Recovery of heavy metals from spent Ni–Cd batteries by a potentiostatic electrodeposition technique

Chun-Chen Yang[*]

Department of Chemical Engineering, Ming-Chi Institute of Technology, 84 Gungjuan Road Taishan, Taipei, Hsein 243, Taiwan, ROC

Abstract

Two heavy metals, Cd and Ni, have been separately recovered from spent AA-size Ni–Cd batteries by the potentiostatic electrodeposition and chemical precipitation methods, respectively. Various types and concentrations of HCl, H_2SO_4, and HNO_3 acids had been used as leach extractants. Experimental results indicate that the acid with the best leach capability is 4 M HCl. Three complexing reagents of NH_3, sodium acetate, sodium citrate have been chosen and tested. The most effective buffer is sodium citrate. The optimum mole ratio of metallic ion to citrate ion is 1:1. The recovery process for Cd metal is conducted by the potentiostatic electrodeposition in a leach electrolyte with a sodium citrate complex. The optimum applied potential for Cd recovery is in the range -1100 to -1120 mV (versus saturated calomel electrode (SCE)). The current efficiency for the recovery process is between 70 and 90% and depends strongly on the process parameters, e.g. liquor, concentration, applied potential, temperature, type of complex reagents, mole ratio, mass-transfer rate.
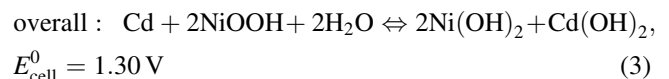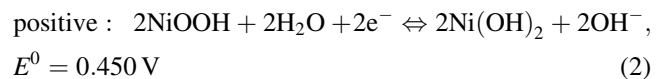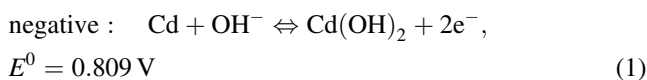
1. Introduction

The alkaline nickel–cadmium (Ni–Cd) battery still remains widely used in variety of applications and devices due to its high-rate capability. Although various types of Ni–Cd batteries are available on the market, the problem of the toxicity of cadmium has still not been completely resolved.

To date, there have been several processes available for the recycling or recovery of spent Ni–Cd, nickel–metal-hydride (Ni–MH), and lithium-ion batteries [1–13]. Yang and Cheh [14,15] have studied the preparation process for thin Cu/Ni multi-layers by the galvanostatic and potentiostatic pulse electrodeposition techniques based on experimental and theoretical work. The Ni–Cd cell is a secondary rechargeable battery, widely used in many 3C electronic devices and tool applications. It is composed of a positive electrode with $Ni(OH)_2$ active material, a negative electrode with $Cd(OH)_2$ active material, a Ni-based current-collector, and a polyethylene/polypropylene (PE/PP) separator. The reactions at the two electrodes are as follows:

$$\text{negative}: \quad Cd + OH^- \Leftrightarrow Cd(OH)_2 + 2e^-,$$
$$E^0 = 0.809\,V \tag{1}$$

$$\text{positive}: \quad 2NiOOH + 2H_2O + 2e^- \Leftrightarrow 2Ni(OH)_2 + 2OH^-,$$
$$E^0 = 0.450\,V \tag{2}$$

$$\text{overall}: \quad Cd + 2NiOOH + 2H_2O \Leftrightarrow 2Ni(OH)_2 + Cd(OH)_2,$$
$$E^0_{cell} = 1.30\,V \tag{3}$$

A major concern with Ni–Cd batteries is the environmental pollution problem. Cadmium is a hazardous and toxic material. Thus, the dumping or incineration of spent Ni–Cd may cause serious environmental problems. Since a huge amount of spent Ni–Cd batteries needs to be treated, the recycling of these batteries becomes urgent and important. The purpose of the work reported here is to develop an electrochemical technique for the separation and recovery of Cd and Ni metals from spent Ni–Cd batteries. Experiments have been carried out to leach out the positive and negative active materials and current collector by the strong acids, followed by Cd metal recovery by a potentiostatic electrodeposition technique.

2. Experimental

2.1. Disassembly and leaching of spent batteries

All spent Ni–Cd batteries were first fully discharged, then disassembled; the metal can was separated from the internal

---

[*] Tel.: +886-2-2908-9899; fax: +886-2-2904-1914.
E-mail address: ccyang@ccsun.mit.edu.tw (C.-C. Yang).

battery rolls. The PE/PP separator was removed from the roll. The whole roll was leached in 250 ml of 4–8 M HCl, H_2SO_4, HNO_3 and aqua regia solutions, under agitation for 24 h over a temperature range of 25–90 °C. After acid-leaching, the small amount of residue (that was comprised of small particles) was removed by two-stage filtration. The resulting liquor had a green colour. The pH of the leach liquor was found to be less than unity. The chemical compositions of Cd, Ni, and Co in the leach liquor were quantitatively analyzed. All the chemicals used in this work are reagent grade.

2.2. Chemical composition analysis

The concentration of heavy metals in the leach liquor were analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES) using a Perkin-Elmer DV 2000 system. Stock solutions of the metals were prepared from commercially available 1000 ppm standard solutions (Perkin-Elmer). In order to assure repeatability of data, a standard stock solution, which comprised a specified concentration for Ni (2 ppm), Cd (1 ppm), and Co (1 ppm), was analyzed before each experiment.

2.3. Recovery of Cd and Ni metals

A suitable amount of leach liquor which contained 2000–5000 ppm Cd, was diluted with double-distilled water and adjusted to a pH of 6–7 with 8 M NaOH solution. Prior to adjustment, the amount of organic complex reagents, e.g. NH_3, sodium acetate and sodium citrate (Aldrich), were added to the above leach liquor. The organic complex reagents help to stabilize and buffer the liquor electrolyte. The organic reagent associated strongly with the metallic ions to avoid forming precipitates of metal hydroxides during the pH adjustment. The citrate complex was found to be the most efficient reagent for stabilizing the metallic ions. The mole ratio of Cd metal to citrate complex varied between 1:1 and 1:4.

Recovery of Cd by an electrochemical technique was carried out in a 300 ml, three-electrode, electrochemical cell. The working electrode was either a flat copper plate (7 cm × 10 cm) or a lab-made porous carbon electrode (area = 1 cm^2). The latter electrodes were made by pressing carbon powder of high surface-area on to a Ni-foam substrate. A saturated calomel electrode (SCE) was used as the reference electrode; all potentials are reported with respect to this electrode. A platinum-screen or Ti-screen electrode was used as the counter-electrode. A carbon rotating disc electrode (RDE) with a 5-mm diameter was used as a working electrode for current–potential measurements in the simulated solution. The simulated solution comprised the individual metal ion plus a suitable amount of Cl^- and citrate complex to maintain a constant ionic strength. A potentiostat (Eg&G 273A) was used to run the potentiostatic Cd recovery by varying the applied potential in the range −1000 to

−1300 mV. The deposition temperature was varied between 25 and 60 °C. After finishing Cd recovery, concentrated NaOH solution was added to the resulting solution and Ni was recovered as $Ni(OH)_2$ particle powder. A scanning electron microscope (Hitach 2600) was used to investigate the surface morphology of the porous carbon electrode.

3. Results and discussion

3.1. Chemical composition analysis

Spent Ni–Cd batteries with a mean weight of 25 g (AA-size) were chosen in this investigation. The weight percent of each component in the spent Ni–Cd battery was analyzed, as listed in Table 1. It was experimentally revealed that the weight percentages of the positive electrode, $Ni(OH)_2$, and of the negative electrode, $Cd(OH)_2$, in the spent battery were 31.36 and 35.97 wt.%, respectively. The weight percentage of the remaining components (separator, can, cap, etc.), was about 32.67 wt.%.

3.2. Leaching

The major components that are leached are the active materials of the battery and the Ni-based current-collector. The type and strength of the leaching acids strongly affect the leach capability. The experimental results for three leached metal ion concentrations are shown in Table 2. Acids with 1–2 M strength exhibit a much lower leaching capability; compared with 4–8 M acids and aqua regia. Further, the leaching capability of HCl and aqua regia solutions is much better than that of HNO_3 and H_2SO_4.

Experimental results reveal that the mean leached concentrations of Cd, Ni, and Co are 20–25, 26–29, and 1.5–1.7 g l^{-1}, respectively, from a single spent Ni–Cd cell. The chemical composition of the major elements in the leach liquor are 41–46 wt.% Cd and 49–55 wt.% Ni; together Cd and Ni metals comprise to 96–97 wt.%. By contrast, Co is only a minor species; its content is <3 wt.%.

The experimental temperature for the leaching process was controlled between 25 and 90 °C. Studies show that the leach temperature exerts a strong influence on the leaching time. Specifically, Cd and Ni metals can be almost

Table 1
Component analysis of AA-size Ni–Cd cell

Component	Mass (g)	Composition (wt.%)
Positive ($Ni(OH)_2$)	7.3386	31.36
Negative ($Cd(OH)_2$)	8.4169	35.97
Separator (PE/PP)	1.2535	5.36
Can (stainless steel)	4.6586	19.91
Cap	0.9876	4.22
Residue	0.7463	3.19
Total weight	23.4015	100.00

Table 2
Chemical composition of leach liquor from a spent 1300 mAh Ni–Cd cell

Acid	Positive mass (g)	Negative mass (g)	Cell mass after disassembly	$[Cd^{2+}]$ (ppm)	$[Ni^{2+}]$ (ppm)	$[Co^{2+}]$ (ppm)
HCl (4 M)	7.3386	8.4169	23.4015	24500	29000	1669
HCl (8 M)	7.2079	8.3358	23.5126	23500	28500	1700
Aqua regia (4 M)	7.1060	8.4343	23.6439	24000	26500	1544
HNO₃ (4 M)	7.3791	8.3391	23.2775	20500	27250	1625
H₂SO₄ (2 M)	7.2589	8.3261	23.3712	21000	26500	1775

completely leached by the acid in 2 h at a temperature of 60 °C. The higher the leaching temperature, the shorter is the leaching time. Nevertheless, the leaching process was difficult to maintain at high temperature due to the loss of a large amount of water. The leaching efficiency is much higher under stirring conditions.

The ratio of liquid leach acid (L) to spent solid (S) was controlled in the range 15–45. The amounts of Cd and Ni metals leached from spent Ni–Cd batteries are not significantly affected by the L:S ratio. Experimental results reveal the optimum conditions for the acid-leaching processes to be 4 M HCl, a temperature of 60 °C, at leach time of 2 h, and stirring conditions.

3.3. Current–potential curves for simulated solution

The polarization curves for simulated solutions of constant ionic strength and containing individual metal ions with a suitable amount of Cl⁻ and citrate anion were examined on a carbon RDE. The experiments were performed at a temperature of 50 °C at a constant rotation speed of 600 rpm.

The current–potential curves for Cd, Ni, and Co elements on a RDE at a scan rate of 1 mV s⁻¹ in various simulated solutions are shown in Figs. 1 and 2. The reversible potential of Cd ($E_{rev, Cd}$) is at −830 mV in 0.01 M CdSO₄ + 0.5 M NaCl solution without sodium citrate, while the reversible potential for Co ($E_{rev, Co}$) in 0.01 M CoSO₄ + 0.5 M NaCl without sodium citrate is −835 mV. Thus, the reversible potentials of Cd and Co are almost identical, and it is not possible to recover the two metals independently by an electrochemical technique. The reversible potential of Ni ($E_{rev, Ni}$) in 0.01 M NiSO₄ + 0.5 M NaCl without sodium citrate is −950 mV, as shown in Fig. 1. From a comparison of the reversible potentials of the three metals, it is seen that the polarization of Ni in a simulated solution without sodium citrate is the most significant.

By contrast, the reversible potential of Cd ($E_{rev, Cd}$) is shifted to −910 mV in 0.01 M CdSO₄ + 0.5 M NaCl with sodium citrate; moreover, the reversible potential of Co ($E_{rev, Co}$) in 0.01 M CoSO₄ + 0.5 M NaCl with sodium citrate is shifted to −940 mV, and the reversible potential of Ni ($E_{rev, Ni}$) in 0.01 M NiSO₄ + 0.5 M NaCl with sodium
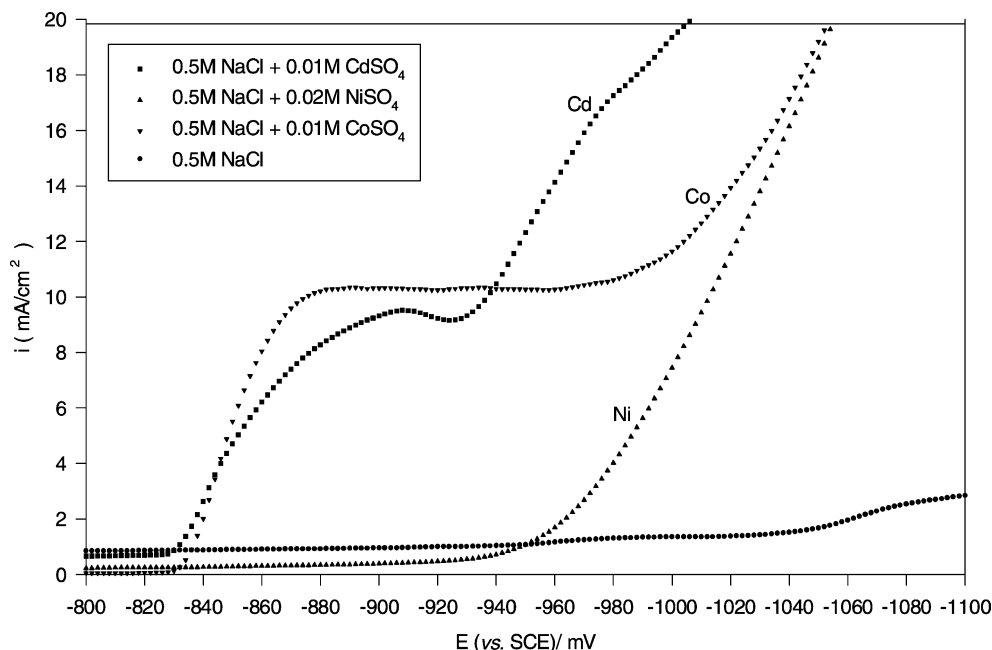

Fig. 1. Polarization curves on carbon RDE at scan rate of 1 mV s⁻¹ at 50 °C; simulated solution without sodium citrate complex reagent.
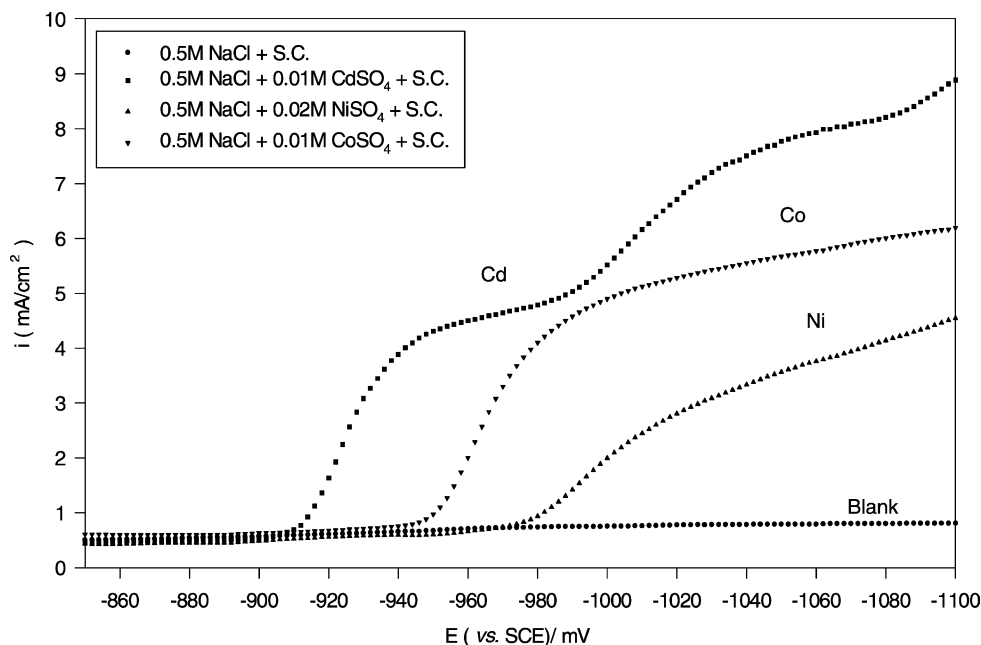
Fig. 2. Polarization curves on carbon RDE at scan rate of 1 mV s^{-1} at 50 °C; simulated solution with sodium citrate complex reagent (at mole ratio = 1:1).

citrate is −975 mV, as shown in Fig. 2. Thus, the reversible reduction potentials of Cd, Co, and Ni are all shifted in a negative direction when the sodium citrate complex reagent is added. Further, the current densities of Cd, Co, and Ni are all decreased. It can be understood that the addition of organic complex additives increases the polarization of the electrode and depresses the recovery rate. Sodium citrate serves as a wetting and buffer medium. Experimental results show that the wetting and buffer capabilities of sodium citrate are more effective than those of other complex reagents, e.g. acetate ion (Ac^{-}), $S_2O_3{}^{2-}$, tartrate ions. It is also found that the optimum mole ratio of metal ion to sodium citrate is 1:1.

3.4. Cd metal recovery

Recovery of Cd metal was carried out on a flat Cu electrode in the leach electrolyte with sodium citrate reagent at a constant temperature of 50 °C. The potential of electrode was varied from −1000 to −1300 mV. The chemical composition of the metal deposits under static conditions are given in Table 3, while the chemical composition of Cd, Ni, and Co elements for metal deposits as a function of applied working potential are presented in Fig. 3. It is observed that the weight percentage of Cd in metal deposits gradually declines with increase in negative applied potential; conversely, the weight percentage of Ni increases. Moreover, the weight percentage of Co is 2–4 wt.%. Investigations show that the optimum potential window for Cd recovery is −1080 to −1130 mV, and that at −1120 mV, the current efficiency (CE) is 90.75%. The recovery of Cd element from leach liquor is around 95%.

3.5. Temperature effects

Current–time curves at a constant applied potential of −1120 mV at various temperatures in a leach electrolyte with a concentration of 1772 ppm [Cd^{2+}], 2608 ppm [Ni^{2+}], and 144 ppm [Co^{2+}] are given in Fig. 4. The current density increases when the recovery temperature is raised; the current density for metal recovery under static conditions at 60 °C is over 1 mA cm^{-2}.

3.6. Mass-transfer effects

The chemical compositions of metal deposits at different rotation speeds are listed in Table 4. The rate of Cd metal recovery increased when the mass-transfer rate is enhanced. The Cd composition in the deposit can reach as high as 98–99% under convection conditions at a potential of

Table 3
Chemical analysis of metal deposits (wt.%) at different applied potentials; static conditions with electrolyte concentration: [Cd^{2+}] = 1772 ppm; [Ni^{2+}] = 2608 ppm; [Co^{2+}] = 144 ppm

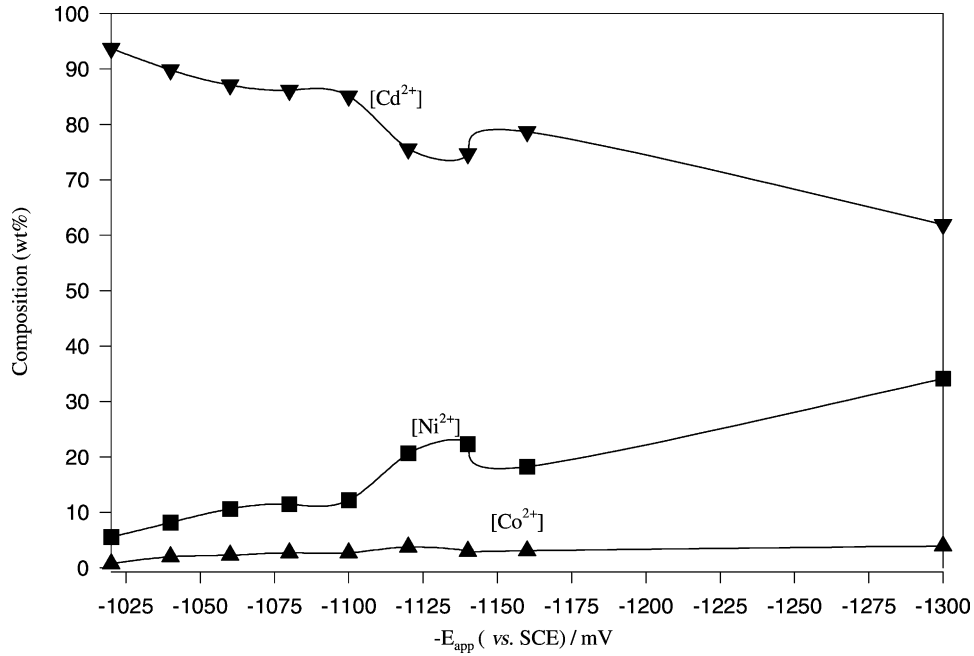| Run	E_{app} (mV)	Cd (wt.%)	Ni (wt.%)	Co (wt.%)
1	−1020	93.69	5.55	0.76
2	−1040	89.81	8.18	2.01
3	−1060	87.09	10.62	2.29
4	−1080	86.12	11.49	2.73
5	−1100	85.1	12.19	2.72
6	−1120	75.56	20.67	3.77
7	−1140	74.67	22.31	3.02
8	−1160	78.654	18.25	3.1
9	−1300	61.91	34.14	3.95

Anode: Ti-screen; cathode: copper plate.

Fig. 3. Chemical composition of metal deposits as function of applied potential at 50 °C; electrolyte composition: $[Cd^{2+}] = 1772$ ppm, $[Ni^{2+}] = 2608$ ppm, $[Co^{2+}] = 144$ ppm.
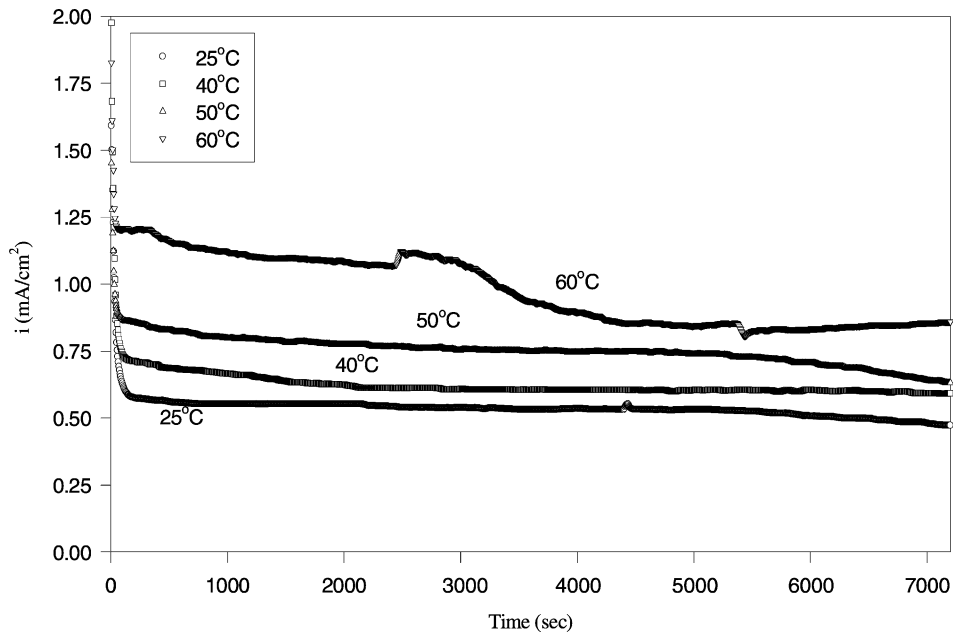

Fig. 4. For Cd recovery at constant potential of -1120 mV at various temperatures; deposition time: 2 h; electrolyte composition: $[Cd^{2+}] = 1772$ ppm, $[Ni^{2+}] = 2608$ ppm, $[Co^{2+}] = 144$ ppm.

Table 4
Chemical analysis of metal deposits (wt.%) at various rotation speeds (wt.%)

Run	Speed (rpm)	E_{app} (mV)	Time (s)	Cd (wt.%)	Ni (wt.%)	Co (wt.%)
1	0	-1120	7200	75.56	20.67	3.77
2	100	-1120	7200	98.16	1.31	0.45
3	200	-1120	7200	99.43	0.51	0.05

Anode: Ti; cathode: copper plate.

-1120 mV, as displayed in Table 4. Results indicate that Cd metal can be recovered independently and separated from the nickel by a potentiostatic electrodeposition technique in a leach liquor with sodium citrate.

3.7. Complex reagent mole ratio effect

Current–time curves are shown in Fig. 5 for various ratios of sodium citrate complex at a constant potential of
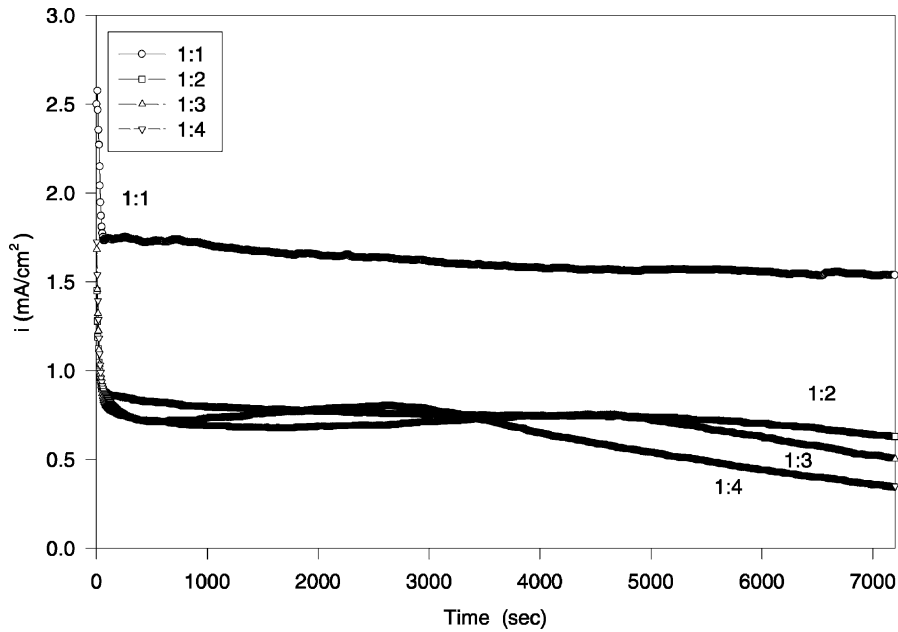
Fig. 5. Current–time curves for Cd recovery at constant potential of -1120 mV at various mole ratios of sodium citrate complex reagent at 50 °C; electrolyte composition: $[Cd^{2+}] = 1772$ ppm, $[Ni^{2+}] = 2608$ ppm, $[Co^{2+}] = 144$ ppm.

-1120 mV and a temperature of 50 °C in a leach liquor. The current density for Cd metal recovery is the highest (viz. 1.75 mA cm^{-2}) when the mole ratio is kept at 1:1. At the other mole ratios of 1:2, 1:3, and 1:4, the current density for Cd recovery is less than 1 mA cm^{-2}. Thus, the higher the mole ratio of complex, the lower is the current density.

3.8. Porous carbon electrode for recovery process

Current–time curves are shown in Fig. 6 for a flat Cu electrode and a porous carbon electrode at a constant potential of -1100 mV at 50 °C in leach electrolyte with the concentration of 5005 ppm $[Cd^{2+}]$, 5300 ppm $[Ni^{2+}]$, and 355 ppm $[Co^{2+}]$. The current density for Cd recovery is
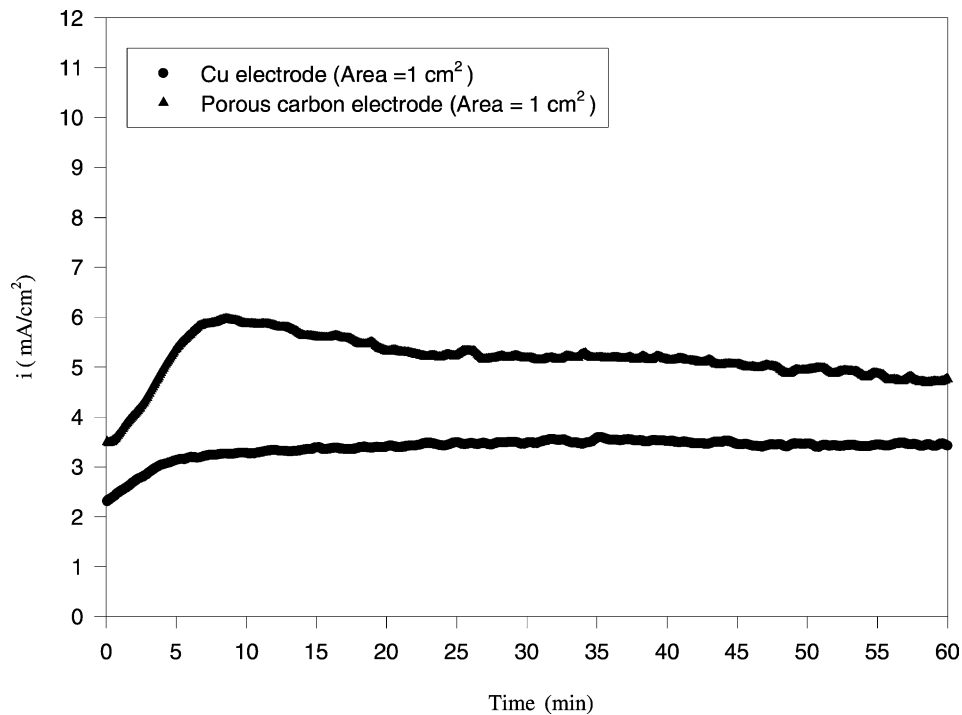

Fig. 6. Current–time curves for Cd metal recovery with different types of electrode at 50 °C; deposition at constant potential of -1120 mV; electrolyte composition: $[Cd^{2+}] = 5005$ ppm, $[Ni^{2+}] = 5300$ ppm, $[Co^{2+}] = 355$ ppm.

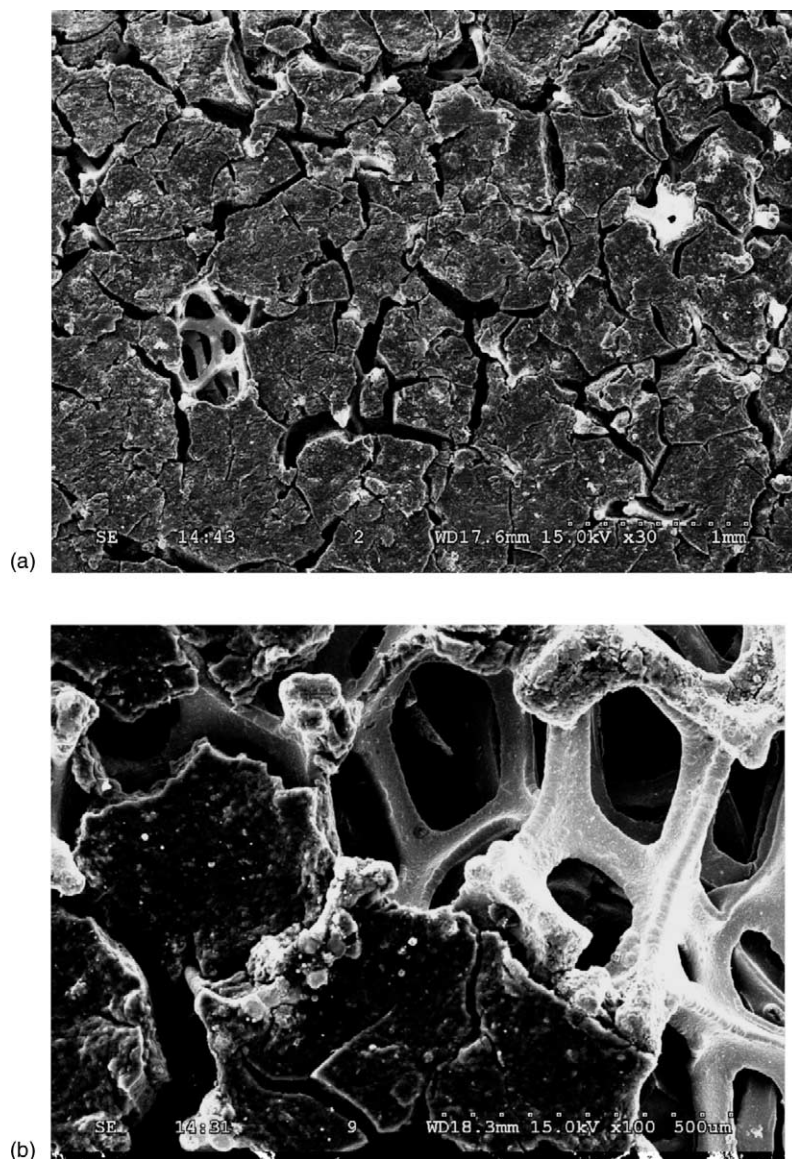Fig. 7. Scanning electron micrographs of porous carbon electrode: (a) 30×; (b) 100×.

higher on the porous carbon electrode for the same recovery conditions. Scanning electron micrographs of the carbon porous electrode are shown in Fig. 7. The surface morphology of the carbon electrode is highly porous and consists of irregular pancake shapes. The recovery rate (i.e. current density) can be effectively increased to 50% when the real surface-area of the electrode is increased, as demonstrated by the data in Table 5.

4. Conclusions

Cd and Ni have been separately recovered from spent AA-size Ni–Cd batteries by an electrochemical technique and by chemical precipitation, respectively. Various concentrations of HCl, H_2SO_4, and HNO_3 acids have been used as leaching agents. It is found that 4 M HCl had the best leaching capability.

A leach liquor with a Cd concentration of 2000–5000 mg l^{-1} is used as an electrolyte and is adjusted by adding organic complex reagents and then neutralizing with NaOH. The most effective complexing reagent is sodium citrate. It is found that the optimum mole ratio of

Table 5
Comparison recovery rates for different electrodes (in terms of current density)

Run	Anode	Cathode (1 cm^2)	Time (min)	E_{app} (mV)	i_{avg} (mA cm^{-2})
1	Ti-screen	Cu	60	−1120	3.2
2	Ti-screen	Porous carbon	60	−1120	5.2

Conditions: static; leach electrolyte with volume of 300 ml; electrolyte composition: $[Cd^{2+}]$ = 5005 ppm; $[Ni^{2+}]$ = 5300 ppm; $[Co^{2+}]$ = 308 ppm.

metallic ion to citrate ion is at 1:1. The Cd recovery process is performed by means of a potentiostatic electrodeposition technique in a leach electrolyte which contains sodium citrate. The Ni element is recovered from the resulting solution by treatment with NaOH to precipitate $Ni(OH)_2$ fine powders. The recovery of Ni from leach liquor is approximately 97%. The optimum applied potential for Cd recovery is in the range -1100 to -1120 mV. The current efficiency for Cd recovery is 70–90%. The rate of Cd recovery increases when the electrochemical system is under convection conditions. It has been shown that a porous carbon electrode can be used for the Cd recovery process in preference to a flat Cu electrode. With the carbon electrode, the recovery rate of Cd can be increased by more than 50%.

Acknowledgements

References

[1] C.A. Nogueira, F. Delmas, Hydrometallurgy 52 (1999) 267–287.
[2] B. Mauro, B. Gaetano, B. Stefania, M.F. Pier, J. Power Source 55 (1995) 247–250.
[3] Z. Pingwei, Y. Toshiro, I. Osamu, M. Yo-shito, M.S. Toshishige, I. Katsutoshi, Hydrometallurgy 50 (1998) 61–65.
[4] J. David, J. Power Sources 57 (1995) 71–73.
[5] Z. Pingwei, Y. Toshiro, I. Osamu, M. Yo-shito, M.S. Toshishige, I. Katsutoshi, J. Power Sources 77 (1995) 116–122.
[6] Z. Pingwei, Y. Toshiro, I. Osamu, M. Yo-shito, M.S. Toshishige, I. Katsutoshi, Hydrometallurgy 47 (1998) 259–271.
[7] X. Zhihual, H. Zongling, Y. Naiyi, C. Shouyo, Sep. Sci. Technol. 27 (2) (1992) 213–221.
[8] J. David, J. Power Sources 57 (1995) 71–73.
[9] F. Putois, J. Power Sources 57 (1995) 67–70.
[10] F. Siegmund, S. Dirk, J. Power Sources 57 (1995) 27–30.
[11] S. Panero, C. Romoli, M. Achilli, E. Cardarelli, B. Scrosati, J. Power Sources 57 (1995) 9–12.
[12] L. Oliver, J. Power Sources 57 (1995) 3–7.
[13] J.W. Lyman, G.R. Palmer, in: Proceedings of the Electrochemical Society, vols. 27–94, 1994.
[14] C.C. Yang, H.Y. Cheh, J. Electrochem. Soc. 142 (1995) 3034.
[15] C.C. Yang, H.Y. Cheh, J. Electrochem. Soc. 142 (1995) 3040.