The Cadmium Electrode Revisited: Kinetic Data

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Abstract

Cadmium has been employed as negative electrode material in nickel-cadmium batteries for decades. Cadmium has been employed also as the negative electrode in less popular Cd/AgO and Cd/HgO-systems. The large hydrogen overpotential is a particular advantage of this metal because it makes any additives otherwise required to suppress hydrogen evolution in aqueous electrolyte solutions unnecessary.

A particular and popular use of cadmium in a galvanic cell is the Weston cell invented by Edward Weston in 1893. In a typical configuration, a Weston cell is set up in a H-shaped glass vessel with cadmium amalgam as the negative electrode on one side and plain mercury on the other side. Electrical connections to the mercury and the cadmium amalgam are made by platinum wires fused through the bottom of the glass vessel and typically a saturated cadmium sulfate electrolyte solution is used. Weston cells are only used for calibration of instruments in laboratory because of the low temperature coefficient, which leads to a highly stable cell voltage.

However, cadmium is an undesirable material because of its toxicity. Over 1.5 billion Ni-Cd batteries were produced worldwide annually in 2000. However, in the EU the sale of Ni-Cd batteries and of devices containing such batteries has been subject to severe restrictions since 2006 (Restriction of Hazardous Substances Directive (RoHS), Battery Directive). Nevertheless, Ni-Cd-batteries still have a huge market share, which may be ascribed to their advantages, including low cost, high power capability, and easy construction despite the well-known memory effect of Ni-Cd-batteries attributed to the cadmium electrode. Additionally, the raw materials used can be recycled almost completely; the technical rates of recovery of nickel and cadmium are very high, 96% and 99%, respectively.

In recent years, most research related to cadmium as an electrode material has focused on Ni-Cd-batteries and redox flow batteries. However, alkaline or acidic electrolyte solutions as used in Ni-Cd batteries or in single flow Cd-PbO2 redox batteries, respectively, cause serious corrosion of equipment and this also worthy of study.

Despite of the particular popularity of Ni-Cd batteries, studies of the kinetics of this electrode material are limited. Kinetic data collected elsewhere are mostly related to cadmium amalgam. Some data collected earlier are available mostly for strongly alkaline and acidic electrolyte solutions, but very few for neutral solutions as collected following. Lorenz used a current step technique and reported a polarization resistance $R_{pol} = 2 \times 6 \Omega \cdot \text{cm}^2$; in a further study he obtained $j_0 = 1.5 \cdot 10^{-2} \text{ A} \cdot \text{cm}^{-2}$ with a neutral electrolyte solution containing 0.4 - 0.75 M Na$_2$SO$_4$ and 5 - 10$^{-3}$ M Cd$^{2+}$ ions. Brodh$^{22}$ found $j_0 = 1.4 \cdot 10^{-2} \text{ A} \cdot \text{cm}^{-2}$ with impedance measurements and an aqueous electrolyte solution of 0.71 M CdSO$_4$. Hampson et al. obtained a rate constant $k_0 = 3.8 \cdot 10^{-5} \text{ cm} \cdot \text{s}^{-1}$ with a current-step method at various Cd-concentrations. Hampson and Latham used impedance measurements and an aqueous electrolyte solution of 1 M NaClO$_4$ containing 0.175 M Cd$^{2+}$-ions, they reported $j_0 = 5.8 \cdot 10^{-2} \text{ A} \cdot \text{cm}^{-2}$. Pan et al. obtained values of $j_0$ with an aqueous electrolyte solution of 2 M H$_2$SO$_4$ + 1 M CdSO$_4$. With no additive DPE-3 $j_0 = 0.3161 \text{ A} \cdot \text{cm}^{-2}$ was found, at the highest concentration 1 g dm$^{-3}$ of added DPE-3 $j_0 = 0.07577 \text{ A} \cdot \text{cm}^{-2}$. Itoh et al. electrodeposited cadmium from a solution of 0.5 M H$_2$SO$_4$ + 0.7 M CdSO$_4$ onto single crystal copper surfaces, $j_0 \cong 10^{-2} \text{ A} \cdot \text{cm}^{-2}$ was obtained. Hampson and Latham used an alkaline solution of 7 M KOH with 0.0099 M Cd$^{2+}$-ions and found $j_0 = 3.1 \cdot 10^{-2} \text{ A} \cdot \text{cm}^{-2}$ with impedence and $j_0 = 2.6 \cdot 10^{-2} \text{ A} \cdot \text{cm}^{-2}$ with current step measurements.

The investigation reported here will close the data gap with respect to the range of applied pH-values. In addition, the results will provide kinetic and thus electrode impedance data needed for the evaluation of cell impedance data obtained elsewhere with Cd/LiCoO$_2$ cells. The electrolyte solution used in Ref. 27 is also used here, because it avoids the risks associated with the strongly acidic and alkaline solutions used in the other systems briefly listed above. Beyond fundamental interest in kinetic data of metal electrode reactions a wider database could be helpful in the study and design of electrochemical energy conversion and storage systems, in particular when selecting electrolyte systems. The recent surge of interest in cadmium-based systems (see9–17) attests to this.

Beyond closing the indicated data gap this study will also help further develop impedance data obtained with complete batteries reported in Ref. 27. The cadmium electrode impedance data can be entered as a set of fixed equivalent circuit element values into the fitting procedure of the cell data. The frequently observed confusion of electrode impedance data with cell impedance data resulting in the fundamentally erroneous assignment of the actually recorded cell impedance to one electrode in the cell only can thus be avoided. This major – and frequently overlooked – distinction has been pointed out before, see e.g. 28.

Experimental

Cadmium acetate (Cd(AC)$_2$ · 2H$_2$O) and lithium sulfate (Li$_2$SO$_4$) were used as received without further purification. An aqueous electrolyte solution containing 0.5 M Li$_2$SO$_4$ and 10 mM Cd(AC)$_2$ was used as anodic and cathodic electrode reaction, respectively. Accordingly the standard exchange current density $j_0$ can be calculated: 

$$j_0 = j_0 \frac{c_{\text{red}}}{c_{\text{ox}}}$$

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prepared with deionized ultrapure 18 MΩ water (Seralpur Pro 90 C). The pH of the solution was found to be pH = 5.5.

A cadmium rod (9.7 mm diameter, technical purity) was wrapped with PTFE-tape and coated with heat-shrinkable sleeve leaving only the frontal surface exposed. Because of the low hardness (Mohs hardness 2.0) of cadmium, no attempt of mechanical polishing was made. After grinding with emery paper (360), the oxide film on the surface was removed by etching in 50% acetic acid using an ultrasound bath for 2 minutes, this etchant is a modified version without the strongly oxidizing nitric acid of the etchant described in Ref. 29 With the aqueous electrolyte solution used here, the etching process had to be repeated frequently because formation of a surface film of poorly defined composition negatively affected the reproducibility of the experimental results.

For electrochemical impedance measurements, a potentiostat (Solartron SI 1287) connected to a frequency response analyzer SI 1255 interfaced to a PC was used. The measurements were carried out at the spontaneously established open circuit voltage (OCV) with a modulation amplitude of 5 mV in the frequency range from 0.1 to 10⁶ Hz. Evaluation of the impedance data was performed with Boukamp software (version 2.4). Cyclic voltammetry (CV) and potentiodynamic polarization measurements (linear scan voltammetry) were performed on a potentiostat IVIUMSTAT Electrochemical Interface. A three-electrode electrochemical cell designed specifically for AC-measurements using a piece of cadmium metal as the reference and a platinum flag as the counter electrode was used. No attempt was made to equilibrate electrolyte solutions at the working or the reference electrode, which was separated with a fine glass frit between the respective compartments. Therefore, small deviations between both electrode potentials, even at rest since $E_0 \neq 0$ V, were observed. All electrochemical measurements were performed at ambient temperature.

Results and Discussion

Fig. 1 shows the cyclic voltammogram of a metallic Cd electrode at 0.1 V·s⁻¹ in the aqueous electrolyte solution of 0.5 M Li₂SO₄ and 10 mM Cd(Ac)₂ in the range $-0.5 < E_{\text{vs.Cd}^{2+/0}}/\text{Cd} < 0.05$ V. Potential limits were selected to examine whether the following Tafel-evaluation could be performed without interference from further electrode processes. Comparison can be made with a CV of a cadmium electrode in an aqueous 6 M KOH solution reported by Suhirtharani et al. 30 In the negative going part (with respect to $E_0$) dissolution yielding fairly soluble products is observed. Suhirtharani et al. observed a current peak instead caused by electrode passivation due to formation of poorly soluble Cd(OH)₂. Evidence of a current loop observed during cadmium deposition on silicon from a slightly acidified sodium sulfate solution 31 indicative of a particular growth mechanism could not be seen here. The anodic peak observed in that study is due to the limited cadmium supply provided by the thin cadmium film deposited in the preceding scan into the electrodeposition region, which is not the case here.

Evaluation of the potentiodynamic polarization measurements (linear scan voltammogram in an electrode potential range ±0.1 V to $E_0$) according to Tafel was done by applying extrapolation lines at $\eta > \pm 118/2 = 59$ mV (i.e. within the “Tafel” region) with respect to the spontaneously established rest potential $E_0$ at current $I = 0$ A·cm⁻². A typical plot is shown in Fig. 2; the extracted value of $j_0$ is listed in Table I.

A complex plane (Nyquist) impedance plot of the cadmium electrode in contact with the electrolyte solution of 0.5 M Li₂SO₄ and 10 mM Cd(Ac)₂ at the open circuit potential is shown in Fig. 3. Evaluations are based on an equivalent circuit with known details of structure and dynamics of the electrochemical interface. The double layer capacitance is modelled as a constant phase element (CPE, $Q$) taking into account recent reports attributing this behavior to roughness, surface/interface inhomogeneities 32,33 including non-uniform charge distribution at grain interfaces 34 and resistivity distribution in films on electrode surfaces 35,36. Based on previous reports 35,36 extraction of $C_{DL}$ from $Q$ is justified. Further, the electrolyte solution resistance $R_{aq}$, the charge transfer resistance $R_{ct}$, and as suggested by Gerischer 37 a further impedance ($R_1$ and $C_1$, elsewhere called crystallization impedance) assigned to the crystallization step were assumed. The additional element assigned to hindered surface diffusion suggested by Fleischmann et al. 38 was not found to be necessary to obtain satisfying fits. Taking into account a diffusion process (see Fig. 4b) did not improve fit quality and was thus not further considered.

A nonlinear least square fit (NLLSF) method 40–44 employing the equivalent circuit given in Fig. 4a was applied. 40–44 Obtained numerical values of the mentioned circuit elements are collected in Table II. Conversion of $R_{ct}$ into $j_0$ was done according to

$$j_0 = \frac{R \cdot T}{n \cdot F \cdot R_{ct}} \quad [2]$$

with $n = 2$ and all other symbols have their standard meaning. Further results are collected in Table I. The value of the double layer capacity as extracted from the value of the constant phase element $C_{DL} =$
Table I. Reported kinetic data of the cadmium electrode in contact with various aqueous electrolyte solutions.

| Solution                          | $j_0$ A cm$^{-2}$ | $j_{00}$ A cm$^{-2}$ | Method* | Reference |
|----------------------------------|-------------------|----------------------|---------|-----------|
| 0.75 M Na$_2$SO$_4$ + 5·10$^{-3}$ M Cd$^{2+}$ | 1.5·10$^{-3}$     | 1.5·10$^{-2}$        | I-step  | 21        |
| 0.71 M CdSO$_4$                 | 1.4·10$^{-2}$     | 1.6·10$^{-2}$        | imp     | 22        |
| 1 M NaClO$_3$ + 0.028 , 0.452 M Cd$^{2+}$ | 3.8·10$^{-5}$   |                      | I-step  | 23        |
| 1 M NaClO$_3$ + 0.175 M Cd$^{2+}$ | 5.8·10$^{-2}$     | 1.39·10$^{-1}$       | imp     | 24        |
| 0.5 M Li$_2$SO$_4$ + 0.01 M Cd(AC)$_2$ | 6.6·10$^{-4}$   | 6.6·10$^{-3}$        | mp      | This work |
| 0.5 M Li$_2$SO$_4$ + 0.01 M Cd(AC)$_2$ | 5.03·10$^{-4}$  | 5.03·10$^{-3}$       | ppm     | This work |
| 2 M H$_2$SO$_4$ + 1 M CdSO$_4$   | 0.316             | 3.16·10$^{-1}$       | ppm     | 16        |
| 2 M H$_2$SO$_4$ + 1 M CdSO$_4$ + 0.3 g · dm$^{-3}$ | 0.1129         | 1.13·10$^{-1}$       | ppm     | 16        |
| 2 M H$_2$SO$_4$ + 1 M CdSO$_4$ + 0.6 g · dm$^{-3}$ | 0.09381       | 9.38·10$^{-2}$       | ppm     | 16        |
| 2 M H$_2$SO$_4$ + 1 M CdSO$_4$ + 1 g · dm$^{-3}$ | 0.07577       | 7.58·10$^{-2}$       | ppm     | 16        |
| 0.5 M H$_2$SO$_4$ + 0.7 M CdSO$_4$ | ~10$^{-2}$       | ~1.20·10$^{-2}$      | ppm     | 25        |
| 7 M KOH + 0.0099 M Cd$^{2+}$     | 3.1·10$^{-2}$    | 0.312                | imp     | 26        |
| 7 M KOH + 0.0099 M Cd$^{2+}$     | 2.6·10$^{-2}$    | 0.261                | I-step  | 26        |

*I-step: Current step method, imp: electrochemical impedance method, ppm: potentiodynamic polarization measurements, all calculations were made assuming $\alpha = \alpha_c = 0.5$.

Figure 3. Complex plane plot (Nyquist plot) of a cadmium electrode in contact with an aqueous electrolyte solution of 0.5 M Li$_2$SO$_4$ and 10 mM Cd(AC)$_2$.

729 μF or 985 μF · cm$^{-2}$ is in qualitative agreement with the significant roughness of the electrode as pointed out above, in the absence of an established value of $C_{DL}$ for an ideally smooth cadmium electrode surface calculation of a roughness factor is not warranted. Recalculation of the charge transfer resistance and derived kinetic data taking into account the double layer capacity as a measure of the true electrode surface area was thus not performed. Values of $j_0$ obtained with both methods independently agree reasonably well. In comparison to previously reported data obtained with neutral electrolyte solutions (see Table I), they are slightly lower; a straightforward explanation is not apparent.

Conclusions

Standard exchange current densities of a cadmium electrode in contact with a neutral electrolyte solution determined with impedance and linear polarization measurements were found to be in good agreement because they are within the range of previously reported data obtained with a wide variety of electrolyte solutions.

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Figure 4. Equivalent circuits used for fitting measured impedance data: a) without diffusion, b) with diffusion; for explanation of symbols see text.
