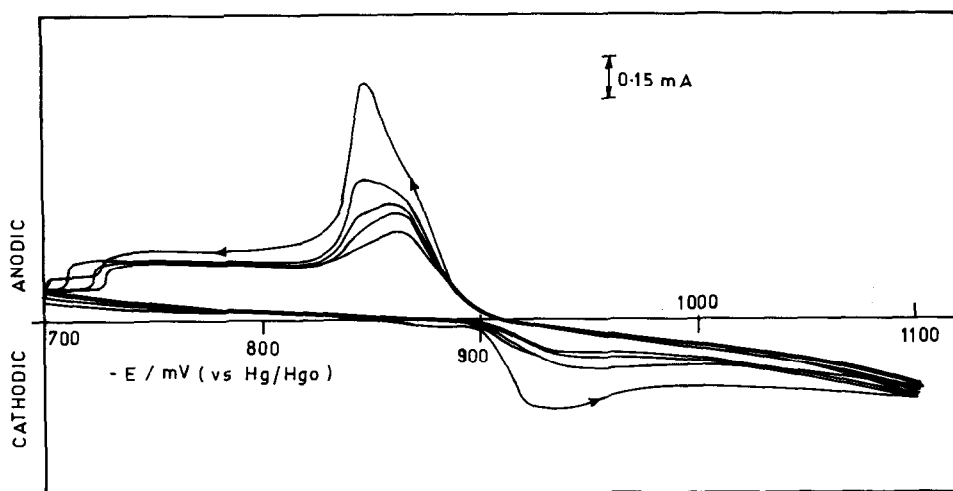


Fig. 8. Cyclic voltammograms for planar cadmium electrode between -1100 mV and -700 mV; sweep rate 1 mV s^{-1} .

a film at this potential has been obtained [12] by low frequency impedance measurements. A cathodic peak is obtained at -940 mV and, after the first cathodic peak, a considerable amount of unreduced hydroxide remains; this explains the diminished anodic peak on the subsequent positive-going scan. Figure 9 shows the voltammograms obtained for cadmium electrodes containing 0 wt.%, 10 wt.%, 20 wt.% and 30 wt.% Fe. As can be seen from

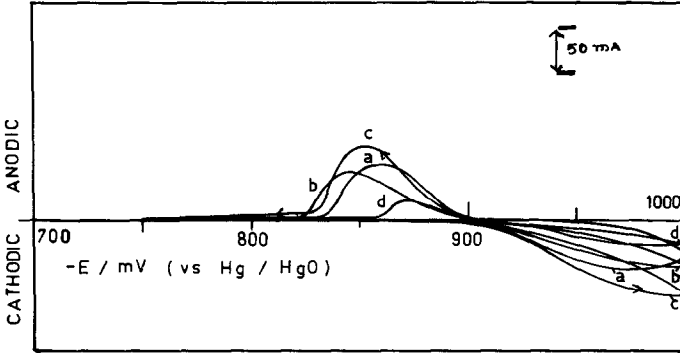


Fig. 9. Cyclic voltammograms for sintered cadmium electrode cycled between -1000 mV and -700 mV (sweep rate 1 mV s^{-1}) with iron additions: (a) 0 wt.%; (b) 10 wt.%; (c) 20 wt.%; (d) 30 wt.%.

these traces, a cathodic peak appears corresponding to the reduction of $\text{Cd}(\text{OH})_2$. Concomitant with the conversion of cadmium is the evolution of hydrogen. Upon reversal, a rather large oxidation peak appears at -860 mV. The size of this peak has been reported [13] as due predominantly to the oxidation of adsorbed hydrogen; only a very small portion of the peak is attributable to $\text{Cd}(\text{OH})_2$ formation. The effective area available for the anodic reaction is maximum in the case of a cadmium electrode containing 20 wt.% Fe after various extents of charge and discharge. This can be seen from Table 1.

Cyclic voltammetry was performed in order to determine the role of iron at the electrode surface. None of the voltammograms exhibits a separate peak for iron and it is concluded, therefore, that iron does not participate in the electrochemical reactions occurring at the cadmium electrode but merely enhances the active surface area.

TABLE 1

Effective areas of cadmium electrodes doped with iron

Iron (%)	Effective area available for the anodic reaction (mA cm^{-2}) ^a
0 (100% Cd)	32.5
10	27.5
20	45.0
30	10.0

^aCycled (after various extents of charge and discharge) sintered Cd electrode.

Conclusions

Charge/discharge characteristics of sintered cadmium electrodes with, and without, iron show that an addition of 20 wt.% Fe is beneficial. Beyond this iron concentration, only decrease of performance can be expected.

Cyclic voltammetric experiments prove that iron does not participate in the electrochemical reactions occurring at the cadmium electrode. A cadmium electrode containing 20 wt.% Fe provides the largest area for the reaction.

The better charge acceptance of sintered electrodes compared with planar ones is clearly demonstrated, confirming earlier observations [5].

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