MECHANISM OF CADMIUM DEPOSITION FROM AN ACIDIC CHLOROALUMINATE MELT

Rajeeva R. Agarwal
Department of Chemical Engineering
University of Connecticut
Storrs, CT 06269

ABSTRACT

Cyclic voltammetry was applied to study cadmium deposition on nickel from purified AlCl₃-NaCl-BaCl₂ (Eut., 50°C) containing 2.1 and 4.25 wt.% CdCl₂. Both diffusion and adsorption peaks formed between 1-1000 mV/s and 95-175°C. Whereas cadmium deposition gave three peaks, its dissolution involved three to five peaks. Based on the formation of Cd²⁺ and Cd₂⁺ ions in chloroaluminate melts, a mechanism involving step-wise electrochemical reactions, intermediates, adsorption, disproportionation, and lattice incorporation is deduced for cadmium deposition.

INTRODUCTION

Molten solutions of cadmium chloride in aluminum chloride or chloroaluminates (AlCl₃ melts) form the complexes, Cd(AlCl₄)₂ and Cd₂(AlCl₄)₂ (1-2). Acidic melts (> 50 mole % AlCl₃) stabilize the cadmium subhalide as Cd₂(AlCl₄)₂ (2). During cadmium deposition from such melts, one expects to note the above and the overall chemical (3) and electrochemical reactions (4-5). In this work (6), (in mole percent) 63.5 AlCl₃-34 NaCl-2.5 BaCl₂ (mp= 50°C) (7) containing (in weight percent) 2.1 and 4.25 CdCl₂ was studied between 95-175°C under a helium atmosphere.

EXPERIMENTAL

Cadmium electrochemistry was studied in the following electrochemical cell:

Cd/ AlCl₃-NaCl-BaCl₂ (Eut.), CdCl₂/ Ni
where an excess 8.8 wt.% AlCl₃ was added. The melt was purified by constant potential electrolysis between aluminum electrodes, and then CdCl₂ (99.995%) was added to the chloroaluminate melt. A cadmium (99.998%) counter electrode was used, and the working electrode consisted of a 5 mm dia. nickel disc electrode in teflon. The working electrode was replaceable between the experiments.

The electrolyte was contained inside a thick-walled pyrolytic coated graphite crucible. A well-fitted teflon cover carried the electrodes and a chromel-alumel thermocouple. The nickel working electrode was typically polished to 0.05 microns. The actual melting point of the melt varied from 66 to 83°C.

Cadmium deposition and dissolution was studied by cyclic voltammetry in 2.1 and 4.25 wt.% CdCl₂ solutions. Experiments were carried out at 1-1000 mV/s and at constant temperatures between 95-175°C. Typically, potentials were first scanned between nickel dissolution and aluminum deposition. Then cadmium peaks were individually separated from these and the background peaks. All potential scans were carried out after steady-state rest potentials were achieved.

RESULTS AND DISCUSSION

Figure 1 shows the cyclic voltammetric cadmium peaks soon after the addition of CdCl₂ (2.1% by wt.) to the melt, at 100 mV/s and 172°C. Peaks 1-2-3 and 1'-2'-3' appeared during cadmium deposition and dissolution, respectively. With an increase in the scan rate (1000 mV/s), 3' decreased, 2' increased and became symmetrical, and the apparent peak current ratio ip₂'/ip₃ >1. At lower temperatures, peaks were smaller (lower fluxes) and 3' appeared at smaller scan rates (20 mV/s). In 4.25% CdCl₂, the ratio ip₂'/ip₃ reduced to <1 as the scan rate was decreased from 1000 to 100 mV/s at 170-119°C. Based on the redox potential range, it was concluded that 1-1' was the Cd²⁺/Cd²⁺⁺ couple; 2-2' and 3-3' were due to the cadmium monolayer and its bulk deposition-dissolution, respectively.

Further, in 4.25% CdCl₂ melt the peak currents 3-3' increased but 1 remained about the same. Moreover, the E_eq. became more cathodic, the concentration overpotentials (E_p-E_eq.) for 1 decreased and for 1' increased. Thus, the Cd²⁺⁺ ions appeared
to stabilize when Cd\(^{2+}\) ions were added. This was an indication of complexation. Also, 1' became symmetrical and was composed of a pair of pre and post peaks.

Figure 2 shows the CV in 2.1% CdCl\(_2\) melt at 1 and 4 mV/s and 119°C. At low scan rates (1-10 mV/s), resolution of peaks 2-2' was weak, thus other peaks could be studied. The peak current of 1 was diffusion limited, but "z" based on \(E_p - E_{p/2}\) increased from 2 to 2.8 between 172-118°C. Further, peak 3 was diffusion limited with z=1 \([8]\) and only 72-78% of the cadmium was recovered in peak 3' at 118°C. Finally, the peak current of 3' varied with scan rate according to the product-adsorbed CV theory \([9]\).

In 4.25% CdCl\(_2\) melt, the peak currents and potentials for 3 showed quasi-reversible form between 2-100 mV/s (the effect of convection became apparent at 1 mV/s and at the higher temperature) and 170-120°C. But \(ip/v^{1/2}\) decayed with an increase in scan rate \([10]\), which indicated disproportionation at the cadmium surface during slow scan rates. Also, as expected from the disproportionation reaction, there was an excess of dissolved cadmium in the melt.

From the above studies, a mechanism for cadmium deposition from an acidic chloroaluminate melt would be expected to involve step-wise electrochemical reactions, adsorption, disproportionation, and lattice incorporation steps. This is described below:

\[
\begin{align*}
\text{Cd}^{2+} + e^- &\rightarrow \text{Cd}^+ \quad \text{(ad)} \quad [1] \\
2\text{Cd}^+ \quad \text{(ad)} &\rightarrow \text{Cd}^{2+} \quad [2] \\
\text{Cd}^+ \quad \text{(ad)} + e^- &\rightarrow \text{Cd} \quad \text{(ad)} \quad [3] \\
\text{Cd}^{2+} + e^- &\rightarrow \text{Cd}^+ \quad \text{(ad)} \quad [4] \\
\text{Cd}^+ &\rightarrow \text{Cd} \quad \text{(ad)} + \text{Cd}^+ \quad \text{(ad)} \quad [5] \\
\text{Cd} \quad \text{(ad)} &\rightarrow \text{Cd} \quad \text{(incorp.)} \quad [6] \\
\text{Cd}^{2+} + \text{Cd} &\rightarrow \text{Cd}^{2+} \quad [7]
\end{align*}
\]

Further, one would expect that the cadmium adsorption, surface diffusion, and lattice incorporation are affected by temperature and substrate.
SUMMARY

The deposition and dissolution of cadmium was studied from a new acidic chloroaluminate melt, AlCl₃-NaCl-BaCl₂ (Eut., 50°C) containing 2.1 and 4.25 wt.% CdCl₂, by cyclic voltammetry on nickel electrode and against the cadmium reference. Multiple diffusion and adsorption peaks formed between 1-1000 mV/s and 95-175°C. Based on the formation of Cd²⁺ and Cd₂⁺ ions in the chloroaluminates, a step-by-step mechanism is deduced for the cadmium "deposition" onto nickel from the cyclic voltammograms obtained.

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REFERENCES

1. J. D. Corbett, W. J. Burkhard, and L. F. Druding, J. Am. Chem. Soc., 83, 76, (1961).

2. J. D. Corbett, and R. K. McMullan, J. Am. Chem. Soc., 78, 2906, (1956).

3. K. Grjotheim, F. Gronvold, and J. Krogh-Moe, J. Am. Chem. Soc., 77, 5824, (1955).

4. T. C. F. Munday and J. D. Corbett, Inorg. Chem., 5, 1263, (1966).

5. D. A. Hames and J. A. Plambeck, Can. J. of Chem., 46, 1727, (1968).

6. R. R. Agarwal, "Electrodeposition, Nucleation, and Film Formation of Cadmium from a Low Melting Molten Salt", PhD Preliminary Thesis, Illinois Institute of Technology, Chicago, Illinois, (1988).
7. G. J. Janz, R. P. T. Tomkins, and C. B. Allen, "Physical Properties Data Compilations Relevant to Energy Storage I. Molten Salt: Eutectic Data." Report NSRDS-NBS 61, Part 1, (1978).

8. G. Mamantov, D. L. Manning, and J. M. Dale, J. Electroanal. Chem., 9, 253, (1965).

9. R. H. Wopschall and I. Shain, Anal. Chem., 39, 1514, (1967).

10. R. S. Nicholson and I. Shain, Anal. Chem., 36, 706, (1964).
Figure 1. Cyclic voltammogram after the addition of CdCl₂ (2.1 Wt.%) to purified AlCl₃-NaCl-BaCl₂ (Eut., 50°C) melt containing 8.8 Wt.% excess AlCl₃, at 100 mV/s and 172°C on nickel (0.306 cm²), against a cadmium reference. Peaks 1-2-3 and 1’-2’-3’ appeared during cadmium deposition and dissolution respectively.

Figure 2. Cyclic voltammogram in purified AlCl₃-NaCl-BaCl₂ (Eut., 50°C), CdCl₂ (2.1 Wt.%) melt containing 8.8 Wt.% excess AlCl₃, at 1 mV/s and 4 mV/s, and 119°C on nickel (0.306 cm²), against a cadmium reference. Peaks 1-2-3 and 1’-3’ formed during cadmium deposition and dissolution respectively.