

VOLTAMMETRIC STUDIES OF DyBa₂Cu₃O_{7-δ} (DyBCO) PREPARED VIA SOLID-STATE (SS) AND CO-PRECIPITATION (COP) TECHNIQUE.

E.F. Kadri¹, W.T. Tan¹, Z. Zainal¹ and I. Hamadneh²

¹ *Department of Chemistry, Faculty of Science, Universiti Putra Malaysia,
43400 UPM Serdang, Selangor, Malaysia*

² *Chemistry Department, Faculty of Science, University of Jordan,
11942 Amman, Jordan.*

ABSTRACT

This paper describes a series of electrochemical measurements design to explore the reactivity of the oxide superconductor, DyBa₂Cu₃O_{7-δ} (DyBCO). The reproducible voltammetry was obtained in the potential window of 1.0 V to -1.0 V vs Ag/AgCl reference electrode. DyBa₂Cu₃O_{7-δ} was prepared via co-precipitation and conventional solid state technique. Parameters used in this study including the effect of potential cycling, scan rate, temperature and pH as well as chronoamperometry (CA) and chronocoulometry (CC). The electrochemical reduction and oxidation can be recognized easily by the solid-phase voltammetric technique. The cyclic voltammogram for DyBCO prepared in both techniques showed four major peaks attributed to first and second redox couple. The peaks are due to the redox reaction of Cu(NH₃)₄²⁺ complex. The peak current is highly dependent upon the formation of the Cu(NH₃)₄²⁺ complex which shows that the copper planes in the superconductor played major role in producing the peaks observed in the voltammograms. A complex surface process was found in the redox reaction through the scan rate study. After thorough investigations, it was found out that DyBCO prepared in both techniques responses strongly under acidic (pH ≈ 2.00), high temperature (80°C) condition with slight differences in voltammetric behaviors. The cyclic voltammetric behavior exhibited by both samples is found to depend greatly on the parameters used in this study. From CA and CC studies, the amount of charge, Q that was presence on the electrode surface is 17.0 μC/cm² and 25.0 μC/cm² and diffusion coefficient, D is 4.6 x 10⁻⁶ cm²/s and 4.0 x 10⁻⁶ cm²/s for co-precipitation and conventional solid state technique, respectively. From the chronocoulometry (CC) measurement, the estimated mass of sample that was attached on the glassy electrode is 65 ng and 96 ng for sample prepared via conventional solid state and co-precipitation technique, respectively.

INTRODUCTION

Understanding the surface chemistry of materials such as high-temperature superconductors, could lead to more rapid developments in basic scientific research and in practical applications. Since the discovery of YBa₂Cu₃O_{7-x} (YBCO) superconductor, the scientists have already prepared well oriented bulk YBCO superconductor. Some researchers substituted almost rare earth metals instead of yttrium (Y) in YBCO

compound in order to find a cuprate-oxide-based superconductor with higher transition temperature (T_c) [1-3]. In this paper, we will report the electrochemical studies of another cuprate-oxide-based superconductor, $\text{DyBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (DyBCO) prepared via conventional solid state [3] and co-precipitation technique [4]. Electrochemistry is an extremely powerful ambient pressure method for assessing the properties of conductive surfaces. It is possible to study voltammetrically insoluble, redox active solids adhered abrasively at electrode surfaces and placed in contact with an electrolyte (solvent). This technique, involving the voltammetry of microparticles immobilized on electrode surfaces, was introduced earlier by Scholz and Lange [5]. Numerous electrochemical studies has been done on superconductors, mainly on $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (YBCO-123 system) [6-9], BSCCO system [10] and also on other type of superconductors [11-12]. However, 123 systems are being chosen in this paper because this system has better characteristics in terms of reactivity in comparison of the common copper-oxide superconductors [12]. Finally, DyBCO was selected because it exhibits a better chemical stability and higher corrosion resistance against moisture than YBCO [13]. The material being investigated is the same compound, a superconductor $\text{DyBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (DyBCO). However, the only difference is in the synthesizing technique, which is prepared through co-precipitation and conventional solid state technique. The critical temperature is higher for sample prepared through co-precipitation technique ($T_{c(R=0)} = 92.3 \text{ K}$) than the one prepared through conventional solid state technique ($T_{c(R=0)} = 85.0 \text{ K}$). This voltammetric studies is being carried out to investigate the electrochemical properties of the compound and also to elucidate the mechanisms of the electrochemical reaction taking place at the electrode-solid-electrolyte.

METHODOLOGY

Cyclic voltammetric measurement

All reagents were of analytical reagent or electrochemical grade purity. All solutions were prepared using distilled water. All solutions were deoxygenated with nitrogen gas for 10 minutes prior to recording the voltammogram. The solid compound DyBCO was transferred to the surface of the glassy carbon electrode as follows: Sample amounts of 1-3 mg of microcrystalline DyBCO were placed on a coarse grade filter paper. The glassy carbon electrode was pressed onto the substance and rubbed over the material, causing some of the compound to adhere to the electrode surface as an array of microcrystalline particles of 0.1-10 μm sizes. For electrochemical measurement, the electrode was transferred into the solution. The clean glassy carbon electrode surface could be renewed after the measurement by polishing with 0.5 μm alumina slurry, followed by ultrasonic cleaning for about 2-3 minutes, rinsing with distilled water and drying with acetone.

Instrumentation and apparatus

An Electrochemical Analyzer (BAS-50W) was used for cyclic voltammetry (CV), chronoamperometry (CA) and chronocoulometry (CC) measurements. It was equipped with an electrochemical cell which consists of three (BAS type) electrodes namely:

- 1) Working electrode

- A glassy carbon electrode (3mm diameter)
- 2) Reference electrode
 - A silver/silver chloride element (Ag/AgCl in 3M NaCl)
- 3) Counter electrode
 - A platinum wire
- 4) Basal plane graphite electrode (for SEM purposes)

Scanning electron micrograph

For the scanning electron microscopy (SEM) studies, the solid compound (DyBCO) was mechanically attached to a basal plane graphite electrode disk surface. The basal plane graphite electrode disk with microcrystalline DyBCO attached was platinum wired by using epoxy glue and was subjected to oxidative electrolysis for about 5 minutes using the controlled potential bulk electrolysis (BE). The surfaces of both graphite disks before and after electrolysis were examined using the SEM equipment. Scanning electron micrograph of the sample was conducted using LEO 1455 VPSEM. The samples were coated with an ultrathin coating of electrically-conducting material which is gold, deposited on the sample using low vacuum sputter coater (Bal-Tech SCD 005) and the image captured at a magnitude of 5000x.

RESULTS AND DISCUSSION

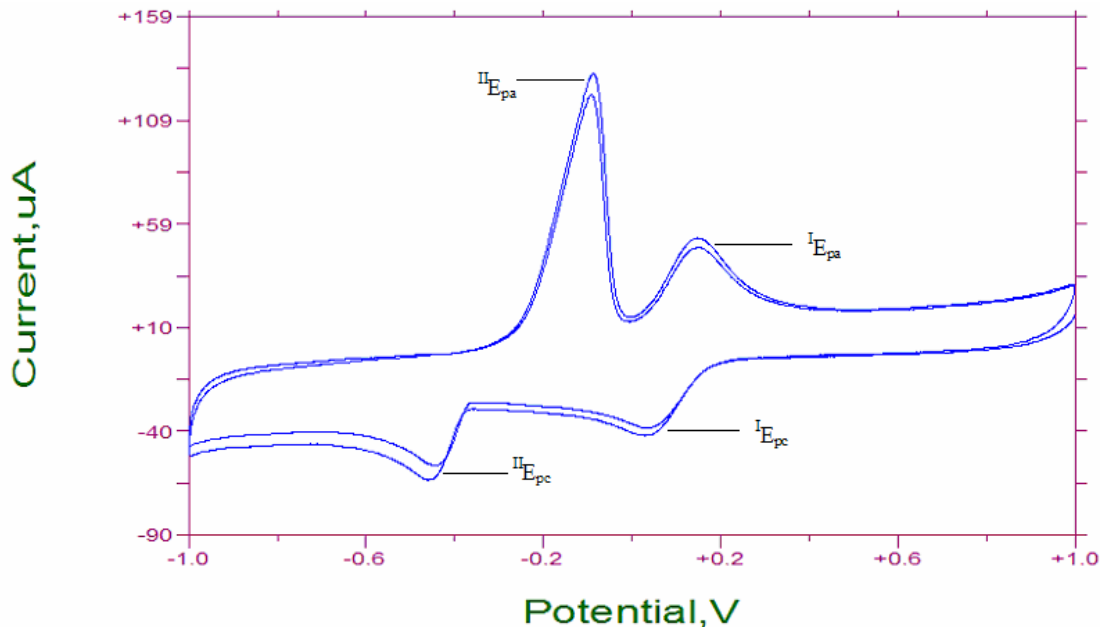
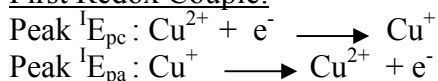


Figure 1: Cyclic voltammogram of DyBCO attached to glassy carbon electrode.

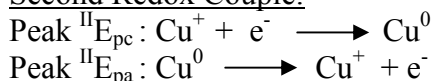
Figure 1 shows cyclic voltammogram of $\text{DyBa}_2\text{Cu}_3\text{O}_{7-\delta}$ attached mechanically at a 3 mm diameter glassy carbon electrode versus Ag/AgCl reference electrode. Unless otherwise specified, the supporting electrolyte used is 0.5 M NH_4Cl in aqueous media at

room temperature. When the voltammograms is compared with the cyclic voltammograms of the parent materials, it is obvious that the reaction peaks are due to the copper species, as only the copper species produced a reduction and oxidation peaks under steady state reaction. Anodic peak $^{II}E_{pa}$ has been identified by Miller [14] using a split ring-disk electrode technique and others [15-18] using cyclic voltammetric technique. The other anodic and cathodic peaks have also been identified by researchers [15-18] and therefore, the peaks obtained are based on the following reaction mechanism:

First Redox Couple:



Second Redox Couple:



The cyclic voltammogram for DyBCO showed four major peaks. The peak potential for first reduction peak, $^{II}E_{pc}$, and second reduction peak, $^I E_{pc}$, occurred at 37.9 and -453.7 mV, respectively whereas the first reoxidation peak, $^I E_{pa}$, and second reoxidation peak $^{II}E_{pa}$, occurred at 147.2 and -89.5 mV, respectively.

3.1 Repetitive cycles of potential

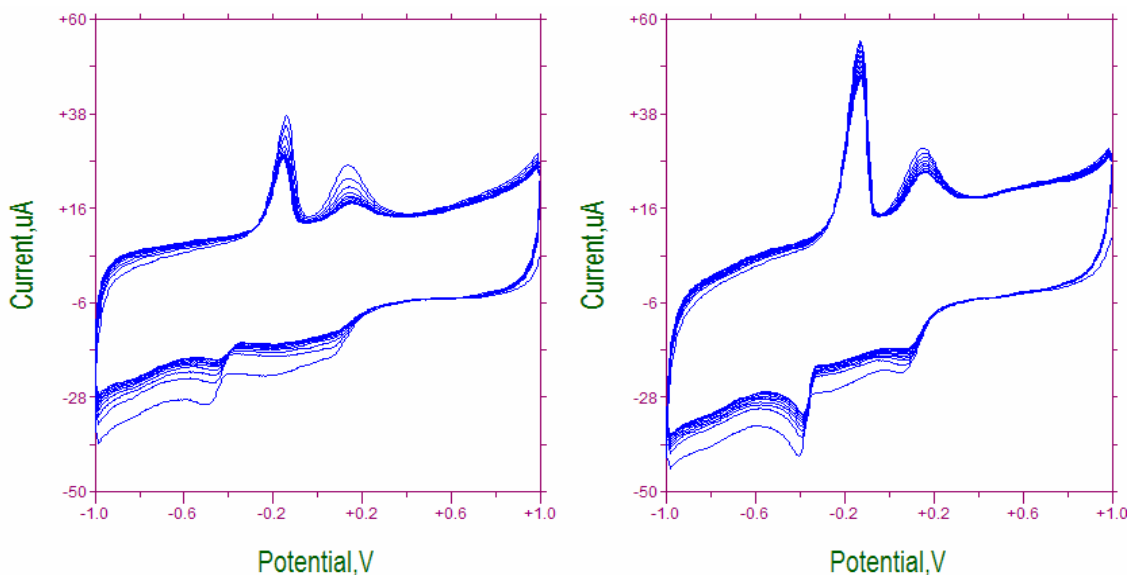


Figure 2: Cyclic voltammogram of DyBCO prepared via (a) conventional solid state technique and (b) co-precipitation technique during potential cycling of 10 cycles, at 25°C using scan rate of 100mV/sec.

The continuous potential cycling was carried out in the potential range of +1.0 V to -1.0 V against Ag/AgCl reference electrode with scan rate of 100mV/s for both techniques. From the voltammogram obtained (Fig. 2), it shows that both samples gives almost the same results. Both voltammograms show that the peak current increases upon repetition scanning. The peak current keeps on increasing up to 10 cycles. However, sample prepared through co-precipitation method gives higher current value compared to the one prepared through conventional solid state method. As mentioned earlier, all the peaks belongs to the copper species and the corrosion behavior of copper has long been investigated either in alkaline [7, 9, 18-19] or acidic media [6]. Also, it has been reported that superconductor is very sensitive to water contact and humidity in agreement with previous results [7, 9 12, 18-19]. This may be partially caused by the relatively high porosity of oxide samples formed by sinter pressing [7]. The ΔE_p value can be used as a diagnostic criterion for determining the integrity of superconductor electrode surfaces. The ΔE_p values for both samples decreases from 280 to 50 mV/s as the number of cycle increases. Even though the theoretical value of ΔE_p is 59 mV/n for an ideal reversible reaction, in situation where electron transfer kinetics is slow with respect to mass transport, larger ΔE_p values are expected. It was reported [19] that the increase in ΔE_p values are influenced by the resistance of the sample itself, and reveals that low carrier density electrode material, a superconductor, is more sensitive to electron transfer kinetic processes.

Table 1: Values of ΔE_p for both samples

Cycle	Solid state		Co-precipitation	
	$\Delta^I E_p$	$\Delta^{II} E_p$	$\Delta^I E_p$	$\Delta^{II} E_p$
1	63.7	346.0	75.8	276.2
2	63.7	312.6	72.8	264.0
3	63.4	309.6	72.8	257.9
4	60.7	306.5	69.8	257.9
5	60.7	300.5	69.8	255.0
6	59.5	297.4	69.8	255.0
7	58.5	297.4	66.8	254.9
8	54.7	294.3	63.8	254.9
9	54.7	285.3	63.8	254.9
10	51.6	285.3	60.7	251.9

$\Delta^I E_p$ = peak separation due to redox process I
 $\Delta^{II} E_p$ = peak separation due to redox process II

Effect of varying scan rate

Varying the scan rate in the range of 10-1000 mVs^{-1} , led to a marked change in the peak heights. From figure 3, it can be seen that the peak has the same form but it is apparent that the total current increases with increasing scan rate. This can be rationalized by considering the size of the diffusion layer and the time take to record the scan. Clearly, 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. In a slow voltage scan the diffusion layer will grow much further from the electrode in comparison to a fast scan. Consequently, the flux to the electrode surface is considerably smaller at slow scan rates than it is at faster rates. As the current is proportional to the flux towards the electrode, the magnitude of the current will be lower at slow scan rates and higher at high rates. Based on the results obtained, the oxidative current of DyBCO prepared in both techniques showed a 0.7 – 0.8 dependence on scan rate as expected for a complex surface process [21].

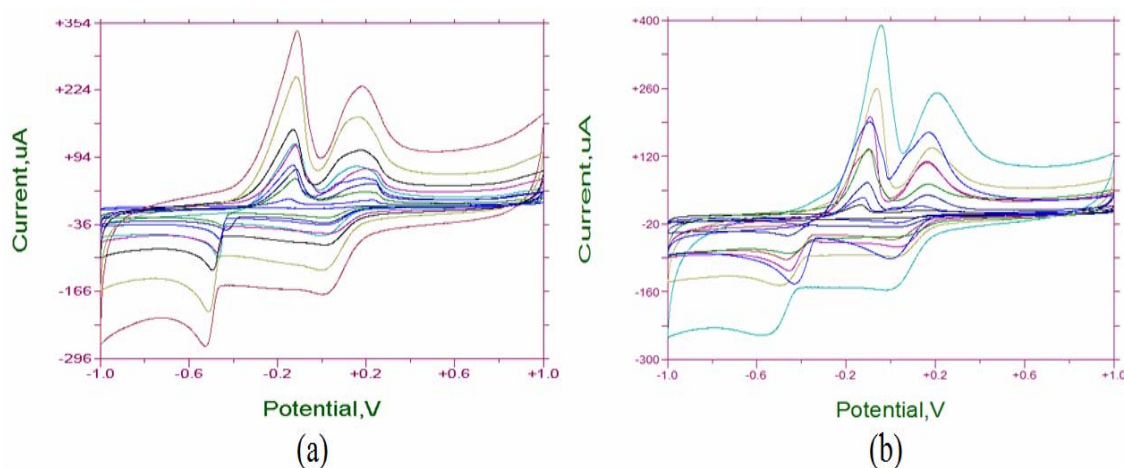


Figure 3: Cyclic voltammogram of DyBCO prepared via (a) co-precipitation and (b) solid state technique.

The scan rate study can also be used to determine the value of E_p^0 for both oxidation (E_{pa}^0) and reduction (E_{pc}^0) process. From graph of current versus peak potential, the value of E_p^0 for both preparation method is within error range of ± 5 mV. At zero-current, value E_{pa}^0 obtained is 133 mV and 138 mV for sample prepared through solid state and co-precipitation method, respectively. While, value of E_{pc}^0 at zero-current is 436 mV and 440 mV for sample prepared through solid state and co-precipitation method, respectively. Therefore, from the values obtained, we can conclude that the E_p^0 values is not dependent on the method of preparation as the value for both samples is fairly similar.

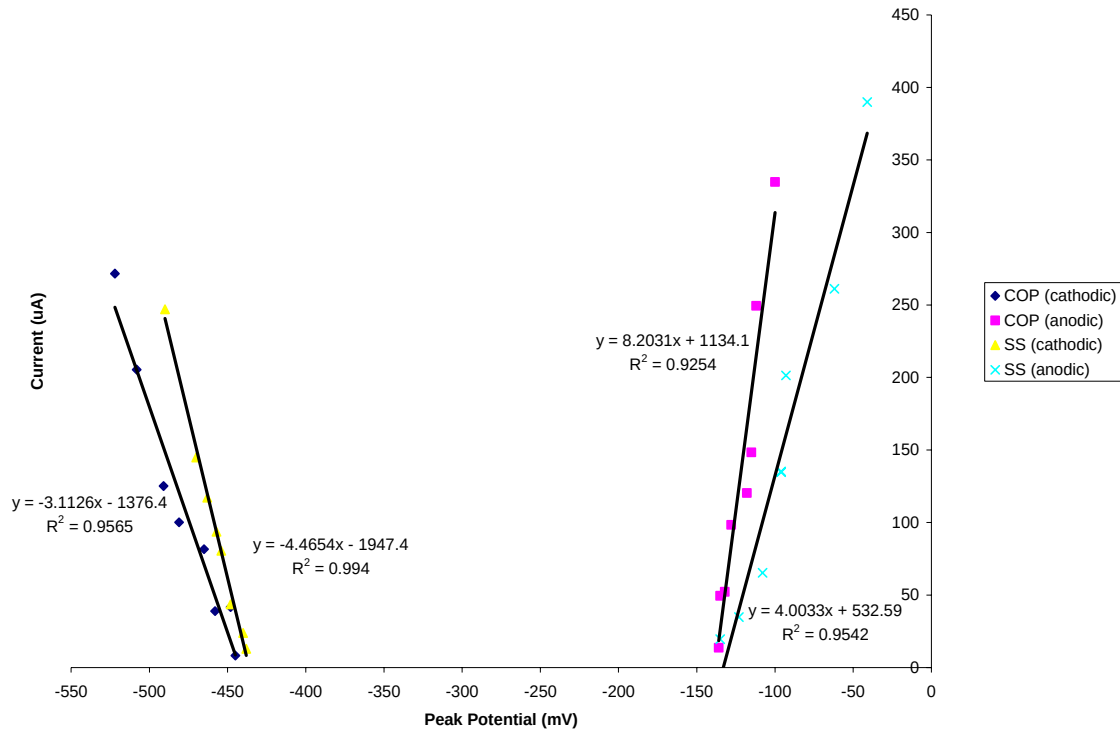


Figure 4: Plot of current versus peak potential for sample prepared solid state (SS) and co-precipitation (COP) method.

Effect of varying temperature

The oxidation and reduction current of DyBCO is definitely temperature dependant as the peak current is increasing with increment of temperature in the range from 10 – 80°C. The increment is small from 30°C to 60°C, however a marked rise in current produced can be noted at 80°C for sample prepared through conventional solid state method. This latter enhancement may be attributed to changes in the diffusibility or diffusion coefficient, D of DyBCO which increases exponentially with temperature [20] as described in Eq. 1:

$$D = D^0 \exp \frac{(-\Delta H)}{RT} \quad (1)$$

where D^0 is a constant and ΔH is the heat of formation. Consequently as the diffusivity, 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. Nevertheless, both samples demonstrate the same effect that can be observed in the peak current enhancement. Arrhenius's equation (2) can be used to determine the activation energy (E_a) that was produced by the compound. From equation (3), k can be referred as current, i . From graph of $\log i$ versus $1/T$ (K^{-1}), the value of activation energy (E_a) is

16.5 kJ.mol⁻¹ for DyBCO prepared through co-precipitation method and 15.7 kJ.mol⁻¹ for DyBCO prepared through conventional solid state method. The activation energy can be associated with the morphology of the sample itself. As the end product of the sample prepared via co-precipitation method is denser than the solid state sample, therefore it is only logical that the activation energy value for co-precipitation sample is higher than solid state sample because with larger surface area, higher energy must be overcome in order for a chemical reaction to occur.

$$k = Ae^{-E_a/RT} \quad (2)$$

$$\text{Log } k = \frac{-E_a}{R} \frac{1}{T} + \log A \quad (3)$$

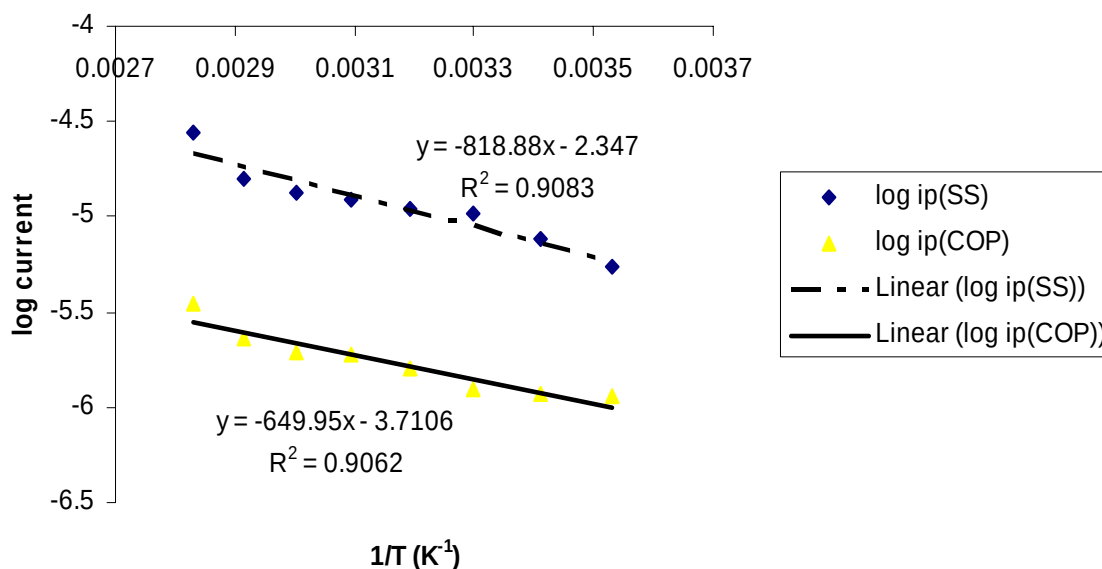


Figure 5: Graph of log current versus 1/T (K⁻¹) of DyBCO in 0.5M NH₄Cl at room temperature.

Effect of varying pH

From the results obtained, the current shows an increment with increasing acidity. At lower pH value (pH ~2.00), there is significant enhancement in peak current in pH ranging between pH 2.00 to 11.00. This happens due to the fact that acidic solution will dissolve the particles of DyBCO that attached on the GC electrode surface and therefore, will produce more soluble species (Cu²⁺ and Cu⁺ cations). This will eventually lead to a higher current produced under strongly acidic condition. However, as the solution become more alkaline (pH >7.00), the compound (DyBCO) that attached on the electrode become less soluble. Hence, the amount of electroactive soluble species formed will be less and eventually lead to a lower current response as observed experimentally. This has been proved by previous reports. The best surface stability was found in alkaline solutions, whereas a rapid surface decomposition was observed in acid solutions in agreement with the findings of Rosamilia et al. [6].

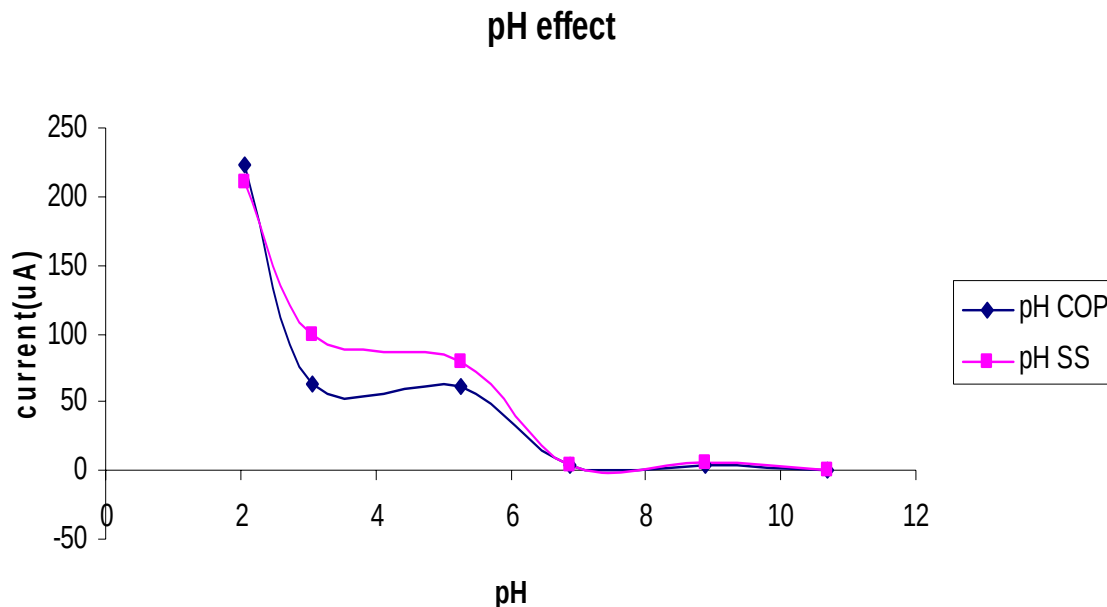


Figure 6: Graph of current versus pH of DyBCO in 0.5M NH_4Cl at room temperature.

Chronoamperometry (CA)

Chronoamperometry (CA) provides heterogeneous kinetics information of the electrode reaction of DyBCO microcrystalline compound. For CA, if the point in time where the potential is stepped 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:

$$i = nFAD^{1/2}C\pi^{-1/2}t^{-1/2} \quad (4)$$

From the Cottrell's equation, the diffusion coefficient, D can be calculated. The value is $4.6 \times 10^{-6} \text{ cm}^2/\text{s}$ and $4.0 \times 10^{-6} \text{ cm}^2/\text{s}$ for sample prepared via conventional solid state and co-precipitation technique, respectively. The diffusion coefficient of co-precipitation sample is lower probably due to its morphology. The compactness and less porous surface [4] make the situation harder for the electrolyte ions to penetrate right into the sample compared to solid state sample.

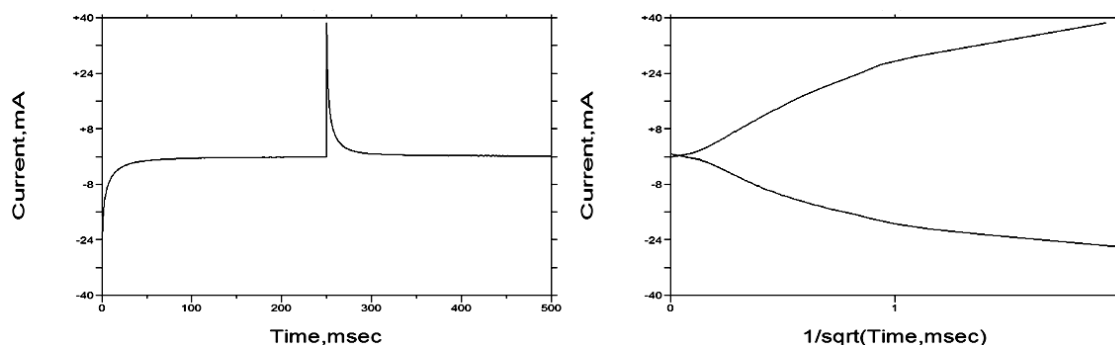


Fig. 8: (a) Chronoamperograms of microcrystalline DyBCO prepared via solid-state technique mechanically attached to a 3mm diameter glassy carbon electrode and immersed in 0.5 M NH_4Cl electrolyte at 25°C.

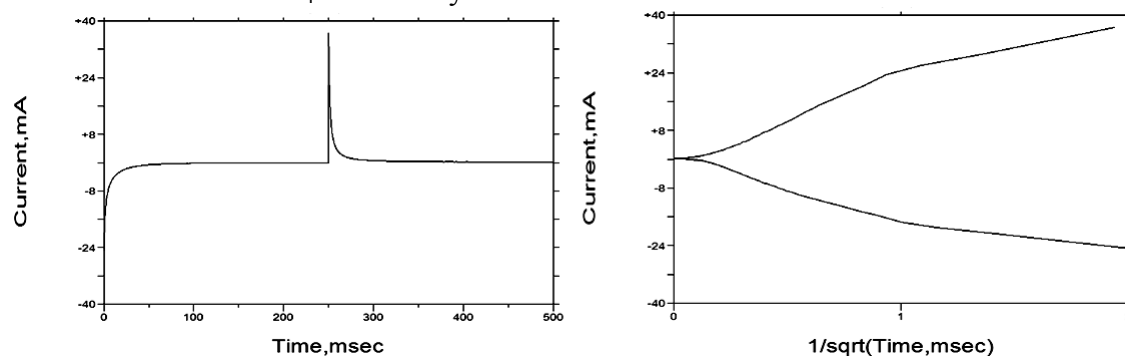


Fig. 8: (b) Chronoamperograms of microcrystalline DyBCO prepared via co-precipitation technique mechanically attached to a 3mm diameter glassy carbon electrode and immersed in 0.5 M NH_4Cl electrolyte at 25°C.

Chronocoulometry (CC)

Chronocoulometry (CC) is the integral analog of the corresponding chronoamperometric approaches. The charge injected by the reduction of DyBCO molecules was withdrawn by oxidation in reversed scan. At $t = 0$, the potential is shifted to a point which is sufficiently negative to enforce a diffusion-limited current. The integral form of Cottrell equation gives the cumulative charge passed in reducing the diffused component:

$$Q = 2nFAD^{1/2}C2\pi^{1/2}t^{1/2} \quad (5)$$

Hence, Anson plot that showed dependency of Q upon $t^{1/2}$ was also plotted to assess the kinetics of the 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 $17.0 \mu\text{C}/\text{cm}^2$ and $25.0 \mu\text{C}/\text{cm}^2$ for sample prepared via conventional solid state and co-precipitation technique, respectively. From this charge value, we can also estimate the mass of sample that was attached on the glassy carbon electrode, which is

0.065 μg and 0.096 μg for sample prepared via conventional solid state and co-precipitation technique, respectively.

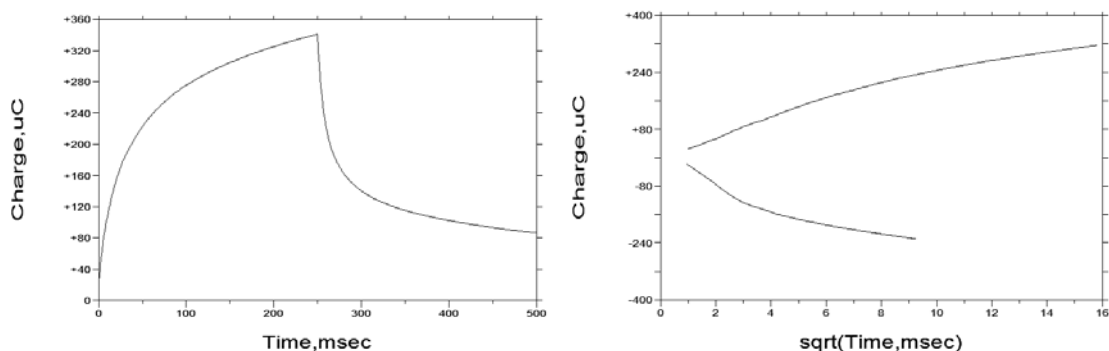


Fig. 9: (a) The chronocoulomogram and Anson plot of charge, Q vs $t^{-1/2}$ for DyBCO prepared via solid-state technique in the presence of 0.5 M NH_4Cl electrolyte at 25°C .

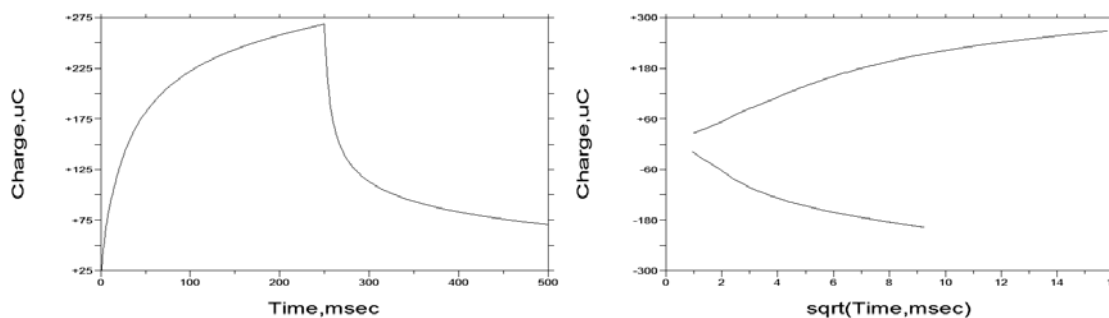
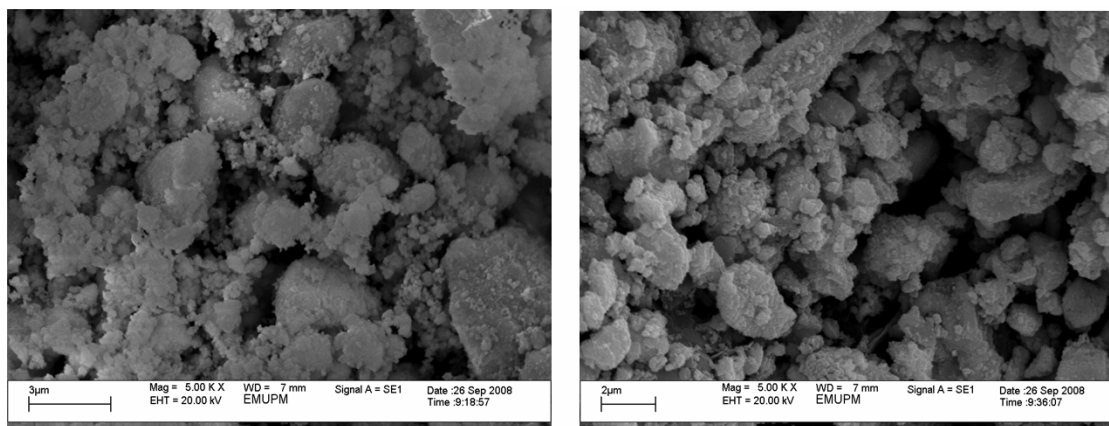


Fig. 9: (a) The chronocoulomogram and Anson plot of charge, Q vs $t^{-1/2}$ for DyBCO prepared via co-precipitation technique in the presence of 0.5 M NH_4Cl electrolyte at 25°C .

Scanning Electron Micrograph



(a)

(b)

Figure 10: Scanning electron micrograph of $\text{DyBa}_2\text{Cu}_3\text{O}_{7-\delta}$ prepared via co-precipitation technique (a) before and (b) after electrolysis process.

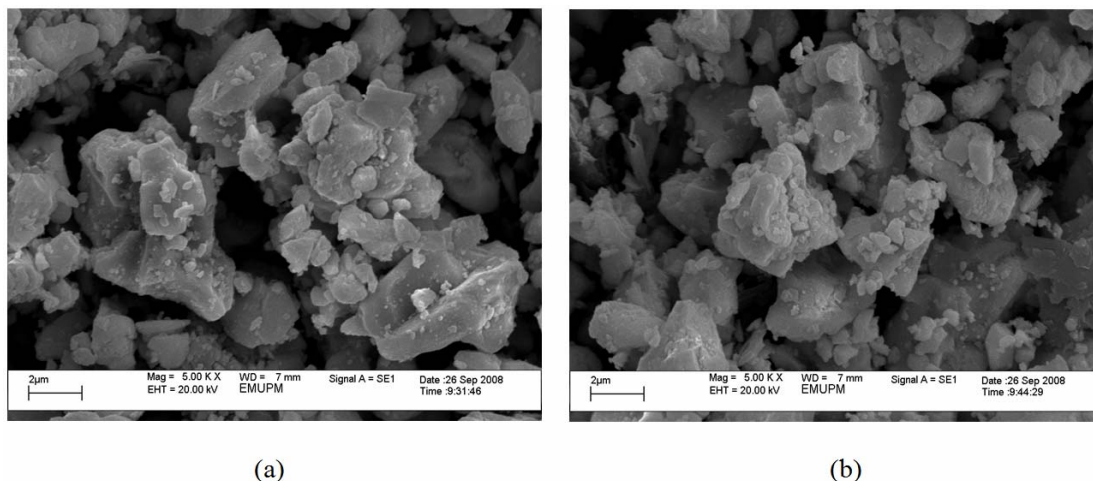
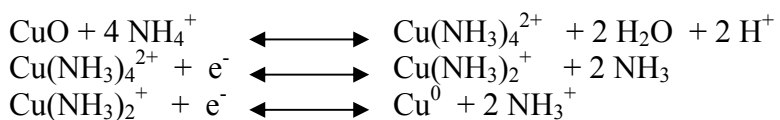


Figure 11: Scanning electron micrograph of $\text{DyBa}_2\text{Cu}_3\text{O}_{7-\delta}$ prepared via conventional solid state technique (a) before and (b) after electrolysis process.

There are differences in shape and sizes for both samples. Before the electrolysis process, the sample prepared via co-precipitation method is smaller with the biggest size about $3\text{ }\mu\text{m}$, and tend to agglomerate due to its nano-scale size [4] while the sample prepared via conventional solid state method is a lot bigger and have a more defined edges with sizes 4 to $6\text{ }\mu\text{m}$. However, after the electrolysis process, there seems to have an increment in sizes for the sample prepared via co-precipitation method with range size between $0.5\text{ }\mu\text{m}$ to $4\text{ }\mu\text{m}$. However, there is not much of a difference in term of size for sample prepared via conventional solid state method. Assumption was made to describe the difference in structure before and after the electrolysis. The difference in the structure can be associated with the electrolyte used which is ammonium chloride. In the presence of NH_4^+ ions, the following electrochemical reactions were thought to have taken place at the electrode-solid compound-electrolyte interfaces.



From the micrograph, it can be seen the stability of the material that was attached on the surface of the electrode after the electrolysis process. It shows that even after 10 cycles of cyclic voltammetric measurements, DyBCO microcrystals still appear stable voltammetrically indicating its usefulness as an electrode or sensing material of a chemically modified solid electrode.

CONCLUSION

High temperature superconductor (HTS) has been prepared via conventional solid state (SS) and co-precipitation (COP) method. For the electrochemical studies purposes, both samples was mechanically attached to a glassy carbon (GC) electrode in $0.5\text{ M NH}_4\text{Cl}$ as an electrolyte and the investigations was done through cyclic voltammetric technique. The cyclic voltammograms show four major peaks attributed to the redox

couples of $\text{Cu}(\text{NH}_3)_4^{2+/+}$, $\text{Cu}(\text{NH}_3)_4^{+/0}$ which shows that the copper planes in the superconductor played major role in producing the peaks observed in the voltammograms. The cyclic voltammetric behavior exhibited by both samples is found to depend greatly on the parameters used in this study, such as type of electrolyte, concentration, temperature and pH. Although DyBCO performed optimally in acidic (pH~2.00) and higher temperature (80°C) condition, it appears stable voltammetrically based on the result from SEM indicating its usefulness as an electrode or sensing material of a chemically modified electrode favoring working range at 0.3 V onwards under weakly to acidic conditions and a wider working range of -1.0 V to 1.0 V under alkaline condition as no mineralization of DyBCO occurs. The research potential for these investigations is DyBCO has potential to be used as a good chemically modified electrode which can be employed in electrocatalysis studies of some rather electro-inactive biochemical compounds. Also, based on the evidences shown above, DyBCO prepared via co-precipitation method can be a better chemically modified electrode than DyBCO prepared via solid-state method.

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