

Cyclic Voltammetry of Zinc Selenide at Hanging Mercury Drop Electrode

G SEETHA RAMA RAO & S JAYARAMA REDDY*

Electrochemical Laboratories, Sri Venkateswara University, Tirupati 517 502

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The electrochemical reduction of semiconductor grade zinc selenide has been studied by cyclic voltammetry at the hanging mercury drop electrode in different aqueous supporting electrolytes such as 1.0 *M* potassium chloride, 0.1 *M* potassium iodide, 1.0 *M* hydrochloric acid, saturated tartaric acid and 0.1 *M* potassium iodide saturated with tartaric acid (0.1 *M* KISTA). Zn(2+) has been found to reduce reversibly to Zn(0) in 0.1 *M* KISTA and irreversibly in other supporting electrolytes. The Spuel effect has been observed in Zn(2+) reduction. Se(4+) is reduced to Se(-2) via Se(0), irreversibly in all the supporting electrolytes except in 0.1 *M* KISTA. Diffusion coefficients and forward rate constants of the electrode processes involved are reported. The electrochemical results have been utilised to evaluate the stoichiometric composition of zinc selenide thin films obtained on a glass substrate.

We have been interested in the study of electrochemical reduction of semiconductor thin films, and as a part of our programme we investigated the chronoamperometry of cadmium selenide at hanging mercury drop electrode (HMDE)¹. In the present paper an attempt is made (i) to study the basic electrochemical properties of Zn(2+) and Se(4+) and (ii) to estimate them in glass impregnated thin films prepared by vacuum evaporation technique.

Materials and Methods

A multipurpose electrochemical module (model 370) and a three-electrode assembly (both supplied by Princeton Applied Research Corporation, USA) were used to record cyclic voltammograms. The HMDE used had an effective area of 0.02695 cm². A high vacuum coating unit (model 12 A4, Hind) was used for the preparation of thin films. Purified nitrogen gas was used for deoxygenation and to maintain inert atmosphere in the cell.

A semiconductor grade sample of zinc selenide (purity, 99.99%) (Ventron GmbH, West Germany) was used. All other chemicals and solvents employed were of analar grade. The stock solutions of supporting electrolytes, namely 1.0 *M* potassium chloride, 0.1 *M* potassium iodide, 1.0 *M* hydrochloric acid, saturated tartaric acid (STA) and 0.1 *M* potassium iodide saturated with tartaric acid (0.1 *M* KISTA) were prepared in doubly distilled water using AR samples.

Results and Discussion

Typical cyclic voltammograms obtained for the reduction of zinc selenide in acidic medium (STA) as well as in neutral medium (0.1 *M* KI) are shown in Figs. 1 and 2 respectively. Selenium is found to exist in Se(4+) state from the conventional qualitative tests. As observed from Fig. 1 during the first cathodic scan,

two cathodic peaks (*c*₁, *c*₂) due to Se(4+) → Se(0) and Zn(2+) → Zn(0) are noticed, whereas in the second cathodic scan an additional peak (*c*₃) due to Se(0) → Se(-2) is noticed. In neutral medium (Fig. 2), two cathodic peaks (*c*₂, *c*₃) due to Zn(2+) → Zn(0) and Se(0) → Se(-2) are noticed. Though no anodic peak is observed in reverse scan in STA, three ill-defined humps (*a*₃, *a*₂, *a*₁) are noticed in 0.1 *M* potassium iodide corresponding to the reduction peaks *c*₁, *c*₂ and *c*₃. The present results establish the consecutive reduction of Se(4+) → Se(0) → Se(-2) which is in agreement with our earlier cyclic voltammetric experiments² with Se(4+) and the cyclic and stripping voltammetric experiments of Jarzabek and Kublik³ with Se(4+) and Se(-2). It is observed that peak (*c*₃) which is absent in the first scan in STA, makes its appearance in 0.1 *M* potassium iodide. The high viscous nature of STA is probably responsible for this behaviour. Moreover, Zn(2+) → Zn(0) reduction does not allow Se(0) → Se(-2) reduction to take place in the

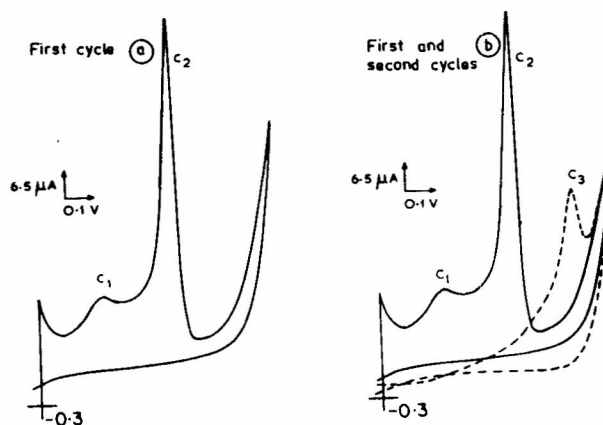


Fig. 1—Typical cyclic voltammograms for the reduction of zinc selenide in saturated tartaric acid; [Conc. = 7.08 mM; sweep rate = 0.1 V s⁻¹ (a) First cycle; (b) first and second cycles]

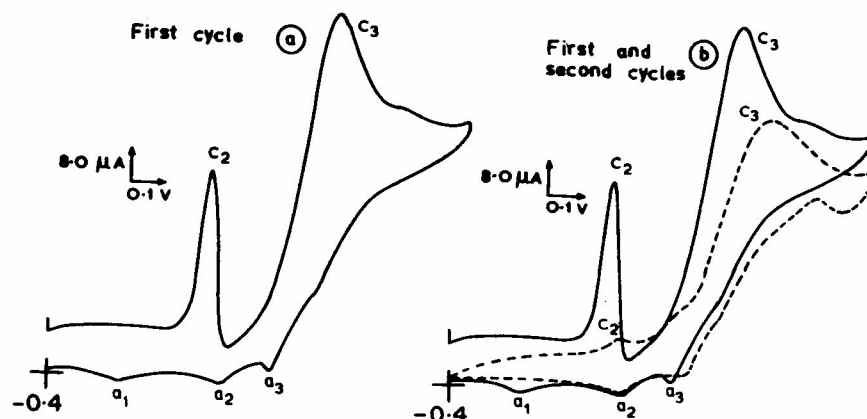


Fig. 2—Typical cyclic voltammograms for the reduction of zinc selenide in 0.1 *M* potassium iodide [Conc. = 2.26 mM; Sweep rate = 0.1 V S⁻¹ (a) First cycle; (b) first and second cycles]

Table 1—Typical Cyclic Voltammetric Data for the Reduction of Zinc and Selenium Sweep Rate: 0.1 V s⁻¹

Sl. No.	Supporting electrolyte	Conc./mM	E _p / -V vs SCE	i _p /μA	αn _a	D × 10 ⁶ / Cm ² s ⁻¹	k _f , h/ cm s ⁻¹
Zn(2+) → Zn(0)							
1	1.0 <i>M</i> KCl	1.92	0.81	40.0	2.4	6.86	5.24 × 10 ⁻³⁶
2	0.1 <i>M</i> KI	0.82	0.84	16.0	1.92	7.47	1.95 × 10 ⁻³⁰
3	1.0 <i>M</i> HCl	1.44	0.73	17.2	1.60	3.38	4.02 × 10 ⁻²³
4	STA	4.32	0.70	31.6	1.60	1.26	1.59 × 10 ⁻²²
5	0.1 <i>M</i> KISTA	0.98	0.99	3.08	—	0.23	—
Se(0) → Se(-2)							
6	1.0 <i>M</i> KCl	1.02	1.30	29.6	0.48	0.69*	1.56 × 10 ⁻¹³
7	0.1 <i>M</i> KI	1.57	1.21	64.0	0.48	1.31*	1.17 × 10 ⁻¹²
8	1.0 <i>M</i> HCl	7.28	0.98	97.6	0.96	7.25	8.56 × 10 ⁻¹⁹
9	STA	5.77	0.97	9.6	0.96	0.11	5.68 × 10 ⁻²⁰

* × 10⁻⁴

first scan as it precedes the latter reduction very closely. But in the second scan where *c*₁ and *c*₂ peaks are absent, the peak due to Se(0) → Se(-2) reduction, i.e. peak (*c*₃) makes its appearance. It may also be seen that no anodic peak is observed in the first or second scan in STA. Besides the viscous nature of the supporting electrolyte (STA), in the other acidic solution (i.e., 1.0 *M* hydrochloric acid) early hydrogen evolution, the Spuel effect associated with Zn(2+) reduction and the relatively vitiated electrode surface due to the deposition of Se(0) produced at peak (*c*₁) may be responsible for the absence of peak (*c*₃) in the first scan. In all the above cases, *c*₃ is visible only in the second scan. Of the peaks *c*₁, *c*₂ and *c*₃ only *c*₂ and *c*₃ are well-defined and therefore have been studied in detail. The data obtained for the reductions Zn(2+) → Zn(0) (*c*₂ peak) and Se(0) → Se(-2) (*c*₃ peak) in various supporting electrolytes employed are presented in Table 1.

The variation of peak potential with concentration and sweep rate and the absence of anodic peak suggest the Se(0) → Se(-2) and Zn(2+) → Zn(0) reductions to

be irreversible. The *i*_p and *v*^{1/2} and *i*_p versus *C* plots are linear passing through the origin indicating the reductions to be diffusion-controlled in spite of complication⁴ arising due to adsorption as also reported in our earlier studies on cadmium selenide² and cadmium telluride⁵.

In neutral media and at very slow scan rates such as 5 mV s⁻¹, an additional peak at -1.40 V (vs SCE) is observed. This peak is also attributed to the reduction of Se(0) → Se(-2) besides peak (*c*₃). The selenide ion formed at peak (*c*₂) moves away rapidly from the electrode surface due to electrical interaction and reacts with Se(4+) ions to produce Se(0) again. The elemental selenium thus formed is reduced at more negative potentials forming an additional peak. Such type of reduction behaviour for Se(4+) and Te(4+) ions is already observed by us^{2,5} and is also reported in literature³.

The absence of anodic peak and variation of peak potential with concentration and sweep rate indicate the Zn(2+) → Zn(0) reduction to be irreversible (except in 0.1 *M* KISTA) and a linear plot of *i*_p versus *v*^{1/2},

passing through the origin suggests the process to be diffusion-controlled. It is interesting to observe that while $\text{Zn}(2+)$ reduction is irreversible in 0.1 M potassium iodide or STA, it is reversible in the presence of 0.1 M KISTA, as shown by a well-defined anodic peak (a_2) (Fig. 2). It is also seen that though the cathodic and anodic half-reactions are reversible (the peak and half-peak potentials are separated by 30 mV), the total reduction is found to deviate from reversibility, as the cathodic and anodic peak potentials are separated by 50 mV.

Except in 0.1 M KISTA, the $\text{Zn}(2+)$ reduction is found to be associated with Spuel effect⁶. The elemental zinc thus formed gets amalgamated with mercury drop. The amalgam while flowing into the electrode produces a vigorous stirring effect resulting in sharp maxima as observed in the present study (Fig. 3).

In spite of Spuel effect, reasonably good diffusion coefficient values are obtained for $\text{Zn}(2+) \rightarrow \text{Zn}(0)$ reduction (Table 1) and are comparable with the literature values⁷. The relatively lower values in STA and 0.1 M KISTA are attributed to the viscosity of the medium which decreases the current substantially. Though $\text{Se}(0) \rightarrow \text{Se}(-2)$ reduction is used to evaluate the diffusion coefficients of $\text{Se}(4+)$, the formation of $\text{Se}(0)$ is governed by the diffusion of $\text{Se}(4+)$ only and hence the values are attributed to $\text{Se}(4+)$. The higher values in neutral media can be due to high diffusion current as a result of adsorption process, and relatively lower values in acidic media are due to the fact that the current values are taken from the second cycle. The heterogeneous forward rate constants for the irreversible reductions of $\text{Zn}(2+) \rightarrow \text{Zn}(0)$ and $\text{Se}(0) \rightarrow \text{Se}(-2)$ are, in general, found to increase with increase in concentration.

Zinc selenide thin films of different thicknesses, obtained on a glass substrate by vacuum evaporation technique have been analysed for their stoichiometric compositions. The calibration plots obtained between concentration and peak current have been used for this purpose. The peak current values obtained for film solutions under identical experimental conditions are substituted into the respective calibration plots, from which the concentration of the electroactive species and in turn the composition is obtained. A fairly good

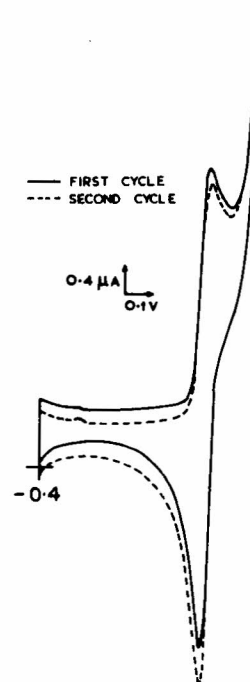


Fig. 3—Typical cyclic voltammogram for the reduction of zinc selenide in 0.1 M potassium iodide saturated with tartaric acid; [Conc. = 0.98 mM; sweep rate = 0.2 V s^{-1}]

agreement is noted between literature⁸ (45.29% of Zn and 54.70% of Se) and experimental (44.82% of Zn and 53.69% of Se) values.

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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 Jarzabek G & Kublik Z, *J electroanal Chem*, **114** (1980) 165.
- 4 Meites L, *Polarographic techniques* (Interscience, New York) 1965, 187.
- 5 Seetha Rama Rao G & Jayarama Reddy S, *J electrochem Soc (India)*, (In press).
- 6 Popova T I, Bogotskii V S & Kahanov B N, *Zh fiz Khim*, **36** (1962) 1432.
- 7 Lingane J J, *Ind Engng Chem (Anal Ed)*, **15** (1943) 583.
- 8 Zachariasen W, *Z phys Chem*, **124** (1926) 440.