Formation of Cadmium Chlorides via Cadmium Dissolution in Chloride Melts

V. F. Kozin and A. A. Omel'chuk

Institute of General and Inorganic Chemistry, National Academy of Sciences of Ukraine, pr. Akademika Palladina 32/34, Kiev, 03142 Ukraine

e-mail: omelchuk@ionc.kar.net Received June 2, 2005

Abstract—The kinetics and mechanism of the formation of complex Cd(I) ions via the reaction of metallic cadmium with Cd^{2+} ions in the Cd^0 – $CdCl_2$ – $ZnCl_2$ – NH_4Cl system are studied spectroscopically. The formation of

 Cd_2^{2+} and Cd_2^{3+} is evidenced by absorption bands around 270 and 335 nm, respectively, in the electronic spectrum of the melt. The anode current efficiency is determined for cadmium electrorefining in a chloride melt. A mechanism is proposed for the anodic dissolution of cadmium at different current densities and process temperatures.

DOI: 10.1134/S0020168506010158

INTRODUCTION

High-purity cadmium is one of the starting materials for the synthesis of II-VI compound semiconductors [1, 2] and CdTe–CdS, $Cd_{1-x}Zn_xTe$, and $Cd_xHg_{1-x-y}Zn_yTe$ solid solutions [3–5], which find application in opto- and microelectronics. In addition, high-purity cadmium is used in the fabrication of lightemitting diodes [6], solar cells [7, 8], and detectors based on the wide-gap semiconductors CdTe and CdZnTe for radiation monitoring at nuclear power plants [9]. CdTe/CdS p-n junctions and CdTe are used in high-efficiency solar energy conversion and storage applications [10, 11]. Ultrapure cadmium possesses a large capture cross section for thermal neutrons and is used to fabricate neutron-absorbing control rods for nuclear reactors [12]. The physicochemical properties of cadmium are attractive for nuclear power engineering applications, in particular for recovering and refining spent nuclear fuel in molten salt systems [13, 14].

The steady growth in the world market for highpurity cadmium in recent years entails ever more stringent requirements on cadmium purity and a need for a significant cadmium production scale-up.

High-purity cadmium can be prepared using a variety of methods and approaches, of which the most widespread are electrolysis with the use of solid electrodes [15], distillation followed by zone melting [16], and zone refining in flowing hydrogen [17]. In most instances, the purity of the resulting cadmium does not meet semiconductor industry's requirements. Only by combining several refining processes can high-purity cadmium be obtained. At present, new refining methods are being developed in order to enhance the purification efficiency, reduce the number of consecutive steps, and increase the number of elements that can be removed in a single process. One such method is electrolysis in molten electrolytes [18]. Electrode processes in molten electrolytes involve subvalent cadmium compounds [19]. For this reason, detailed information about the state of cadmium ions in electrode layers is crucial for the ability to control such processes.

Chemical equilibria in the systems $Cd^0-CdHal_2$ (Hal = Cl⁻, Br⁻, I⁻) have been studied extensively (see, e.g., [20, 21]). Metal dissolution was shown to be accompanied by changes in the anion component of the salt and process temperature [20, 21]. In particular, the equilibrium Cd⁺ concentration is 21.0 mol % in the Cd⁰-CdCl₂ system at 800°C, 20 mol % in the Cd⁰-CdI₂ system at 700°C, and 15 mol % in the Cd⁰-CdI₂ system at 700°C [17].

Taking into account Cd⁺ dimerization, the formation of subvalent cadmium compounds, and the presence of Cd⁺, Cd²⁺, Cd²⁺, Cd³⁺, and finely dispersed cadmium metal in the Cd⁰–CdHal₂ systems, it is of interest to monitor the anode current efficiency in the process of cadmium dissolution.

Molten cadmium is known to react with cadmium halides to form subvalent cadmium compounds [20–28] according to the scheme

$$Cd^0 + CdHal_2 \longrightarrow 2CdHal,$$
 (1)

where $Hal = Cl^{-}$, Br^{-} , or I^{-} .



Fig. 1. Time variation of the intensity of absorption bands in the electronic spectra of Cd⁰–CdCl₂–ZnCl₂–NH₄Cl melts.

In this paper, we describe the formation of cadmium subchlorides via the reaction of cadmium with Cd²⁺containing melts.

EXPERIMENTAL

In our preparations, we used extrapure-grade salts, which were purified further and carefully dehydrated. Purified anhydrous CdCl₂ was prepared by passing hydrogen chloride through molten cadmium at 650-750°C. Chemical analysis for impurities showed that the resultant cadmium chloride contained Al 5×10^{-5} , Bi 2.6×10^{-4} , Fe 3.3×10^{-4} , In 1.3×10^{-4} , Co 2.0×10^{-4} , Mn 7.4 × 10⁻⁴, Cu 2.3 × 10⁻⁵, Ni 1.4 × 10⁻⁵, Pb 1.7 × 10^{-5} , Sb 2.8 × 10^{-4} , Tl 1.5 × 10^{-4} , and Zn 2.0 × 10^{-4} wt %.

Prior to electrolysis, the electrolyte was held in contact with extrapure-grade (99.9999%) cadmium metal at 600°C for 3 h in order to saturate it with subchlorides:

$$CdCl_2 + Cd^0 = Cd_2Cl_2.$$
(2)

The resultant melt was dark pink.

To elucidate the mechanism and follow the kinetics of the formation of intermediate cadmium compounds, we used spectrophotometry (Specord UV-VIS instrument). The melt was enclosed in a leak-tight quartz cuvette with plane-parallel windows and a 1-cm optical path. The kinetics of Cd⁺ formation were evaluated by monitoring the absorbance of the melt of known com-

position in which a cadmium plate 2 cm² in area had been immersed. The light beam was passed along the surface of the cadmium plate. The absorbance of the melt in the cuvette was taken into account using a solution of the same composition in a reference cuvette. To reduce the electrolysis temperature, cadmium chloride was dissolved in the 45 wt % ZnCl₂ + 55 wt % NH₄Cl eutectic [29], which melts at 180°C.

RESULTS AND DISCUSSION

Cadmium is a transition metal with the $4d^{10}5s^2$ outer shell configuration. It has a tendency to form metalmetal bonds stable in melts [24]. In earlier studies [25, 26], pulse radiolysis in aqueous solutions made it possible to identify a monovalent cadmium compound, which had a strong absorption band at 295 nm.

In molten salts, the equilibrium of reaction (1) in the Cd^{0} – $CdCl_{2}$ system is shifted to the right [22, 27, 28]. To identify the intermediate compounds in the reaction system under consideration, it is reasonable, in our opinion, to use spectrophotometry.

Figure 1 illustrates the time variation of the intensity of absorption bands in the electronic spectra of Cd⁰-CdCl₂–ZnCl₂–NH₄Cl melts. The lowermost spectrum was recorded 1 min after the cadmium plate had been immersed in the melt, and the other spectra were taken at 2-min intervals.

As seen in Fig. 1, the introduction of a cadmium plate into the melt gives rise to a strong absorption peaked near 270 nm. Owing to the fast rate of reaction (1) and the shift of equilibrium to the right, the Cd²⁺ concentration in the melts studied was 5.0 mmol/cm³.

As shown earlier using pulse radiolysis [25], the Cd⁺ intermediate is a highly reactive species which tends to dimerize:

$$Cd^+ + Cd^+ \rightleftharpoons Cd_2^{2+}$$
. (3)

The formation of the Cd_2^{2+} dimer, a more stable species, is responsible for the strong absorption band around 270 nm (Fig. 1). The shift of equilibrium to the right increases the lifetime of the Cd_2^{2+} ion, in accordance with the results reported by Borresen *et al.* [30].

The absorption spectra in Fig. 1 show a shoulder at about 335 nm, which may be due to the reaction

$$Cd^{+} + Cd^{2+} = Cd_2^{3+}$$
. (4)

According to Ershov [31], in concentrated aqueous solutions Cd^+ reacts with Cd^{2+} to form Cd_2^{3+} clusters. Note that, in the spectral range corresponding to the formation of Cd_2^{2+} and Cd_2^{3+} cations, the absorbance of the reaction mixture as a function of Cd_m^{x+} content

76

INORGANIC MATERIALS No. 1 Vol. 42 2006 obeys the Bouguer–Lambert–Beer law (Fig. 2). This finding suggests that, measuring the absorbance as a function of time, one can spectroscopically follow the kinetics of Cd_2^{2+} and Cd_2^{3+} formation according to schemes (3) and (4).

Let A_0 be the absorbance of the reaction mixture at the instant in time when equilibrium (3) set in, A_{τ} be the absorbance at time τ , and A_{∞} be the absorbance after a time sufficiently long for the complete transition of cadmium ions from one oxidation state to another. The difference $A_{\tau} - A_{\infty}$ is then proportional to the Cd⁺ concentration at time τ , and $A_0 - A_{\infty}$ is proportional to that at the beginning of the measurements. Under the assumption that equilibrium (3) is described by a firstorder rate law, the equilibrium concentration of monovalent cadmium compounds in the reaction system can be represented by the equation

$$(A_{\tau} - A_{\infty}) = (A_0 - A_{\infty})\exp(-k\tau)$$
(5)

or

$$\log(A_{\tau} - A_{\infty}) = \log(A_0 - A_{\infty}) - k\tau/2.303, \qquad (6)$$

where *k* is the rate constant for the formation of the corresponding compound. The plot of $\log(A_{\tau} - A_{\infty})$ versus τ will then give a straight line with a slope *k*/2.303.

Analysis of the present data indicates that, in the case of Cd_2^{2+} and Cd_2^{3+} formation, the variation in the absorbance of the reaction mixture is well represented by Eq. (6) (Fig. 3).

The rate constants for the formation of the Cd_2^{2+} and Cd_2^{3+} complex cations evaluated from the slope of lines *l* and *2* in Fig. 3 are 4.22×10^{-3} and 3.50×10^{-3} s, respectively. Thus, our experimental data provide clear evidence that cadmium reacts with molten $CdCl_2$ to form Cd_2^{2+} and Cd_2^{3+} .

Figure 4a shows the anode current efficiency as a function of current density *j* for the anodic cadmium dissolution. The current efficiency of cadmium dissolution rises from 100% at *j* = 0.05 A/cm² to 124% at *j* = 1.0 A/cm², which is associated with side reactions and the participation of Cd⁺ ions in electrode processes. In the range of current densities 0.05–0.2 A/cm², the current efficiency is close to the value predicted theoretically for Cd²⁺ compounds:

$$Cd^0 = Cd^{2+} + 2e^{-}.$$
 (7)

The observed tendency for the current efficiency to rise with increasing current density is due to the formation of subvalent cadmium compounds. The same is evidenced by the observed changes in the color of the melt. Therefore, increasing the current density leads, in

INORGANIC MATERIALS Vol. 42 No. 1 2006



Fig. 2. Absorbance of Cd^0 – $CdCl_2$ – $ZnCl_2$ – NH_4Cl melts as a function of (a) Cd_2^{2+} and (b) Cd_2^{3+} concentrations upon the formation of the corresponding complex cations.



Fig. 3. Semilog plots of absorbance vs. time for Cd^{0} – $CdCl_{2}$ – $ZnCl_{2}$ – $NH_{4}Cl$ melts upon the formation of (1) Cd_{2}^{2+} and (2) Cd_{2}^{3+} complex cations.

addition to the formation of stable Cd²⁺ ions, to the formation of subvalent cadmium compounds:

$$Cd^0 = Cd^+ + e^-.$$
 (8)

The stability of these compounds is enhanced owing to



Fig. 4. Current efficiency as a function of (a) current density at 600° C and (b) electrolysis temperature at a current density of 0.2 A/cm² for the anodic dissolution of cadmium.

the dimerization reaction (3), which ensures the formation of an unshared pair of 5*s* electrons [20]. The dimeric ions forming by reaction (3) undergo electro-

Characteristics of cadmium dissolution in a cadmium chloride electrolyte at 600° C

0.051.4792.0952.000.13.0202.1371.9620.26.1602.1791.925	Current density, A/cm ²	Amount of Cd dissolved at the anode, g	Anode current efficiency, g/(A h)	Oxidation state of cadmium resulting from anodic dissolution
0.13.0202.1371.9620.26.1602.1791.925	0.05	1.479	2.095	2.00
0.2 6.160 2.179 1.925	0.1	3.020	2.137	1.962
	0.2	6.160	2.179	1.925
0.4 13.032 2.306 1.819	0.4	13.032	2.306	1.819
0.6 20.430 2.409 1.741	0.6	20.430	2.409	1.741
0.8 28.430 2.515 1.667	0.8	28.430	2.515	1.667
1.0 36.724 2.599 1.614	1.0	36.724	2.599	1.614

chemical oxidation,

$$Cd_2^{2+} - e = 2Cd^{2+}$$
 (9)

followed by the chemical reaction

$$Cd^+ + Cd^+ \iff Cd_2^{2+} \iff Cd^0 + Cd^{2+}.$$
 (10)

Increasing the current density favors the reaction

$$Cd^{+} + Cd^{2+} \longrightarrow Cd_{2}^{3+}.$$
 (11)

Convincing evidence for the formation of the paramagnetic dimeric ion Cd_2^{3+} was provided in an ESR study by Eachus and Symons [32]. The Cd_2^{3+} ion is stabilized owing to the bonding between two metal ions via an electron in a σ -orbital. As pointed out by Aleksandrov *et al.* [33], an insignificant axial anisotropy of the *g*-factor and an only slight deviation of *g* from 2.00 point to a small contribution of the *p* and *d* orbitals to the σ molecular orbital.

As the temperature is raised, the current efficiency of the anodic dissolution of cadmium increases. As shown above, increasing the temperature drives the equilibrium in reaction (1) toward the formation of Cd⁺ ions, in accordance with earlier results [22, 27, 28]. Figure 4b shows a typical plot of the anode current efficiency versus temperature for chloride electrolytes at j = 0.2 A/cm².

The high current efficiency of the anodic dissolution of cadmium indicates that the electrolyte contains cadmium ions in different oxidation states. We evaluated the average oxidation state of cadmium from the reduction in the amount of cadmium on the anode under different electrolysis conditions using the formula n = $A/(26.8\eta)$, where η is the current yield of the anodic dissolution of cadmium, g/(A h), and A is the atomic weight of cadmium. The results are presented in the table. The average oxidation state of the cadmium resulting from anodic dissolution is seen to depend on the electrolysis conditions and to be below 2. At i = 0.05 A/cm^2 , the oxidation state of cadmium is 2+, which confirms that the electrode process involves two electrons. With increasing current density, the oxidation state of cadmium decreases, which attests to the formation of subvalent cadmium compounds by reactions (3), (4), and (10).

CONCLUSIONS

The kinetics and mechanism of the formation of subvalent cadmium complexes in the Cd^0-CdCl_2- ZnCl₂-NH₄Cl system were studied spectroscopically.

INORGANIC MATERIALS Vol. 42 No. 1 2006

The results indicate that metallic cadmium reacts with Cd^{2+} ions in the melt to form Cd_2^{2+} and Cd_2^{3+} complex cations. The formation of Cd_2^{2+} and Cd_2^{3+} is evidenced by the absorption bands around 270 and 335 nm, respectively, in the electronic spectrum of the melt.

The variation of the intensity of absorption bands during the reaction between Cd^{2+} and metallic cadmium was used to evaluate the kinetics of Cd_2^{2+} and Cd_2^{3+} formation. The rate constants for the formation of the Cd_2^{2+} and Cd_2^{3+} complex cations evaluated from the slope of the plot of $\log(A_0 - A_\infty)$ versus time are 4.22×10^{-3} and 3.5×10^{-3} s⁻¹, respectively.

The effect of the electrolysis conditions on the rate of cadmium exchange between the electrodes was examined. The anode current efficiency of cadmium dissolution was found to increase with current density and temperature and to exceed the theoretically predicted value, which was attributed to the formation of subvalent cadmium compounds.

The present results may be helpful in assessing parameters of cadmium electrorefining.

REFERENCES

- Abrikosov, N.Kh., Bankina, V.F., Poretskaya, L.V., et al., Poluprovodnikovye soedineniya, ikh poluchenie i svoistva. Khal'kogenidy elementov II, IV i V grupp Periodicheskoi sistemy (Preparation and Properties of Compound Semiconductors: Chalcogenides of Group II, IV, and V Elements), Moscow: Nauka, 1967.
- Poluprovodnikovye veshchestva. Voprosy khimicheskoi svyazi (Chemical Bonding Aspects of Semiconductors), Zhuze, V.P., Ed., Moscow: Nauka, 1960.
- Rakhshani, A.E., Heterojunction Properties of Electrodeposited CdTe/CdS Solar Cells, *J. Appl. Phys.*, 2001, vol. 90, no. 8, pp. 4265–4271.
- Atroshchenko, L.V., Galkin, S.V., and Galchinetskii, L.P., Crystals Cd_{1-x}Zn_xTe—A Promising Material for Noncryogenic Semiconductor Detectors: Preparations, Structure Defectness, and Electrophysical Properties, *Semicond. Phys. Quantum Electron. Optoelectron.*, 1999, vol. 2, no. 4, pp. 81–85.
- Belov, A.G. and Denisov, I.A., Optical Properties of Semiconductor Solid Solutions, *Izv. Vyssh. Uchebn. Zaved., Mater. Elektron. Tekh.*, 2001, no. 4, pp. 62–66.
- Che Song-Bek, Nomura Ichirou, and Takada Tomoyuki, Growth and Characterization of ZnCdSe/BeZnTe II–VI Compound Type-II Superlattices on InP Substrates and Their Application of Visible Light Emitting Devices, *Jpn. J. Appl. Phys., Part 1*, 2001, vol. 40, no. 12, pp. 6747–6752.
- Okamoto Tamotsu, Kitamoto Shinji, and Yamada Akira, Native Defect Control of CdTe Thin Film Solar Cells by Close-Spaced Sublimation, *Jpn. J. Appl. Phys., Part 1*, 2001, vol. 40, no. 5, pp. 3089–3092.

INORGANIC MATERIALS Vol. 42 No. 1 2006

- El Assali, K., Boustani, M., and Khiaza, A., Some Structural and Optical Properties of CdS Thin Films Prepared by RF Sputtering, *Phys. Status Solidi A*, 2000, vol. 178, no. 2, pp. 701–708.
- Azhazha, V.M., Kutnii, V.E., and Rybka, A.V., Application of Detectors Based on the Wide-Gap Semiconductors CdTe, CdZnTe, and GaAs in Radiation Monitoring at Nuclear Power Plants, *At. Energ.*, 2002, vol. 92, no. 6, pp. 473–476.
- Mackowski, S., Smith, L.M., and Jackson, H.E., Optical Properties of Annealed CdTe Self-assembled Quantum Dots, *Appl. Phys. Lett.*, 2003, vol. 83, no. 2, pp. 254–256.
- Zhou, S.M., Feng, Y.S., and Zhang, L.D., Growth and Optical Characterization of Large-Scale Crystal Cd_xZn_{1-x}S Whiskers via Vapor Reaction, *J. Cryst. Growth*, 2003, vol. 252, nos. 1–3, pp. 1–3.
- 12. Cook, M.E., Cadmium, Met. Miner. Annu. Rev., 1992, vol. 20, no. 1, pp. 87–88.
- 13. Kobayashi, T., Fujita, R., and Nakamura, H., Electrorefining Experiments to Recover Uranium with a Cadmium Lithium Anode and Their Theoretical Evaluation, *J. Nucl. Sci. Technol.*, 1999, vol. 36, no. 3, pp. 283–296.
- Li, S.X., Sofu, T., Johnson, T.A., and Wigeland, R.A., Experimental Observations on Electrorefining Spent Nuclear Fuel in Molten LiCl–KCl/Liquid Cadmium System, *J. New Mater. Electrochem. Syst.*, 2000, vol. 3, no. 3, pp. 259–268.
- 15. Kozin, L.F. and Marochevskii, A.G., Preparation of High-Purity Metals by Reaction Electrolysis, *Zh. Prikl. Khim.* (Leningrad), 1990, vol. 63, no. 9, pp. 1913–1926.
- Zudov, V.G. and Aleksandrov, B.N., Behavior of Impurities in Cadmium during Vacuum Distillation, *Izv. Akad. Nauk SSSR, Met.*, 1974, no. 1, pp. 43–47.
- Kalashnik, O.N., Movshits, B.I., and Petrenko, V.R., Optimization of Zone Refining of Cadmium in Flowing Hydrogen, *Izv. Vyssh. Uchebn. Zaved.*, *Tsvetn. Metall.*, 1987, no. 5, pp. 49–52.
- Kozin, V.F. and Omel'chuk, A.A., Cadmium Refining in Chloride Melts using a Bipolar-Electrode Electrolyzer, *Neorg. Mater.*, 2002, vol. 38, no. 3, pp. 270–275 [*Inorg. Mater.* (Engl. Transl.), vol. 38, no. 3, pp. 207–211].
- Heusler, K.E. and Gaiser, L., The Mechanism of the Cadmium Electrode, J. Electrochem. Soc., 1970, vol. 117, no. 6, pp. 762–767.
- Ukshe, E.A. and Bukun, N.G., Dissolution of Metals in Halide Melts, Usp. Khim., 1961, vol. 30, no. 2, pp. 243–273.
- Heymann, E., Martin, R.J.L., and Mulcahy, M.F.R., Distribution Equilibria between Molten Metals and Molten Salts, with Reference to the Stability of Intermetallic Compounds in the Molten State, *J. Phys. Chem.*, 1943, vol. 47, no. 1, pp. 473–484.
- 22. Emons, H.H., Uder das Verhalten von Metallen in ihren geschmolzenen Salzen, *Chem. Zvesti*, 1974, vol. 28, no. 4, pp. 433–446.
- Spravochnik po plavkosti sistem iz bezvodnykh neorganicheskikh solei (Melting Relations in Anhydrous Inorganic Salt Systems: A Handbook), Voskresenskaya, N.K., Ed., Moscow: Metallurgiya, 1961, vol. 1, p. 845.

- 24. Cotton, F.A. and Wilkinson, G., Advanced Inorganic Chemistry, New York: Wiley, 1966, vol. 2. Translated under the title Sovremennaya neorganicheskaya khimiya, Moscow: Mir, 1969.
- Ershov, B.G., Metal Ions in Unusual and Unstable Oxidation States in Aqueous Solutions: Preparation and Properties, Usp. Khim., 1997, vol. 66, no. 2, pp. 103–116.
- Ershov, B.G., Atoms in Unusual Oxidation States and Small Metal Clusters in Aqueous Solutions, *Zh. Neorg. Khim.*, 2002, vol. 47, no. 4, pp. 644–653.
- Urazov, G.G. and Karnaukhov, A.S., On the Solubility of Metals in Their Chlorides, *Dokl. Akad. Nauk SSSR*, 1954, vol. 96, no. 3, pp. 535–538.
- Rodionov, Yu.I. and Klokman, V.R., Cadmium Solubility in CdCl₂–ZnCl₂ Melts, *Radiokhimiya*, 1966, vol. 8, no. 1, pp. 59–63.
- 29. Meyerstein, D. and Mulac, W.A., Reductions by Monovalent Zinc, Cadmium, and Nickel Cations, *J. Phys. Chem.*, 1968, vol. 72, no. 3, pp. 784–788.

- Borresen, B., Voyiatzis, G.A., and Papatheodorou, G.N., The Cd₂²⁺ in Molten Halides and at Electrode Interfaces, *Phys. Chem. Chem. Phys.*, 1999, vol. 1, no. 14, pp. 3309–3314.
- Ershov, B.G., Metal Ions in Unusual and Unstable Oxidation States and Electrochemical Reaction Stages, *Usp. Khim.*, 1981, vol. 50, pp. 2137–2166.
- Eachus, R.S. and Symons, M.C.R., Unstable Intermediates: Part XXIX. An Electron Spin Resonance Investigation of the [Ag–Cd]²⁺ and Cd₂³⁺ Diatomic Cations, *J. Chem. Soc. A*, 1970, no. 18, pp. 3080–3084.
- 33. Aleksandrov, A.I., Ershov, B.G., Pikaev, A.K., and Spitsyn, V.I., Electron Spin Resonance Spectra of Irradiated Frozen Aqueous Solutions: 15. Aqueous Solutions of Cadmium and Mercury Salts, *Izv. Akad. Nauk SSSR*, *Ser. Khim.*, 1976, no. 2, pp. 249–256.