

CADMIUM — A REVIEW OF THE RECENT LITERATURE

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Summary

Recent electrotechnological aspects of the cadmium electrode have been reviewed. Forty-four references are included and the electrode characteristics in the alkaline battery systems are highlighted.

Introduction

The electrochemical behaviour of the cadmium electrode has previously been reviewed by Milner and Thomas [1], Hampson and Latham [2], Armstrong *et al.* [3] and more recently by Barnard [4], as well as in Falk and Salkind's [5] excellent monograph on alkaline battery systems. The established processes of impregnation in sintered plaque electrodes have also been recently reviewed [6]. Research work connected with the electrochemistry of cadmium has been scarce in recent years, but there have been a number of papers dealing with alkaline cadmium battery systems: this review presents the electrochemical aspects of the cadmium electrode used in such alkaline battery systems published since the last review [4]. Electrometric methods, the effect of additives, morphological aspects and porosity of the cadmium electrode are the main headings under which the published work has appeared, and these form our major review headings.

Electrometric methods

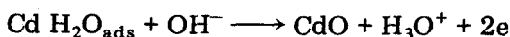
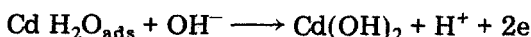
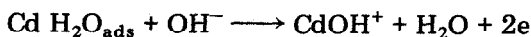
A cyclic voltammetric study [7] on planar cadmium in various concentrations of potassium hydroxide achieved good agreement with the previously reported work of Barnard *et al.* [8], showing the sharp anodic oxidation peak, and the development of a shoulder on the main peak becoming more pronounced at high sweep speeds, $>200 \text{ mV s}^{-1}$ before the electrode passivated. The usual single reduction peak was also observed. A

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square root dependence for the peak currents was obtained and the peak potentials varied linearly with sweep rate at high speeds. Potentiostatic work in the anodic region revealed a Tafel relation, slopes of $4/7 RT/F$ in 0.5 M KOH and $3/4 RT/F$ for all other concentrations were found. A very complex, multistep electrode process was proposed, involving the formation of CdO and Cd(OH)₂ films.

A galvanostatic study [9] was used to confirm the mechanism in identical experimental conditions. A further galvanostatic study [10] of the reduction of oxide films formed on cadmium led to a proposed mechanism derived from the electrochemical parameters obtained at various current densities.

Burnstein [11] analysed the transient electrochemical behaviour of freshly generated cadmium surfaces produced by scratching the metal with a diamond stylus whilst immersed in various concentrations of potassium hydroxide. The anodic reaction rate of the metal surface was found to follow Tafel's law with a slope of 63 mV/decade and a reaction order of 1.1. The equilibrium parameters were defined by $E_0 = 18$ mV (N.H.E.) and $i_0 = 2$ mA cm⁻². These results were interpreted as showing the simultaneous loss of two electrons per cadmium atom in a single reaction step. No evidence of any Cd(I) species was found. The rate determining step was thought to be one of the following:



Lobanova *et al.* [12] used the technique of chronopotentiometry and impedance to study the anodic oxidation of cadmium in KOH. At low current densities the process was found to be controlled by a homogeneous chemical reaction (*i.e.*, formation of the cadmate ions) following a transition step, but at higher currents the controlling factor became the diffusion rate of the cadmate ions.

Barton *et al.* [13] also used the impedance technique to study the sintered cadmium electrode in alkali. Measurements were made on 1 cm² mini-electrodes over the frequency range 10 kHz - 300 mHz. It was shown that the electrode behaviour conforms to that of a porous film electrode under charge transfer and diffusion control. A Randles circuit, modified for porosity and the presence of films, was found to match the data over the specified range of frequency. In the lower frequency domain the electrode behaviour becomes more complicated due to slow processes which are effectively masked out at the higher frequencies.

L'vova *et al.* [14] studied the effect of the structure of Cd(OH)₂ on its chemical dissolution in alkali using pressed pellets of Cd(OH)₂ as disc electrodes and Cd metal as a ring electrode. The rotating ring disc measurements were used to determine the chemical dissolution rate of β - and γ -polymorphs of cadmium hydroxide. The results were compared with the

dissolution of CdO. The rate of dissolution was found to increase on passing from the β - to the γ - phase, owing to an increase in electrochemical activity. Polarisation curves were presented for the reduction on a rotating ring disc.

Additives

Addition of polyvinyl alcohol (PVA) to the cadmium pocket electrode helps to prevent crystal growth and, hence, safeguard capacity. Munshi *et al.* [15] measured the impedance of such electrodes over the active and passive regions at different PVA concentrations in KOH electrolyte. The addition of PVA markedly increased the double layer capacity of the electrode and decreased the solution resistance. The impedance data were interpreted using an equivalent circuit containing two double layer capacitors in series, together with a resistance proportional to the conductivity of the electrolyte.

Polyethylene oxides and their derivatives have been used [16] to improve the structure of cathodic metal deposits and to hinder the growth of dendrites, which has led to improved characteristics and service life. The compounds act as surfactants, with a high surface activity.

Sathyanarayana [17] incorporated an alkali-stable colloidal surfactant (ethyl cellulose) into the cadmium electrode during fabrication such that both crystal growth and cadmium hydroxide migration were suppressed. The doped electrode was capable of $96 \pm 2\%$ capacity utilization even at the end of fifty deep discharge cycles. The beneficial effects of ethyl cellulose were lost, however, when subjected to severe overdischarge. Excessively thick coatings of the ethyl cellulose reduced capacity due to the large ohmic resistance of the film.

Mrha and co-workers [18] studied the rate of oxygen recombination on plastic (poly(tetrafluoroethylene)) bonded Cd electrodes for use in nickel-cadmium cells. A comparison of results obtained with pocket-type and plastic bonded cadmium electrodes showed that oxygen was reduced on metallic conductors of the electrodes which were covered with a thin electrolyte layer, are easily accessible to oxygen, and are short-circuited by the electroactive Cd/Cd²⁺ material. The latter has a sufficiently negative potential and electronic conductance to allow the electro-reduction of O₂ to take place.

Various additions have been made to the plastic bonded cadmium electrode to enhance the rate of oxygen recombination. The inclusion of a metal screen [19] of optimum geometry allowed ideal conditions for the existence of a uniform electrolyte film covering the total screen surface. The oxygen recombination rate was also increased if an Ag-plated rather than a steel or nickel screen was used.

The rate of oxygen recombination on plastic bonded cadmium electrodes in sealed Ni-Cd cells can be controlled by the use of a catalytic mix of active carbon, carbon black and poly(tetrafluoroethylene) [20]. A rate of oxygen recombination was claimed which surpassed that obtained on

commercial pocket type electrodes. Further increase in the rate of oxygen recombination has been achieved [21] by addition of $\text{Ni}(\text{OH})_2$, Fe_3O_4 and carbon black to the plastic bonded cadmium electrode.

Munshi *et al.* [22] investigated the dissolution of iron from the additive $\alpha\text{-Fe}_2\text{O}_3$ in the negative cadmium pocket electrode. Iron poisoning of the positive electrode is a common failure mode in flooded Ni-Cd cells. The investigation revealed some dissolution of the $\alpha\text{-Fe}_2\text{O}_3$, though the amount was found to be much lower than the amount dissolved from the perforated mild steel ribbons used to enclose the active material.

Al-Mosawi *et al.* [23] studied the hydrogen evolution reaction on porous cadmium pocket electrodes containing iron oxide and graphite, under commercially relevant conditions in lithiated potassium hydroxide. Their results showed how the relatively slow reaction on cadmium was influenced by the electrode structure, mixed expander, and powder lubricant, and, hence, suggested that these additional materials promote the hydrogen reaction, possibly by a synergistic mechanism.

Reshetov *et al.* [24] investigated the formation mechanism of the intermetallic compound $\text{Ni}_5\text{Cd}_{21}$ which occurs when a charged cadmium electrode containing $\text{Ni}(\text{OH})_2$ is stored in alkaline solution. Formation of this compound causes capacity loss. The kinetics of accumulation of the compound were studied as a function of temperature and quantity of $\text{Ni}(\text{OH})_2$ introduced. The kinetic curve exhibited a two-step form, thus indicating that the intermetallic compound could be formed during storage of cadmium electrodes according to two parallel mechanisms, both involving Ni^0 and Ni^{2+} .

Morphology

Popkov and co-workers [25 - 28] studied the surface morphology of cadmium deposits obtained with periodic current under different solution stirring conditions at pH 5. At a stationary electrode, spongy deposits were formed, whilst at a rotation speed of 25 Hz only compact, fine, crystalline deposits with spiral forms were obtained. This change in morphology was attributed to the effect of the d.c. and periodic currents on the concentrations of species of intermediate valency. The spongy deposits were eliminated, however, when the ionic strength of the solution was increased by the addition of neutral salts such as aluminium sulphate.

In a kinetic investigation [29] of the growth of cadmium dendrites on planar cadmium and nickel electrodes, approximately 30 μm long dendrites were found after 6 days at overpotentials of -300 mV (Hg/HgO) in 10 M KOH and a Cd(II) concentration of 2.8×10^{-4} M. When small quantities of $\text{Cd}(\text{OH})_2$ were placed in suspension the growth time was reduced.

Barnard *et al.* also studied the growth of cadmium dendrites in both alkaline [30] and acidic media [31]. In potassium hydroxide, 2D fern dendrites were observed at an overpotential of -150 mV, needle-like dendrites at -200 mV and large, 'filled in' fern dendrites at -300 mV. At higher over-

potentials crystalline aggregate dendrites were observed. Under the well defined condition of a rotating disc electrode only small ferns were seen over a wide range of overpotentials.

In another study of dendrite growth in acidic media [31] the morphology and induction time were found to be concentration or overpotential dependent. Barnard's theoretical treatment [32] was in good agreement with the earlier work of Diggle *et al.* [33]. The total current-time behaviour for the alkaline system can be predicted using the exponential limiting form of the equations with the assumption that the dendrites approximate to rectangular rods and follow first order progressive initiation law. The very different behaviour in acidic media was predicted from the linear limiting form of the equations, with the assumption that the dendrites approximate to cylindrical rods and follow an instantaneous law.

Popov and co-workers [34] studied the morphology of cadmium deposits obtained on foreign substrates at high overpotentials in acidic media. Their short communication confirmed the earlier work of Barnard [31, 32]. Kazarinov and co-workers [35] showed how the structural characteristics (crystal lattice period, unit size, specific surface area, and structural water content) of β -modifications of $\text{Cd}(\text{OH})_2$ affected the cathodic reduction behaviour in alkaline media. A relationship was found between the particle size of the $\text{Cd}(\text{OH})_2$, the rate of chemical dissolution, and the electrochemical activity.

Fritts and Dueber [36] used time lapse microphotography to study the surface morphology of cadmium. The technique revealed numerous migration regions growing during the life of a single cell. The dominant transport mechanism of the active material was hydrodynamic in nature and was due to molar volume changes occurring in the electrode. Migration was found to occur *en masse* with the migration region charging and discharging with the electrode. Scanning electron microscopy was used to inspect individual migration regions; these were shown to consist of both crystalline and amorphous forms of Cd. The amorphous material contained metallic Cd which allowed for an electrical connection to the negative electrode. Growth of the migration regions occurs through a precipitation-dissolution mechanism of the active material until a short circuit developed between the two electrodes.

Mrha *et al.* [37] investigated the anomalous behaviour of deeply discharged, sealed Ni-Cd cells. After polarity reversal the cell voltage resides in the range -60 to -260 mV, and the situation can sometimes persist for an unlimited time without any increase in overpressure in the cell. A necessary condition for the appearance of this discharge voltage level was found to be a capacity reserve of the cadmium electrode, and the presence of cadmium in the separator as a result of migration from the negative electrode. The cadmium particles form bridges across the separator leading eventually to a short circuit and consequent cell failure.

Marek and co-workers [38] studied the temperature behaviour of plastic bonded cadmium electrodes in sealed Ni-Cd cells. A decrease in capacity was

found for temperatures below room temperature. At elevated temperatures, large crystals of active material were formed accompanied by a decrease in specific surface area.

Fiala *et al.* [39] studied the experimental conditions for the formation of cadmium bridges to protect sealed Ni-Cd cells from cell voltage reversal. They found that a common polyamide separator, used as the electrolyte carrier, could also function as a carrier for the Cd/Cd²⁺ system, the deposition method being the same as that in the preparation of sintered cadmium electrodes. The separator was found to be suitable if cycled at least once in excess alkali prior to sealing and, if the cell capacity is limited by the positive electrode, the explosion hazard of the sealed cell can be eliminated. Cadmium bridges formed in the separator under these conditions prevent gas formation on either electrode, their properties depending on the quality of the separator and its loading with cadmium.

Pores

Palanisamy and co-workers [40] reported the electrochemical aspects of the cadmium impregnation process where they employed electroanalytical methods to investigate the cathodic deposition, on a nickel plaque, of cadmium hydroxide from cadmium nitrate solution. Two different deposition products were generated depending on the potential. At potentials positive of -0.6 V a grey, non-crystalline cadmium hydroxide was produced and at potentials negative of -0.8 V a black precursor to cadmium hydroxide was deposited. The black material was thought to be a cadmium complex of a nitrate reaction product. Although both compounds readily converted to crystalline, hexagonal cadmium hydroxide, the grey cadmium hydroxide deposited with minimal concurrent gas evolution and achieved high cadmium hydroxide loadings in the pores of the nickel plaque.

Pensenson [41] used the theory of transient liquid and gas filtration to describe electrolyte displacement by gas in sealed Ni-Cd battery separators. The author has modified this theory to describe electrolyte displacement from the pores of the cadmium electrode, taking into account that the displacing oxygen is reduced at the cadmium (beneath an electrolyte film) electrode occurring under diffusion control.

Novak and Grachev [42, 43] showed that the effective electrolyte resistance in the pores of the cadmium electrodes increased several-fold during discharge. Results obtained in measurements of effective electrolyte resistance in the pores were compared with results for the total porosity of the electrode. The change in effective resistance of the electrolyte in the pores was found to be caused by the change in structure of the pores during charge and discharge. The technique of contact standard porosimetry has been used to study the size distribution of pore volumes in cadmium electrodes [44]. The pore size of the active material was found to be 0.04 μm and the intervals between particles of active material were about 1 μm .

A specific surface area of 14 - 15 m² g⁻¹ for a fully charged electrode was quoted, whilst the B.E.T. method on the same electrode was 3.5 m² g⁻¹. The reason suggested for this difference was the blocking of large pores by fine particles in porous materials with complex shaped pores.

Final remarks

Research on the cadmium electrode has been limited in recent years, although work on the morphology of the electrode, particularly on the formation of cadmium bridges, seems on-going. Recent advances in lithium primary battery systems has highlighted the relatively poor energy density characteristics of the traditional alkaline battery systems incorporating cadmium. This inadequacy has been solved to some extent by the introduction of plastic bonded electrodes which have stimulated new interest in this area.

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