

Electrochemical Recovery of Cadmium from Simulated Waste Nickel–Cadmium Battery Solutions

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Abstract The selective recovery of Cd from simulated spent nickel–cadmium battery solutions was achieved using a Cd working electrode in a laboratory cell with a three-electrode arrangement in hydrochloric, nitric, and sulfuric acids. The latter was selected for further study of the recovery step. Nitrate media were found to be unsuitable for Cd recovery since nitrates are reduced at the required deposition potentials. Cd(II) deposition on Cd electrodes is favored in sulfate or chloride media since it occurs at a potential some 200 mV less negative than that of Ni(II). A good percent Cd recovery (>90%) with high selectivity (approximately 0% Ni) and a reasonably high current efficiency (>80%) can be achieved under appropriate conditions. The irreversible nature of Ni(II) reduction provides the necessary framework to achieve such a selective separation.

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1 Introduction

Spent nickel–cadmium (NiCad) batteries still represent an important pollution problem. In fact, the US, Japan and some European countries have established tight regulations for their disposal, mainly due to the high toxicity of cadmium. Nickel compounds possess different degrees of toxicity, but that of cadmium compounds is typically more acute and bioaccumulation may represent important threats (Topperwien et al. 2007). Even though NiCad's tend to be phased out in some developed countries, they still cover a large portion of the market for emergency lights, alarms, portable electric tools, and other home and portable devices that require rechargeable batteries (Fujimoto 1997). In Canada alone, the annual shipments of NiCad consumer battery units were 9.1×10^6 in 2000, and the projection is 22.4×10^6 for 2010 (Environment Canada 2007). Such an increase is most likely due to their lower cost as compared to that of the alternative Li-ion and Ni-hydride batteries (Lam et al. 2007).

Sales of sealed NiCad batteries in the US, Japan and Europe totaled nearly 10^9 units in 1998 (Hake 1998); in spite of the lack of precise data, it can be anticipated that very few of them have been recycled. For example, only 1% of the consumer secondary

batteries were recycled in 2001 in the United Kingdom (Environment Canada 2007). In addition, consumers tend to store their batteries for long periods of time; for example, in Belgium a very slow consumer clearance rate for NiCad's of only 5% was estimated after 5 years of their sale, 33% after 15 years, and the remaining 62% were cleared by 25 years (Belgium Federal Department of the Environment; Environment Canada 2007). A key consideration is that improperly disposed batteries may be mixed up with waste that ends up in municipal incinerators, where cadmium readily volatilizes (b.p. 767°C) (Rajeshwar and Ibanez 1997). In addition, those that remain in open landfills may undergo lixiviation as a result of acid deposition; such lixiviates may enter groundwater streams and create a potential danger to nearby users.

Recycling processes applicable to this case can be grouped into hydrometallurgical and pyrometallurgical (Van Deelen 1989). The first group normally entails several separation stages including acid dissolution, solvent extraction, and pH-precipitation. In the second group, high temperatures are utilized to volatilize the main components. Some technological processes involve the combination of both types of recovery schemes. Other approaches are based on physicochemical adsorption and solvent extraction (Lam et al. 2007; Srivastava et al. 2006).

Alternatively, electrochemical techniques offer the possibility of achieving the selective separation and recovery in two steps. This selectivity depends on the composition of the solution containing the desired metals, since phenomena like complex formation and standard potential modification may play a key role in their recuperation. For example, in the electrochemical recovery of Cd from the anodes in spent NiCad batteries it is important to avoid as much as possible the presence of Fe from the battery shell, since the reduction of Fe(III) to Fe(II) occurs at a less negative potential than that required for the reduction of Cd(II) to Cd(0). In this case, the undesired Fe + Cd codeposition is possible (Scott and Paton 1993). Another case in point is that of Cd(II), which suppresses the Ni electrodeposition from a Ni(II) + Cd(II) sulfate solution and shifts its deposition potential to more negative values (Mohanty et al. 2004).

We present here a study of the electrochemical separation of Ni and Cd from simulated waste battery solutions by means of Cd electrodeposition. Various electrodes have been used to study Cd deposition (e.g., hanging mercury drop, paraffin impregnated graphite,

vitreous carbon, and tin oxide; Rozik and Trnkova 2006). Even though Cd recovery in the presence of nickel has been reported earlier (Armstrong et al. 1996), the effect of convection (which is of paramount importance for reactions under mass-transfer control) has not been—to the best of our knowledge—reported yet. Acids used for the dissolution step of NiCad's include HNO₃, HCl and H₂SO₄. Since anions are known to influence the metal deposition potentials, their effect was also analyzed. The acidic medium that yielded the best results with constant potential electrolysis in this screening stage (i.e., a sulfate medium) was then selected for further study. Since the electrochemical behavior during Cd deposition is different with the various electrodes (Rozik and Trnkova 2006), we selected Cd metal as the substrate in order to promote surface recognition by the depositing ions, and analyzed the effect of mass transfer with a rotating disk electrode. The targeted selective Cd recovery was achieved in a simple system (i.e., without an ion exchange membrane) as discussed below.

2 Experimental Details

Constant potential electrolyses were used for the deposition experiments and linear potential sweeps for process characterization. For both techniques, a CV-50 W Voltammetric Analyzer (Bioanalytical Systems) was employed. A controlled growth mercury drop electrode (CGME, BAS) was used for the polarographic analysis. An analytical rotator (AF-ASR, Pine Instruments) was used for the convection experiments. An Ag/AgCl electrode (BAS) was the reference electrode (all potentials in this work are referred to it), and a platinum square flag electrode (Strem Chemicals, 99.9%, 1 cm²) was used as counter electrode. High purity nitrogen gas was bubbled through each solution for at least 5 min before the experiments, and a nitrogen blanket was kept above the solution during the experiments to prevent dioxygen interference.

The reagents were Na₂SO₄ (J. T. Baker Analyzed, 100%), H₂SO₄ (J. T. Baker Analyzed, 97.9%), CdSO₄ (3CdSO₄·8H₂O, J. T. Baker Analyzed, 105.95%), NiSO₄ (NiSO₄·6H₂O, Sigma Chemical Co., N-4882), KCl (J. T. Baker Analyzed, 99.9%), HCl (J. T. Baker Analyzed, 38%), CdCl₂ (CdCl₂·2.5H₂O, J. T. Baker Analyzed, 80%), NiCl₂ (NiCl₂·6H₂O, J. T. Baker Analyzed, 97%), KNO₃ (J. T. Baker Analyzed, 100%),

ammonium citrate (J. T. Baker Analyzed, 99.5%), and HNO_3 (J. T. Baker Analyzed, 65%). Deionized water was used throughout this work.

2.1 Anion Effects on the Ni and Cd Deposition from Solutions Containing Each Metal

These experiments were performed in a conventional three electrode cell using a Cd wire (Aldrich, 99.9%, 1 mm diameter) with the end transversal area (i.e., the bottom face) exposed to the solution; the rest of the electrode surface was insulated with Teflon tape. The other electrodes were described above. A scan rate of 50 mV s^{-1} was routinely applied.

The following solutions were employed:

1. *Sulfate media*: A blank 1.0 M Na_2SO_4 solution was used and its pH adjusted to 4 with H_2SO_4 (acidic conditions are needed in order to avoid precipitation of Cd or Ni hydroxides). Then, Cd or Ni sulfates were added to obtain the following three solutions:
 - (a) 1.0 M Na_2SO_4
 - (b) 1.0 M Na_2SO_4 + 0.01 M CdSO_4
 - (c) 1.0 M Na_2SO_4 + 0.01 M NiSO_4
2. *Chloride media*: In the same fashion, enough HCl was added to a 0.5 M KCl blank to reach a pH=3. Then, Cd or Ni salts were added to obtain the following solutions:
 - (a) 0.5 M KCl
 - (b) 0.5 M KCl + 0.01 M CdSO_4
 - (c) 0.5 M KCl + 0.01 M NiSO_4
3. *Nitrate media*: In the same manner, HNO_3 was added to a 1.0 M KNO_3 blank to reach a pH=3, and then Cd or Ni salts were added to obtain the following solutions:
 - (a) 1.0 M KNO_3
 - (b) 1.0 M KNO_3 + 0.01 M CdSO_4
 - (c) 1.0 M KNO_3 + 0.01 M NiSO_4

2.2 Anion Effects on the Ni and Cd Deposition from Solutions Containing Both Metals

The same set up described above was employed, except that a Cd foil (Aldrich, 99.9998%, 35 mm^2) replaced the Cd wire in order to decrease the deposition time. The 10-mL solutions were not stirred

during the experiments. The changes in Ni and Cd concentration were monitored with an Atomic Absorption Spectrometer (Varian SpectrAA 250 plus). The solutions were made as follows:

1. *Sulfate medium*: 1.0 M Na_2SO_4 + 0.01 M CdSO_4 + 0.01 M NiSO_4 . Here, H_2SO_4 was added as needed to reach a pH of 4.
2. *Chloride medium*: 0.5 M KCl + 0.01 M CdSO_4 + 0.01 M NiSO_4 . Here, HCl was added as needed to reach a pH of 3.
3. *Nitrate medium*: 1.0 M KNO_3 + 0.01 M CdSO_4 + 0.01 M NiSO_4 . Here, HNO_3 was added as needed to reach a pH of 3.

2.3 Effect of Controlled Convection Upon the Deposition Potentials of Ni(II) and Cd(II) in Separate Solutions. An RDE Study

A conventional three electrode set up was used as described earlier. The working electrode was a Cd disk (Aldrich, 99.9998%, 8 mm diameter) embedded in Teflon. A scan rate of 10 mV s^{-1} was employed. As will be described below, the experiments in sulfate medium gave the best results and this medium was selected for further study. The solutions hereby used were 1(a), 1(b) and 1(c).

2.4 Constant Potential Electrolysis of Solutions Containing Ni(II) and Cd(II): An RDE Study

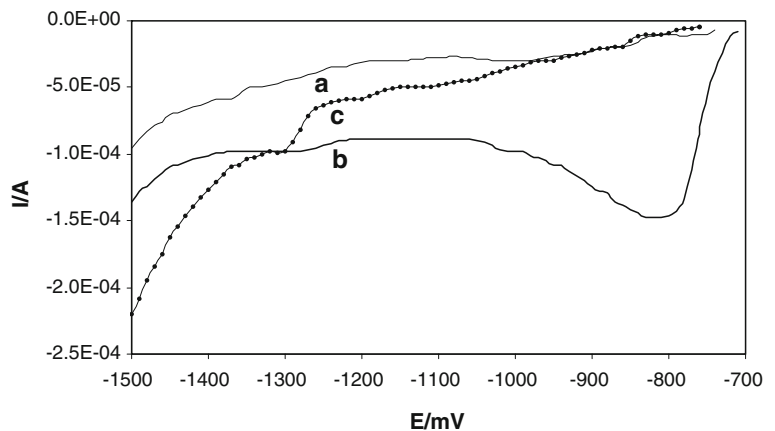
The same set up as in the previous section was employed. The solution under study was 1.0 M Na_2SO_4 + 0.01 M CdSO_4 + 0.01 M NiSO_4 . Here, H_2SO_4 was added as needed as to reach a pH of 3.

The change in metal ion concentration was monitored by differential pulse polarography (DPP)

Table 1 Parameters used in the polarographic experiments

Instrumental parameter	Set point
Upper potential scan limit	-600 mV
Lower potential scan limit	-1,300 mV
Scan rate	4 mV s^{-1}
Pulse amplitude	50 mV
Sampling time	17 ms
Pulse time	50 ms
Drop time	1,000 ms

Fig. 1 Linear sweep voltammetry on a Cd electrode for the following solutions: *A* 1.0 M Na₂SO₄+H₂SO₄ (pH=4); *B* 1.0 M Na₂SO₄+H₂SO₄ (pH=4) + 1 × 10⁻² M CdSO₄; *C* 1.0 M Na₂SO₄+H₂SO₄ (pH=4) + 1 × 10⁻² M NiSO₄. Scan rate: 50 mV s⁻¹



using a conventional three electrode cell with the CGME as the working electrode and the Pt flag electrode as counter electrode. We developed an analytical protocol so as to have a linear response of the current peaks of each metal ion with their molar concentrations (Mayen-Mondragon et al. 2002). Such conditions include the use of a buffer (5 mL) composed of 1.0 M ammonium citrate/1.0 M ammonium hydroxide (28.2%) to which 75 μ L of the analyte were added. An automatic volumetric pipet (Eppendorf 20–200 μ L) and volumetric glassware were used throughout the analysis. Potential sweeps were performed immediately after terminating the nitrogen bubbling described earlier. A nitrogen blanket was maintained above the solution during the analysis. Other working parameters are given in Table 1.

Constant potential electrolyses were performed during 68 min (i.e., the maximum electrolysis time allowed by the instrument) under different conditions as dis-

cussed below. Samples were taken every 10 min (unless otherwise specified) to monitor metal concentrations.

3 Results and Discussion

3.1 Anion Effects on the Metal Deposition Potentials

1. *Sulfate medium.* Figure 1 shows linear sweeps with and without Ni and Cd in sulfate media. The supporting electrolyte gives a significantly smaller electrochemical response than that of the target processes in the voltage range studied. We measured the open circuit potentials for systems A, B and C and found them to be -0.730, -0.710 and -0.780 V (vs. Ag/AgCl), respectively. This means that the Cd(II) deposition has the least negative potential and thus it is expected to be easier to achieve. In fact, Cd(II) starts depositing

Fig. 2 Linear sweep voltammetry on a Cd electrode for the following solutions: *A* 0.5 M KCl + HCl (pH=3); *B* 0.5 M KCl + HCl (pH=3) + 1 × 10⁻² M CdCl₂; *C* 0.5 M KCl + HCl (pH=3) + 1 × 10⁻² M NiCl₂. Scan rate: 50 mV s⁻¹

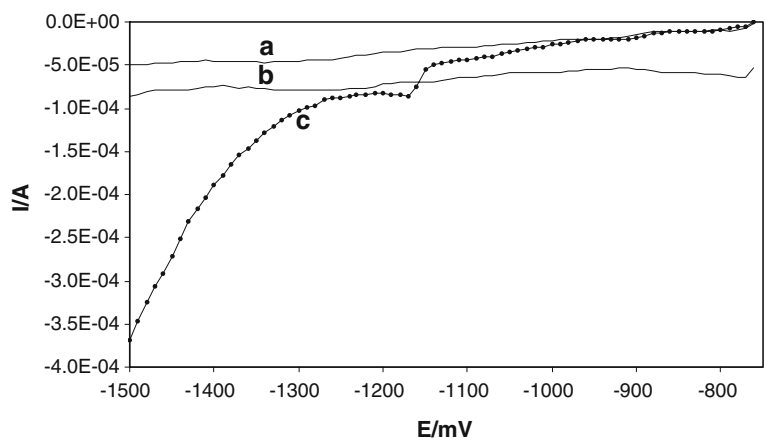
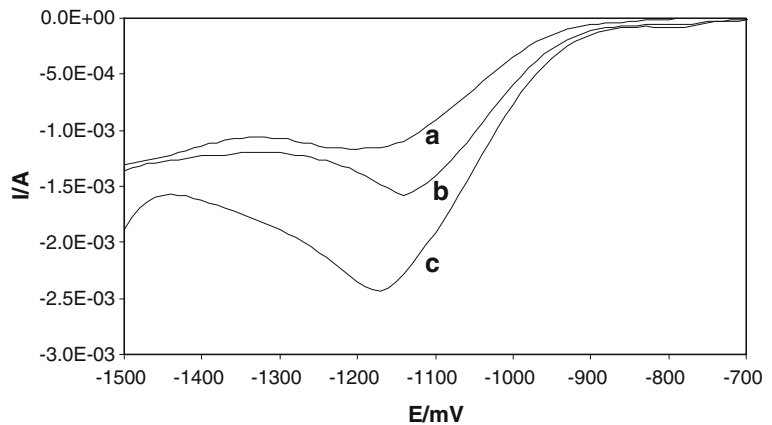


Fig. 3 Linear sweep voltammetry on a Cd electrode for the following solutions: *A* 1.0 M $\text{KNO}_3 + \text{HNO}_3$ (pH=3); *B* 1.0 M $\text{KNO}_3 + \text{HNO}_3$ (pH=3) + 1×10^{-2} M CdSO_4 ; *C* 1.0 M $\text{KNO}_3 + \text{HNO}_3$ (pH=3) + 1×10^{-2} M NiSO_4 . Scan rate: 50 mV s^{-1}



immediately after the rest potential (i.e., the natural potential of the system at $I=0$) and a diffusion peak is observed at approximately -800 mV ; Ni(II) starts depositing at approximately $-1,000 \text{ mV}$. Thus there is a 200 mV difference in deposition potentials under these conditions that should allow for a good separation of both metals upon deposition. In addition, the diffusional peak near the rest potential indicates that the Cd(II) deposit is kinetically favored whereas that of Ni(II) is not, and the latter occurs simultaneously with appreciable solvent decomposition. This is consistent with recent findings at a paraffin impregnated graphite electrode (PIGE), where the initial stage during Ni deposition in this medium was found to be proton reduction and the charge carrying species is NiOH^+ (Orinakova et al. 2006). On the other hand, Cd(II) reduction is mass-transport limited and quasi-reversible on a Cd electrode; in a sulfate medium it can form sulfate complexes (Armstrong

1996) and the deposition occurs in two steps, involving an adsorbed Cd(II) intermediate species (Montiel et al. 2000). Lastly, the $[\text{Ni(II)}]/[\text{Cd(II)}]$ ratio affects the potential range in which pure Cd can be deposited from a mixed solution. However, even at a 100:1 ratio the deposition potential difference should be sufficient as to obtain pure Cd deposits (Armstrong et al. 1996).

2. *Chloride medium.* Figure 2 shows the linear sweeps with and without Ni and Cd in chloride media. We measured the open circuit potentials for systems A, B and C (Fig. 2) and found them to be -0.77 V vs. Ag/AgCl for the three systems, which is consistent with previous findings (Badawy et al. 1999). As in sulfate media, the supporting electrolyte does not produce a significant electrochemical response in the region of interest, and a small diffusional reduction peak for Cd(II) is observed at the beginning of the experiment (i.e., at approximately -750 mV).

Fig. 4 Constant potential electrolysis I vs. t curve on a Cd electrode with the following solutions: *A* 1.0 M $\text{Na}_2\text{SO}_4 + \text{H}_2\text{SO}_4$ (pH=4) + 1×10^{-2} M $\text{CdSO}_4 + 1 \times 10^{-2}$ M NiSO_4 ; *B* 0.5 M $\text{KCl} + \text{HCl}$ (pH=3) + 1×10^{-2} M $\text{CdCl}_2 + 1 \times 10^{-2}$ M NiCl_2 ; *C* 1.0 M $\text{KNO}_3 + \text{HNO}_3$ (pH=3) + 1×10^{-2} M $\text{CdCl}_2 + 1 \times 10^{-2}$ M NiCl_2

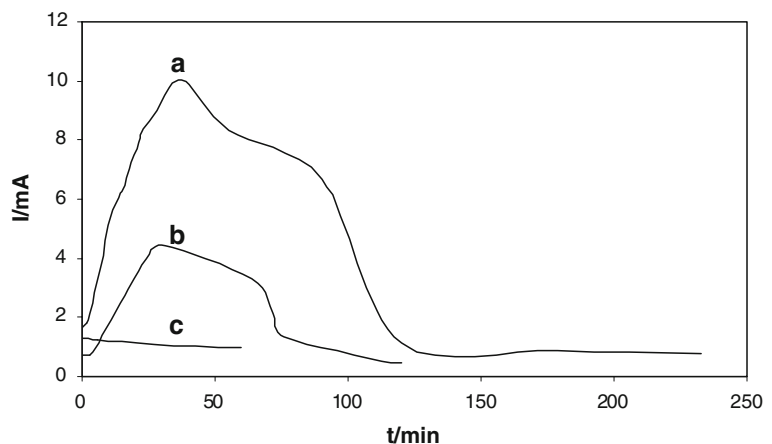


Table 2 Percent Ni and Cd recovery after electrolysis (conditions as in Fig. 4)

Curve	Electrolysis time (min)	Electrode potential (V vs. Ag/AgCl)	% Ni recovery	% Cd recovery
A	233	-0.850	2.6	>88 ^a
B	120	-0.850	9.6	>75 ^a
C	60	-0.900	49.0	8.2

^aThe absorbance measured for the final solution was smaller than the minimum value used for the corresponding calibration curve.

Again, Ni(II) starts depositing at the point where its reduction curve begins deviating appreciably from that of the blank (i.e., near $-1,000$ mV); the initial stage in this medium was found to be Ni^{2+} reduction, with NiCl^+ as the charge carrying species (at a PIGE; Orinakova et al. 2006).

3. *Nitrate medium.* Figure 3 shows that both metals deposit at similar potentials in this medium (i.e., -900 mV). We measured the open circuit potentials for systems A, B and C (Fig. 3) and found them to be: System A: -0.810 V vs. Ag/AgCl, System B: -0.700 V vs. Ag/AgCl, System C: -0.710 V vs. Ag/AgCl. Nitrate ions are known to be reduced at PIGE during Cd deposition (Rozik and Trnkova 2006), which is consistent with our results on Cd metal. Nitrate reduction is observed, as evidenced by the broad peak shown in the supporting electrolyte scan. Nitrate ions inhibit somewhat the deposition of Cd, whereas they facilitate the deposition of Ni (i.e., it deposits at approximately 100 mV less negative potentials than in sulfate or chloride media). In addition, nitrate ions may react with Cd metal itself (Rozik

and Trnkova 2006). Furthermore, nitrate reduction typically produces OH^- ions (Rajeshwar and Ibanez 1997) that may yield the corresponding insoluble metal hydroxides on the electrode surface (see below), thus impeding electron transfer. From these results and considerations it is clear that the nitrate medium is not adequate for the targeted selective deposition of Cd.

3.2 Constant Potential Electrolysis of Sulfate, Chloride, and Nitrate Solutions Containing Ni(II) and Cd(II)

These systems were studied under constant potential electrolysis conditions. Based on the above results, a potential of -850 mV was selected for the sulfate and chloride media whereas -900 mV was used for the nitrate medium (see Fig. 4). An initial current increase characterizes the electrolyses in the sulfate and chloride media, most likely due to the formation of dendritic deposits that increase the electrode surface area and promote mass transfer in its vicinity. The current then falls due to the decrease in Cd ion concentration. For the nitrate medium, the current is much smaller and starts decreasing slightly from the beginning of the electrolysis. Table 2 shows the results obtained in such electrolysis. It is clear that the percent recovery of Cd in sulfate and chloride media is quite reasonable (the numbers given are *minimum* values), whereas that in the nitrate medium is rather low. Furthermore, in sulfate and chloride media the undesirable codeposition of Ni is relatively small, whereas in the nitrate medium it is much higher

Fig. 5 Linear sweep voltammetry with a Cd rotating disk in 1×10^{-2} M $\text{CdSO}_4 + 1.0$ M $\text{Na}_2\text{SO}_4 + \text{H}_2\text{SO}_4$ (pH=3). Rotation rate: A 0 rpm, B 1,000 rpm, C 1,500 rpm, D 2,000 rpm, E 2,500 rpm. Scan rate: 10 mV s^{-1}

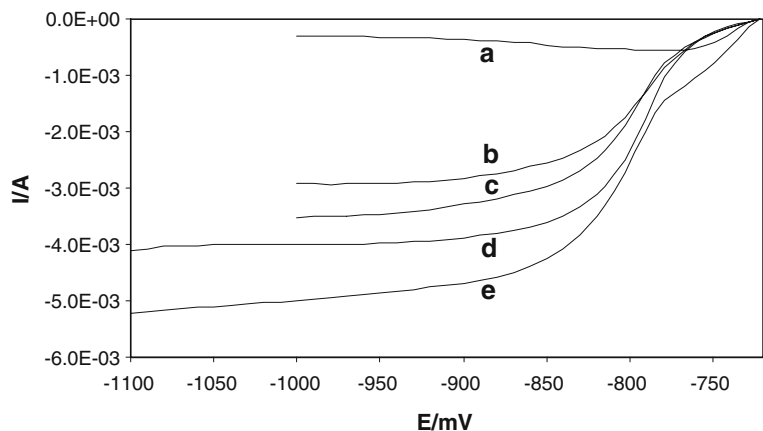
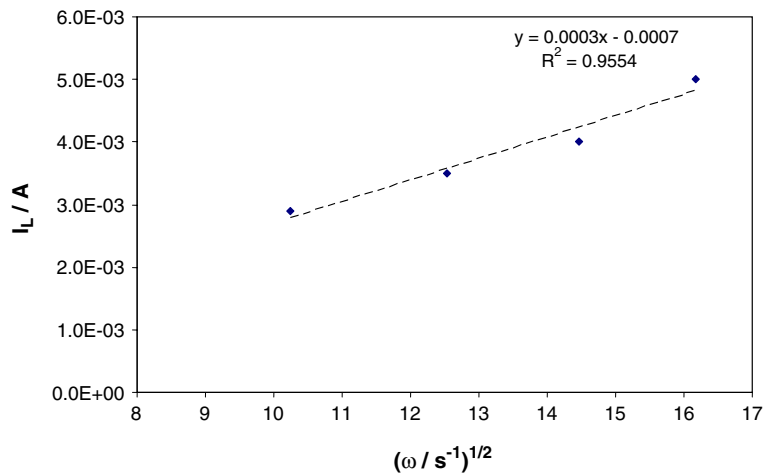


Fig. 6 Plot of the limiting current as a function of rotation rate for system B, 1.0 M $\text{KNO}_3 + \text{HNO}_3$ (pH=3) + 1×10^{-2} M CdSO_4

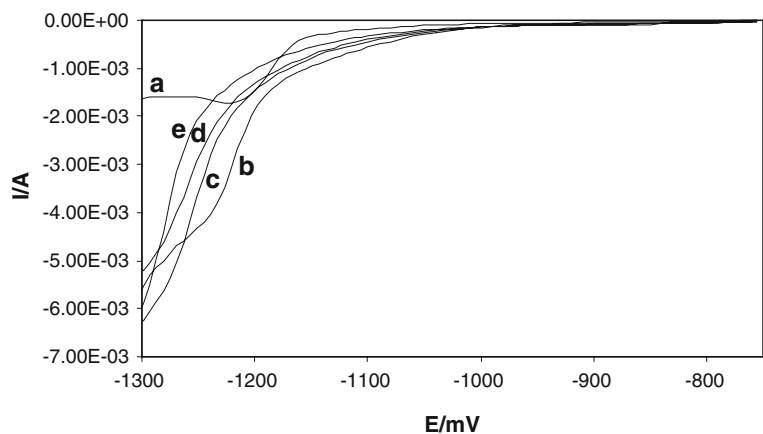


than that of Cd. In spite of the fact that the electrolysis times were different, it can be affirmed that the sulfate medium is the most suitable of the three media tested for the selective recovery of Cd.

3.3 Effect of Controlled Convection Upon the Deposition Potentials of Ni(II) and Cd(II) in Separate Solutions: An RDE Study

Figure 5 shows the rotating disk electrode (RDE) linear scans in sulfate media for the reduction of Cd (II). Upon comparison of curves A and B it becomes apparent that forced convection increases Cd deposition. A plateau signals that the limiting current is reached. When the diffusion layer decreases (i.e., at higher rotation rates) the limiting current increases, confirming that Cd deposition is in the mass-transfer controlled region.

Fig. 7 Linear sweep voltammetry with a Cd rotating disk in 3×10^{-2} M $\text{NiSO}_4 + 1.0$ M $\text{Na}_2\text{SO}_4 + \text{H}_2\text{SO}_4$ (pH=3). Rotation rate: A 0 rpm, B 1,000 rpm, C 1,500 rpm, D 2,000 rpm, E 2500 rpm. Scan rate: 10 mV s^{-1}

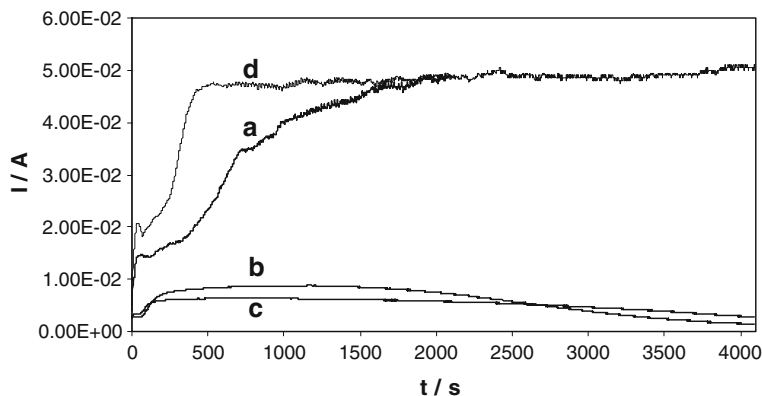


From Levich's equation,

$$I_L = 0.62AnFD^{2/3}\nu^{-1/6}c\omega^{1/2} \quad (1)$$

we calculated the diffusion coefficient for Cd(II) in our particular solution as follows. Here, I_L is the limiting current (in amperes), A is the electrode area (in meters squared), n is the number of electrons involved in the electrochemical reaction, F is Faraday's constant ($96,485 \text{ C/mol e}^-$), D is the diffusion coefficient (in meters squared per second), ν is the kinematic viscosity of the solution (in meters squared per second), c is the bulk concentration of the reactant (in mole per cubic meter) and ω is the rotation rate of the disc (in radian per second). From the viscosity of the solution and its density, the kinematic viscosity was calculated to be $9.98 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$. This was then used together with the obtained Levich's slope (Fig. 6) to calculate a diffusion coefficient of $3.5 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$

Fig. 8 Constant potential electrolysis of 1.0 M $\text{Na}_2\text{SO}_4 + 1 \times 10^{-2}$ M $\text{CdSO}_4 + 3 \times 10^{-2}$ M $\text{NiSO}_4 + \text{H}_2\text{SO}_4$ on a rotating cadmium disk. A $\omega=1,000$ rpm, $V=-1,300$ mV; B $\omega=1,000$ rpm, $V=-800$ mV; C $\omega=1,500$ rpm, $V=-800$ mV; D $\omega=1,500$ rpm, $V=-1,300$ mV



for Cd(II), which is consistent with the typical range of values given (i.e., $3-7 \times 10^{-10} \text{ m}^2\text{s}^{-1}$; Walsh 1993).

Figure 7 shows the RDE linear scans in sulfate media for the reduction of Ni(II). The deposition current onsets are consistent with those observed earlier (approximately $-1,000$ mV). The same rationale as above can be applied to the comparison of curves A (0 rpm) and B (1,000 rpm). However, there is not an appreciable current increase from 1,000 to 2,500 rpm. This indicates that Ni(II) deposition under such conditions is still controlled by charge transfer (as opposed to mass transfer). The Ni(II) to Ni(0) deposition process is irreversible and occurs through an adsorbed Ni(I) intermediate that limits the rate of the overall process (Watson and Walters 1991). Furthermore, Ni(II) reduction occurs simultaneously with appreciable water reduction.

3.4 Constant Potential Electrolysis of Solutions Containing Ni(II) and Cd(II): An RDE Study

Conditions were selected by experimental design so as to find a successful combination of potential (high/

low) and rotation rate (high/low). The experiments were limited by the maximum time allowed by the instrument, i.e. 68 min. The linear scans thus obtained are plotted in Fig. 8, and the results tabulated in Table 3. The current increased continuously when the electrolyses were performed at $-1,300$ mV (curves A and D); this effect was promoted by a considerable surface area increase (a dendritic deposit was observed). At the same time water electrolysis at the anode produces H^+ ions that lower the pH of the solution, thus facilitating hydrogen gas production at the cathode. This explains the observed overall decrease in pH since there are two competing reduction processes at the cathode (i.e., metal ion reduction and proton reduction) whereas water electrolysis is the only anodic process. At this very negative potential, some Ni deposition is obtained in addition to Cd deposition as discussed earlier. On the other hand, for the two electrolyses performed at -800 mV (curves B and C), the initial current increase (smaller than that observed at the more negative potentials) is followed by a slow decrease. Here, the

Table 3 Summary of results at constant potential electrolysis

Expt. ^a	E (mV)	rpm	t, min	%Cd recovered (by weight)	%Ni recovered (by weight)	Theoretical charge for complete Cd recovery (C)	Measured charge (C)	Current efficiency (%) ^d
A	-1300	1000	35 ^b	91.3	37.7	17.4	74.8	23.3
B	-800	1000	68	96.7	0 ^c	18.4	24.3	75.9
C	-800	1500	68	91.4	0 ^c	17.4	21.4	81.4
D	-1300	1500	68	98.0	53.4	18.7	189.5	9.9

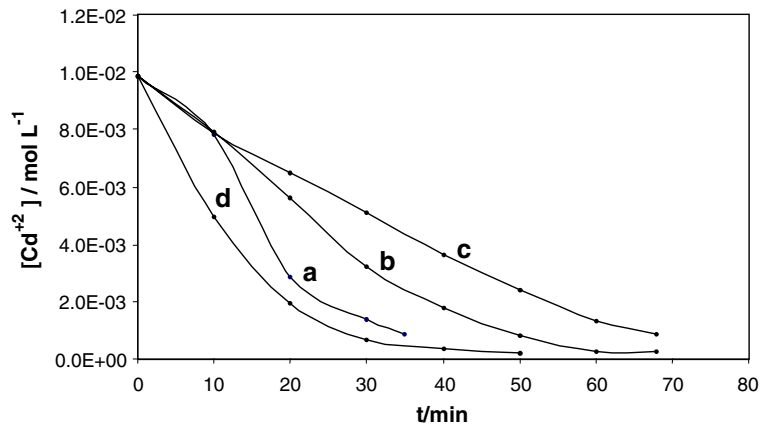
^a 1.0 M $\text{Na}_2\text{SO}_4 + 1 \times 10^{-2}$ M $\text{CdSO}_4 + 3 \times 10^{-2}$ M $\text{NiSO}_4 + \text{H}_2\text{SO}_4$ on a rotating Cd disk

^b This particular experiment was discontinued after 35 min, when a total charge of 74.8 C had passed through the electrode (the theoretical charge required for 100% Cd recovery is 17.4 C).

^c The Ni(II) concentration in solution remained essentially constant.

^d In order to make a straightforward comparison one would need to apply a constant charge.

Fig. 9 Variation of Cd concentration in 1.0 M $\text{Na}_2\text{SO}_4 + 1 \times 10^{-2}$ M $\text{CdSO}_4 + 3 \times 10^{-2}$ M $\text{NiSO}_4 + \text{H}_2\text{SO}_4$ during constant potential electrolysis on a rotating cadmium disk at: A $\omega=1,000$ rpm, $V=-1300$ mV; B $\omega=1,000$ rpm, $V=-800$ mV; C $\omega=1,500$ rpm, $V=-800$ mV; D $\omega=1,500$ rpm, $V=-1300$ mV



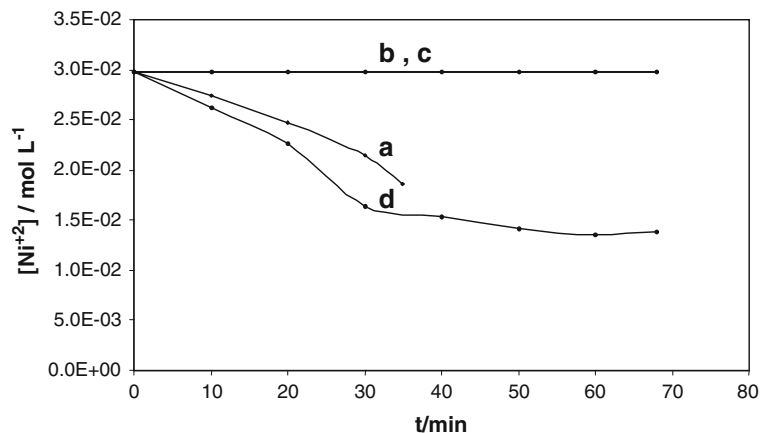
deposit was observed to be composed of fine, compact grains without dendrites. Again, Cd concentration decreases with time and so does the overall current. Ni deposition is not observed here.

In order to analyze the change in concentration of the metal ions in the electrolytic solutions, DPP was performed as described above on the solution at different electrolysis times. A reference datum was obtained by analyzing a solution deliberately prepared with low concentrations of both metal ions (i.e., 2×10^{-3} M $\text{CdSO}_4 + 6 \times 10^{-3}$ M $\text{NiSO}_4 + 1.0$ M $\text{Na}_2\text{SO}_4 + \text{H}_2\text{SO}_4$, at pH=3). In conjunction with the points at the initial concentration values, this reference datum was used for drawing a straight line in order to estimate the concentration at each point. From Table 3, the highest Cd recovery was obtained in experiment D due to the very negative potential applied. Likewise, the highest selectivity was obtained in experiments B and C (i.e., nearly 0% Ni recovery). The physical aspect and morphology of the

deposited Cd are better from a commercial stand point in the second case (i.e., non-dendritic, metallic grayish in color), since at very negative potentials thick deposits with little adherence are obtained. Furthermore, at -800 mV the process involves much higher current efficiencies. Since the conditions in experiment C led to a higher current efficiency than those in experiment B (i.e., 5.5% higher), and at the same time the % Cd recovery is somewhat small (i.e., 5.3% smaller), an economic balance would define the best parameters from an applied standpoint.

Figure 9 shows the variation of $[\text{Cd(II)}]$ as a function of time for the conditions described in Table 3 and Fig. 8. This confirms that Cd deposition occurs much faster under the conditions of experiment D than under those of experiment C. In the experiments run at lower potentials, the decrease in $[\text{Cd(II)}]$ is also slower than that at $-1,300$ mV and 1,500 rpm, although the final recovery is similar. Figure 10 shows that Ni recovery is practically zero at

Fig. 10 Variation of Ni concentration in 1.0 M $\text{Na}_2\text{SO}_4 + 1 \times 10^{-2}$ M $\text{CdSO}_4 + 3 \times 10^{-2}$ M $\text{NiSO}_4 + \text{H}_2\text{SO}_4$ during constant potential electrolysis on a rotating cadmium disk at: A $\omega=1,000$ rpm, $V=-1,300$ mV; B $\omega=1,000$ rpm, $V=-800$ mV; C $\omega=1,500$ rpm, $V=-800$ mV; D $\omega=1,500$ rpm, $V=-1,300$ mV



–800 mV (see Table 3). On the other hand, a higher Ni recovery is noted at –1,300 mV and 1,500 rpm, and the concentration vs. time plot reaches a plateau after about 30 min. At this point, [Ni(II)] is very likely small enough so as to make the applied potential insufficient for its deposition.

The use of a low solution pH can be advantageous since it can inhibit Ni(II) reduction at low metal ion concentrations (Njau and Janssen 1995). In addition, the absence of complexing agents and of a buffer promotes the production of insoluble Ni(OH)₂ at the electrode surface since the production of hydrogen at the cathode uses up nearby H⁺ thus provoking a local pH increase (Njau and Janssen 1995); the solubility of Ni(OH)₂ is two orders of magnitude smaller than that of Cd(OH)₂. These factors contribute to the selectivity for Cd deposition. On the other hand, the recovery of Cd in a batch reactor is favored at somewhat higher pH values, although its morphology is better—from a commercial standpoint—at low pH (i.e., crystalline, compact deposits, Bartolozzi et al. 1991). Such observation is in agreement with the findings of the present work. Additives have been suggested to improve Cd deposition efficiency at more negative potentials, since hydrogen production can be selectively impaired (Franklin et al. 1998).

Generally speaking, low concentrations of metals to be recovered are problematic since they suffer from thermodynamic, kinetic, and transport limitations. This is the reason why large volumes of acid cannot be used for the lixiviation of electrodes from spent batteries. However, a trade off is needed since the usage of smaller volumes implies using lower pH values that favor water reduction as a secondary reaction during Cd deposition.

4 Conclusions

Selective Cd recovery from a solution containing Cd (II) and Ni(II) in approximately the same ratio as that found in solutions containing dissolved electrodes from spent NiCad batteries (i.e., 3:1 mole ratio) was achieved under selected conditions of applied potential and electrode rotation rate. A good percent recovery (>90%) with high selectivity (approximately 0% Ni) and a reasonably high current efficiency (>80%) can be achieved. Cd(II) deposition on Cd electrodes is favored over that of Ni(II) since it occurs

at a potential some 200 mV less negative than that of Ni(II) (in sulfate or chloride media). Cd deposition is a quasi-reversible process, whereas that of Ni is irreversible. Nitrate media were found to be unsuitable for Cd recovery. Forced convection (e.g., using a RDE) facilitates Cd deposition in sulfate media, but plays a much smaller role in Ni deposition.

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