Int. J. Electrochem. Sci., 8 **(2013)** 4818 - 4826

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Voltammetric Oxidation of Potassium Thiocyanate using $ErBa_2Cu_3O_7$ Modified Glassy Carbon Electrode

Mohammed Zidan[*], *Tan Wee Tee, Elyas Sadeq Alaghbari, Mansor Ahmad. Kamyar.Shameli*

Department of Chemistry, Faculty of Science, Universiti Putra Malaysia, 43400 UPM, Serdang, Selangor D.E., Malaysia.
Department of Chemistry, Faculty of Science, University of Sebha, Libya
[*]E-mail: zidanupm@gmail.com

Received: 29 May 2012 / *Accepted:* 18 October 2012 / *Published:* 1 April 2013

The electrochemical analysis of $ErBa_2Cu_3O_7$ (ErBCO) superconductor materials, adhered at a glassy carbon electrode surface placed in an aqueous media has been investigated by cyclic voltammetry technique. Voltammetric determination of the oxidation of Thiocyanate in 0.1 M NH_4Cl electrolyte solution by solid phase voltammetry has shown the effect of copper–thiocyanate complexes. Observation revealed a high peak of ErBCO appears at 220 mV vs Ag/AgCl when there is an absence of thiocyanate, while in the presence of thiocyanate, peak current increases by 3.1. The voltammetric response of the ErBCO was found to depend greatly on the scan rate and pH. From CC studies, the amount of charge, Q that was present on the electrode surface is 5.513 $\mu C/cm^2$. The diffusion coefficient,D, value for the copper–thiocyanate complexes was determined to be 7.48×10^{-05} cm^2/s .

Keywords: $ErBa_2Cu_3O_7{-}\delta$; Modified GC electrode; potassium Thiocyanate; Cyclic Voltammetry

1. INTRODUCTION

In recent years, there has been an increasing interest in the preparation of a complex compounds such as $ErBa_2Cu_3O_7{-}\delta$ superconductor, which needs a crucial approach in order to obtain a high-purity product. Besides, several factors such as time and cost saving effects is needed to be considered during sample processing. This kind of method is called solid-state powder technique, which is conventionally used and most commonly reported in the literature [1, 2].The electrochemical properties of solid materials such as high-temperature superconductor could lead to more rapid developments in basic scientific research and in practical applications. Despite the complexity to obtain voltammetric data for solid state process compared to conventional solution cyclic voltammetry, it has now been known that it is possible to carry out voltammetric studies on redox active solid adhered abrasively at electrode surfaces and placed in contact with an electrolyte solvent [3]. Recently the electrochemical properties of the compound and also the mechanism of the electrochemical reaction taking place at the electrode-solid-electrolyte at different voltammetric condition has been reported and elucidated. [4, 5]. Thiocyanate (SCN^-) is an important ion in metabolism, which is often being affected by the consumption of specific foods or the smoking of tobacco. For the later, thiocyanate measurements can be used to distinguish between smokers and nonsmokers, as thiocyanate is a metabolic degradation product of tobacco smoke [6.7]. Present methods for measuring thiocyanate levels include a variety of spectroscopic and chromatographic methods as well as a number of electrochemical approaches [8]. The fabrication of chemically modified electrode (CME) consisting of a mixture of carbon paste and modifying reagent have been widely used. They can be easily prepared and have a stable electrode response and important analytical properties of electrodes-sensitivity, selectivity, reproducibility [9.14.15]. Since there are very limited electrochemical studies on ErBCO especially via cyclic voltammetry (CV), here we report the electrochemical properties of the compound and also elucidate the mechanism of the electrochemical reaction taking place at the electrode-solid-electrolyte at different voltammetric condition.

2. EXPERIMENTAL

2.1 Instrumentation and electroanalytical analysis methods

Electrochemical workstations of Bioanalytical System Inc. USA: Model BAS 50W with potentiostat driven by electroanalytical measuring softwares were connected to computer to perform cyclic voltammetry (CV), chronoamperometry (CC) and chronoamperometry (CA). An Ag/AgCl (3M NaCl) and platinum wire were used as a reference and counter electrodes respectively. The working electrode used in this study was 3 mm diameter glassy carbon (GC). Unless otherwise stated, the voltammetric experiments were carried out at 25 ± 2^oC using 0.1 M NH_4Cl as supporting electrolyte. Solutions were degassed with nitrogen for ten minutes prior to recording the voltammogram. Scanning electrode microscopy (SEM) was used to characterize the surface of the ErBCO composites at 5 mm diameter basal plane paralytic graphite electrode (BPPGE) (Model JOEL,JSM-64000 machine).

2.2 Reagents

ErBCO sample was prepared via co-precipitation and solid state methods as described by Nazarudin et al., 2011 [10] the samples were in a pellet form. The pellet of ErBCO was then cracked and ground to form fine powder. Deionized water by reverse osmosis (RO) via Elken’s water filteration system (BIO PURE) was used in the preparation of solutions. Unless otherwise specified, the supporting electrolyte was 0.1 M NH_4Cl in aqueous media at room temperature. All solutions were deaerated with oxygen-free nitrogen gas for 15 minutes prior to making the measurement.

2.3. Procedures

2.3.1. Preparation of a ErBCO- modified electrode

The solid compound was transferred to the clean surface of the glassy carbon electrode as follow: 1-3 mg of ErBCO microcrystalline was placed on a coarse grade paper. The working electrode was pressed onto the solid and rubbed over the clean electrode surface to transfer a trace amount of sample as an array of microcrystalline particles. For electrochemical measurement, the electrode was transferred into the solution. Commercial reagent grade chemicals were used as received. All the solutions were prepared using distilled water. All solution was degassed with high purity nitrogen gas for 15 min prior to electrochemical measurement.

3. RESULTS AND DISCUSSION

3.1. Enhancement Study

Figure 1 shows the cyclic voltammograms obtained for the oxidation of ErBCO in 0.1 M NH_4Cl supporting electrolyte at pH 3.0 at modified GC electrode (a), and in the presence of 0.2 mM thiocyanate (b). In Figure (a) the CV for ErBCO showed four major peaks. The first cathodic peak (E_p^c) was due to the reduction of Cu^{2+} to Cu^{1+} and second cathodic peak (E_p^c) was due to the reduction of Cu^{1+} to Cu^0 . The corresponding anodic peak (E_p^a) was due to the oxidation of Cu^0 to Cu^{1+} and of Cu^{1+} to Cu^{2+} as represented by the first and second oxidation peak (E_p^a) respectively. It is therefore evident that the electrolyte containing $NH4^+$ ion was responsible for the formation of some copper(II) complex as $Cu(NH_3)_4^{+2}$ complexes were easily formed and the following stepwise reduction may occur (reaction [1] and [2]). Presumably, $Cu(NH_3)_4^{2+}$ might have been formed which would rendered Cu^{2+} in ErBCO to be more electro-active. In Figure (b) the voltammogram showed that the peaks of ErBCO have two redox processes. The first cathodic peak oxidation potential of ErBCO appears at 220 mV vs Ag/AgCl in the absence of thiocyanate, while in the presence of thiocyanate, peak current increase by 3.1. In the second cathodic peak, a shift of 400 mV towards high positive region was observed for $^-$SNC. The peaks obtained are based on the following reaction of copper–thiocyanate complexes in processes (3) and (4):

$$Cu(NH_3)_4^{+2} + e^- \rightleftharpoons Cu(NH_3)^{2+} + 2NH_3 \qquad (1)$$

$$Cu(NH_3)^{2+} + e^- \rightleftharpoons Cu(s) + 2NH_3 \qquad (2)$$

$$Cu(s)+SCN^- \rightleftharpoons CuSCN+ e- \qquad (3)$$

$$Cu(s)+2SCN^- \rightleftharpoons Cu(SCN)_2{}^- + e- \qquad (4)$$

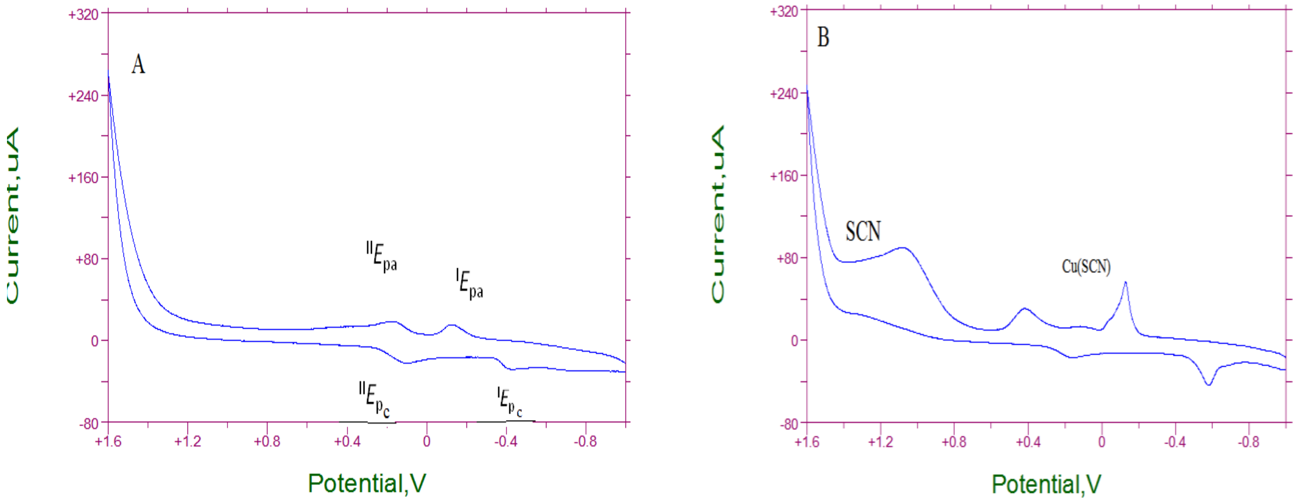


Figure 1. Cyclic voltammogram of ErBCO in 0.1 M NH_4Cl, at pH3.0 for the (a) absence of analyte, (b) presence of 0.2 mM thiocyanate

3.2. Effect of varying pH

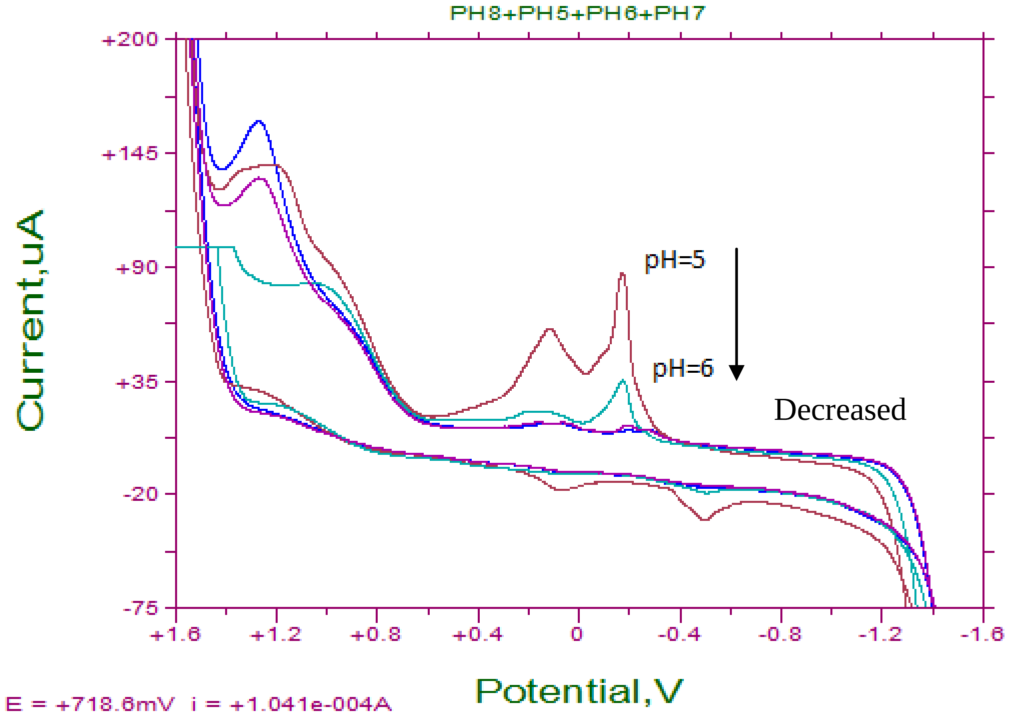


Figure 2. Graph of current versus pH for 0.2 mM thiocyanate in 0.1 M NH_4Cl in different pH, for the GC modified electrode with ErBCO/GC modified electrode.

The solution was varied from pH 2.0 to 11 in order to determine its effect on the oxidation of ErBCO /GC modified electrode. Figure 2 shows that the oxidation current of copper in the presence of 0.2 mM thiocyanate decreases with an increase in pH with maximum current response at pH3.0. However, when the pH increases, it was observed that there is an increment in the peak current of the

SCN^- due to the addition of the OH group as shown in the following reactions by Figuroa., et al 1986 [12]:

$Cu\ (SCN\text{-})_{ad} + H_20 \rightleftharpoons Cu(H_2O)_{ad} + SCN^-$ (5)

$CU\ (H_2O)_{ad} \rightleftharpoons Cu(OH)_{ad} + H^+ + e^-$ (6)

$xCu(OH)_{ad} \longrightarrow x^-\ Cu,O$ (hydrous). (7)

3.3. Effect of potential cycling

The stability of the ErBCO/GC modified electrode and its effect on the thiocyanate oxidation current were assessed by continuous potential cycling over the potential range where copper-thiocyanate is complexes. Fig. 3 shows that the current associated with the oxidation of copper-thiocyanate decreased slightly after the first cycle and remains unchanged from the fourth cycle onward. Even after the 20th potential cycle, the oxidation peak of copper-thiocyanate remains high; reflecting the stability of ErBCO/GC coating. This result can be related to the realization of steady condition in solid state cyclic voltammogram and the reaction is in equilibrium condition.

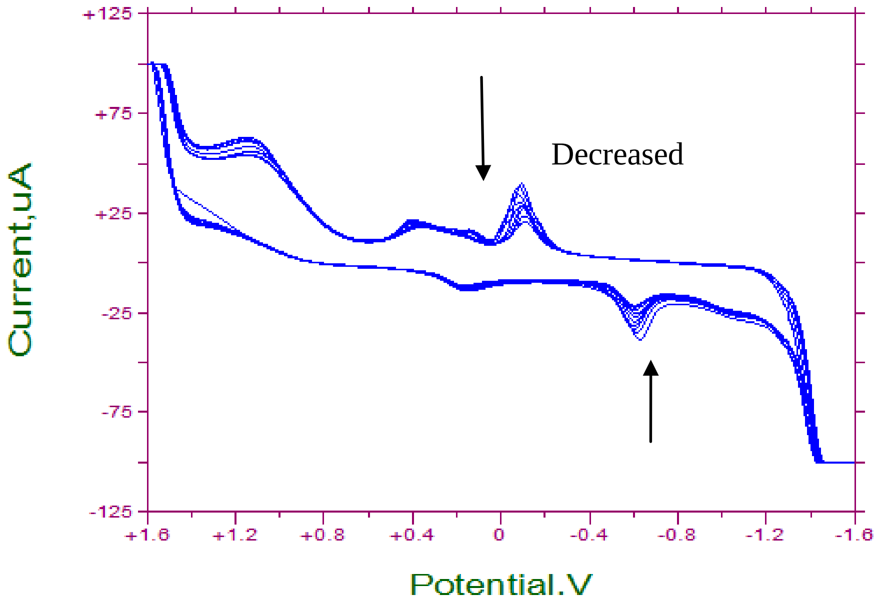


Figure 3. Multiple Cyclic voltammogram of 0.2 mM thiocyanate in 0.1 M NH_4Cl at pH 3.0, for the GC modified electrode with ErBCO- modified electrode.

3.4. Effect of varying scan rate

The effect of varying scan rates on the cyclic voltammograms of 0.2 mM thiocyanate using ErBCO modified working electrode in 0.1 M NH_4Cl supporting electrolyte was studied over scan rates in the range of 5 – 1000 mV/s. Oxidation currents of thiocyanate was observed to increase with scan rate due to heterogeneous kinetics. Based on a plot of log peak current versus log scan rate (Figure 4), v for oxidation current of thiocyanate , a straight line was obtained fulfilling the equation y = 0.81x + 7.32 with R^2=0.99. A slope of 0.47, which is quite comparable with theoretical slope of 0.8 for a complex surface process is obtained. [12-13]

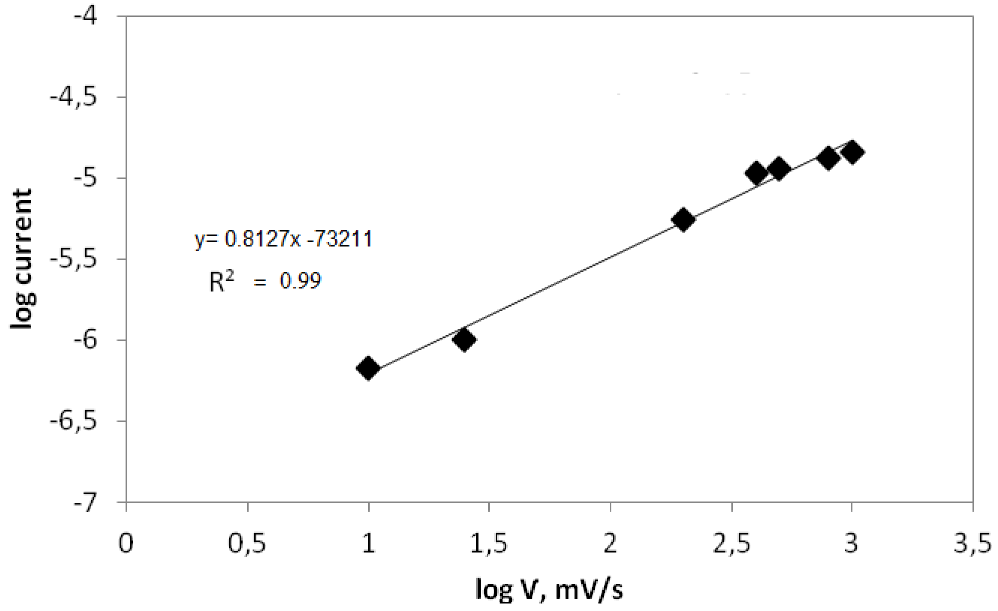
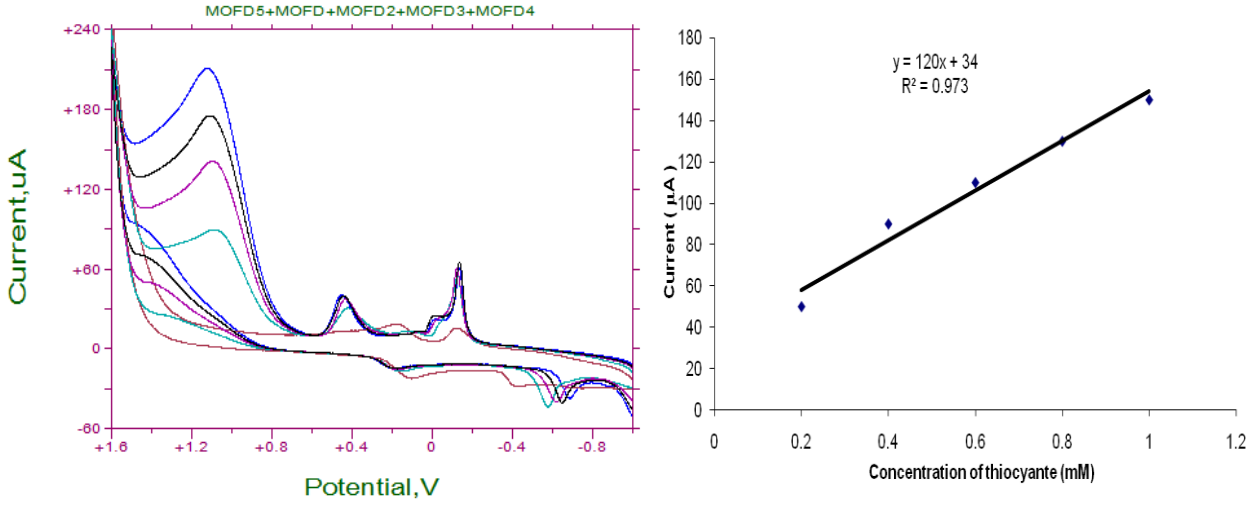


Figure 4. Graph of log peak current versus log scan rate for 0.2 mM thiocyanate in 0.1 M NH_4Cl in different scan rate, for the GC modified electrode with ErBCO- modified electrode.

3.5. Effect of varying thiocyanate concentrations



(a) **(b)**

Figure 5. (a) Typical cyclic voltammograms of various thiocyanate concentrations at ErBCO-modified electrode, immersed in 0.1 M NH_4Cl, pH 3.0, at scan rate of 100 mV/s (b) Calibration graph of thiocyanate (Similar conditions as above).

Figure 5 shows the calibration graph of thiocyanate in 0.1 M NH_4Cl. A linear response was achieved over the concentration range from 0 to 1 mM, which showed correlation of 0.974 R^2 value. The sensitivity of the modified electrode obtained from the linear equation slope was close to 102 mA L M^{-1}. The measured electrochemical response to thiocyanate concentration, [SCN^-], suggests that the sufficiently large thiocyanate concentration led to an increase in the adsorption of thiocyanate on the surface area of the electrode.

3.6. Chronocoulometry

Chronocoulometry (CC) is the integral analogs of the corresponding chronoamperometry approaches. From Figure 6, it was observed that the charges injected by the reduction of ErBCO were withdrawn by oxidation in reversed scan. The integral form of Cottrell equation gives the cumulative charged passed in reducing the diffused component:

$$Qd = 2nFAD1/2C\pi-1/2t1/2 \qquad (8)$$

Based on Anson's plot of the above, surface charge can be calculated by taking the difference between two intercepts of forward and reverse steps at t=0. It was found that the ErBCO/GC has a total charge transferred of 5.513 μC/cm2. The diffusion coefficient value, D, is 7.48×10-05 cm^2/s. This indicates that the ($Cu^{2+}L$) complexes sample produce a higher current in the redox reaction. The metal ions L =(NH_4^+, SCN^-)are highly diffusive for the sample (according to its diffusion coefficient value)

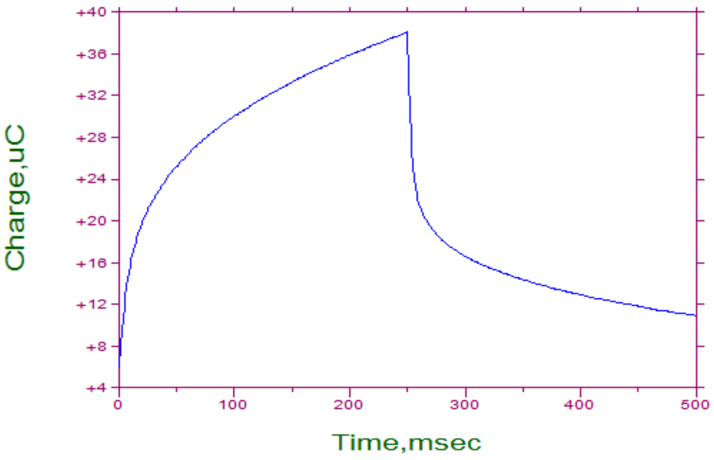
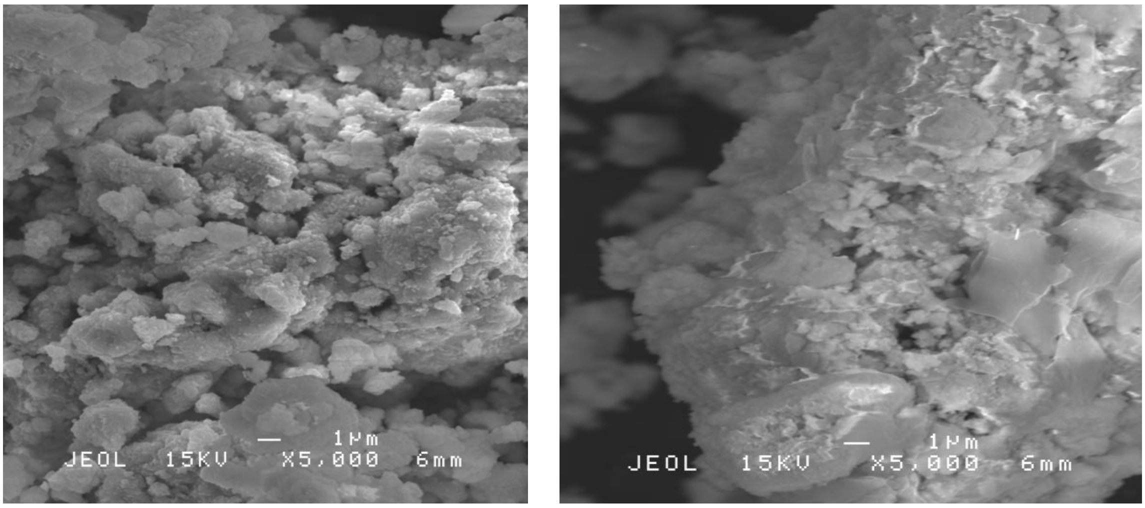


Figure 6. The chronocoulomogram of thiocyanate at the ErBCO/GC modified electrode in the presence of 0.1 M NH_4Cl electrolyte at 25^oC.

3.7. Scanning Electron Microscopy (SEM)

Before electrolysis (Figure 7a), the ErBCO appears rather loose and granular in form, while after electrolysis (Figure 7b), it showed a somewhat compact and crystalline in shape. As shown in

Fig. 7 (b), the size of particle agglomeration increased to crystallite size after electrolysis with the magnification of 5000 times.



(a) **(b)**

Figure 7. Scanning electron micrographs of ErBCO mechanically attached to a basal graphite electrode (5 mm diameter) and immersed in 0.1 M NH_4Cl electrolyte (a) before electrolysis (b) after electrolysis with an enlargement of 3000 times

4. CONCLUSION

ErBCO/GC electrode was successfully fabricated and has exhibited the complexity of the interactions effect on the oxidation of thiocyanate. The oxidation current of thiocyanate at ErBCO/GC modified electrode appeared with an enhancement of 3.1 times compared to in the absence of thiocyanate. The thiocyanate ions were adsorbed onto the reaction surface of the modified electrode. Although ErBCO performed optimally in acidic (pH3.00) condition, it appears to be stable voltammetrically. The voltammogram obtained for ErBCO sample showed four major peaks which are attributed to the first and second redox couples. The peaks are due to the redox reaction of $Cu(NH_3)_4^{2+}$ complex. The peak current is highly dependent on the formation of the $Cu(NH_3)_4^{2+}$ complex which shows that the copper planes in the superconductor played a major role in producing the peaks observed in the voltammograms. The investigation of the research shows that ErBCO has the potential to be used as a good chemically modified electrode which can be employed in electro catalysis studies of some rather electro-inactive biochemical compounds.

ACKNOWLEDGEMENT
The authors wish to thank Universiti Putra Malaysia for providing research facility and financial support for the accomplishment of this work.

References

1. T.J. Cardwell, J.H. Santosa, A.M. Bond. .*Analytica Chimica Acta* 340 (1997) 169-174
2. A.J. Bard, and L.R. Faulkner, *In: Electrochemical Method*, Wiley, New York (1980).
3. Cattien V Nguyen, Kuo-Jen Chao, Ramsey M. D. Stevens., *Nanotechnology* 12 (2001) 363.
4. M. F. Nazarudin, Z. Zainal, W.T. Tan, I. Hamadneh. E.F. Kadri *Int. J. Electrochem. Sci*., 7 (2012) 2970
5. M. F. Nazarudin, I. Hamadneh, W. T. Tan, Z. Zainal, *The journal.Supercond Nov Magn*. 24(5) (2011) 1745.
6. M. Arvand, M. A. Zanjanchi, L. Heydari, *Sensor and Actuator* B 122 (2007), 301-308
7. M. J. Segu, J. Lizondo-Sabater, R. Mart_nez-Ma´n˜ ez, F. Sanceno´ n, J. Soto, *Talanta* 2006, 68, 1182-1189
8. M. P. Sánchez, M. Barrera, S. González, R. M. Souto, R. C. Salvarezza, A.J Arvia, *Electrochimica Acta* . 35(9) (1990) 1337-1343
9. M. G. Figuroa , R. C. Salvarezza and A. J. Arvia **,** *Electrochimica Acta* (1986.)Vol. 31, No. 6. pp. 67 1480-1492
10. S. Nariki, M .Murukami. *Supercond. Sci. Technol*. 15, (2002)786.
11. S. Dong, X. Yuanwu , C. Guangjin,. *Electroanalytical chemistry* 513 (2001) 52-58
12. S.Tanaka and H.yashida,. *Talanta*., 36(1989)1044-1049
13. K .A. Yahya., R .Abd-Shukor., *Supercond. Sci. Technol*. 11, (1998)173-178

© 2013 by ESG (www.electrochemsci.org)