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Abrasive Stripping Voltammetric (Abrsv) Studies of $ErBa_2Cu_3O_{7-\delta}$ Superconductor Synthesised Via Co-Precipitation and Solid State Methods

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The electrochemical analysis of $ErBa_2Cu_3O_{7-\delta}$ (ErBCO) superconductor ceramic materials, adhered abrasively at a glassy carbon electrode surface placed in an aqueous media has been investigated by abrasive stripping voltammetry, AbrSV technique. ErBCO samples were prepared via co-precipitation (COP) and solid state (SS) method. Powder x-ray diffraction (XRD) patterns showed both samples to be single-phased 123 of an orthorhombic structure. Details studies on the reduction-oxidation of ErBCO involved the variation of scan rate, temperature and pH of electrolyte as well as chronoamperometry (CA) and chronocoulometry (CC). The voltammogram obtained for ErBCO prepared in both methods showed four major peaks attributed to 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 upon the formation of the $Cu(NH_3)_4^{2+}$ complex which shows that the copper planes in the superconductor played major role in producing the peaks observed in the voltammograms. The voltammetric response of the ErBCO was found to depend greatly on the scan rate, pH and temperature. From CA and CC studies, the amount of charge, Q that was presence on the electrode surface is 4.7 $\mu C/cm^2$ and 5.4 $\mu C/cm^2$ and diffusion coefficient, D is 3.4 x $10^{-6} cm^2/s$ and 4.0 x 10^{-6} cm^2/s for solid state and co-precipitation method respectively.

Keywords: $ErBa_2Cu_3O_{7-\delta}$, abrasive stripping voltammetry, $Cu(NH_3)_4^{2+}$ complex, chronoamperometry (CA) and chronocoulometry (CC), diffusion coefficient

1. INTRODUCTION

The electrochemical analysis of solid materials was designed to identify or analyses the redox state composition of solid mixture and characterize their electrochemistry-related properties.

Understanding 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 of complexity to obtain voltammetric data for solid state process compared to conventional solution cyclic voltammetry, it has a now been renowned 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) [1]. This analytical technique, involving the voltammetry of micro particles immobilized on electrode surfaces and has known as Abrasive stripping voltammetry (AbrSV) [2]. AbrSV could be employed and extensively use to investigate and elucidate the mechanism of electrochemical reaction taking place at the electrode-solid-electrolyte interface [3-7]. The advantages of AbrSV technique are this method can be applied to all solid compounds that include at least one of electrochemically active element and can elucidate the very complex condition on the surface electrode. In addition, it also required very small quantities of a sample to give easily measurable currents. This technique is especially useful for the voltammetric studies of compounds that are insoluble in important solvents such as water. However, the electrochemical studies on high-temperature superconductor via AbrSV method are less reported.

Since the discovery of high temperature ceramic superconductors by Nobel Prize winner, J. G. Bednorz and K. A. Müller in 1986, the studies on the superconducting materials are actively done. Nowadays, scientific research activity not limited to the discovery of new class of superconductor but also to elucidate the disproportionate theory of high-temperature superconductivity and then to invent the future application for the society. Numerous electrochemical studies have been done on superconductors, mainly on rare earth, (RE), $YBa_2Cu_3O_{7-\delta}$ (YBCO-123 system) [8-11], BSCCO system [12] and also on other type of superconductors. Nevertheless, 123 systems are being chosen in this research study because this system has better characteristics in terms of reactivity in comparison of the common copper-oxide superconductors [13]. In this paper, we reported the electrochemical reduction-oxidation of cuprate-oxide-based superconductor 123 systems, $ErBa_2Cu_3O_{7-\delta}$ (ErBCO) prepared via different type of preparation which is chemically synthesized, co-precipitation (COP) and physical mixtures of oxides and carbonates, solid state (SS) method. The critical temperature, T_c is slightly higher for sample prepared through COP method ($T_{c(R=0)}$ = 91 K) than prepared through SS method ($T_{c(R=0)}$ = 90 K). Er ions were selected to replace Y in YBCO because it is significantly smaller than Y and is abundant [14].

The differences among $REBa_2Cu_3O_{7-\delta}$ may be related to the crystal chemistry which changes with the RE ionic size [15]. Since there are very limited electrochemical studies on ErBCO especially via AbrSV, here we report 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.

These data were discussed in more detailed and comparisons were made between samples prepared via COP and SS to realize whether the preparation methods might or might not affect the electrochemical properties of the sample. Further information from data obtained such as the activation energy (E_a) of the compound and diffusion coefficient, D also provided from the resulting current response.

2. EXPERIMENTAL

2.1 Cyclic voltammetric measurement

ErBCO sample was prepared via co-precipitation and solid state methods as described by Nazarudin *et al.*, 2011 and Yahya *et al.*, 1997[16-17]. The samples were in a pellet form. The pellet of ErBCO then was cracked and ground to form fine powder.

Prior to mechanical transfer of solid compound, the electrode surface was cleaned using polishing kit. 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.

In this study, 20ml of 0.1 M NH_4Cl supporting electrolyte was used. All solution was degassed with high purity nitrogen gas for 15 minutes prior to electrochemical measurement. All of the voltammetric measurements were performed at room temperature (25°C ± 2°C) at the scan rate of 100 mV/s, unless otherwise stated.

2.2. Instrumentation and Apparatus

An electrochemical analyzer (BAS 100W) was used for cyclic voltammetry (CV) chronoamperometry (CA) and chronocoulometry (CC). All the electrochemical measurements were carried out in a voltammetry cell consisted of 3 mm glassy carbon (GC) as a working electrode (WE), Ag/AgCl in 3.0 M NaCl as a reference electrode (RE) and 1 mm Pt as a counter electrode (CE).

2.3. Parameters

2.3.1. General Solid State Voltammetry Study of ErBCO

For the electrochemical reduction-oxidation of the GC electrode, the potential was initially scanned to 1.0 V (vs. Ag/AgCl), held for 2 min, and reversed to -1.0 V in 0.1 M NH_4Cl (unless otherwise specified). Repeated scans between 0.4 and -1.0 V after the reduction-oxidation treatment gave a stable background current. The potential window was selected between 0.4 V to -1.0 V. The sample mechanically attached onto GC electrode was placed in voltammetry cell electrochemical measurements. The cyclic voltammogram was recorded.

2.3.2. Effect of Repetitive Cycle of Potential

The effect of multiple cycling of both samples was studied in 0.1 M NH_4Cl with a scan rate of 100 mV/s at 25 ± 2 ^{o}C for five cycles.

2.3.3. Effect of Varying Temperature

The temperature of 0.1 M NH_4Cl electrolyte was varied from 10°C to 80°C. The bath temperature was controlled by a thermostat where and ice was used wherever necessary.

2.3.4. Effect of Varying pH

In order to obtain a series of pH range, 0.1 M NH_4Cl with pH 5 was titrated with 1.0 M HNO_3 to form an acidic solution and 1.0M NaOH to form a basic solution. The pH range was from pH 2.0 to 9.0.

2.3.5. Effect of Varying Scan Rate

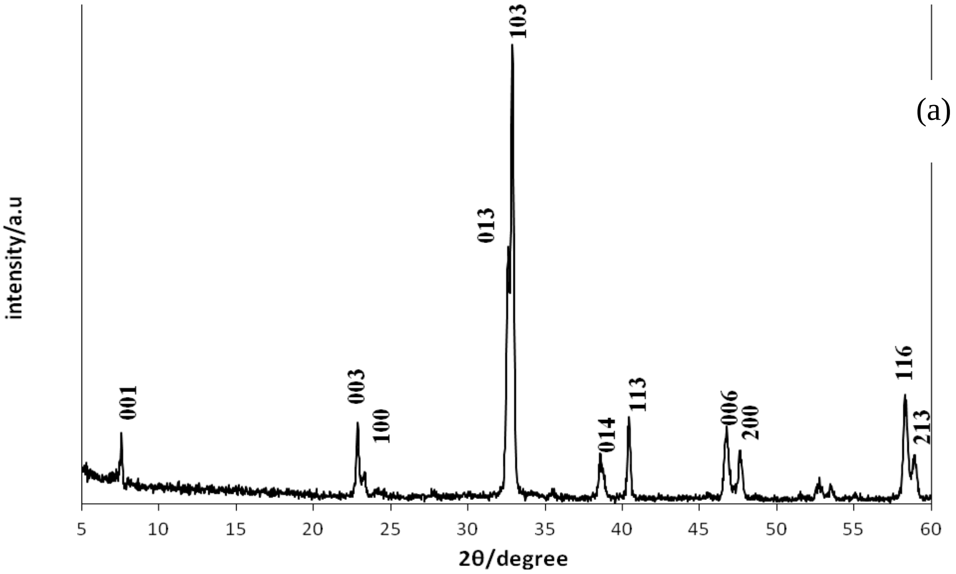
The cyclic voltammogram was examined for ErBCO in 0.1 M NH_4Cl with different scan rate ranging from 5 to 1000 mV/s. Other conditions were the same as described before.

2.3.6. Chronoamperometry (CA) and Chronocoulometry (CC)

ErBCO was studied with the techniques of double potential step chronoamperometry and chronocoulometry in 0.1 M NH_4Cl by using 3 mm GC electrode as working electrode.

3. RESULTS AND DISCUSSIONS

3.1. Powder X-Ray Diffraction and General Solid State Voltammetry Study of ErBCO



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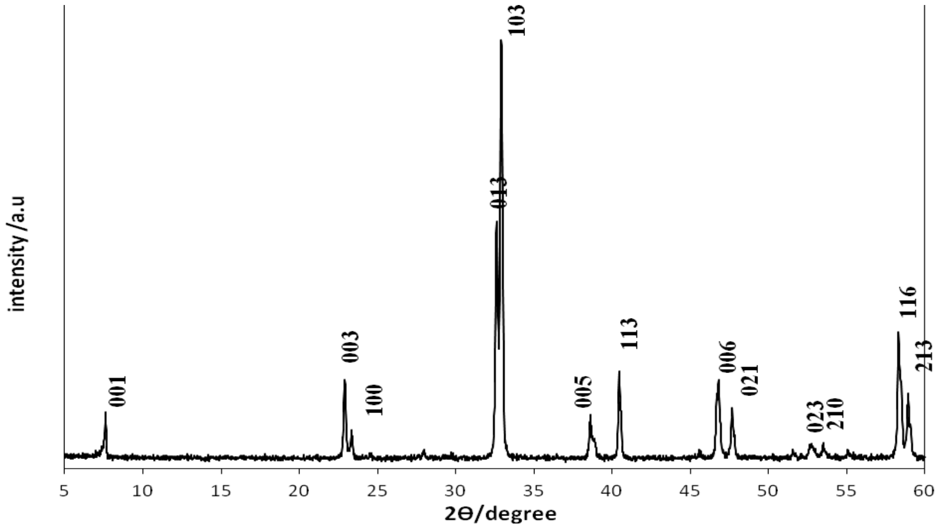

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Figure 1. X-ray powder diffractograms for samples prepared via a) co-precipitation and b) conventional method.

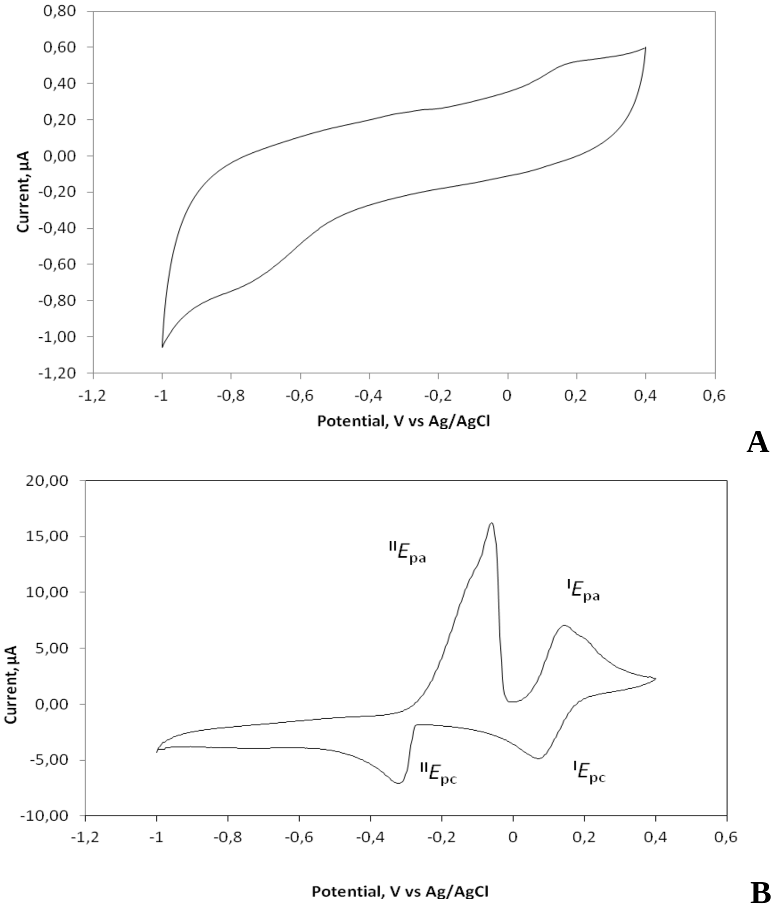


Figure 2. Cyclic voltammogram obtained for the oxidation-reduction of a) bare electrode (GC) and b) ErBCO mechanically attached to GC electrode surface in presence of 0.1 M NH_4Cl at 25°C using scan rate 100mV/s.

Powder X-Ray Diffraction pattern (Figure 1a-b) confirmed that ErBCO sample consist of essentially single phased orthorhombic 123 structures. Figure 2a and b shows a cyclic voltammogram (CV) of a GC bare electrode (without sample) and ErBCO powder mechanically attached at a 3 mm glassy carbon electrode surface. From the voltammogram obtained, there were no peak appear for a bare electrode. Meanwhile four peaks were observed which are two cathodic peaks and two anodic peaks for ErBCO. These peaks show that ErBCO has the two redox processes. First redox process is from the first cathodic peak and anodic peak, while the second redox process was from the second cathodic and anodic peaks. The changes in CV upon continuing cycling show a well defined and symmetrical reduction-oxidation process.

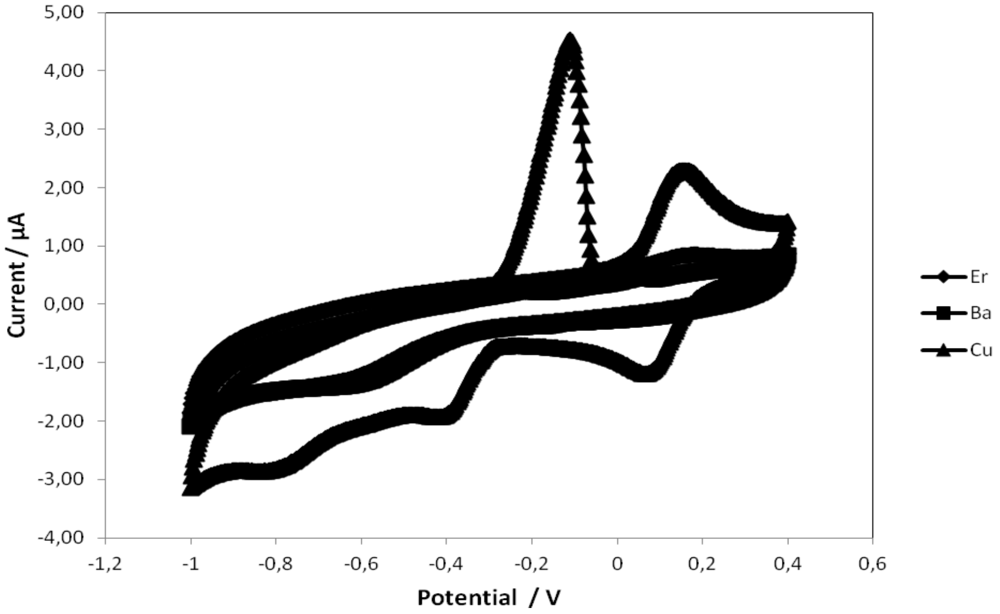


Figure 3. Cyclic voltammogram obtained for the oxidation-reduction of parent material.

When the voltammograms is compared with the CV of the parent materials (Figure 3) it is obvious that above reaction was due to copper species as only the copper species produced four pronounced peaks [18-19]. Cathodic peaks, ${}^{I}E_{pc}$ and ${}^{II}E_{pc}$, occurred at 64.2 mV and -329.4 mV and anodic peak, ${}^{I}E_{pa}$ and ${}^{II}E_{pa}$ appeared at 146.6 mV and -60.8 mV *vs* Ag/AgCl respectively. These results also agreed to finding by other researchers [8], when they assigned the positive peak to the reduction of Cu^{2+} to Cu^{+} and negative peak represent the reduction of Cu^{+} to Cu^{0}. Therefore, the peaks obtained are based on the following reaction mechanism:

Process I:

Peak ${}^{I}E_{pc}$: $Cu^{2+} + e^{-} \longrightarrow Cu^{+}$ 64.2mV [1]

Peak ${}^{I}E_{pa}$: $Cu^{+} \longrightarrow Cu^{2+} + e^{-}$ 146.6mV [2]

Process II:

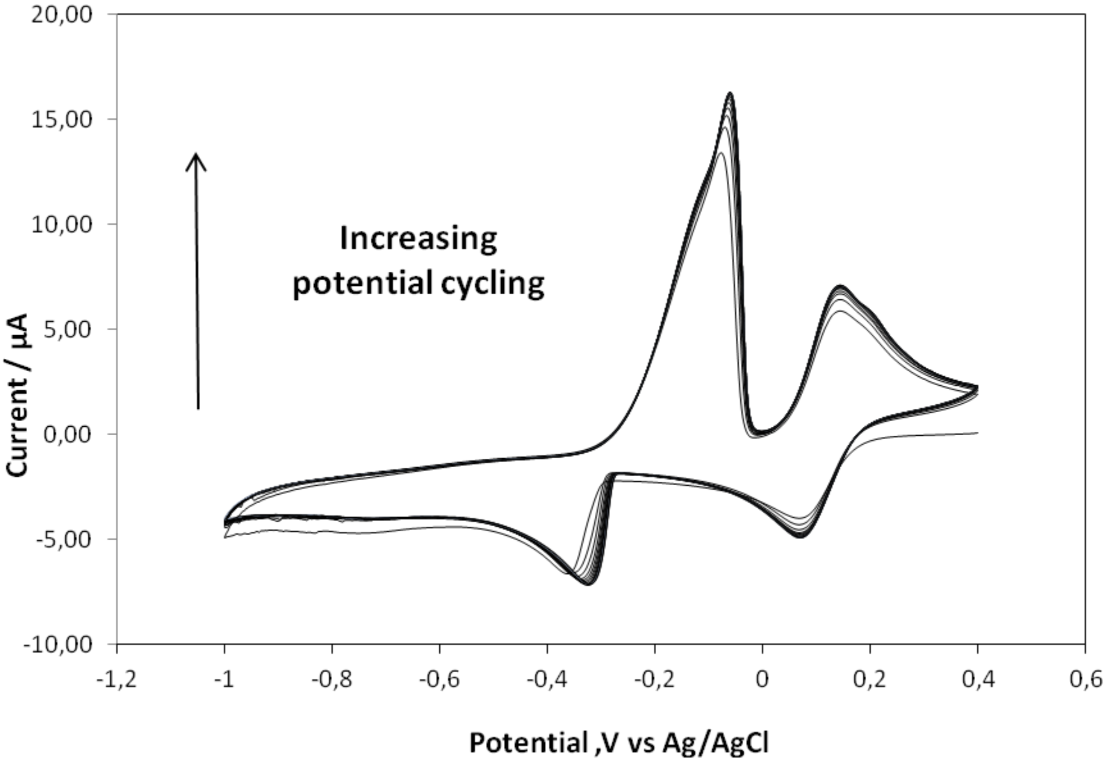
Peak $^{II}E_{pc}$: $Cu^+ + e^- \longrightarrow Cu^0$ -329.4mV [3]

Peak $^{II}E_{pa}$: $Cu^0 \longrightarrow Cu^+ + e^-$ -60.8mV [4]

Other parent materials emerge to be electro inactive within the potential range electrode since no redox peaks has been traced under similar experimental conditions. Besides, it is also shows that NH_4^+ electrolytes have strong complexing ability with copper ions as it has a ligand bearing group.

3.2. Effect of Repetitive Cycle of Potential

Continuous potential cycling was carried out in the potential range of 0.4 V to -1.0 V against Ag/AgCl with scan rate of 100 mV/s for both COP and SS samples. Fig. 4 shows that the peak current keeps on increasing upon repetition scanning. The peak current keeps on increasing up to 5th cycles. Results obtained from multiple cycling also show that cyclic voltammogram waveform for first cycle was unstable. This may due to a small amount of ErBCO on the electrode has yet to be reduced completely. Nonetheless from the 2nd cycle onwards, symmetrical reduction-reoxidation process appears to be at steady state associated with the stability of ErBCO upon continuous cycling. This result can be related to the realization of steady condition in solid state cyclic voltammogram and the reaction is in equilibrium condition.



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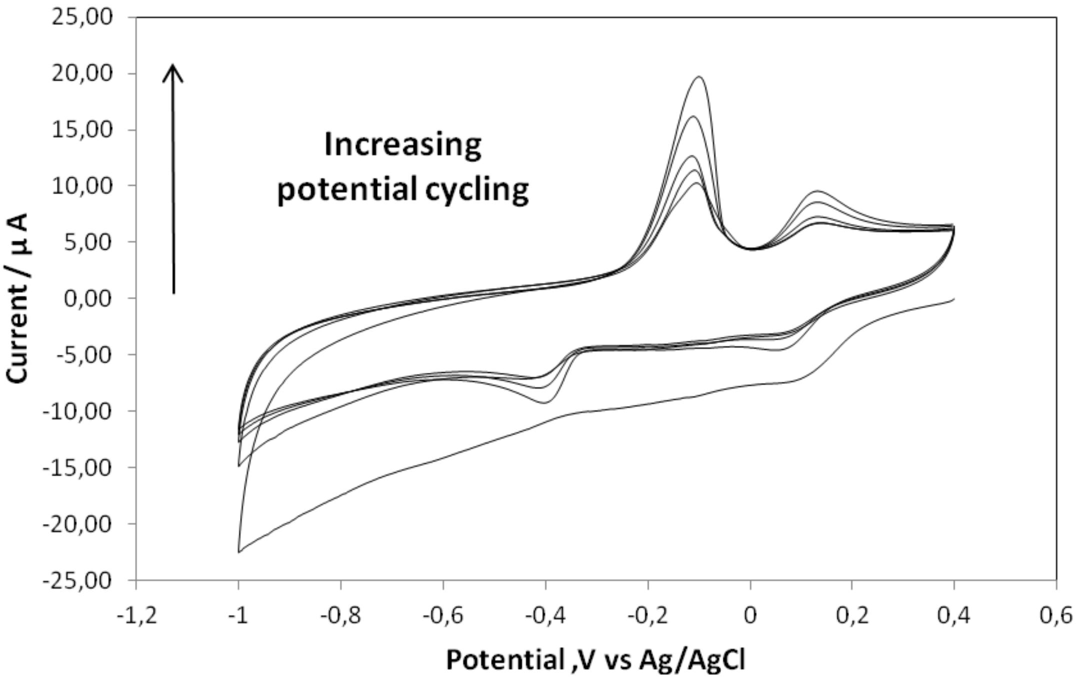

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Figure 4. Cyclic voltammogram of ErBCO prepared via (a) co-precipitation and (b) conventional solid state technique during potential cycling of 5 cycles, at 25^{o}C using scan rate of 100 mV/sec.

3.3. Effect of varying temperature

The change in temperature led to the significant effect on peak current of ErBCO. According to the studies by Tan *et al* 2002 [20], an increment in temperature aided the dissolution of the solid surface solid. This latter enhancement may be attributed to changes in the diffusibility or diffusion coefficient, D of ErBCO which increases exponentially with temperature as described in Eq. 5:

$$D = D^{\circ} exp\frac{(-\Delta H)}{RT} \qquad [5]$$

where D^o is a constant and ΔH is the heat of formation. Consequently as the diffusity, D increases, the current for the oxidation and reduction peak will increase. However while use at elevated temperature can give an increase in current in a practical sense, applications need to be under taken close to ambient temperature.

From Arrhenius's equation [6], the activation energy (E_a) that was produced by the compound can be determined. From equation [7], k can be referred as current, i.

$$k = Ae^{-Ea/_{RT}} \qquad [6]$$

$$logk = \frac{-Ea}{R}\frac{1}{T} + logA \qquad [7]$$

From the plot of log *i* versus 1/T (K^{-1}), (Fig. 5), the value of activation energy (E_a) is 6.2 kJ.mol^{-1} and 8.6 kJ.mol^{-1} for ErBCO prepared through co-precipitation and solid state method respectively.

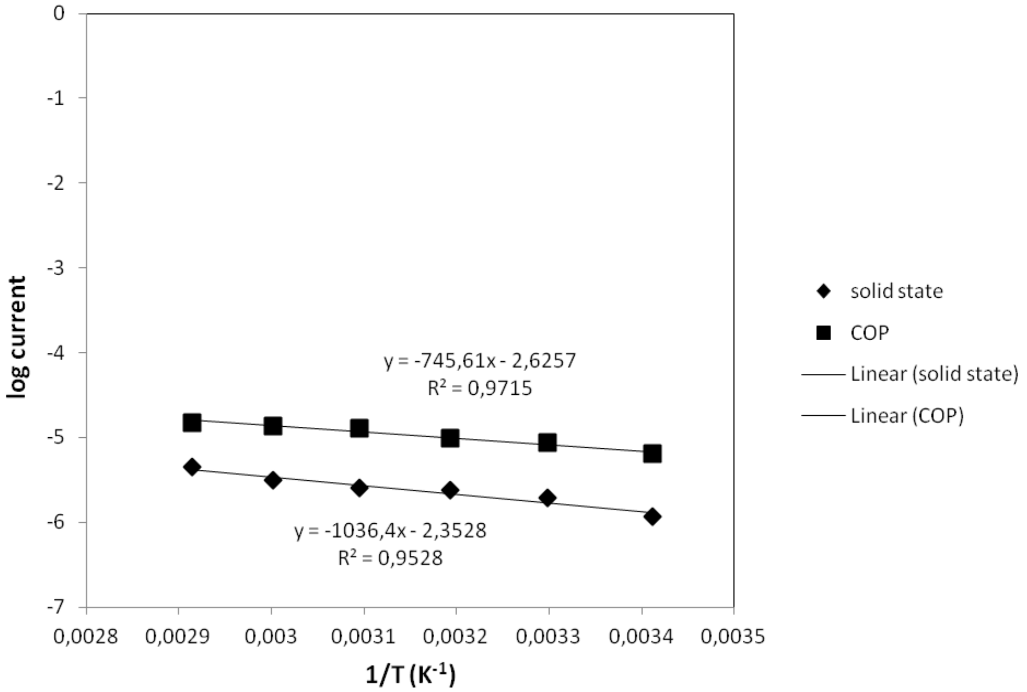
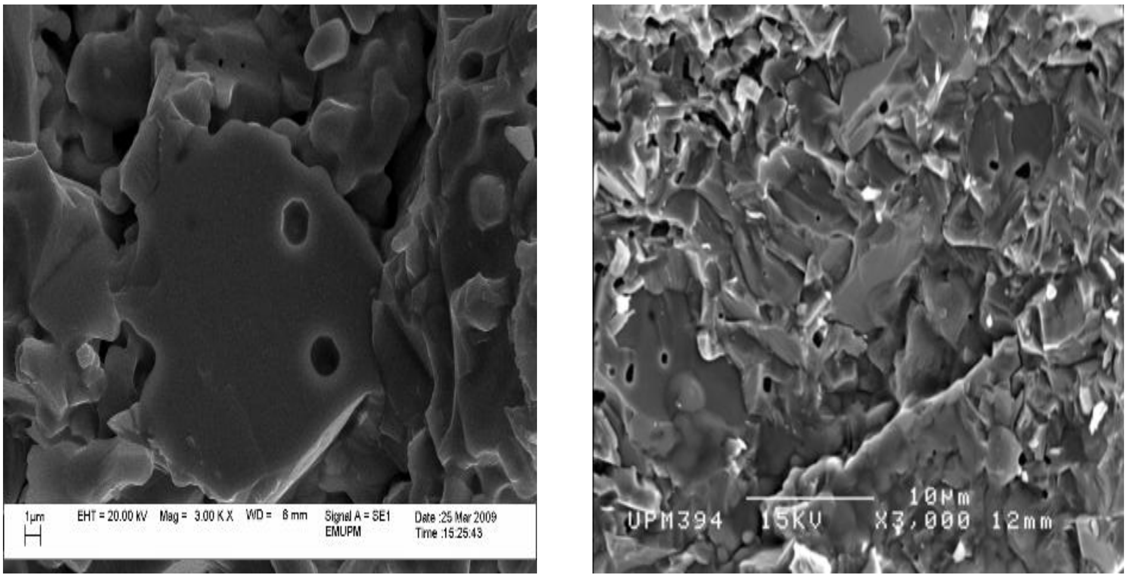


Figure 5. Graph of log current versus 1/T of different temperature of electrolyte on both ErBCO GC modified electrodes.

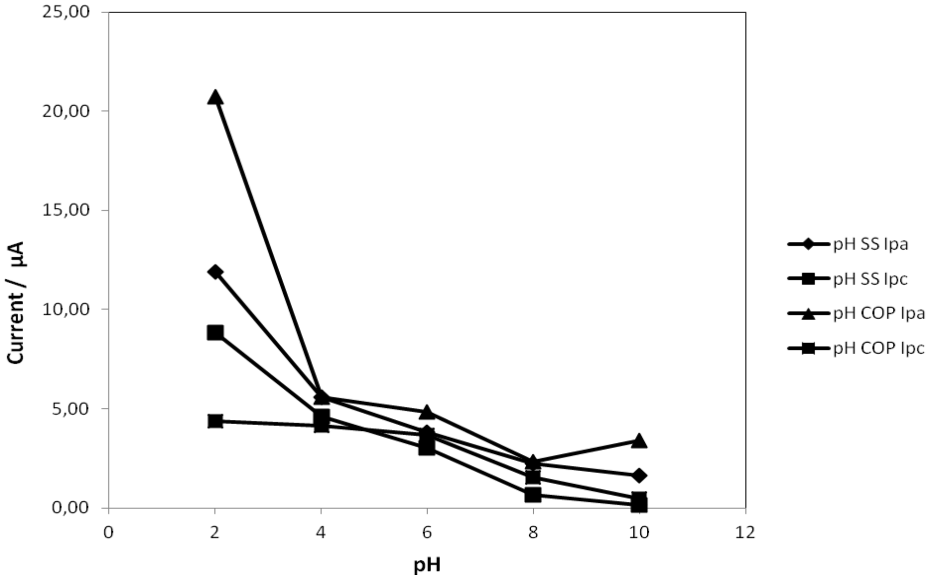


A **B**

Figure 6. Scanning electron micrograph of sample (a) solid state and (b) co-precipitation.

The activation energy value for SS sample is higher than COP sample probably due to the SS sample is denser than COP sample as shown in Fig 6a and b. This is because activation energy can be related with the morphology of the sample where higher energy must be overcome in order for a chemical reaction to occur especially in the samples with large surface area and denser.

3.4. Effect of varying pH



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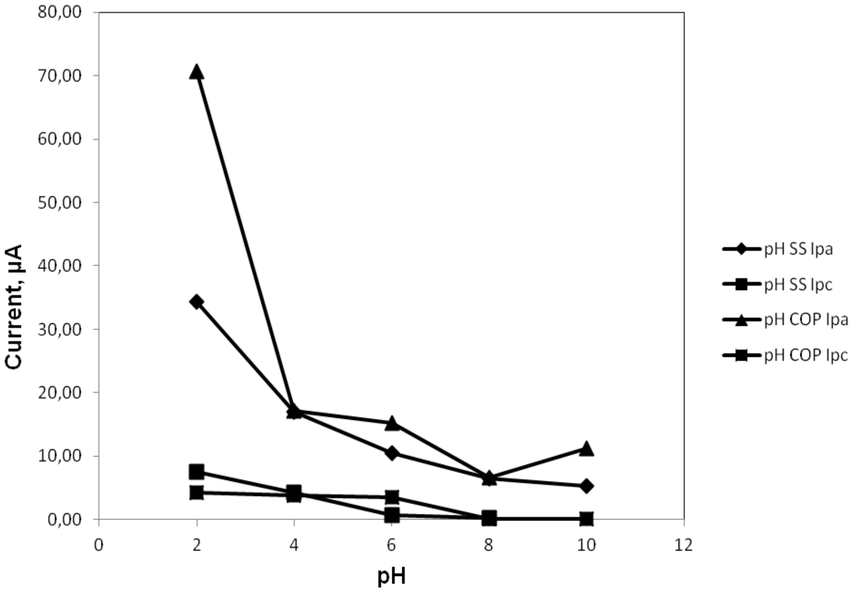

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Figure 7. Plot of peak current (I_p) versus pH for ErBCO (COP) mechanically attached to GC electrode surface in presence of 0.1M NH_4Cl using scan rate 100 mV/s for a) first redox couple and b) second redox couple.

The role played by pH gives an impact on the solubility of soluble species which indirectly control the stability and influence the peak potential and resultant current of the redox couples of the metal complex. There are other effects to be considered, such as the amount of ErBCO that had to be controlled. The pH of the electrolyte solution was varied from pH 2.42 to pH 10.11 to determine its effect on reduction and oxidation of ErBCO by titrating the NH_4Cl aqueous electrolyte with dilute H_2SO_4 acid during cyclic voltammetry. It was found that the cyclic voltammogarm of ErBCO were more stable in acidic medium rather than in basic medium. Moreover the enhancements of peak current occur at low pH and the peaks become ill defined in basic medium. This is due to rapid surface decomposition occurs in acidic medium where more electro active species formed agreed to study done by Rosamilia *et al*. (1987) [9]. At very low pH, the acidic solution dissolve more ErBCO adhered to glassy carbon surface thus produced more Cu^{2+} and Cu^{+} cations and led to the higher current response. In addition, the lowering of pH would also bring about a change in diffusion rate and affecting the redox reaction.

In general, peak current increase as pH of solution decreased, for both anodic and cathodic for first and second redox couple (Figure 7a-b). The peak current for pH 2 has the highest current, and started to decrease with the increase in pH. At higher pH, least amounts of electro active soluble species would be formed since the solid compound become less soluble.

3.5. Effect of varying scan rate

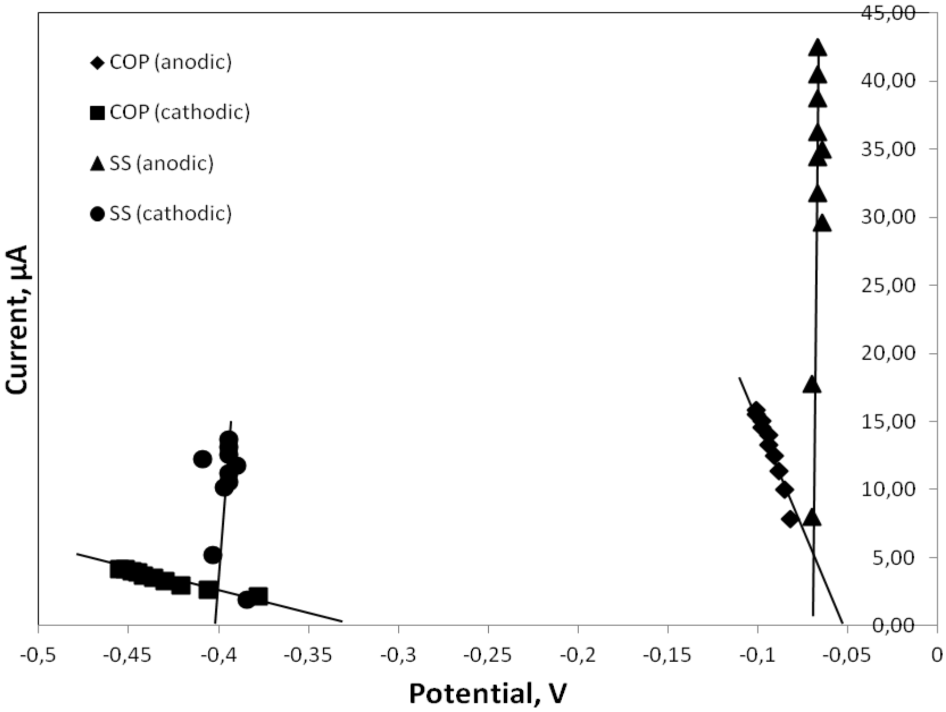
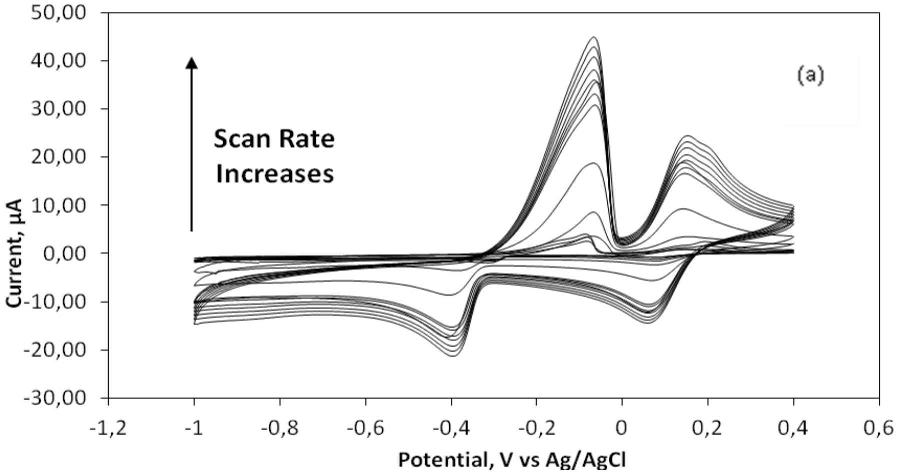


Figure 8. Plot of current versus peak potential for sample prepared solid state (SS) and co-precipitation (COP) method.

A series of scan rate studies was carried out to determine the zero-current potential of ErBCO (prepared via co-precipitation and solid state) in NH_4^+ electrolytes solution. The scan rate study determines the value of E^o_p', (i.e. potential at zero current) for both oxidation (E^o_{pa}') and reduction (E^o_{pc}') processes. A linear plot of peak current versus peak potential is shown in Figure 8. These linear dependencies allow extrapolation of peak potential data to zero current. From graph of current versus peak potential, the value of E^o_p' for both preparation method is within error range of ± 5 mV. At zero-current ($i = 0$), value E^o_{pa}' obtained is 70 mV and 50 mV for sample prepared through solid state and co-precipitation method, respectively. While, value of E^o_{pc}' at zero-current ($i = 0$) is 385 mV and 320 mV for sample prepared through solid state and co-precipitation method, respectively. Therefore, we can end that the E^o_p' values is not dependent on the method of preparation as the value for both samples are fairly similar. This is expected as E^o_p' is independent on the morphology of the micro particles attached to the electrode surface.



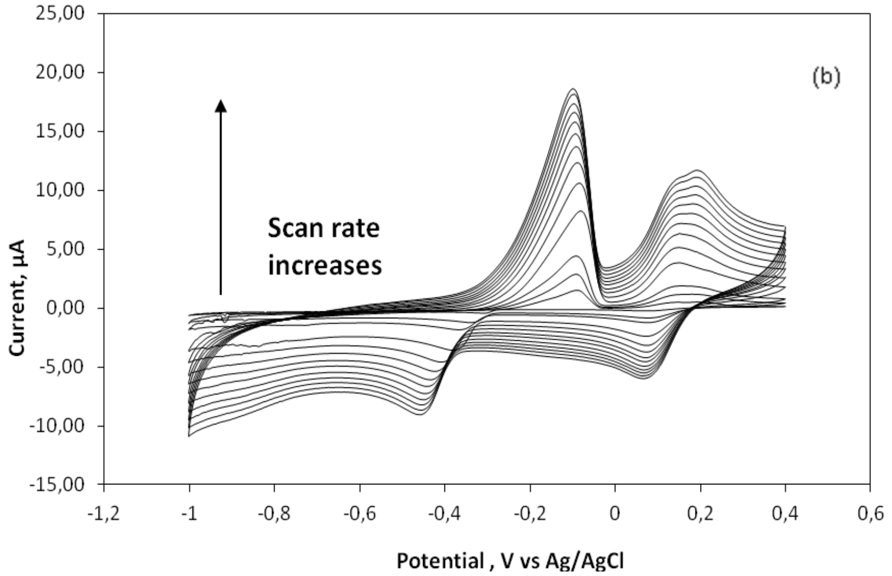


Figure 9. Cyclic voltammogram of ErBCO prepared via (a) co-precipitation and (b) solid state technique.

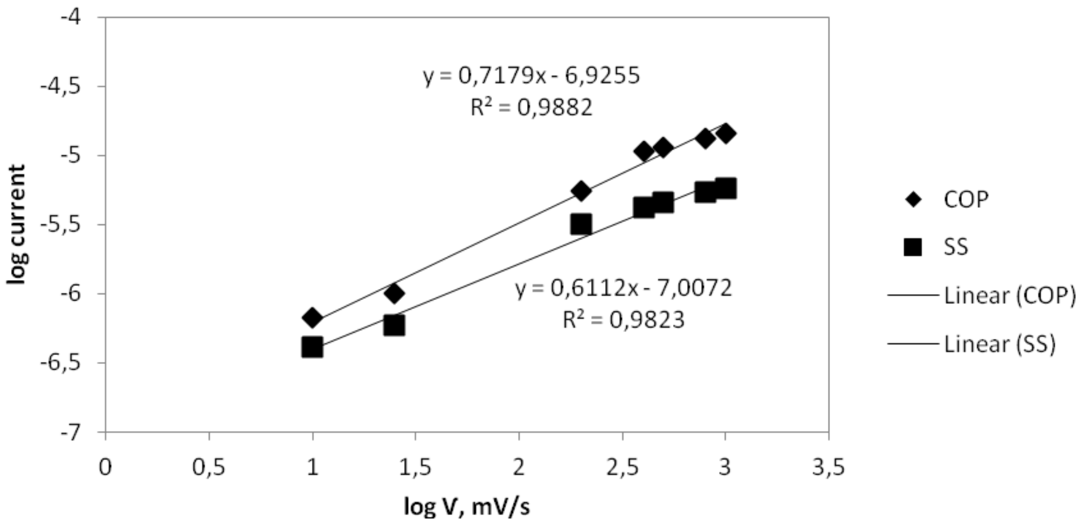


Figure 10. Dependence of log reductive current on log scan rate for ErBCO-GC electrode for both prepared sample in 0.1 M NH_4Cl.

The affects of varying scan rate which varied from 5 to 1000 mV/s in 0.1M aqueous ammonium chloride are illustrated in the Fig.9. The result showed that the peak has the same formation but apparently that the total current of oxidation and reduction processes increase with an increasing scan rate due to the size of the diffusion layer and the time took to record the scan. The cyclic voltammogram will take longer to record as the scan rate is decreased. Therefore, the size of the diffusion layer above the electrode surface will be different depending upon the voltage scan rate used. At higher scan rates, the signals broadened significantly accordingly of an increase in heterogeneous kinetics and/or IR drop allied with increasing scan rate. Figure 10 shows the ErBCO reductive current demonstrated the dependence of log current (i) on log scan rate (v). Based on the results obtained, the slope of the oxidative current of ErBCO prepared in both techniques is between 0.6 – 0.8 which is expected for a complex surface process [21].

3.6. Chronoamperometry (CA)

Chronoamperometry, (CA) provides heterogeneous kinetics information of the electrode reaction of the ErBCO microcrystalline compounds. For CA, if the point in time where the potential step is taken as time zero, the Cottrell equation describes how the current, I, decays as a function of time, t. Cottrell’s equation for a planar electrode is as below:

$$I = \mathrm{n}FAD^{1/2}C\pi^{-1/2}t^{-1/2} \qquad [7]$$

Figure 11 and 12 showed the observation of monatomic transient current with a maximum from double potential step chronoamperometric experiments. The experiments were carried out with an initial potential step from 0.4 V to 0.6 V *vs* Ag/Ag$^+$. From the Cottrell's equation, the diffusion coefficient, D can be calculated.

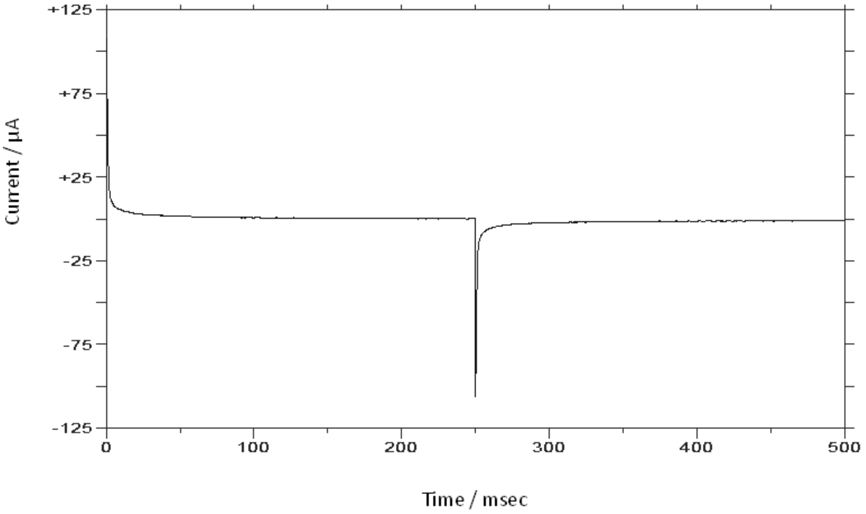


Figure 11. Chronoamperograms of microcrystalline ErBCO prepared via co-precipitation technique mechanically attached to a 3mm diameter glassy carbon electrode and immersed in 0.5 M NH_4Cl electrolyte at 25°C.

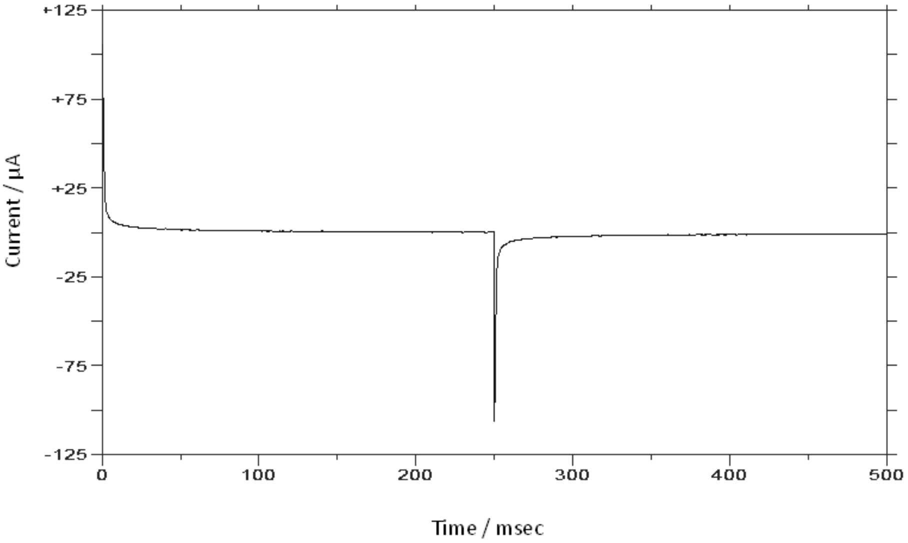


Figure 12. Chronoamperograms of microcrystalline ErBCO prepared via solid-state technique mechanically attached to a 3mm diameter glassy carbon electrode and immersed in 0.5 M NH_4Cl electrolyte at 25°C.

The value is 3.4 x $10^{-6}cm^2/s$ and 4.0 x 10^{-6} cm^2/s for sample prepared via conventional solid state and co-precipitation technique, respectively. The diffusion coefficient, D of co-precipitated sample is larger than solid state sample probably due to its morphology. This indicates that the co-precipitated sample produces higher current in the redox reaction. The metal ions are highly diffusive for the co-precipitated sample (according to its diffusion coefficient value) and hence it undergoes faster redox reaction. This result supported with temperature study when it shows the lower E_a value of co-precipitated sample.

3.7. Chronocoulometry

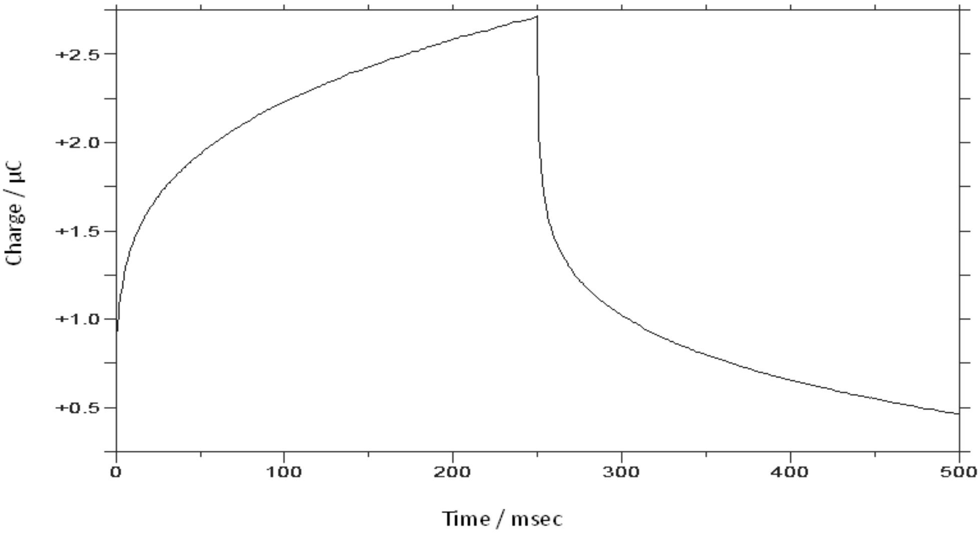


Figure 13. The chronocoulomogram for ErBCO prepared via co-precipitation technique in the presence of 0.5 M NH_4Cl electrolyte at 25°C.

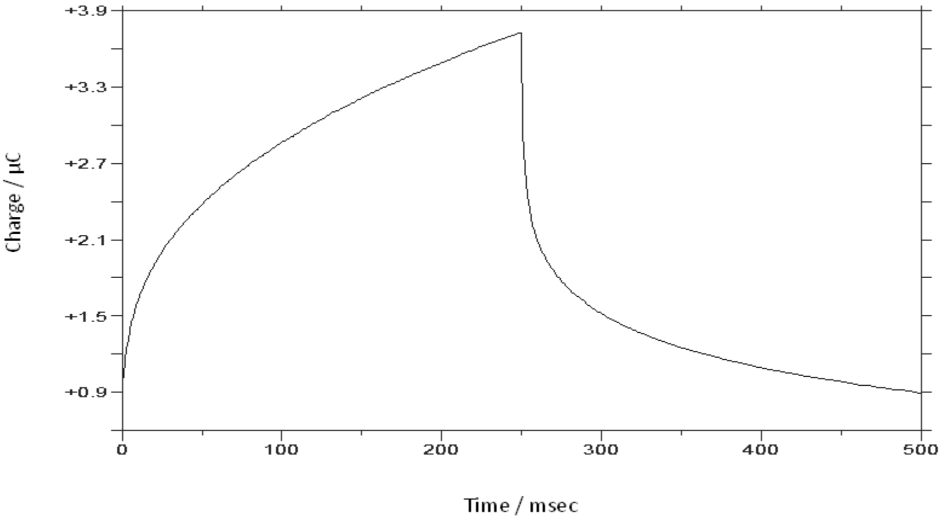


Figure 14. The chronocoulomogram for ErBCO prepared via solid-state technique in the presence of 0.5 M NH_4Cl electrolyte at 25°C.

In chronocoulometry (CC), the potential excitation function is step from initial potential where no redox reaction occurs to a final potential where the reaction of interest does occur. Instead of measuring current directly, it is integrated and the charge is measured. Chronocoulometry is the integral analogs of the corresponding chronoamperometric approaches. It is a technique used to determine the amount of charge per unit surface area. The chronocoulogram were scanned with 250 msec pulse width at potential range between +400 mV to +600 mV. The forward step was the oxidation process followed by reduction in the reversed step.

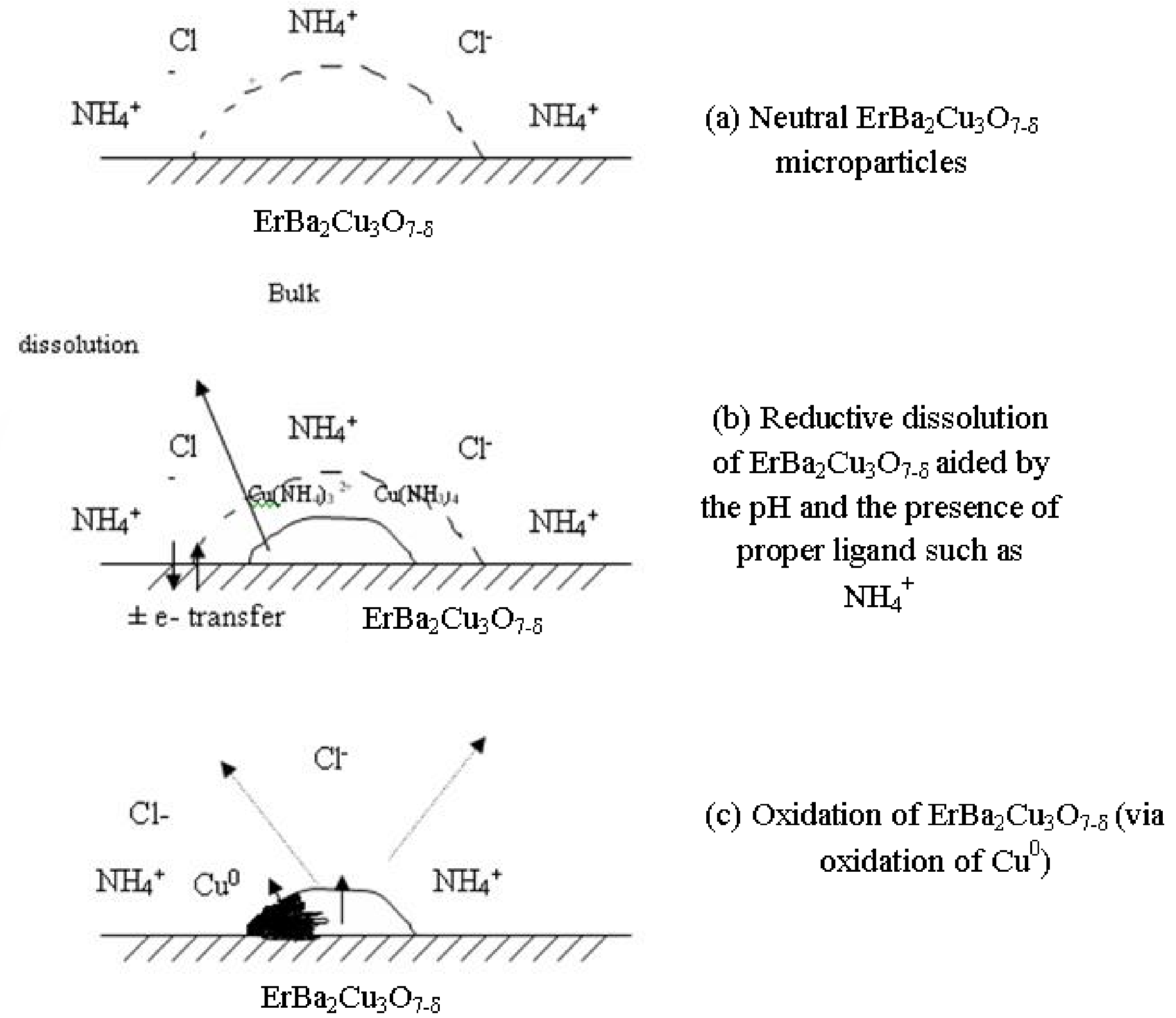
At $t = 0$, the potential is shifted to a point which is sufficiently negative to enforce a diffusion-limited current. From Figure 13 and 14, it was observed that the charges injected by the reduction of ErBCO were withdrawn by oxidation in reversed scan. The integral form of Cottrell equation gives the cumulative charged passed in reducing the diffused component:

$$Q_{\mathrm{d}} = 2\mathrm{n}FAD^{1/2}C\pi^{-1/2}t^{1/2} \qquad [8]$$

Hence, the Anson plot that showed dependency of Q, upon $t^{1/2}$ was also plotted to assess the kinetics of reactants. The equation above shows that the diffusion component to the charge is zero at $t = 0$. Therefore, the value charge, Q presence on the surface of the electrode is 4.7383 μC/cm^2 and 5.4413 μC/cm^2 for sample prepared via co-precipitation and conventional solid state technique, respectively.

4. CONCLUSION

The electrochemical behavior of $ErBa_2Cu_3O_{7-\delta}$ (ErBCO) micro crystalline ceramics prepared via co-precipitation (COP) and solid state (SS) method has been studied. Both samples were mechanically attached to glassy carbon (GC) electrode surface in 0.1M NH_4Cl. The electrochemical behaviors for both samples appear voltammetrically stable showing its usefulness as an electrode of a chemically modified solid electrode. Four characteristics peaks were detected in cyclic voltammogram of ErBCO. There are two redox couples (${}^{\mathrm{I}}E_{\mathrm{pc}}$, ${}^{\mathrm{I}}E_{\mathrm{pa}}$, ${}^{\mathrm{II}}E_{\mathrm{pc}}$, ${}^{\mathrm{II}}E_{\mathrm{pa}}$) observed and the peaks could be attributed to the Cu^{2+}/Cu^{1+} and Cu^{1+}/Cu^0 redox couple which shows that the copper planes in the superconductor played major role in producing the peaks observed in the voltammograms. The cyclic voltammetric behaviors exhibited by both samples are found to depend greatly on the parameters used in this study, such as type of electrolyte, concentration, temperature and pH where the presence of a surface reaction were summarized in Scheme 1. Although ErBCO performed optimally in acidic (pH~2.00) and higher temperature (80$^{\mathrm{o}}$C) condition, it appears stable voltammetrically. The $E^{\mathrm{o}}{}_{\mathrm{p}}$’ values are not dependent on the method of preparation as the value for both samples are fairly similar. The research potential for these investigations are 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.



Scheme 1. Schematic diagrams of the electrode reactions believed to be associated with the electrochemical reduction and reoxidation of microcrystalline solids of $ErBa_2Cu_3O_{7-\delta}$ abrasively attached and placed in contact with NH4Cl electrolyte.

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