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Electrochemical Study of Zn-Doped ErBCO Superconductor Synthesized via the Coprecipitation Method

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Electrochemical analyses of $Er_{1-x}Zn_xBa_2Cu_3O_{7-\delta}$ superconductor series were studied using solid phase cyclic voltammetry technique. Samples were synthesized via coprecipitation method, and the powder X-ray diffraction (XRD) patterns showed a minor phase of Er_2BaCuO_5 (211) at higher content of Zn. The higher electrochemical response of current appeared at x=0.2 where the secondary phase was investigated. This phase played a major role in the electrochemical behavior. Cyclic voltammetry of the sample on glassy carbon electrodes in 0.1 M NH_4Cl at pH 4.12 showed four major peaks attributed to first and second red-ox couple due to the formation of copper complexes. The sensitivity under conditions of cyclic voltammetry is significantly dependant on pH and scan rate. From chronocoulometry (CC) and chronoamperometry (CA) studies, the amount of charge, Q increased from 497.25 $\mu C/cm^2$ for the pure sample up to 808.01 $\mu C/cm^2$ for doped 0.2 mole of Zn while the diffusion coefficient, D recorded for the pure and 0.2 mole doped samples were 7.47×10^{-05} and 7.31×10^{-05} cm^2/s, respectively.

Keywords: Cyclic Voltammetry; Superconductor; Doping; Coprecipitation

1. INTRODUCTION

As a superconducting material, it is a meaningful to study the electrochemical properties of the sample in a particular content and concentration in which the electrical properties can be affected by the doping process. This electrochemical behavior can be studied by several procedures and instruments. The electrochemical behavior of superconductors, especially cuprate superconductors, have been studied by many researchers [1-5] using different ways of characterization.

The cyclic voltammetry is the suitable method for assessing the conductive surface, in which the red-ox active solids abrasively adhered to the electrode surface and placed in contact with an electrolyte. This technique was introduced by Scholz and Lange as a voltammetry of micro-particles immobilized on electrode surfaces using fine ground minerals in the micro-scale as a study material [6].

Zakharchuk, et al., 1991, studied the electrochemical behavior of $YBa_2Cu_3O_{7-x}$ and $Ba(CuO_2)_2{\cdot}nH_2O$ using solid state voltammetry and reported that it is possible to identify the individual phases of 0^- ion peak for each superconducting phase [7]. In addition, a study of electrochemical properties on $YBa_2Cu_3O_7$ using abrasive stripping voltammetry showed that there is an evidence on several transitions of Cu^{3+}-Cu^{2+}-Cu^+ [8].

In this paper, we report the electrochemical behavior of a series of Zn-doped ErBCO synthesized via coprecipitation method. The most affected doping content was studied at variant parameters to conclude the change of condition in the compound.

2. METHODOLOGY

Preparation of samples:

Series of $Er_{1-x}Zn_xBa_2Cu_3O_{7-\delta}$ x= 0.0, 0.05, 0.1, 0.15 and 0.2 were successfully prepared by coprecipitation method (COP) as described in our previous work [9]. Fine ground sample was mechanically attached into the working electrode for testing. The supporting electrolyte used in this study was 0.1 M NH_4Cl due to the best result and smooth curve obtained according to the recent work for DyBCO synthesized via COP method [2]. The experiment was carried out at room temperature using pH of 4.12. All samples have a fixed scan rate of 100 m Vs^{-1}.

Instruments and Apparatus:

The final compound was pulverized using mortar and pestle and was used in the phase determination. The powder samples were examined by X-ray powder diffraction (XRD) with Cu-Kα radiation using PANalytical's X'Pert PRO X-ray diffraction system at 40 kV and 30 mA with a step of 0.02 ° over the range 4–60 °.

Cyclic Voltammetry (CV) Chronocoulometry (CC) and Chronoamperometry (CA) were run by Electrochemical Analyzer (BAS-50W), equipped with an electrochemical cell which consists of three (BAS type) electrodes. These electrodes are: a working electrode of glassy carbon electrode (GC), a reference electrode of silver/silver chloride (Ag/AgCl in 3 M NaCl), and a counter electrode of a platinum wire.

In the cyclic voltammetry experiment, a clean cell was equipped with a glassy carbon electrode, a standard calomel electrode (SCE) and a platinum auxiliary platinum electrode. Then, the electrochemical cell was filled with the pure electrolyte solution. The electrode was de-oxygenated with nitrogen for 10 minutes prior to voltammogram recording. Removing of oxygen from the electrolyte solution is important to avoid its interferences.

3. RESULTS AND DISCUSSION

3.1 Structural study

The XRD study for pure and Zn-doped samples of ErBCO superconductor discussed in our previous work [9], showed that a phase of the tetragonal phase of Er_2BaCuO_5 presented in the doped content of 0.15 and 0.2 accompanying with the orthorhombic structure of Er-123 at 2θ= 27.38, 28.24 and 29.08 with an intensity of (0-12%).

Scanning electron microscopy of $Er_{1-x}Zn_xBa_2Cu_3O_{7-\delta}$ x=0.0, 0.05, 0.1, 0.15 and 0.2 presented in figure 1 shows a significant change in the microstructure of the sample by the variation of the Zn content in the sample. For instance, the first doped sample with the content of Zn of x=0.05 the grain size increased with lower porosity while the higher content of Zn showed a fuse-like structure with more pores in the structure. This has happened due to the presence of the secondary phase of Er_2BaCuO_5.

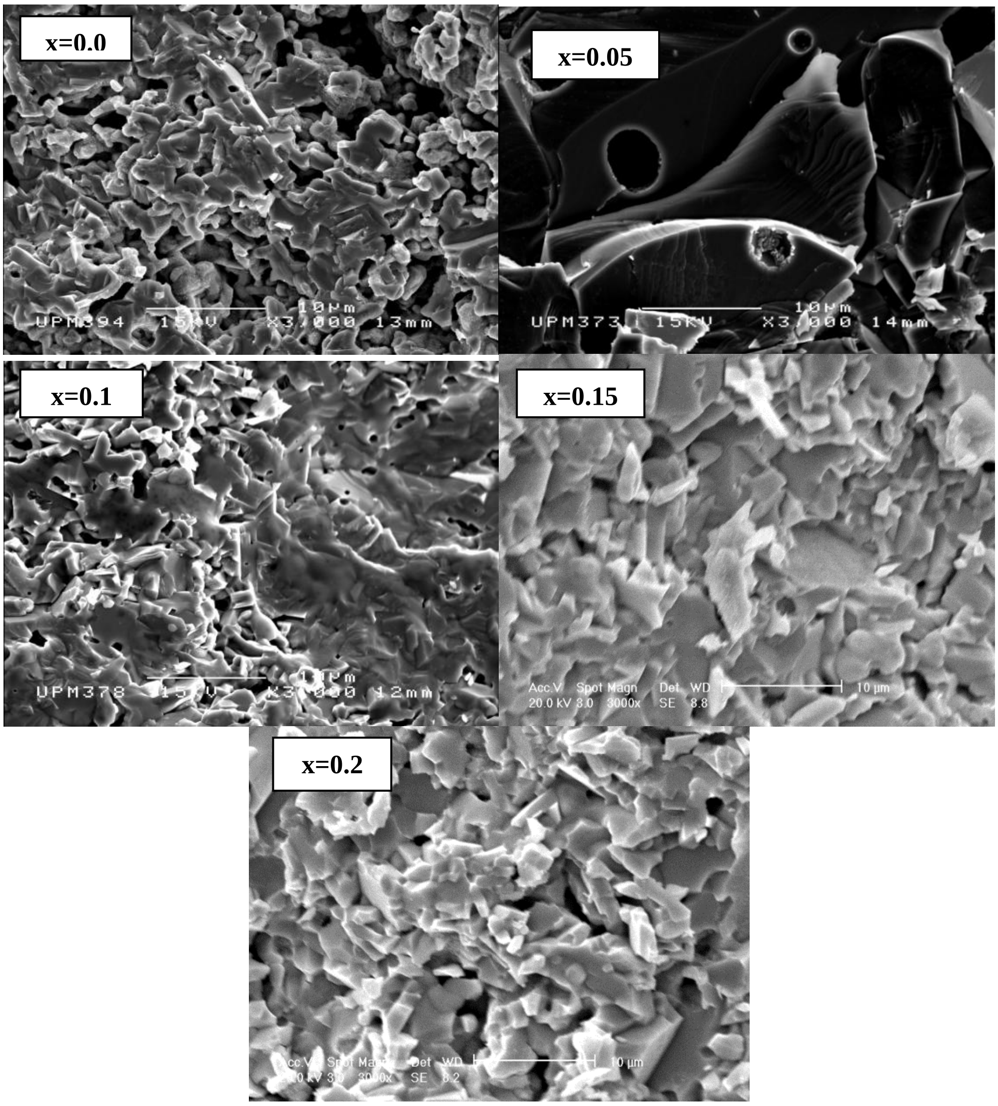

Figure 1. SEM microstructure for $Er_{1-x}Zn_xBa_2Cu_3O_{7-\delta}$ prepared via coprecipitation method

3.2 Cyclic voltammetry study

It is clearly known in solid-state voltammetry that the most affected part is the potential change in the electrode, where the current changes according to the amount of the sample attached into the working electrode[10,6]. The cyclic voltammogram of pure and x=0.2 Zn-doped ErBCO is presented in figure 2. Four major peaks were clearly observed. The most effective part of the electrochemical reaction is the Cu ions where the red-ox reaction occurred at the faint potential applied. For RE-123 superconducting system, two red-ox reactions were presumed to have taken place:

$$\textbf{\textit{Process I:}} \quad Cu^{2+}+e^{-} \rightleftharpoons Cu^{+}$$

$$\textbf{\textit{Process II:}} \quad Cu^{+}+e^{-} \rightleftharpoons Cu$$

The peak potential for the first reduction peak, ${}^{1}E_{pc}$, was the one in which the reduction of Cu^{2+} into Cu^{+} occurred, while the peak potential for the second reduction peak, ${}^{2}E_{pa}$, was the one in which the reduction of Cu^{+} into Cu^{0} happened in the presence of 0.1 M NH_4Cl. Presumably, $Cu(NH_3)_4^{2+}$ might have been formed which would have rendered Cu^{2+} in ErBCO more electro-active. Furthermore, the peak potential for the second oxidation peak, ${}^{2}E_{pc}$, was the one in which the oxidation of Cu^{0} into Cu^{+} occurred, and the peak potential for the first oxidation peak, ${}^{1}E_{pc}$, was the one in which the oxidation of Cu^{+} into Cu^{+2} happened.

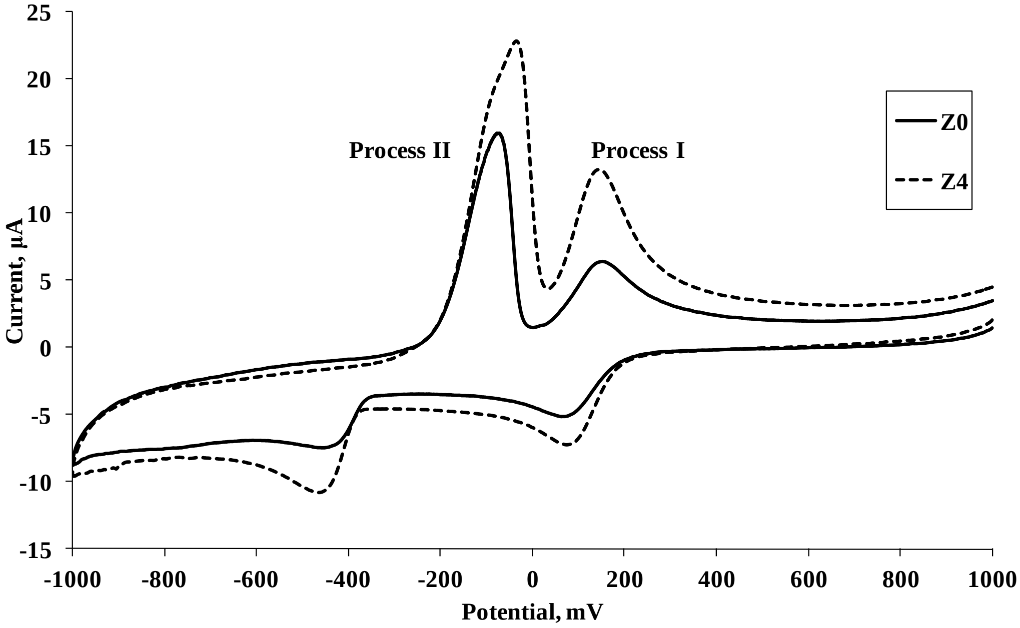

Figure 2. Cyclic voltammograms for $Er_{1-x}Zn_xBa_2Cu_3O_{7-\delta}$ samples (x=0.0, and 0.2) attached to a glassy carbon electrode in the presence of 0.1 M NH_4Cl

The cyclic voltammetry data of the first and second couples are presented in tables 1 and 2. From the result, there is a reduction in first couple peak separation, Δ^1E_p, and increasing of second couple peak separation, Δ^1E_p, amounts by increasing the Zn content in the sample in general. This was due to change in the charge carrier in the compound. At x=0.05 and x=0.1, the decrease in the amount of Δ^1E_p appeared with increase in the Δ^2E_p amount, which might be due to the replacement of Zn in the Cu^{2+} ions. On the other hand, at x=0.15, the amount of Δ^1E_p increased and the amount of Δ^2E_p decreased, which can be caused by the replacement of Zn in the Cu^+ ion. This implies that, the doping of Zn into ErBCO can happen in each of Cu_2O plane and CuO chain according to the Zn content in the sample. However, the oxygen coefficient may change due to a change in the valence of the cupper in the sample.

Table 1. The first couple cyclic voltammetry data of pure and doped Zn samples

	Mole	$^1E_{pc}$ mV	$^1i_{pc}$ A	$^1E_{pa}$ mV	$^1i_{pa}$ A	Δ^1E_p mV	Δ^1i_p A	Δ^1i_p µA
Er	0.0	71	-4.67×10^{-06}	151	4.91×10^{-06}	80	9.58×10^{-06}	9.58
Z1	0.05	71	-5.55×10^{-06}	143	7.57×10^{-06}	72	1.31×10^{-05}	13.12
Z2	0.1	72	-5.81×10^{-06}	136	7.96×10^{-06}	64	1.38×10^{-05}	13.77
Z3	0.15	73	-5.50×10^{-06}	150	8.25×10^{-06}	77	1.37×10^{-05}	15.57
Z4	0.2	75	-6.51×10^{-06}	144	8.84×10^{-06}	69	1.53×10^{-05}	15.35

Table 2. The second couple cyclic voltammetry data of pure and doped Zn samples

		$^2E_{pc}$ mV	$^2i_{pc}$ A	$^2E_{pa}$ mV	$^2i_{pa}$ A	Δ^2E_p mV	Δ^2i_p A	Δ^2i_p µA
Er	0.0	-454	-4.03×10^{-06}	-75	1.60×10^{-05}	379	2.00×10^{-05}	20.02
Z1	0.05	-457	-5.15×10^{-06}	-48	1.65×10^{-05}	409	2.16×10^{-05}	21.61
Z2	0.1	-464	-6.28×10^{-06}	-51	2.05×10^{-05}	413	2.67×10^{-05}	26.74
Z3	0.15	-503	-5.42×10^{-06}	-45	1.80×10^{-05}	458	2.34×10^{-05}	23.44
Z4	0.2	-465	-6.23×10^{-06}	-35	2.28×10^{-05}	430	2.90×10^{-05}	28.98

The electrochemical behavior of the doping content of Zn proves that the replacing of Zn is going into the Cu^+ site this may supported by the shifting of the second red-ox couple peaks.

The enhancement of potential peaks in Z4 sample shown in Figure 2 compared with the Zn free sample in all peaks shows that the presence of Er_2BaCuO_5 has a significant effect in the electrochemical response of the compound, where the change in the first and second couple peaks is around 1.5 times.

Figure 3 shows the cyclic voltammograms of oxidation reduction response of bare electrode (GC), $ErBa_2Cu_3O_{7-\delta}$, and $Er_{0.8}Zn_{0.2}Ba_2Cu_3O_{7-\delta}/ErBa_2Cu_3O_{7-\delta}$ electrode mechanically attached to GC electrode. It is clear that the electrochemical response increased two times in the presence of the doped

Zn sample in the second couple peaks, $^{2}E_{pc}$ and $^{2}E_{pa}$ where the enhancement is affected by the Er_2BaCuO_5 phase appeared in the XRD patterns due to the presence of Cu^+ in the 211 phase. Furthermore, the first couple peaks, $^{1}E_{pc}$ and $^{1}E_{pa}$ have a lower effect compared with the first couple peaks.

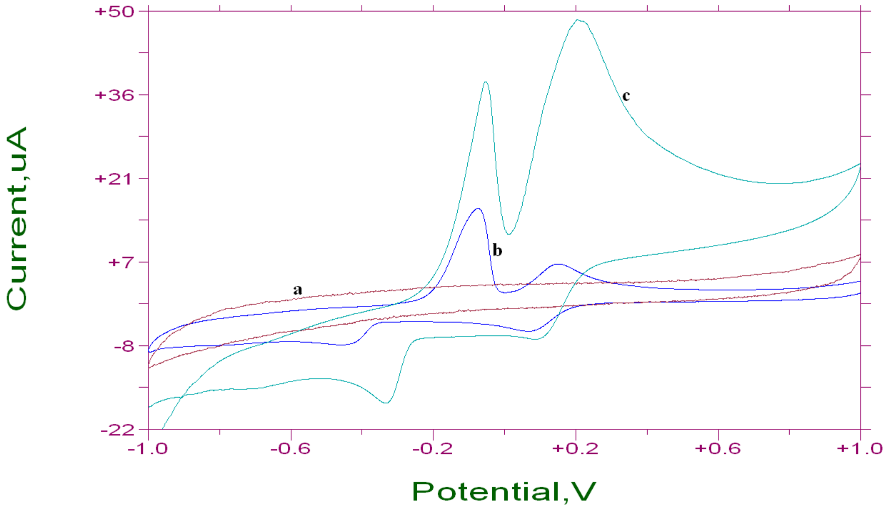

Figure 3. Cyclic voltammogram obtained for the oxidation-reduction of a) bare electrode (GC) and b) $ErBa_2Cu_3O_{7-\delta}$ and c) $Er_{0.8}Zn_{0.2}Ba_2Cu_3O_{7-\delta}/ErBa_2Cu_3O_{7-\delta}$ mechanically attached to a GC electrode surface in the presence of 0.1 M NH_4Cl at 25 °C using scan rate 100mV/s.

3.3 Effect of scan rate

Varying scan rate from 5-300 mVs^{-1}, led to changes in the peak height and position. Figure 4 shows that the second and first peak reduction have a considerable change in the reduction peaks where at lower scan rate of 5 and 20 mV/s the second reduction peak $^{2}E_{pc}$ has the lower electrochemical response compared with the first reduction peak, $^{1}E_{pc}$. In general, the current increased with an increase in the scan rate which may be due to the size of the diffusion layer and the time taken to record the scan [2].

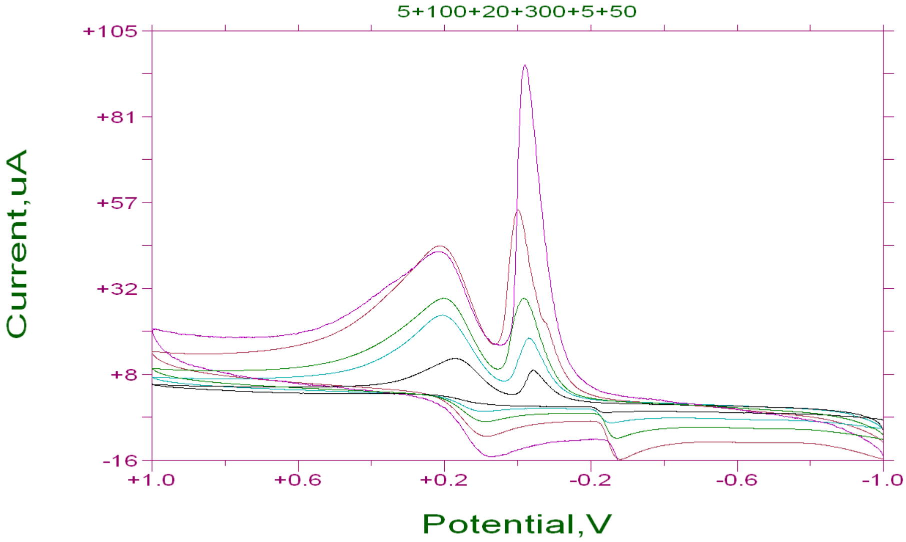

Figure 4. Cyclic voltammogram data for $Er_{0.8}Zn_{0.2}Ba_2Cu_3O_{7-\delta}/ErBa_2Cu_3O_{7-\delta}$

The oxidative current demonstrated the dependence of log oxidative current, I on log scan rate, υ using doped $Er_{0.8}Zn_{0.2}Ba_2Cu_3O_{7-\delta}$ modified working electrode in 0.1 M NH_4Cl as a supporting electrolyte was studied over 5 – 700 mV/s.

The result shows that the current increased with an increase in the scan rate. The slope of the graph of log I versus log υ was 0.7 indicating that the $Er_{0.8}Zn_{0.2}Ba_2Cu_3O_{7-\delta}$/GC complex species was not strongly adsorbed on to the GC electrode surface (Fig 5). This value is far from 1, this is due to the change in chemical properties of metal ion.

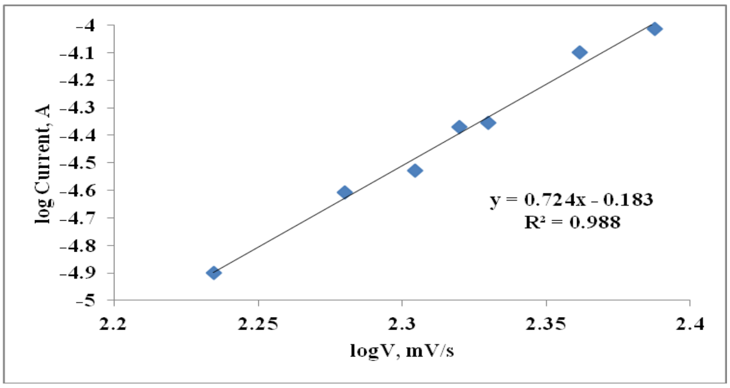

Figure 5. dependence of log reductive current on log scan rate for in $Er_{0.8}Zn_{0.2}Ba_2Cu_3O_{7-\delta}$ /GC 0.1 M NH_4Cl

3.4 Effect of Repetitive Cycle of Potential

The continuing potential cycling was carried out at 100 mV/s scan rate in the potential range of +1.0 V to -1.0V for the $Er_{0.8}Zn_{0.2}Ba_2Cu_3O_{7-\delta}/ErBa_2Cu_3O_{7-\delta}$ sample. Figure 6 shows that the repetition of scanning led to increase in the current up to the 10th cycle. This could have happened because ~~a~~ small amount of the deposited compound might not have reduced completely.

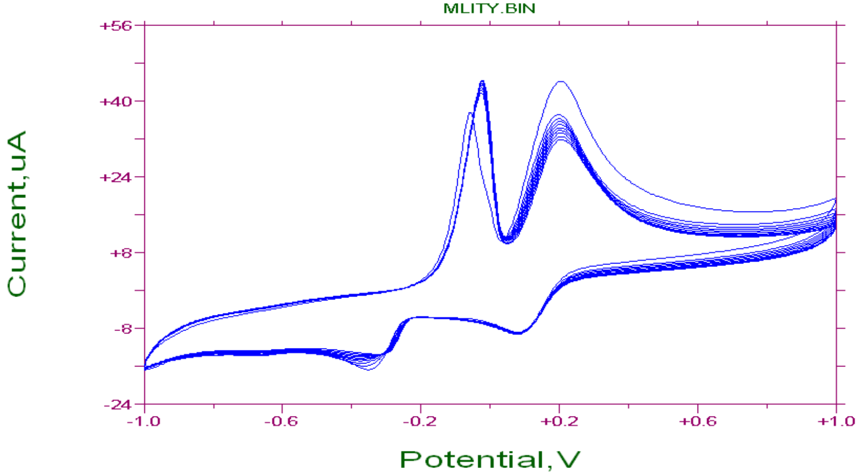

Figure 6. Cyclic voltammogram of $Er_{0.8}Zn_{0.2}Ba_2Cu_3O_{7-\delta}/ErBa_2Cu_3O_{7-\delta}$ during the potential cycling of 10 cycles, at 25 °C using scan rate of 100 mV/s.

3.5 Effect of pH

Figure 7 shows the effect of pH value in the electrochemical response of $Er_{0.8}Zn_{0.2}Ba_2Cu_3O_{7-\delta}/ErBa_2Cu_3O_{7-\delta}$ attached to 3 mm GC electrode in the presence of 0.1 M NH_4Cl as a supporting electrolyte. The results showed an increment in the current as the acidity increased. This result is summarized in figure 7 where the change of current has a semi-linear relation with the acidity. The explanation of this current increment had been rendered by many researchers [2,11-12], where the acidic media dissolved the compound attached to the electrode to release more soluble species (Cu^{2+} and Cu^{+} cations)

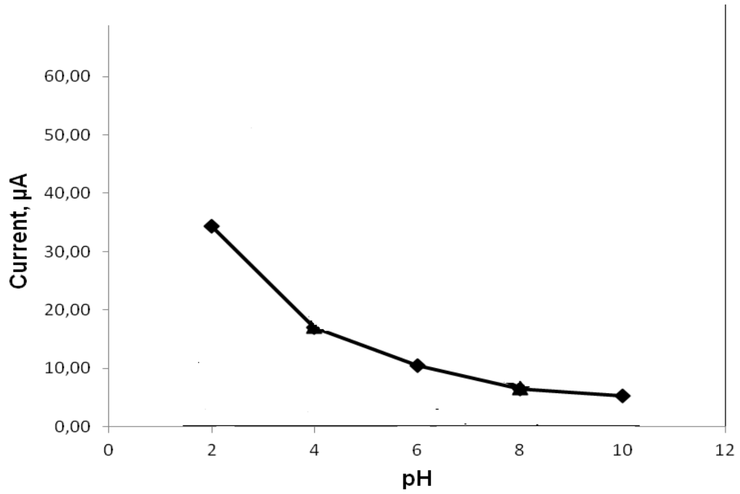

Figure 7. The current versus pH for $Er_{0.8}Zn_{0.2}Ba_2Cu_3O_{7-\delta}/ErBa_2Cu_3O_{7-\delta}$ attached to 3 mm GC electrode in the presence of 0.1 M NH_4Cl as a supporting electrolyte

3.6 Chronocoulometry (CC) and Chronoamperometry (CA)

Double potential step experiment, CC and CA for $Er_{1-x}Zn_xBa_2Cu_3O_{7-\delta}$ x= 0.0, 0.05, 0.1, 0.15 was performed using GC electrode in the presence of 0.1M NH_4Cl aqueous solution as a supporting electrolyte.

Chronoamperometry (CA) as a relation between time versus current provides heterogeneous kinetics information of the electrode reaction. The Cottrell equation can be applied in the potential stepped at time zero to estimate the diffusion coefficient of the sample.

$$i = \frac{nFAC_0\sqrt{D_0}}{\sqrt{\pi t}}$$

The diffusion coefficient D values shown in table 3 indicates that, the value increased with an increase in the Zn content of the sample. However, at higher content of Zn, the value dropped down below the un-doped sample, which might be due to the lower distribution of the Zn in the sample in the morphology structure.

The chronocoulometry (CC) known as the charge-time behavior of the electrode in the solution in which it provides the electrode kinetics information and the value of charge can be estimated according to the Cottrell equation as shown below:

$$Q = \frac{2nFAC_0\sqrt{D_0 t}}{\sqrt{\pi}}$$

The estimated values of charge in the electrode presented in table 3 indicated an increase in the value by increasing the Zn content in the sample

Table 3. Diffusion coefficient and value of charge of $Er_{1-x}Zn_xBa_2Cu_3O_{7-\delta}$ mechanically attached to 3 mm glassy electrode.

	Mole of dopant	D cm^2/s	Value of Charge $\mu C/cm^2$
Er	0.0	7.47×10^{-05}	497.25
Z1	0.05	7.52×10^{-05}	441.07
Z2	0.1	7.78×10^{-05}	629.11
Z3	0.15	7.85×10^{-05}	651.24
Z4	0.2	7.31×10^{-05}	808.01

4. CONCLUSIONS

In this paper, the Zn-doped ErBCO was successfully prepared via coprecipitation method. The electrochemical study of pure and doped sample was characterized using a solid phase cyclic voltammetry method by attaching the sample to a glassy electrode at a fixed parameter of 100 mV/s scan rate in the presence of 0.1 M NH_4Cl. The effective electrochemical response happened in the Z4 sample where the content of Zn was higher. The higher effective response sample studied in variant parameter showed that the presence of the second phase of Er_2BaCuO_5 promoted the activity of the electrochemical behavior of $Er_{0.8}Zn_{0.2}Ba_2Cu_3O_{7-\delta}/ErBa_2Cu_3O_{7-\delta}$. In addition, the scan rate and the repetitive scanning of sample had a proportional effect due to the time needed for the over layer response. The current increment by the acidity was due to the dissolution of the solid phase in the electrode. All the samples showed an increase of the charge value on the surface and the diffusion coefficient increased with increase in Zn content. The decreasing of diffusion value in Z4 sample led to the effect of the secondary phase of 211.

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