

Fabrication of Copper Foam from Copper - Polymer composite By Powder Metallurgy Technique for using as Electrode

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Abstract— Copper foam was prepared using copper powder and epoxy resin with sodium bicarbonate as a foaming agent by powder metallurgy technique. Copper powder was prepared by water atomization technique; it was mixed with 12.5, 25 and 50 wt. % epoxy resin, then sintered at 600 °C and 800 °C in an argon atmosphere for one hour. Microstructure was estimated by both optical and FE-SEM which indicated the homogeneous distribution of irregular shape pores all over copper matrix. Phase structure was investigated by XRD that gives only peaks corresponding to copper metal in all samples. Density and porosity were measured by Archimedes principle, which indicated that sample containing 25 wt. % epoxy resin Cu foam sample has the highest relative porosity at 800 oC. Compressive strength for samples sintered at the 800 oC indicated that sample containing 50 wt. % epoxy has the lowest compressive strength value. The three copper foam samples have been tested as an electrode for electro analysis processes, zinc oxide thin film has been successfully prepared by electrode position onto copper foam substrates using zinc nitrate, aqueous solution at room temperature, and the deposition was conducted using the cyclic voltammetric technique. The effect of substrate type on the deposition and dissolution currents was fully analyzed. Also, it has good effect on the corrosion behavior of the copper foam samples. The results showed that sample containing of 25 wt. % epoxy at 800 O C resin is the most suitable one for these purposes..

Keywords — Copper foam, Powder metallurgy, Polymers, Epoxy resin, Porosity, Foaming materials, Electrochemical deposition; Corrosion resistance.

I. INTRODUCTION

Metal foams are a new class of materials with low density and novel physical (thermal and electrical), mechanical and acoustic properties. They offer potential for lightweight structures, for energy absorption and thermal management. It possesses unique characteristics such as low density, high stiffness in conjunction with very low specific weight and high gas permeability combined with high thermal conductivity [1- 4]. In the last decades, there was a considerable interest metal foams that have recently increased, due to the process developments promising a better quality of the foamed material [3]. For functional applications, such as sound absorption, thermal insulation,

heat dissipation and catalyst support, the cells need to be open and small. The metal matrix may be Cu, Fe, Ti or Ni based alloy, these metals have much higher melting point than Al. Solid route manufacturing technologies are then often adopted [5]. For instance, in automotive industries, aluminum foam material has been applied to increase fuel efficiency due to its weight reduction. It is also utilized in automotive structure to absorb impact during a car accident. Other applications of metal foam, e.g. copper foam, have been also developed, such as thermal pipe, heater plate, and cooling fins [3-5]. Requirements for using bare electrodes in electrochemical analysis with strong catalytic activity in the reduction of ions and good stability under the test conditions. After screening several cathode materials, various investigators have converged to identify copper [6 – 8] or its alloys, especially Cu-Ni [9, 10], as the most suitable ones. Open cell foams are manufactured via foundry or powder metallurgy technique in which metal powders are the most widely used. These methods have a good control over the cell shape, cell size and porosity distribution. Some investigators have used the Sintering and Dissolution Process (SDP) to manufacture the metal based foams [4, 5], and recently, the Lost Carbonate Sintering (LCS) process became the subject of some research in this area [6]. Copper foam is a popular metallic foam which characterized by excellent ductility as well as good thermal and electrical conductivities. Therefore, they are very attractive for potential in industrial applications such as porous electrodes in rechargeable batteries, fuel cells, heat exchangers, catalytic substrates for chemical reactions and filtration applications. For such applications, the pore structure is considered a key factor for the sustainable design of high performance porous components and should therefore exhibit a high degree of porosity uniformity and controllable porosity distribution [1-4]. The Fabrication of porous copper by unidirectional solidification under hydrogen and its properties were investigated by Nakajima et al. [10]. Recently, LCS process was used for manufacturing open cell copper foams [5, 6].

The aim of this research is to investigate of manufacture

copper foams by using polymeric materials for electrochemical analysis application and to understand the effect of epoxy resin on performance copper foam electrode in an electrochemical cell, corrosion rate and mechanical behavior of copper foam products.

II. MATERIALS & METHODOLOGY

In this study the copper powder fabricated by a water atomization method with particle size 150 μm and 99% purity was mixed with an epoxy resin by three percent 12.5, 25 and 50 wt. % in the presence of 1wt.% foaming agent . A dispersing agent of 1wt.% was also added for improving the wettability and dispersity of Cu particles with the polymeric material. They are mixed with each others at room temperature with rotation speed of 50 RPM, then sintered at two different temperatures 600 & 800oC under argon atmosphere to prevent the oxidation process. The density was estimated by Archimedes principle, in which the actual density of the prepared samples was determined according to ASTM D1217 standard, using water as a floating liquid according to MPIF standard 42, 1998. The sintered specimens were weighed in air and in distilled water after its capsulation with paraffin wax to prevent entering of water in the pores, then their densities (D) were calculated according to the following equation:-

$$D = W_a / (W_a - W_w)$$

Where, W_a and W_w are the masses of the sample in air and water respectively. The relative density of the composite is the ratio of the measured sintered density (actual density) to the theoretical one. The degree of porosity of the sintered compacts was calculated according to the following equation:-

$$\text{Porosity\%} = (D_{th} - D_o) / D_{th}\%$$

Where, D_{th} is the theoretical density of the sintered sample and D_o is the actual density. The phase constituent of the sintered specimens was achieved by x-ray diffraction analysis using x-ray diffractometer model x, pert PRO PANALYTICAL with Cu α radiation ($\lambda=0.15406$ nm). The sintered samples were ground successively with 600, 800, 1000, 1200, 2000 and 3000 grit SiC papers. Then, the specimens were polished with 3 micrometer alumina paste using a machine model "Buhlertm". The microstructure of the polished samples was investigated by Field emission scanning electron microscope (FE-SEM), model (FE-SEM; QUANTAFEG250, Holland) equipped with energy dispersive X-ray (EDX) spectrometers, and secondary electron (SE) and backscattered electron (BSE) detectors for the determination of particle size, morphology and chemical composition. Compression strength testing of the investigated samples was also measured using uniaxial SHIMADZU universal testing machine UH-F500KN. The area of the specimen is (65.86 mm²) and the applied cross-head speed is 2mm/min. The test was conducted at room temperature. Copper foam can be used as an electrode in electrochemical cells, this is achieved by immersing the Cu foam in an electrolyte in which a conventional three-electrode cell was used with different copper sheets (1 cm²) as a

working electrode, platinum as a counter electrode (1 cm²) and silver / silver chloride (Ag/AgCl) (+220 mV vs. normal hydrogen electrode as a reference electrode (HANNA Instruments, Italy). The electrolyte is 0.05 M KNO₃, and 0.1 M Zn (NO₃)₂, and the analytical grade reagents worked at room temperature. The working and counter electrodes were mounted parallel to each other at a distance of 0.5 cm a part, without stirring. All substrates were cleaned by an ultrasonic bath with deionized water followed by rinsing in an ethanol bath. Copper substrate samples were etched for 15 sec. With dilute hydrochloric acid to eliminate the oxide layer. Prior to the film deposition, the copper substrate was polished with emery paper, followed by an etching process in dilute hydrochloric acid for 30 s and rinsing in distilled water. This preparation method provides chemically clean and smooth surface, which is important for the cyclic voltammetry studies. Cyclic voltammetry curves were measured by sweeping from 1000 to -2000 mV vs and Ag/AgCl electrode at a selected potential was swept by a rate of 10 mV s⁻¹. The voltammetric response was obtained from a high-performance 20 V/1A potentiostat/galvanostat, Volta Lab 21 PGP 201 model, coupled to a computer to record current and potentials. The resulting deposited ZnO film on a copper electrode was rinsed thoroughly with water, ethyl alcohol then dried under vacuum in a desiccator for one hour.

III. RESULTS AND DISCUSSIONS

A. Densification and Porosity Measurements

The relative porosity of Cu-foam samples sintered at 600 and 800 °C are given in figure (1). There are two phenomena the higher porosity percent of samples sintered at 800 °C than those sintered at 600 °C, which may be due to the suitable sintering temperature, for complete decomposition of the polymeric material with a foaming agent that gives a large number of pores. The second phenomena are the higher porosity percent of sample containing 50 wt. % epoxy resin, which may be attributed to the suitable epoxy resin percent with 1 wt%. Foaming agent at 800 oC sintering temperature. While 1 wt. The % foaming agent is not sufficient for 12.5 and 50 wt. % epoxy resin. So, 25 wt% epoxy resin with 1 wt%. Foaming agent added for copper powder and sintered at 800 OC is the most suitable parameters that give the highest.

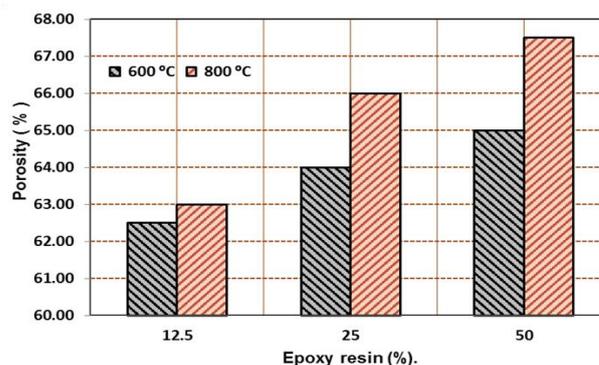


Fig. (1) The density and porosity of the Cu foam with 12.5, 25 and 50 wt. % epoxy resin sintered at 600 and 800 °C.

B. XRD Measurement

The phase structure of copper foam specimens with 12.5, 25 and 50 wt. % epoxy resin are estimated by X-ray diffraction. Figure (2) represents the XRD pattern which indicated that only peaks corresponding to copper metal were observed in all samples sintered at both 600 & 800 Oz. This may be due to the complete dissociation of the epoxy resin to carbon dioxide gas and water vapor during the sintering process.

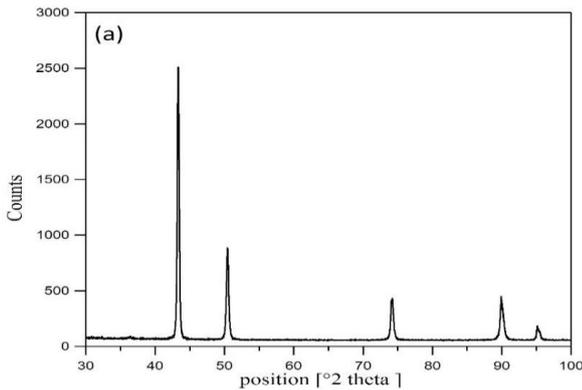


Fig. (2) XRD pattern of sintered Cu foam

C. Photographic Investigations

Figure (3) and (4) show the photo images of copper foam with 12.5, 25 and 50 wt.% epoxy resin samples sintered at 600 & 800 OC respectively. The samples are in the shape of a rectangle or cubic form. The porous structure is clear in all samples and distributed in a homogeneous manner.

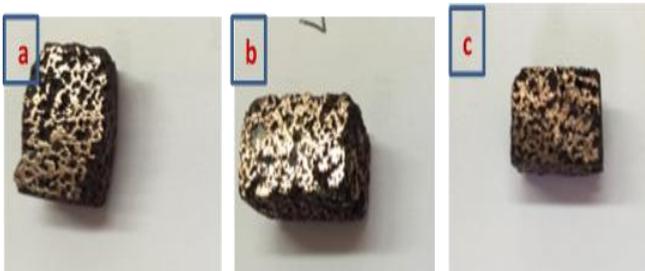


Fig. (3) The photo images of (a)12.5 wt.% , (b) 25wt.%,50 wt.% Epoxy resin copper foam samples sintered at 600 OC.

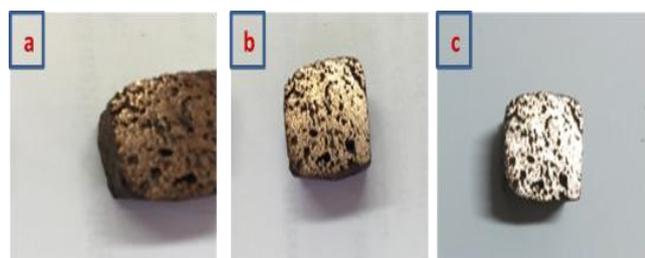


Fig. (4) The photo images of (a)12.5 wt.% , (b) 25wt.%,50 wt.% Epoxy resin copper foam samples sintered at 800 OC.

D. Microstructure Investigations

Microstructure of copper foam was examined by both optical (OM) & field emission scanning electron microscopes (FE-SEM).

1. Optical Microscopic Studies

Figures (5 and 6) show the optical micrographs of 12.5, 25 and 50 wt.% epoxy resin samples sintered at 600 oC and 800 oC respectively . The results indicated the appearance of two types of pores, open pores and closed nearly rounded pores. Samples sintered at 800 oC have connected and irregular pores, this may be due to the higher sintering temperature, which causes the complete dissociation of the epoxy resin and foaming agent, also give the chance for connection of the pores with each others. Also cell wall is dense and only micro pores or voids can be seen and the pores are not uniaxial. The pores are distributed in a nearly homogeneous manner all over the copper matrix, in which copper matrix is well sintered around the pores while samples sintered at 600 oC has a separate and connected pore, as the temperature is not sufficient for complete sinterability and connection of pores [11].

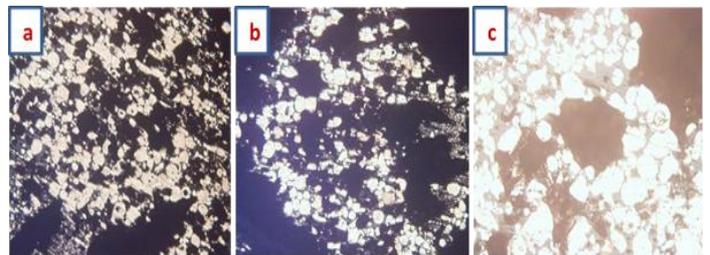


FIG (5) METALLOGRAPHIC CROSS SECTION OF (A)12.5 WT.% , (B) 25WT.%, (C) 50 WT.% EPOXY RESIN COPPER FOAM SAMPLES SINTERED AT 600 OC.

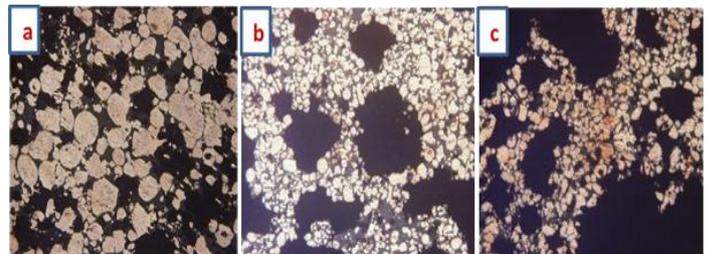


FIG (6) METALLOGRAPHIC CROSS SECTION OF (A)12.5 WT.% , (B) 25WT.%, (C) 50 WT.% EPOXY RESIN COPPER FOAM SAMPLES SINTERED AT 800 OC.

2 Scanning Electron Microscopic Investigation

Figure (7) represents the microstructure of 25wt. % epoxy resin sample sintered at 800 oC at magnifications 70X, 100X and 250X. There are some variations in both pore size and particle size of copper, the pore size ranges from 20 μm to 200 μm. The particles of copper matrix are well sintered around these pores, although interparticle pores are shown. Also higher cell wall porosity and more interconnected pores are observed. This may be attributed to the suitable added epoxy resin percent and foaming agent to copper powder as they are a main factor in formation pore and shape. It is clear that sample containing 25wt. % epoxy has the most homogenous pore distribution in the Cu matrix. There are regular distribution of the pores which related to the

homogenization between Cu powder, epoxy resin and the foaming agent during the mixing process that play an important role in this process, as these pores are attributed to the decomposition and evaporation of polymeric material during the sintering process.

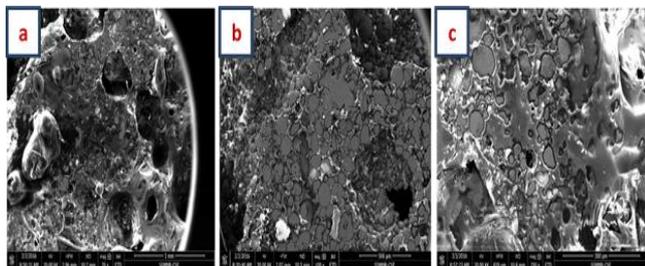


Fig (7) Scanning electron micrographs of 25 wt. % epoxy resin copper foam samples sintered 800 °C at (a) 70 X (b) 100 X (c) 250 X.

E. Compression Strength

The compression strength of a foaming material depends greatly on the density; also pore distribution, size and shape. Figure (8) shows the experimental stress–strain curves for copper foam with 12.5, 25 and 50 wt.% epoxy resin samples sintered at 800 °C. All curves display one behavior for all samples illustrated as follows; in this first step at the beginning of the load the specimens deformed elastically and bending occurs only, in this section the pore remained unharmed. The second step copper foam 50 wt. % epoxy sample has the lowest compressive strength value due to the high porosity percent created by the epoxy and foaming materials percent in which the pore are considered a weak point for crack initiation and propagation [11].

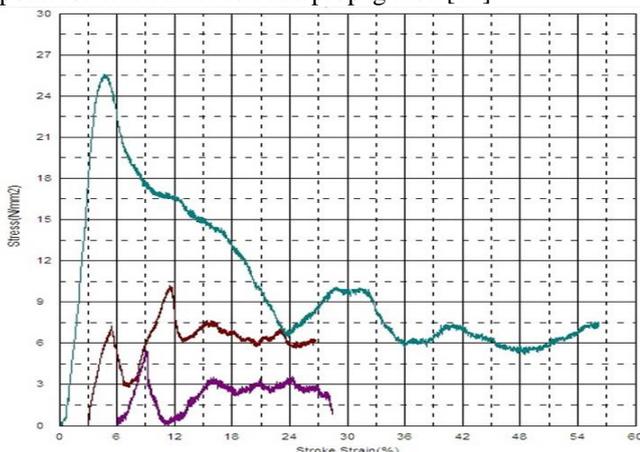
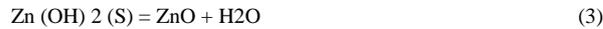
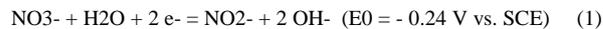


Fig. (8) Compressive stress–strain curves for Cu foam 12.5, 25, 50 wt.% epoxy resin sintered at 800 °C.

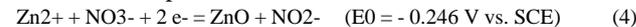
F. Copper Foam as an Electrode for ZnO Film Formation

Porous copper foam can be used, as an electrode for electrochemical deposition of metals, by immersing in an electrolytic solution of an electrochemical cell. In this work Cu-foam electrode was used in cyclic Voltammetry of ZnO film deposition by immersing in Zinc nitrate solution, based on the reduction of nitrate at the copper foam electrode, raising the local pH and causing precipitation of the hydroxide phase and subsequent dehydration to the oxide,

according to the following scheme [12]



The overall expression of the reaction is:



The cathodic electrode position of ZnO thin film from nitrate solution is thought to proceed via the reduction of nitrate ions according to equation (1). The as-generated hydroxide ions would react with Zn²⁺ ions to form Zn(OH)₂ according to equation (2). Subsequently, Zn(OH)₂ is spontaneously dehydrated into ZnO equation (3). During the electrode position of ZnO films, nitrate ions are used as oxygen precursor.

I Copper Foam Samples Sintered at 600 °C

Figure (9) shows four typical cyclic voltammograms recorded with four different copper electrodes in a bath containing 0.05 M Zn (NO₃)₂ + 0.05 M KNO₃. Curve (standard) displays the cyclic voltammogram recorded in the deposition solution of ZnO on solid, non porous copper substrate which is prepared from water atomized copper powder that compacted under 700 MPa pressure, then sintered in a vacuum furnace at 900 °C for 1 hour. This sample was used as a reference sample for the comparison with the three copper foam samples, in this curve, ZnO begins to deposited at potential -100 mV (Ag/AgCl), and cathode potential of -1.2 V vs. Ag/AgCl a steep increase of the cathodic current takes place up to 13 mA cm⁻² which corresponding to nitrate ions reduction and hydrogen gas evolution but observed anodic current is 20 mA cm⁻² associated with anode potential 20 mV and is likely due to oxygen evolution [12, 13]. The rate of ZnO electrode position reaction and rate of anodic reaction are directly proportional to the recorded deposition current value in the voltammogram.

Curve (S1) which represents the cyclic voltammogram of Cu – 12.5 wt% epoxy sample. It displays the cyclic voltammogram recorded in the deposition solution of ZnO on porous copper substrate sintered at 600 °C. ZnO deposition begins at cathodic deposition potential -300 mV higher than that of standard non porous Cu. Also at the cathode potential of -1.5 V a week increase of the cathodic current takes place up to 5 mA cm⁻² that corresponding to hydrogen gas evolution [12]. In the anodic reverse direction, the observed oxygen evolution current of standard non porous Cu is 2 mA cm⁻² and started at anodic potential 500 V [13]. Also the deposition potential is higher than that of standard non porous Cu by -300 mV and the deposition current is lower by 8 mAcm⁻². In additions, the anodic potential is higher by 480 mV and the anodic current is lower than that of curve 1 (standard non porous Cu) by 18 mAcm⁻². Similar behavior was observed with the fourth curve (S3), which displays the cyclic voltammogram of ZnO on porous copper substrate. The deposition potential of curve S3 is higher than that of curve by -400 mV while the deposition current is lower than

that of curve 1 by 11 mAcm⁻². Also the anodic potential of curve S3 is higher than that of curve 1 by 580 mV and the anodic current is lower by 19 mAcm⁻².

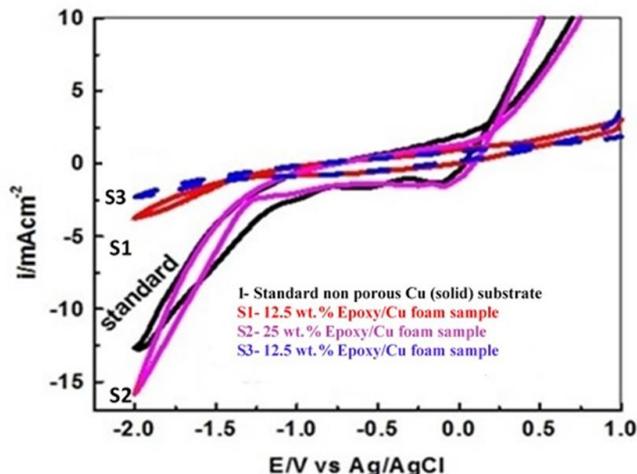


Fig (9) Four typical cyclic voltammograms recorded with copper samples electrodes sintered at 600°C in a bath containing 0.05 M Zn (NO₃)₂ + 0.05 M KNO₃.

Curve S2 displays the cyclic voltammogram of 25 wt% epoxy resin copper foam sample recorded for ZnO film deposition on porous copper substrate. The voltammogram showed a behavior better than curve 1 in both cathodic and anodic directions which indicated that this samples is the best in both deposition and dissolution conditions. In which the deposition potential is lower than that of curve 1 by -40 mV and the deposition current is higher by 5 mAcm⁻²., while the anodic potential is lower by 5 mV and the anodic current is higher by 4 mAcm⁻². So, these results sample.

This can be explained by the porosity of this sample which gives high surface area that is more catalytic for the electro chemical deposition [13]. Figure (9) showed that 25wt.% epoxy resin Cu foam sample (curve S2) is the best in its electrochemical deposition behavior .

2 Copper Foam Samples Sintered at 800 oC.

Figure (10) shows four typical cyclic voltammograms recorded with four different copper foam electrodes sintered at 800°C in a bath containing 0.05 M Zn(NO₃)₂ + 0.05 M KNO₃. As in figure (9) curve 1 displays the cyclic voltammogram recorded in the deposition solution of ZnO on non-porous copper substrate.

Curve S1 displays the cyclic voltammogram recorded in the deposition solution of ZnO on porous copper substrate sample S1 (12.5 wt.% epoxy resin sample sintered at 800 oC). The voltammogram showed better behavior than curve 1 in both cathodic and anodic directions which indicated that copper substrate which is copper foam with 12.5 wt.% epoxy resin sample is the best in electrochemical deposition and dissolution process. The deposition potential of curve S1 is lower than that of curve 1 (standard non porous Cu) by -70 mV while the deposition current is higher by 8 mAcm⁻² and the anodic potential is lower by 20 mV and the anodic current is higher by 4 mAcm⁻².

S2 curve displays the cyclic voltammogram for the deposition solution of ZnO on porous copper substrate contains 25 wt.% epoxy resin. In this curve, ZnO deposition begins at cathodic deposition potential -300 mV higher than that of standard non porous Cu. Also at the cathode potential of -500 mV, in which a small increase of the cathodic current takes place up to 7 mA cm⁻² which corresponding to hydrogen gas evolution [12]. In the anodic reverse direction, the observed oxygen evolution current is 3 mA cm⁻² and started at anodic potential of 500 mV [13].

The deposition potential of curve S2 is higher than that of curve 1 by - 200 mV and the deposition current is lower by 6 mAcm⁻², while the anodic potential is higher by 500 mV and the anodic current is lower by 17 mAcm⁻². All these resulte indicated that 25 wt.% epoxy resin porous copper sample Curve (S1) is the best in its electrochemical deposition behavior.

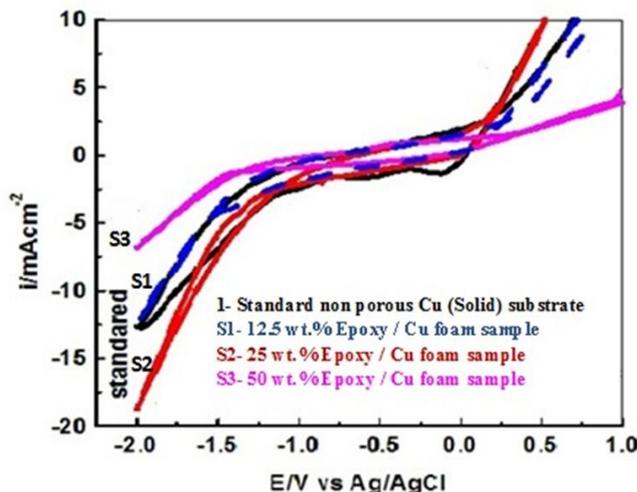


Fig (10) Four typical cyclic voltammograms recorded with copper samples electrodes sintered at 800°C in a bath containing 0.05 M Zn(NO₃)₂ + 0.05 M KNO₃.

G. Corrosion Behavior of Copper Foam

The corrosion behavior of different copper foam samples prepared at 600 0C in 0.1M ZnNO₃ + 0.05 M KNO₃ bath is observed in Figure (11). The results showed that, the corrosion rate of non porous copper sample in bath containing 0.1 MZnNO₃ + 0.05 M KNO₃ is about 1.062 mm/Y at a corrosion current of 0.0908 mA cm⁻².

S1 and S3 samples that contains 12.5 wt.% and 50wt.% epoxy resin showed a higher corrosion rate 1040 and 932 mm/Y respectively with respect to the non porous one copper sample and a higher corrosion current of about 88.92 and 79 mm/Y with respect to the non porous one. For S2 sample that contains 25 wt.% epoxy, the corrosion rate in nitrate bath was about 13.68 mm/Y while the corrosion current was 1.14 mA cm⁻². So S2 is the best in its electrochemical corrosion behavior with respect to the other samples. This my be attributed to the higher density and lower porosity of the samples in which as the porosity increases the surface area increases and the catalytic behavior increases which stimulate

the corrosion [14]. While, as the sample becomes more dense this resists the corrosion.

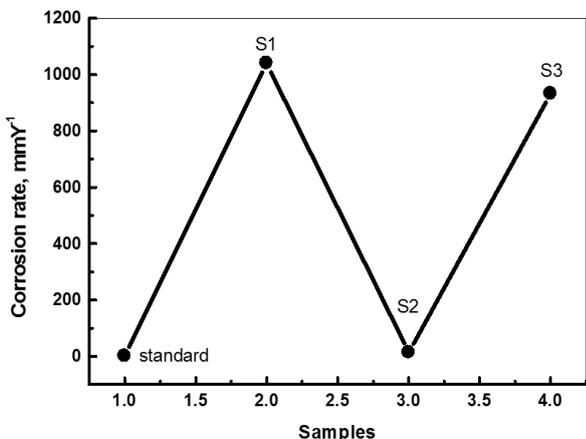


Fig. (11) Corrosion behavior of copper samples prepared at 600 °C.

Figure (12) represents the corrosion rate of copper foam samples prepared at 800 °C in the same a bath containing 0.1 M ZnNO₃ and 0.05 M KNO₃. It was about 1.062 mm/Y while the corrosion current was 0.0908 mA cm⁻². S1 and S3 samples showed a higher corrosion rate of 1040 and 932 mm/Y with respect to the non porous sample, also a higher corrosion current of about 88.92 and 79 mm/Y respectively. For S2 sample the corrosion rate was about 13.68 mm/Y while the corrosion current was 1.14 mA cm⁻².

The results showed that S2 sample sintered at 800 °C is the nearest on to the non porous sample in its electrochemical corrosion behavior. While, S1 sample is the worst one.

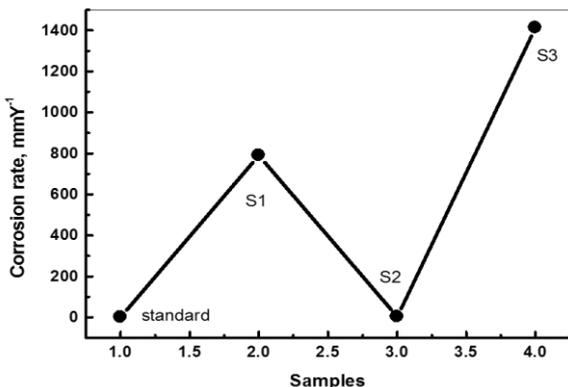


Fig. (12) Corrosion behavior of copper samples prepared at 800 °C.

Fig. (12) showed that, the corrosion rate of copper sample (non porous) sintered at 800 °C in 0.1 M ZnNO₃ + 0.05 M KNO₃ bath is about 1.062 mm/Y while the corrosion current was 0.0908 mA cm⁻². Samples 1 and 3 showed a higher corrosion rate of 120 and 67 mm/Y with respect to non-porous sample. Also, a higher corrosion current of about 1412 and 790 mm/Y with respect to non porous sample, respectively.

The corrosion rate of (Sample number 1) which is the Cu-

foam with 12.5 % wt. epoxy resin in nitrate bath was about 2.535 mm/Y while the corrosion current was 0.21 mA cm⁻². Porous sample number 1 sintered at 800 °C is the nearest and best porous sample in its electrochemical corrosion behavior with respect to other samples. While, sample number 2 showed the worst one.

Copper foams are characterized by excellent ductility as well as good thermal and electrical conductivities this gives it the facilities to use as, pours electrodes, a catalectic substrate for chemical reactions and filtrations applications also the pores structure is considered a mean factor for a uniform distribution of pours which plays a big role in all the above applications.

IV. CONCLUSION

In the present work, Copper foam are fabricated using copper powder with Polymeric materials by powder technology technique to be used as an electrode in electrochemical cell analysis, have been prepared in three electrodes from mixed with 12.5, 25 and 50 wt. % epoxy resin with copper powder, Cu foam specimens were divided based on the sintering temperature at 600 and 800 °C. Based on the mechanical, physical and performance of electrode in electrochemical cell of the investigated electrodes specimens, the following remarks can be highlighted:

- After Cu foam sintered have been complete dissociation of the epoxy resin to carbon dioxide gas and water vapor and homogeneous distribution of irregular shape pores all over copper matrix.
- Increase addition of epoxy resin from 12.5 to 50 wt. % and sintering temperature from 600 to 800 leads to a relative porosity increase.
- Positive effect of the 25 wt. % epoxy resin porous copper sample is the best in its electrochemical deposition and corrosion rate behavior and it is the most suitable one for these purposes.

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