

Cathodic Stripping Voltammetry of Tellurium(IV) at a Bismuth Film Electrode

Noseung Myung,* Sunyoung Ham, Seungun Choi, Yujin Chae, Wooju Lee, Jihye Kwak, and Krishnan Rajeshwar†

Department of Applied Chemistry, Konkuk University, Chungju, Chungbuk 380-701, Korea. *E-mail: myung@kku.ac.kr

†Center for Renewable Energy Science & Technology (CREST), The University of Texas at Arlington, Arlington, TX 76109-0065, USA

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Stripping analysis has been widely employed for the determination of trace metals in solutions due to its high sensitivity which is rooted in the combination of an effective pre-concentration step with advanced electrochemical stripping/quantification possibilities.^{1,2} Although the mercury film electrode (HgFE) has been generally used for stripping analysis,^{1,2} the bismuth film electrode (BiFE) has attracted much attention as an alternative to the HgFE since bismuth is environmentally benign unlike mercury. Another positive feature of BiFE in stripping analysis stems from the proclivity of bismuth, to form alloys with metals, analogous to mercury amalgams.^{3,4} As a result, BiFE have been widely used as the working electrode for the determination of metals and other elements by anodic, potentiometric, and adsorptive stripping voltammetry techniques.⁴⁻¹²

Unlike the extensive application of anodic stripping analysis using a BiFE, there are only few reports on *direct* cathodic stripping analysis at a BiFE.^{13,14} Cathodic stripping voltammetric determination of As(III), Te(IV), Sb(III and V) and Se(IV) using in situ plated BiFEs has been reported.¹⁵⁻¹⁸ However, an *indirect* cathodic stripping analysis was used in these studies where the catalytic hydrogen wave, which was proportional to the analyte concentration, was used as the analytical signal. Considering the high hydrogen overpotential and low background of bismuth, it is therefore surprising that there are only a couple of examples of direct cathodic stripping analysis using BiFEs.^{13,14}

In this report, we describe for the first time alloy formation of Bi₂Te₃ during the pre-concentration stage of Te on the BiFE and its relevance to Te determination. Tellurium (Te) is a constituent of technologically important compound semiconductors such as CdTe and ZnTe.¹⁹ The element itself is a p-type semiconductor and is also a constituent of Bi₂Te₃, which is a benchmark active material for thermoelectric power generation and cooling.²⁰ In what follows, alloy formation on the conventional HgFE electrode will also be discussed. Unlike the cases of metal ions, there have been only few reports on the determination of Te(IV) or Se(IV) by cathodic stripping voltammetry at HgFEs. A Tosflex/8-quinolinol coated HgFE has been reported for Te determination.²¹ Our laboratories developed a stripping voltammetric technique for compositional analysis of electrodeposited CdSe thin films using HgFEs.²² However, there are no reports on the observation of compound formation

during stripping analysis of Te(IV) or Se(IV). Therefore in this study, the conventional HgFE was also deployed to investigate whether alloy formation is a general phenomenon (like in the BiFE instance above) or not. Finally, comparative aspects of Te determination at BiFE and HgFE will be briefly discussed.

Experimental

Bismuth nitrate pentahydrate (purity 99.99 + %), tellurium dioxide (purity 99 + %), sodium sulfate (purity 99 + %), sodium phosphate monobasic (purity 99.0 + %), sodium phosphate dibasic (purity 99 + %), mercury(II) nitrate monohydrate (purity 98 + %), hydrochloric acid (purity 37%) and nitric acid (purity 70%) were from Aldrich. All chemicals were used as received.

For voltammetry and film deposition, an EG&G Princeton Applied Research (PAR) 273A instrument equipped with Model M250/270 electrochemistry software was used. A glassy carbon working electrode, a Pt counter electrode, and a Ag/AgCl/3 M NaCl reference electrode were used. All potentials below are quoted with respect to this reference electrode.

The BiFE was pre-electrodeposited on a well-polished glassy carbon (GC) electrode (area = 0.07cm²) at -0.1 V for 120 s or 240 s in 1 M HNO₃ electrolyte containing 1 mM Bi(NO₃)₃, while the solution was stirred. A fresh BiFE electrode was used for each measurement. A square wave cathodic stripping voltammetric mode was employed with a frequency of 25 Hz, amplitude of 25 mV, scan rate of 10 mV/s and potential step of 2 mV.

Results and Discussion

Figure 1(a) shows representative square wave cathodic stripping voltammograms in 1 M phosphate buffer solutions (pH=7) after pre-concentration of Te(IV) at -0.3 V for 600 s in 0.1 M HCl electrolyte containing Te(IV) ions in the range, 5 μM to 40 μM. The BiFE yielded a well-defined cathodic wave at ~ -0.97 V which is attributed to the cathodic stripping of Te to Te²⁻ and the peak area is clearly proportional to the Te(IV) concentration in the electrolyte. A calibration plot obtained from the voltammograms in Figure 1 is linear (R² = 0.99) up to 40 μM Te(IV) as shown in the inset in Figure

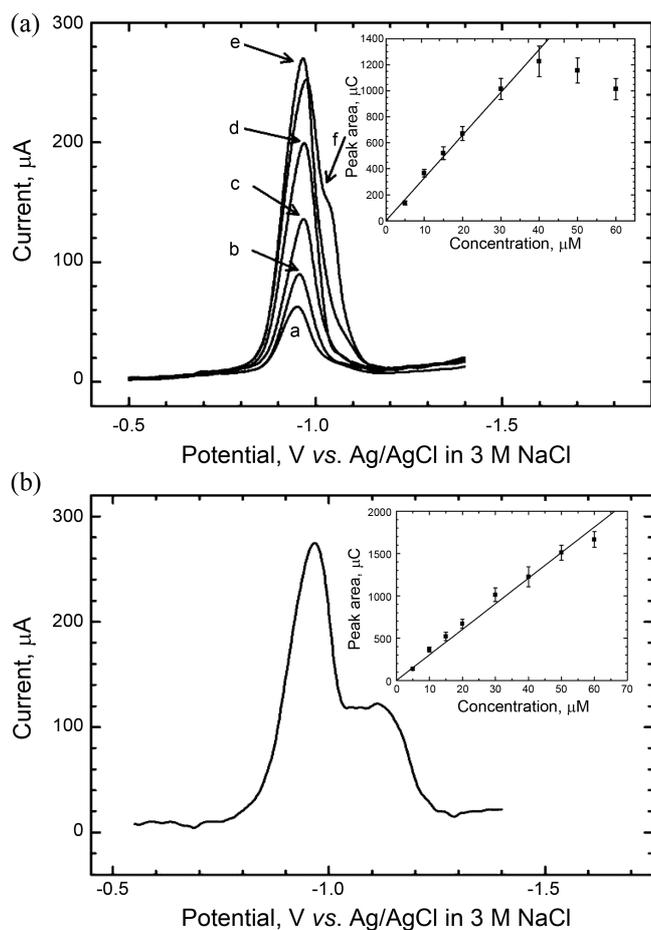


Figure 1. Square wave cathodic stripping voltammograms at Bi film electrode in 1 M phosphate buffer electrolyte. Te was pre-concentrated at -0.3 V for 600 s in 0.1 M HCl containing Te(IV) at (a) a: 5 μM , b: 10 μM , c: 15 μM , d: 20 μM , e: 30 μM , f: 40 μM and (b) 50 μM . The insets contain the calibration plots for the determination of Te(IV) up to 60 μM . Error bars in the calibration curves represent the standard deviation of 7 measurements.

1(a).

Interestingly, a new wave appears at ~ -1.11 V when the BiFE, after analyte pre-concentration at high levels of Te(IV) (for example, 50 μM), was subjected to cathodic stripping in 1 M phosphate buffer of pH 7 as shown in Figure 1(b). The first peak at ~ -0.97 V results from Te reduction ($\text{Te} + 2\text{e} \rightarrow \text{Te}^{2-}$) (as seen in Figure 1(a)) and the second peak -1.11 V results from the reduction of Bi_2Te_3 to $\text{Bi} + \text{Te}^{2-}$ as discussed before by us and others.²⁰ Detailed thermodynamic data on the above reactions were discussed by Stacy and co-workers.²⁴ The appearance of this second stripping peak clearly implies the formation of Bi_2Te_3 during the deposition step according to the following reaction:^{20,23,24}



Figures 1(a) and 1(b) together indicate that the formation of Bi_2Te_3 is dependent on the deposition conditions and is not significant at Te(IV) levels less than ~ 40 μM . When the area of the second peak is included in the total peak area, a calibration plot is obtained with extended linearity ($R^2=0.99$)

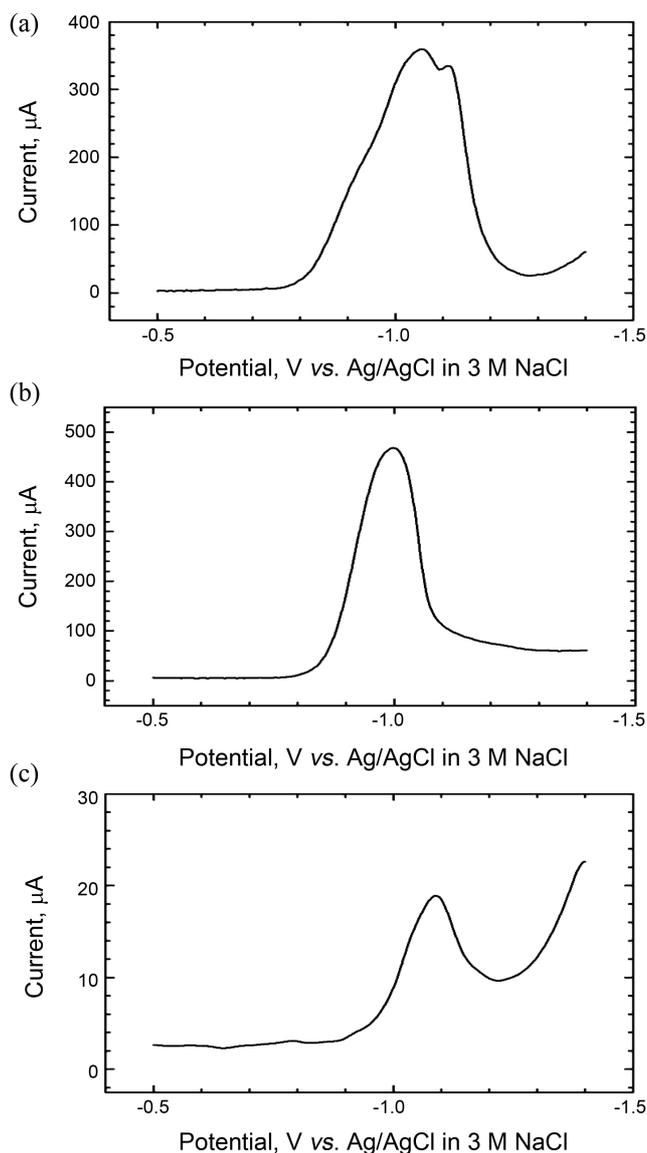


Figure 2. Square wave cathodic stripping voltammogram in 1 M phosphate buffer electrolyte for: (a) Bi_2Te_3 film mixed with Te, which was pre-electrodeposited at a glassy carbon electrode at -0.1 V for 120 s in a 1 M HNO_3 containing 1 mM $\text{Bi}(\text{NO}_3)_3$ and 1 mM TeO_2 , (b) Te film pre-electrodeposited at -0.3 V for 600 s using a 1 M HNO_3 containing only 1 mM TeO_2 and (c) Bi_2Te_3 film which was pre-electrodeposited at a GC electrode at -0.1 V for 120 s in a 1 M HNO_3 containing 1 mM $\text{Bi}(\text{NO}_3)_3$ and 1 mM TeO_2 . Free Te was completely removed by applying -1.0 V for 600 s in a blank electrolyte.

up to 60 μM of Te(IV) as shown in the inset in Figure 1(b) contrasting with the trend in the inset in Figure 1(a).

To further probe the origin of the second wave in Figure 1(b), a Bi_2Te_3 thin film was electrodeposited on the GC electrode at -0.1 V for 120 s from 1 M HNO_3 electrolyte containing 1 mM $\text{Bi}(\text{NO}_3)_3$ and 1 mM TeO_2 .²⁰ The GC electrode was subjected to square wave cathodic stripping in 1 M phosphate buffer electrolyte (pH=7) (Figure 2(a)). Two peaks were found as in Figure 1(b) while the first peak (due to the reduction of Te to Te^{2-}) was slightly shifted to a

negative potential. This could be attributed to kinetics differences in the two cases and poor separation of the peaks.²⁰ Next, a Te film was electrodeposited on the GC electrode at -0.3 V for 600 s using a 1 M HNO_3 containing only 1 mM TeO_2 . Again, the electrode was subjected to square wave cathodic stripping in 1 M phosphate buffer electrolyte (pH=7, Figure 2(b)). Clearly, the first peak in Figure 1(b) as well as the peak in Figure 1(a) results from Te reduction ($\text{Te} + 2e \rightarrow \text{Te}^{2-}$).

Another piece of evidence for the second peak at -1.1 V being due to the reduction of Bi_2Te_3 to $\text{Bi} + \text{Te}^{2-}$ is shown in Figure 2(c). For this, a Bi_2Te_3 film was electrodeposited as in Figure 2(a) and the film was reduced at -1.0 V for 600 s in 0.1 M Na_2SO_4 blank electrolyte to remove free Te.²⁰ After thoroughly cleaning the electrode, the same film was subjected to square wave cathodic stripping in the blank electrolyte again (Figure 2(c)). The peak at -1.1 V is clearly identical to the second stripping peak in Figures 1(b) and 2(a). Therefore, cathodic stripping of the films electrodeposited on the BiFE using a electrolyte containing increased levels of Te(IV) is believed to proceed *via* a two-

step process: reduction of free Te first followed by the cathodic reduction of Bi_2Te_3 to $\text{Bi} + \text{Te}^{2-}$.

In order to further study the conditions under which Bi_2Te_3 is formed, we systematically changed Te(IV) concentration as well as deposition time. Square wave cathodic stripping voltammograms in Figure 3 were obtained in 1 M phosphate buffer electrolytes after Te pre-concentration at -0.3 V with

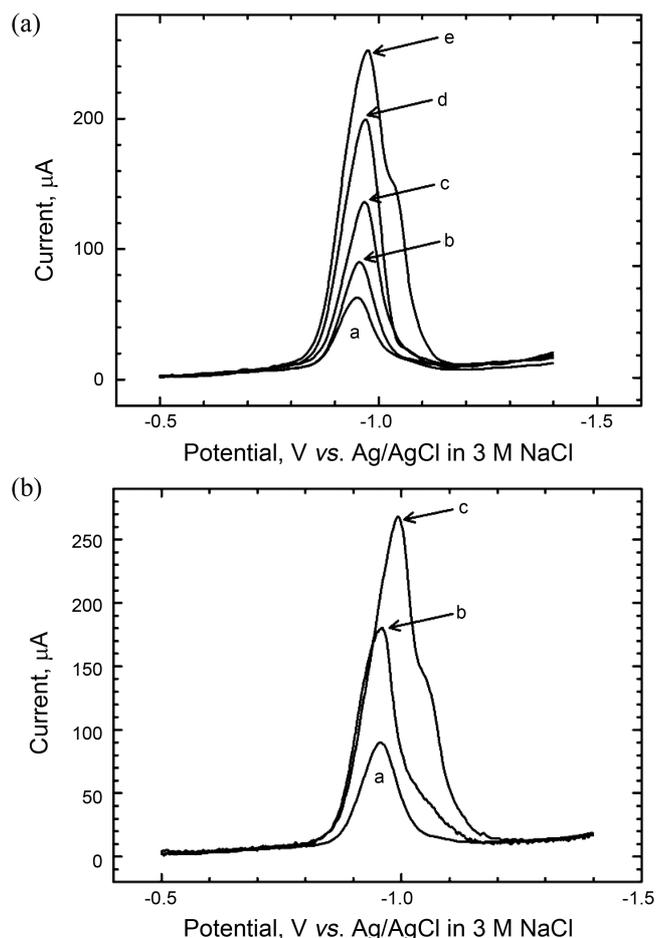


Figure 3. Square wave cathodic stripping voltammograms at Bi film electrode in 1 M phosphate buffer electrolyte. (a) Te was pre-concentrated at -0.3 V in 0.1 M HCl containing 20 μM of Te(IV) for: a: 400 s, b: 600 s, c: 800 s, d: 1000 s, e: 1800 s. (b) Te was pre-concentrated at -0.3 V for 600 s in 0.1 M HCl containing a: 20 μM , b: 40 μM and c: 50 μM of Te(IV).

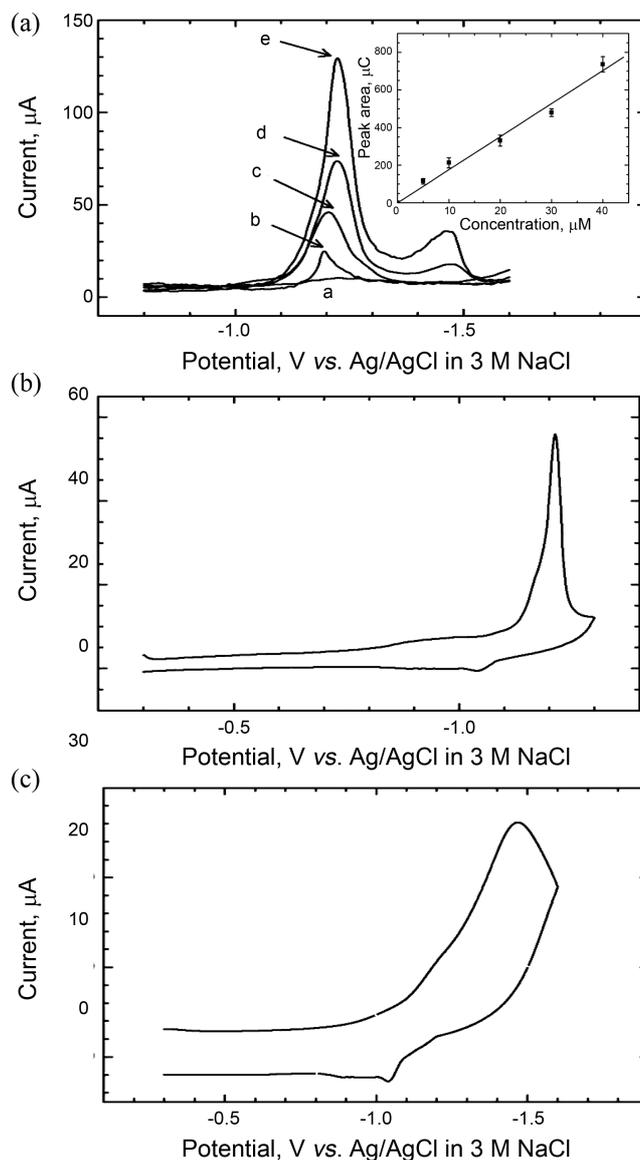


Figure 4. (a) Square wave cathodic stripping voltammograms at mercury film electrode (HgFE) in 1 M phosphate buffer electrolyte. Te was pre-concentrated at -0.3 V for 600 s in 0.1 M HCl containing a: 5 μM , b: 10 μM , c: 20 μM , d: 30 μM and e: 40 μM of Te(IV). The inset contains a calibration plot for the determination of Te(IV) at HgFE and both peaks were included for the calibration curve. Error bars in the calibration curve represent the standard deviation of 7 measurements. Cyclic voltammogram on HgFE in 1 M phosphate buffer electrolyte (b) after pre-concentration of Te(IV) at -0.3 V for 600 s in 0.1 M HCl containing 20 μM of Te(IV) and (c) after pre-concentration of Te(IV) at -0.3 V for 600 s in 0.1 M HCl containing 30 μM of Te(IV) followed by a cathodic scan from -0.3 V to -1.3 V to remove free Te in the film. Potential scan rate: 50 mV/s.

different deposition time and Te(IV) concentration. In the case of 20 μM , it took 1800 s to form Bi_2Te_3 on the BiFE as shown in Figure 3(a). The peak area was increased up to 1200 s and another peak was appeared at 1800 s, instead of showing leveling off of the peak area which is usually observed in stripping voltammetry and other analytical methods.² Figure 3(b) shows that the formation of Bi_2Te_3 is also dependent on the Te(IV) concentration. The peak at -1.1 V was appeared again when square wave cathodic stripping voltammograms were obtained after Te preconcentration at -0.3 V for 600 s in 0.1 M HCl containing 50 μM of Te(IV).

To compare the behavior on a mercury film electrode, HgFEs were prepared on the GC electrode at -0.1 V for 120 s using 1 M HNO_3 electrolyte containing 1 mM $\text{Hg}(\text{NO}_3)_2$. Tellurium was pre-concentrated at -0.3 V for 600 s in 0.1 M HCl containing specified concentration of Te(IV) and square wave cathodic stripping voltammograms were obtained using a series of electrolytes with different concentrations of Te(IV). Two peaks at -1.2 V and -1.5 V were also observed on the HgFE at Te concentrations 30 μM or higher (Figure 4(a)). Not surprisingly, the peak positions were different from the case of the BiFEs. The first peak at -1.2 V is attributed to the reduction of Te to Te^{2-} as in the BiFE case. From the results discussed earlier, it is reasonable to infer that the second peak at ~ -1.4 V results from the reduction of HgTe to Hg and Te^{2-} .

To further probe the origin of the second peak in Figure 4(a), cyclic voltammograms were obtained on the HgFE. Figure 4(b) contains a representative cyclic voltammogram on HgFE in 1 M phosphate buffer electrolyte after pre-concentration of Te at -0.3 V for 600 s in 0.1 M HCl containing 20 μM of Te(IV). During the cathodic scan, only one wave at -1.2 V was observed for the reduction of Te to Te^{2-} . Upon reversing and in the anodic scan, a small peak at -1.04 V was seen which is assigned to the oxidation of Te^{2-} to Te .²⁵ For the cyclic voltammogram in Figure 4(c), Te was pre-concentrated at the HgFE at -0.3 V for 600 s in 0.1 M HCl containing 30 μM of Te(IV). Subsequently, the free tellurium was stripped from the HgFE by applying -1.3 V or a potential scan from -0.3 V to -1.3 V. Only one peak at ~ -1.4 V is seen in the subsequent voltammogram (Figure 4(c)), which is due to the reduction of HgTe to Hg and Te^{2-} . Reduction of HgTe and generation of Te^{2-} is clearly proved by the anodic peak at -1.04 V upon reverse scan which is due to the oxidation of Te^{2-} to Te as in Figure 4(b).²⁵

The inset in Figure 4(a) contains a calibration plot for the determination of Te(IV) at HgFE. Both peaks were utilized to compute the areas shown on the ordinates of these plots. The comparison of calibration curves, i.e., inset in Figure 1(b) and inset in Figure 4(a), showed that the analytical sensitivity (as manifested in the plot slopes) for BiFE is twice that at HgFE. Further optimization in terms of para-

meter settings for pre-concentration and stripping will be carried out in our laboratories.

In summary, both amalgam-forming Hg film electrode and alloy-forming Bi film electrode showed Bi_2Te_3 and HgTe formation on the film, respectively depending on the experimental conditions such as Te(IV) concentration and deposition time. Thus alloy or compound formation is indeed a general property of bismuth and mercury film electrodes as demonstrated in this study. Further studies on the optimization of experimental conditions for the direct determination of Te(IV) using an environmentally benign bismuth film electrode are in progress.

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