

Voltammetric behavior of selenium from H_2SeO_3 solution on solid copper amalgam electrode

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ABSTRACT

Issues concerning the remote monitoring and in-the-field analysis have generated considerable research effort aimed at finding methods with acceptable performance. Voltammetry has been known as one of the methods that are suitable for this purpose. Some of solid amalgam electrodes were designed and used for analysis of selenium, but its voltammetric behavior study was still limited. The electrochemical behavior of selenium from H_2SeO_3 solution by cyclic voltammetry at a solid copper amalgam electrode is described. The aim of this work is to reveal some factors that can influence the shape of voltammogram. Concentration of supporting electrolyte, scan rate, and number of cyclic repetition were examined for their effect on the selenium peak shape and intensity. The best responses were obtained with 0.1M HCl as supporting electrolyte; meanwhile scan rate and number of cyclic repetition have a great influence on selenium peak shape and intensity.

Keywords: cyclic voltammetry, selenium, solid copper amalgam electrode

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I. INTRODUCTION

The detection and analysis of metal ions has been the subject of many research studies [1]. Among these focused on selenium (Se) compounds which are essential for biological system, but will be toxic if it excesses. Toxicological effects of selenium are strongly depends on its chemical form. In general, inorganic selenium compounds are more toxic than organic ones [2]. The most common forms of selenium in water are selenite ($Se(IV), SeO_3^{2-}$) and selenate ($Se(VI), SeO_4^{2-}$). The formation of selenat from selenite is slow, and both forms exist together in solution [3]. Selenite is approximately 10-fold more toxic than selenate [4].

The choice of detection and analysis method depends on the sample, the analyte to be assayed, accuracy, limit of detection, cost and time to complete the analysis [5]. Atomic absorption spectrometry (AAS) with hydride generation is one of the powerful methods for determining selenium due to its low detection limit. For some routine laboratories at several location in Indonesia, this method is very inconvenient and not possible to be applied because of expensive, not easy to use for actual measurements, need some preparation step and using a lot of chemicals. Electrometric are widely diffused as alternative methods due to the capability of quantitatively evaluate concentrations up to the trace levels, low cost instrumentation, and in-the-field detection application.

As is well known, the best material for working electrode is mercury due to its large cathodic window, easily renewable, and atomically smooth surface. However, because of the fears of its toxicity and low mechanical stability, extensive development the nontoxic electrodes of solid amalgams were designed and introduced. Some metals such as gold, platinum, iridium, silver, and copper have been used as the substrate to form solid amalgam electrode. The use of solid copper amalgam as electrode material avoids the use of liquid mercury or mercury salts in voltammetric analysis, and thus offers a nontoxic electrode system.

In this paper, fabricated of both reference (Ag/AgCl) and working (CuHg) electrode were utilized for evaluation the voltammetric behavior of selenium from H_2SeO_3 solution.

II. MATERIALS AND METHODS

2.1 Instrumentation

All the measurements were performed using an eDAQ potentiostat model EA163 with an e-corder unit connected to a PC, in combination with a three electrode cell incorporating platinum wire (Nilaco, Japan) as the auxiliary electrode, a fabricated Ag/AgCl electrode (3M KCl) as the reference, and a fabricated solid copper amalgam (CuHg) as the working electrode. Glassware, polypropylene (PP) nalgene plastic ware were soaked in HNO_3 1:3 for at

least 24 h and then rinsed three times with millipore water and kept dry before ready to use.

2.2 Chemicals

All chemicals were of analytical grade, and Millipore water of $18.2 \text{ M}\Omega\text{cm}^{-1}$ specific resistivity obtained from a Milli-Q purification system (Millipore Co., Bedford, MA, USA) was used throughout. Cu wire was obtained from PT. Freeport Indonesia. Ag wire was obtained from Nilaco, Japan. Sodium chloride, copper sulfate pentahydrate, and hydrochloric acid 32%, acetone, and mercury nitrate were purchased from E.Merck, Indonesia. Sodium selenite pentahydrate 99% was purchased from Sigma Aldrich, Japan. The selenium stock solution and the necessary dilutions were prepared freshly prior to use.

2.3 Procedures

All the experiments were conducted in room temperature. The solution was bubbled with nitrogen before measurements.

Preparation of Ag/AgCl reference electrode

Ag/AgCl reference electrode consists of an Ag wire coated with silver chloride, which was immersed in an aqueous solution containing NaCl 3M. The procedures of preparation were as follow: First, Ag wire was cleaned with a fine sand paper and then subjected to an oxidizing potential (about 2.0V) in a two-electrode system with a platinum wire (for the counter electrode) in 0.1M NaCl for about 10min until a reasonable thickness of a grey Ag/AgCl coating can be seen. Then, coated Ag wire was rinsed with Millipore water and put in the translucent tube filled with 3M NaCl solution. A porous ceramic frit is used for the junction between the reference electrode solution and the sample solution.

Preparation of solid copper amalgam (CuHg)

CuHg working electrode was made by deposition of Cu from 0.1M CuSO_4 at potential deposition of 15V for 35s onto Cu wire with diameter of 0.43cm, and then immersed in saturated mercury salt to form amalgam CuHg. Finally, Millipore water and acetone was used respectively for cleaning the surface of CuHg electrode, and then dried at atmosphere condition.

Cyclic voltammetry of selenium

Cyclic voltammetry (CV) experiment was start at potential -0.3V and swept in the negative direction first then reversed at -0.8V, with scan rate (v) = 0.1V/s for evaluation the electrochemical behavior of selenium at CuHg electrode. 0.1M HCl was used as supporting electrolyte.

III. RESULTS AND DISCUSSION

Calibration of Ag/AgCl reference electrode

Fabricated Ag/AgCl reference electrode was calibrated using commercial Ag/AgCl reference electrode (BASi Electrode RE-5B). Pt-disc and Pt-wire was used as working and auxiliary electrode respectively. A mixture (1:1) of 10mM $\text{K}_3[\text{Fe}(\text{CN})_6]$ and 10mM $\text{K}_4[\text{Fe}(\text{CN})_6]$ in 0.1M NaCl as the supporting electrolyte was scanned with cyclic voltammetry (CV) technique. The parameters set up were: initial potential (E_i) = -0.2V, high potential (E_H) = 0.8V, low potential (E_L) = -0.2V, and scan rate (v) = 0.1V/s. Both voltammogram were compared and analyzed statistically using paired samples t-test. The performance of fabricated Ag/AgCl appears to be comparable with commercial Ag/AgCl reference electrode (Fig. 1).

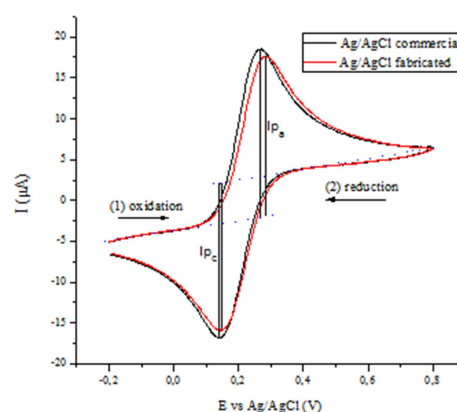


Figure 1. Cyclic voltammogram of fabricated and commercial Ag/AgCl in the mixture of $\text{K}_3[\text{Fe}(\text{CN})_6]$ and $\text{K}_4[\text{Fe}(\text{CN})_6]$, scan rate 100 mV/s

Variation of supporting electrolyte concentration

Since selenium can have multiple oxidation state, which depends on the solution acidity, determination of dominant selenium species in the solution was performed prior to voltammetric analysis. Based on the acid-base equilibrium at 25°C, the possible selenium species resulted from reaction of Na_2SeO_3 with HCl were H_2SeO_3 , HSeO_3^- , and SeO_3^{2-} . The dominant selenium species throughout the discussion in this paper was considered as H_2SeO_3 .

The use of HCl as a supporting electrolyte has been studied before [3, 6-10]. In the current research, the choice of HCl concentration as a supporting electrolyte was determined by its cyclic voltammetry behavior. The onset potential (E_i) was set at -0.3V and reversed at the potential -0.8 mV (E_f) with scan rate 0.1V/s. The experiment was performed at $\text{pH} \approx 1$, using standard solution of 200µM Se(IV). The concentration of HCl was varied at 0.05M, 0.10M, and 0.50M.

In the absence of Se(IV), the cyclic voltammogram of aquamillipore and HCl shows that

there were no oxidation and reduction reaction peaks performed (Fig. 2A). It can be seen that the HCl concentration affected the capacitive current. As the HCl concentration increased, the capacitive current raised (Fig. 2A). The cyclic voltammogram of 200 μ M Se (IV) in *aquamillipore* and in several concentration of HCl can be seen at Fig. 2B. The Figure 2B shows that there was a reduction peak in the region of 0.70V to -0.72V and an oxidation peak in the region of -0.60V to -0.66V toward Ag/AgCl electrode. The highest intensity of reduction current peak was found at 0.50M HCl.

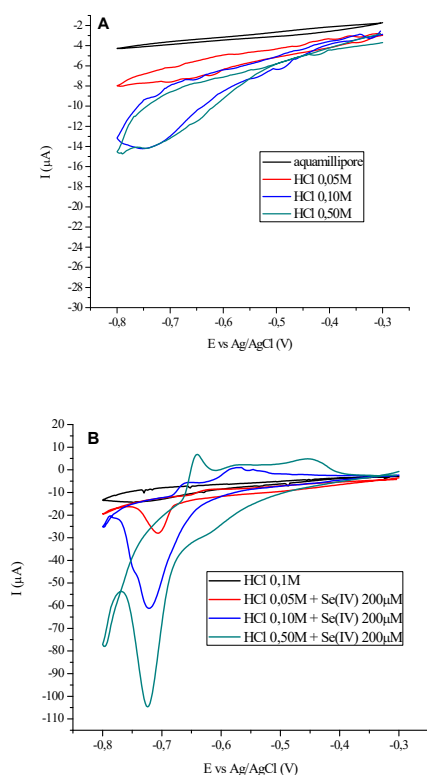


Figure 2. Cyclic voltammogram with scan rate 50 mV/s of (A) *aquamillipore* and HCl, (B) 200 μ M Se(IV) in several concentration of HCl

Based on the I_p values of 200 μ M Se(IV) in HCl, which was calculated from the voltammogram, the sensitivity of selenium detection increased three times when the HCl concentration amplified from 0.05 to 0.10M. Interestingly, the sensitivity of selenium detection was not improved when the HCl concentration multiplied from 0.10 to 0.50M. Therefore, the 0.10M HCl was selected as a supporting electrolyte for the next step, besides to minimize the effect of capacitive current during the measurement of Se (IV).

Determination of reduction and oxidation peakspotential of Selenium

Reduction and oxidation peaks potential of Se(IV) was determined using 1mM Se(IV) in 0.1MHCl. The onset potential was set at -0.3V and reversed at the potential -0.8V with scan rate of 0.1V/s. During the sweeping, two reduction peaks at potential -0.74mV and -0.76mV and two oxidation peaks at potential -0.70mV and -0.62mV were observed toward Ag/AgCl (Fig. 3). The presence of oxidation and reduction peaks was reported as well in the previous reports[11, 12]. Those peaks were presumably related to the redox reaction of Se(IV) at surface of working electrode CuHg, confirmed by the alteration of the peak intensity during variation of Se (IV) concentration.

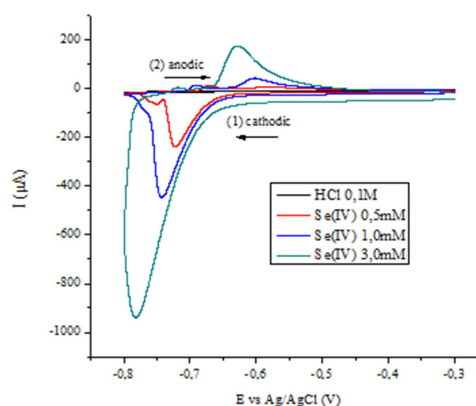


Figure 3. Cyclic voltammetry of Se(IV) at the concentration of 0.5mM, 1.0mM, and 3.0mM in 0.1M HCl, scan rate 100mV/s

Figure 3 showed a linear correlation between peak current and Se(IV) concentration, although the data resulted from I_{p_c} has higher sensitivity than the data resulted from I_{p_a} . The analyte concentration affected the shifting of both cathodic and anodic peaks towards negative potential, but the potential difference of reduction and oxidation peaks are relatively consistent. It was suggested that the electrochemical reaction rate of Se(IV) in the concentration range of 0.5mM to 3.0mM was constant.

Based on the profile of voltammogram, peak current and peak potential of Se(IV) in 0.1M HCl were determined. The cathodic peak current (I_{p_c}) and anodic peak current (I_{p_a}) values can be readily obtained from the cyclic voltammogram as can be seen in Table 1.

Table 1. Peaks current and peaks potential of Se(IV) in 0.1M HCl

Parameters	Concentration of Se(IV)		
	0.5mM	1.0mM	3.0mM
Ep _{c1} (V)	-0.722	-0.742	-0.782
Ep _{c2} (V)	-0.752	nd ^{*)}	nd
Ep _{a1} (V)	-0.672	-0.690	-0.720
Ep _{a2} (V)	-0.582	-0.602	-0.628
ΔEp (V)	0.140	0.140	0.154
Ip _{c1} (mA)	-0.1986	-0.3369	-0.8978
Ip _{c2} (mA)	-0.0282	nd	nd
Ip _{a1} (mA)	0.0182	0.0212	0.0153
Ip _{a2} (mA)	0.0080	0.0416	0.1780

^{*)}nd = not determined

Variation of the scan rate

The effect of different scan rate on the peak height and peak potential of the selenium were evaluated. The Se(IV) concentrations were 1000μM, 500μM and 20μM in 0.1M HCl, and the scan rate was varied from 25mV/s to 125mV/s. For 1000 μM Se(IV) in 0.1M HCl with scan rate from 25mV/s to 125mV/s, one cathodic peak and one anodic peak were observed at the potential -0.750V and -0.650V, respectively. Two cathodic peaks (-0.540V and -0.780V) and two anodic peaks (-0.650V and -0.500V) were observed at scan rate 80mV/s and 100mV/s (Fig. 4A). The number of peaks observed in the lower selenium concentration (500 μM in 0.1M HCl) altered. Some cathodic peaks appeared at potential around -0.700V to -0.800V, while two anodic peaks were observed at potential around -0.650V to -0.550V. The number of cathodic peak affected by scan rate, but the anodic peak was not (Fig. 4B). Different phenomena was observed during the profiling of 20μM Se(IV) in 0.1M HCl (Fig. 4C). Only one cathodic peak and one anodic peak were observed on almost all scan rates, except on scan rate 50mV/s two cathodic peaks were observed.

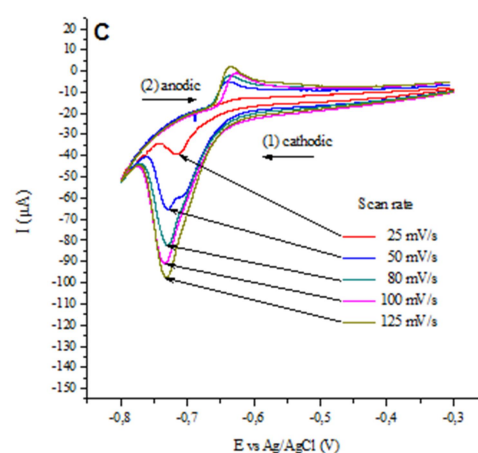
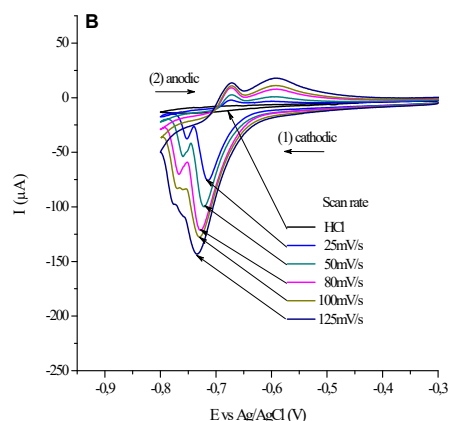
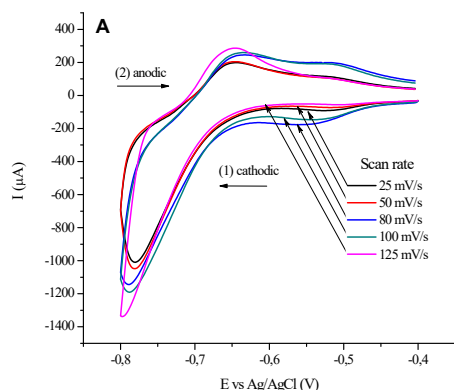


Figure 4. Cyclic voltammogram of Se(IV) at concentration of (A) 1000μM, (B) 500μM, (C) 20μM with variation of scan rate

As mentioned before, the Ip_{c1} were used for further quantitative analysis, and the correlation between Ip and scan rate (v) of Se(IV) at the concentrations of 1000μM, 500μM, dan 20μM can be seen in figure 5. In general, the increase of Ip_c and Ip_a values was in line with the elevation of scan limit. There was a linear correlation between intensity of Ip and v at the Se(IV) concentration of 20μM and 500μM, whilst the linearity decreased in the 1000μM Se(IV) (Fig. 5). It can be interpreted that in the 20μM and 500μM Se(IV), electron transfer performed on the surface of working electrode CuHg, controlled by diffusion, while in the 1000μM Se(IV), the electron transfer was affected by other factors such as adsorption of Se(IV). Moreover, the increase of Se(IV) concentration made the density higher, and in turn it affected the ion mobility. It implied that the working curve of Se(IV) analysis was limited by the concentration.

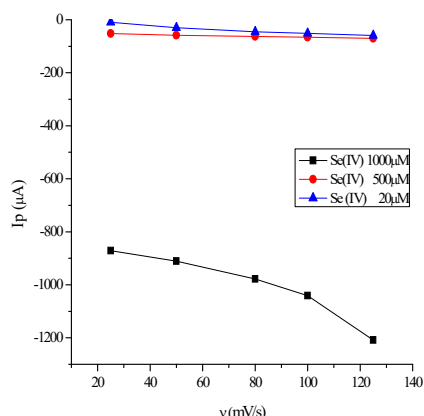


Figure 5. Correlation between peak intensity (I_p) of Se(IV) and scan rate (v)

The effect of cyclic repetition on the voltammetric behavior of selenium also studied. The experiment was performed using Se(IV) $20\mu\text{M}$ in HCl $0,1\text{M}$, with 5 times of repetition and scan rate 25mV/s (Fig. 6). It can be seen that I_{p_c} decreased with the number of repetition. This indicated the change of characteristic of working electrode CuHg due to the layer formation on the amalgam surface.

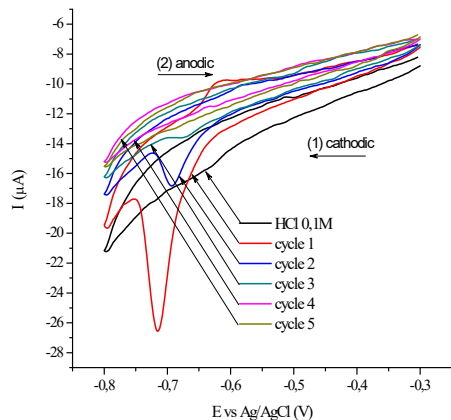
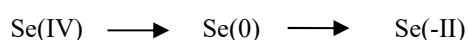
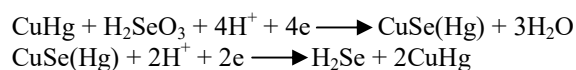


Figure 6. Cyclic voltammogram of $20\mu\text{M}$ Se(IV) in 0.1M HCl with five times cyclic repetition, scan rate 25mV/s

Based on the voltammetric behavior and disproportionation reaction of selenous acid, using Se(IV) in 0.1M HCl, we propose the reaction mechanism of Se(IV) on the surface of working electrode CuHg as follows:



where the reduction of Se(0) performed at the more negative potential. Reduction of Se(IV) followed this equations:



IV. CONCLUSION

Fabricated working electrode CuHg was used to evaluate the voltammetric behavior of selenium from H_2SeO_3 solution using cyclic voltammetry method. The method was performed at the range potential of -0.300mV to -0.800mV . The cathodic and anodic peak potentials, resulted in redox reaction of selenium on fabricated electrode CuHg, were -0.700mV and -0.600mV , respectively, toward reference electrode Ag/AgCl. The cyclic voltammogram profile of Se(IV) in 0.1M HCl was affected by Se(IV) concentration and applied scan rate. In addition, the number of cyclic repetition decreased the reduction peak intensity. This confirmed the adsorption of selenium at the surface of working electrode CuHg. All those phenomena indicated that the reduction of selenium at a certain concentration was a quasi-reversible, and current limitation was controlled by diffusion and adsorption.

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REFERENCES

- [1] Saji, V.S. and C.-W. Lee, Selenium electrochemistry. *RSC Advances*. 3(26), 2013, 10058-10077.
- [2] Tsoi, Y.-K. and K.S.-Y. Leung, Toward the use of surface modified activated carbon in speciation: Selective preconcentration of selenite and selenate in environmental waters. *Journal of Chromatography A*. 1218(16), 2011, 2160-2164.
- [3] Piech, R. and W.W. Kubiak, Determination of trace selenium on hanging copper amalgam drop electrode. *Electrochimica Acta*. 53(2), 2007, 584-589.
- [4] Ochsenkühn-Petropoulou, M. and F. Tsopelas, Speciation analysis of selenium using voltammetric techniques. *Analytica Chimica Acta*. 467(1), 2002, 167-178.
- [5] Potin-Gautier, M., F. Seby, and M. Astruc, Interference of humic substances on the speciation analysis of inorganic selenium in waters and soils by DPCSV. *Fresenius' journal of analytical chemistry*. 351(4), 1995, 443-448.
- [6] Papoff, P., F. Bocci, and F. Lanza, Speciation of selenium in natural waters and snow by DPCSV at the hanging mercury drop electrode. *Microchemical Journal*. 59(1), 1998, 50-76.

- [7] Bryce, D., A. Izquierdo, and M.L. de Castro, Sequential speciation of selenium by flow injection cathodic stripping voltammetry. *Fresenius' journal of analytical chemistry*. 351(4-5), 1995, 433-437.
- [8] Lange, B. and C.M. van den Berg, Determination of selenium by catalytic cathodic stripping voltammetry. *Analytica Chimica Acta*. 418(1), 2000, 33-42.
- [9] Mohamed, R. and L.W. Lee, Analysis of selenium species using cathodic stripping voltammetry. *J Technol*. 44, 2006, 55-66.
- [10] Ashournia, M. and A. Aliakbar, Determination of selenium in natural waters by adsorptive differential pulse cathodic stripping voltammetry. *Journal of hazardous materials*. 168(1), 2009, 542-547.
- [11] de Carvalho, L.M., et al., Redoxspeciation of selenium in water samples by cathodic stripping voltammetry using an automated flow system. *Analyst*. 124(12), 1999, 1803-1809.
- [12] Mattsson, G., et al., Determination of selenium in freshwaters by cathodic stripping voltammetry after UV irradiation. *Talanta*. 42(6), 1995, 817-825.