

Polarography of Cadmium & Selenium in Cadmium Selenide

G SEETHA RAMA RAO & S JAYARAMA REDDY*

Department of Chemistry,

Sri Venkateswara University, Tirupati 517 502

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The electrochemical reduction of semiconductor grade cadmium selenide at the dropping mercury electrode has been studied in various aqueous supporting electrolytes. Both $\text{Cd}(2+)$ and $\text{Se}(4+)$ undergo reduction in almost all the media employed. The n and αn , values, diffusion coefficients and heterogeneous rate constants obtained are reported. The experimental results are utilised to evaluate the stoichiometry of cadmium selenide thin films.

The electrochemical properties of $\text{Se}(4+)$ and $\text{Cd}(2+)$ in the presence of one another and the analysis of thin films of cadmium selenide obtained on glass substrate by vacuum evaporation technique, were studied by us earlier^{1,2} employing chronoamperometry¹ and cyclic voltammetry². The results of similar studies using d.c. polarography are reported in this note.

Aqueous solutions of 1.0 *M* hydrochloric acid, 1.0 *M* potassium chloride, 0.1 *M* potassium iodide, saturated tartaric acid (STA) and 0.1 *M* potassium iodide saturated with tartaric acid (0.1 *M* KISTA) were used as supporting electrolytes in the present study.

A multipurpose electrochemical module (model 370, Princeton Applied Research Corporation, USA) was used to record the polarograms, with dropping mercury electrode (d.m.e.) as working, isolated platinum wire as auxiliary and saturated calomel (SCE) as reference electrodes. A high vacuum coating unit, (Hind, model 12A4) and a Philips X-ray diffractometer (model 1009) were employed for thin film preparation and to ascertain valence states of cadmium and selenium in solid state, respectively.

A semiconductor grade sample (99.99%) of cadmium selenide (Koch-light) was used for preparing stock solution^{1,2} and thin film formation. All other chemicals and solvents used were of AR grade. Doubly distilled mercury and water and purified nitrogen gas were employed in all the experiments.

Diffusion coefficients (D), n and αn , values and heterogeneous forward rate constants ($k_{f,r}^0$) were evaluated using standard methods³. The d.m.e. used had m values in the range of 1.665 to 2.732 mg s^{-1} for a t values of 2.0 to 5.0 s in 1.0 *M* potassium chloride. All polarograms were recorded at $28 \pm 0.1^\circ\text{C}$.

The experimental lattice parameter values ($a = 4.37 \text{ \AA}$ and $c = 7.09 \text{ \AA}$ of the cadmium selenide sample used

compare well with the theoretical values⁴ ($a = 4.71 \text{ \AA}$ and $c = 7.02 \text{ \AA}$), indicating the molecular formula to be CdSe . But selenide ion acquires more stable valence state of $(4+)$, as shown by the conventional qualitative tests, in the presence of strong oxidising agents which were added during solution preparation.

Cyclic voltammetric² and chronoamperometric¹ data of cadmium selenide indicated that $\text{Se}(4+)$ underwent a consecutive reduction as $\text{Se}(4+) \rightarrow \text{Se}(0) \xrightarrow{2} \text{Se}(-2)$. The step (1) being an ill-defined one occurs at a peak potential of about -0.4 V and the second step, a well-defined and totally irreversible step occurs at a peak potential of about -1.40 V (vs SCE). It was also observed that elemental selenium in step (1) got adsorbed and deposited on the electrode surface. The present d.c. polarographic results are in agreement with those obtained earlier^{1,2}. Under polarographic conditions, $\text{Cd}(2+)$ undergoes reduction in all the media employed, while $\text{Se}(4+)$ is reduced to selenide ion, in a well-defined form only in 1.0 *M* potassium chloride and 0.1 *M* potassium iodide. Figures 1 and 2 represent typical polarograms obtained for cadmium selenide reduction in a slightly basic medium (0.1 *M* potassium iodide, $p\text{H}$: 7.75) and in acid medium (1.0 *M* hydrochloric acid) respectively. In Fig. 1, the first wave

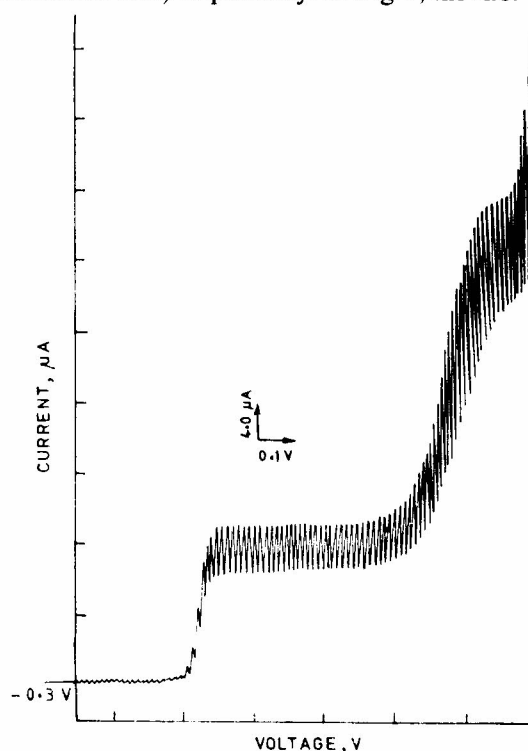


Fig. 1—Typical polarogram for the reduction of cadmium selenide in 0.1 *M* potassium iodide [$p\text{H} = 7.75$; conc. = 1.07 mM; and $t = 3.5 \text{ s}$]

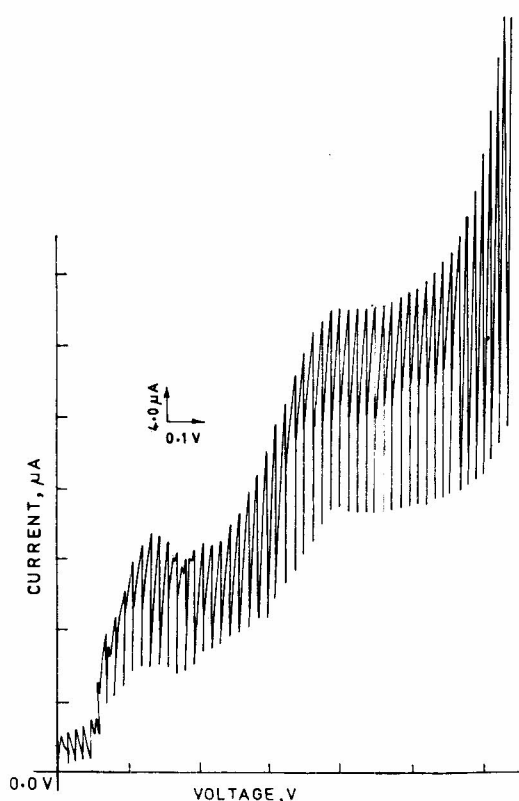


Fig. 2—Typical polarogram for the reduction of cadmium selenide in 1.0 *M* hydrochloric acid [Conc = 1.92 mM; *t* = 2.1 s]

occurring at a half-wave potential ($E_{1/2}$) of -0.65 V can be attributed to a two-electron reduction process $\text{Cd}(2+) \rightarrow \text{Cd}(0)$ and the second one at a $E_{1/2}$ of -1.35 V to $\text{Se}(4+) \rightarrow \text{Se}(-2)$. The fairly defined reduction wave between -0.1 and -0.3 V in Fig. 2 is

considered to be due to the reduction of $\text{Se}(4+) \rightarrow \text{Se}(0)$ and the second one between -0.4 and -0.8 V to $\text{Cd}(2+) \rightarrow \text{Cd}(0)$. The general mechanism of formation of elemental selenium involving a four-electron reduction in acid media and formation of selenide ion with a six-electron addition in neutral and alkaline media is thus observed in the present case. Typical values of half-wave potentials and diffusion currents for the reductions of $\text{Cd}(2+) \rightarrow \text{Cd}(0)$ and $\text{Se}(4+) \rightarrow \text{Se}(-2)$ in the various supporting electrolytes employed are presented in Table 1.

Though $\text{Cd}(2+)$ gets reduced in all the media employed, the reduction is reversible only in 0.1 *M* potassium iodide and 0.1 *M* KISTA, as revealed by Tokes' criterion. In the other media the reduction tends to be irreversible. The linear plot between i_d versus $\sqrt{h}$ passing through the origin suggests the reduction to be diffusion-controlled in all the supporting electrolytes studied. The irreversibility in the media other than 0.1 *M* potassium iodide and 0.1 *M* KISTA may be attributed to the reduction of $\text{Se}(4+) \rightarrow \text{Se}(0)$ preceding that of $\text{Cd}(2+)$. This may be due to the fact that elemental selenium gets adsorbed on the electrode surface thereby preventing the total reduction of $\text{Cd}(2+)$ and making the wave to start from more anodic potentials. Hence the difference between $E_{3/4}$ and $E_{1/4}$ becomes large and the process deviates from reversibility. But in the presence of iodide ion, the current-voltage curve is taken starting from -0.30 V since anodic currents are noticed upto -0.25 V. The step $\text{Se}(4+) \rightarrow \text{Se}(0)$ and in turn the adsorption of $\text{Se}(0)$ are absent, hence in 0.1 *M* potassium iodide and 0.1 *M* KISTA, the reduction of $\text{Cd}(2+) \rightarrow \text{Cd}(0)$ is reversible.

Table 1—Polarographic Characteristics of $\text{Cd}(2+)$ and $\text{Se}(4+)$ in Cadmium Selenide

Sl No.	Supporting electrolyte	$-E_{1/2}$ V vs SCE	i_d μA	αn_a	$D/\text{cm}^2 \text{ s}^{-1}$	$k_{f,m}^\circ/\text{cm s}^{-1}$
Cadmium (2+)						
1	1.0 <i>M</i> HCl (1.27 m <i>M</i>)	0.61	16.8	0.52	3.11×10^{-5}	1.59×10^{-6}
2	1.0 <i>M</i> KCl (1.62 m <i>M</i>)	0.64	26.0	0.65	4.60×10^{-5}	1.52×10^{-7}
3	0.1 <i>M</i> KI (1.07 m <i>M</i>)	0.65	17.2	+	2.36×10^{-5}	+
4	STA (1.48 m <i>M</i>)	0.52	7.2	0.35	4.14×10^{-6}	2.22×10^{-5}
5	0.1 <i>M</i> KISTA (1.05 m <i>M</i>)	0.60	4.1	+	3.02×10^{-6}	+
Selenium (4+)						
6	1.0 <i>M</i> KCl (0.86 m <i>M</i>) (1.70 m <i>M</i>)	1.35	35.2	0.54	1.72×10^{-5}	1.15×10^{-13}
		1.35	71.2	0.54	1.79×10^{-5}	1.17×10^{-13}
7	0.1 <i>M</i> KI (1.07 m <i>M</i>) (1.61 m <i>M</i>)	1.36	38.0	0.57	1.28×10^{-5}	2.19×10^{-14}
		1.36	53.2	0.57	1.12×10^{-5}	2.05×10^{-14}

+ Reversible behaviour

The heterogeneous forward rate constants calculated (see Table 1) in the other three media are in the range of 10^{-5} to $10^{-7} \text{ cm s}^{-1}$, indicating that the reduction just tends to irreversibility as the region for quasi-reversibility lies between 10^{-2} and $10^{-5} \text{ cm s}^{-1}$.

Since the step $\text{Se}(4+) \rightarrow \text{Se}(0)$ is observed in acid media in an ill-defined form, the well-defined reduction of $\text{Se}(4+) \rightarrow \text{Se}(-2)$ in neutral media has, therefore, been studied in detail. The diffusion-controlled nature of the reduction process is indicated by the linear plots of i_d versus $\sqrt{h}$ and i_d versus C , which pass through the origin. The non-applicability of Tokes' criterion proved the process to be irreversible as also seen from the xn_a and $k_{f,h}^0$ values (Table 1).

The diffusion coefficients for the reduction processes have been calculated using Ilkovic equation. The values obtained for $\text{Cd}(2+)$ are in good agreement with the literature value⁵ but in STA and 0.1 M KISTA, a marginal decrease is observed due to the high viscosity of the medium. The diffusion coefficient values for the reduction of $\text{Se}(4+) \rightarrow \text{Se}(-2)$ in 1.0 M potassium chloride and 0.1 M potassium iodide (vide

Table 1) also compare well with the theoretical value⁶ calculated for a similar sized ion, $\text{Te}(4+)$ in 0.1 M ammonium chloride + 0.3 M ammonium hydroxide.

The electrochemical results in the form of calibration plots are utilised to determine the stoichiometry of cadmium selenide thin films (thickness $\sim 1500 \text{ \AA}$) obtained by vacuum evaporation technique. A reasonably good agreement is noticed between theoretical⁴ and experimental results: theoretical: 58.73% of cadmium; 41.26% of selenium; experimental: 57.65% of cadmium; 40.96% of selenium.

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References

- 1 Seetha Rama Rao G & Jayarama Reddy S, *Indian J Chem*, **22A** (1983) 660.
- 2 Seetha Rama Rao G & Jayarama Reddy S, *Transactions SAEST*, **18** (1983) 115.
- 3 Meites L, *Polarographic techniques* (Interscience, New York) 1965.
- 4 Zachariasen W, *Z physik Chem*, **124** (1926) 436.
- 5 Adams R N, *Electrochemistry at solid electrodes* (Marcel Dekker, New York) 1976, 217.
- 6 Schmidt H & Von Stackelberg M, *J Polarogr Soc*, **8** (1962) 49.