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IMPEDANCE RESPONSE AND CHARACTERIZATION OF NANO POROUS CURRENT COLLECTOR

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Abstract

Power crisis is the great concern in electrical charge storage devices. Electrochemical energy storage devices such as supercapacitors are the alternative power sources. Nanoporous gold film is the promising material for supercapacitor current collector fabrication. Nanoporous gold has recently become a desirable material in the field of analytical chemistry. This conductive material has an open, 3D porous structure consisting of nano sized pores with surface areas that are 100s to 1000s of times larger than planar gold of an equivalent surface area. The high surface area tied with an open pore network arrangement makes nanoporous gold a perfect support for the development of supercapacitor. Important features include conductivity, high surface area, ease of preparation and adaptation, tunable pore size, and a continuous open pore network. Nanoporous current collector for supercapacitor is prepared by dealloying Au:Cu alloys. Surface analysis and characterisation are performed by using SEM, FESEM and EDAX analysis. Mathematical modelling of impedance response for a nanoporous current collector is derived and equivalent circuit is also obtained. This current collector can store more charge carriers for large number of charging /discharging cycles and can be used in portable, high power applications.

Keywords:

Supercapacitor, Nanoporous Gold, Scanning Electron Microscope (SEM), Field Emission Scanning Electron Microscope (FESEM), EDAX

1. INTRODUCTION

The rebirth of electrical/electro chemical double layer capacitors is occurring at a phenomenally high rate as the important role of these power storage devices in traction, space flight technology, power electronics and other fields is recognized [1]. Electrochemical supercapacitors store charges through electrostatic charging of a double layer. It also utilize the faradic reactions have higher energy density than electrostatic capacitors as well as higher power density than batteries in general [2]. Supercapacitors can hold electrical charge in the order of ~10^6 Farads and offer extended life cycle than batteries. Supercapacitors can offer high rated voltage and operate in the higher temperature [1]. These characteristics are of growing attention in energy storage applications such as: electric vehicles, backup power systems and electronic components. They are based on a storage mechanism that results from the development of an electric double layer at the boundary between an electronically conductive material and an electrolyte solution.

A usual supercapacitor is formed from two carbon electrodes and a liquid electrolyte supported in a porous matrix introduced between the electrodes. The energy stored in carbon based supercapacitor is predominantly a function of the following parameters: the specific surface area, porous structure of electrodes, ionic conductivity and the voltage stability [3]. Therefore, typical materials used in conventional electrodes must have high surface area, such as activated carbon [4], carbon nano tubes [5] and carbon aerogel [6].Along with various carbonaceous materials, activated carbon is the most popular because of its abundance, cost effectiveness and environmentally benign nature. But its surface properties of the synthesized carbon materials are critical for the electrochemical performance when used as an electrode or current collector material in double layer capacitors [4]. Carbon nano tubes have been believed as the ultimate material for supercapacitors due to their high utilization of surface area, fine conductivity, chemical steadiness and other advantages. In addition, CNT array electrode is found to have low ESR and good cycling stability [5]. Carbon aerogel is promising and innovative material because of its attractive properties. But the conventional method for carbon aerogel synthesis is usually the most time consuming and costly [6]. High electrical conductivity materials such as graphene [7] and crumpled graphene [8] can be used for electrode fabrication. High performance stretchable electrodes are fabricated by using crumpled graphene. Here, the performance is limited by their low stretchability, high cost and complicated fabrication process [8]. These zero gap semiconductor materials will introduce leakage problem. Conducting polymer may be helpful as they are less expensive and able to store energy through redox reactions [9]. But it has lower life cycle and specific capacitance.

'D' block elements in the periodic table are called as transition metal oxides. They are the promising material for supercapacitor electrode fabrication. In transition metal oxides, RuO2 in both crystalline and amorphous forms is of critical importance for theoretical as well as practical purposes, due to unique combination of characteristics, such as sharp conductivity, high chemical and thermal stability, catalytic actions, electrochemical redox properties and field emitting behaviour [10]. It has some major limitations like rigid lattice structure, low availability and expensive in nature [12]. MnO_2 could be used to formulate electrodes in such supercapacitors, because they are predicted to have an elevated capacitance for storing electrical charge, easy synthesis, in expensive, nontoxic, environmental friendly nature and good cycling stability [11, 12]. Advantages of MnO_2 based electrode are,

- It enhances the areal capacitance
- It reduces the electrode size
- Effectively utilize the pseudo capacitive material

This MnO_2 has poor conductivity. It confines the charge/discharge rate. To overcome this problem, high electrical conductivity and porous gold wafer can be used as a current collector [13, 14]. Some perovskite materials can also be used for supercapacitor electrode fabrication [15, 16]. Perovskites are commonly used for solar cell fabrication. It provides very low specific capacitance. From the previous literature, it is known

that the combination of MnO_2 and gold can give more capacitance. MnO_2 nano particles (electrode) are uniformly coated on porous gold wafer current collector by using electrochemical deposition. Electrochemical deposition is a better technique for developing supercapacitor's electrode fabrication [11]. Thickness and morphology of the nano structure can be easily controlled by adjusting the electrochemical parameters. It provides relatively uniform and compact deposits.

In the present study, surface analysis of Nanoporous current collector is given. Nanoporous gold (NPG) thin films, less than 1μm in thickness, have been of great interest in large part due to the fact that such materials show great promise for use in diagnostic applications or other applications that require inertness, conductivity, or increased surface area. Knowledge of the mechanical properties of NPG films is fundamental to an understanding of issues regarding structural integrity in devices which employ such films [13]. High surface area nano structured electrodes have received considerable attention in recent years. These materials are conductive, have high surface areas that are typically 2-1000 times larger than a planar electrode of similar size, and consist of oriented, well defined or random pore morphology. This can potentially lead to larger currents, even for diffusing species, because faradic current typically scales linearly with electrode area [14]. It is believed that this nano porous current collector can improve the charge storing capability of the supercapacitor.

Usually, supercapacitors are modelled using simple RC circuits. However, these models cannot accurately describe the voltage behaviour and the energy efficiency of these devices during dynamic current profiles. Different approaches are used to model the dynamic behaviour of supercapacitors. S. Buller et al. (2002) have proposed the basic approach. It uses the impedance spectroscopy to model the dynamic behaviour of supercapacitor [17]. Equivalent circuit model proposed by E.Tironi et al. (2009) characterizes the dynamic supercapacitor behaviour over a wide charge and discharge frequency [18].

Mathematical and econometric model of Elena Danil et al. (2011) allows the supercapacitor characteristics optimization. In that paper [19], realization of a new complex, adaptive model of a supercapacitor is explained. Supercapacitors are frequently used in Energy Harvesting Wireless Sensor Nodes (EHWSNs) to store harvested energy. Detailed work of Alex S. Weddell et al. (2011) is accurately models real world supercapacitor operation and has a number of important suggestions for the design of low power energy harvesting systems [20].

The implementation of the supercapacitor models using PLECS is illustrated by John Schonberger et al. (2013). Small signal impedance and frequency dependent parameters are calculated to depict the effective internal resistance and capacitance during transient operation [21]. Supercapacitor acts as an energy buffer or energy sources due to their high power density when compared to other charge storing devices as indicated by Rajib Sarkar et al. (2013). In their research, Equivalent Circuit Model (ECM) is projected by considering leakage and self-discharge current. Here all the electrical parameters of supercapacitor realized in to two phases. In first phase leakage or self-discharge current is not considered and in later these losses are considered. Moreover, simulation results are presented to prove the validity of this model. Supercapacitors are better than a battery because it is much more environment friendly, cheap and more over maintenance and hazard free. All these qualities make supercapacitor more preferable for application in power and electronic engineering [22].

2. EXPERIMENTAL ANALYSIS

2.1 MATERIALS AND METHODS

An 18 karat gold substrate was purchased. Gold is the most malleable of all metals. It was beaten to reduce the thickness. Due to the high thermal conductivity and excellent thermal stability, precious metals (Au & Pt) are preferred for supercapacitor current collector fabrication [23]. NPG thin films were prepared by selective etching of copper from gold alloy [13] resulting in a nano porous metal having pore dimensions of 60-80nm. 3.5cm × 1.5cm gold substrates were cleaned and rinsed with ultrapure distilled (DI) (18MΩ-cm) water. After undergoing an additional rinse/dry cycle, gold substrates were immersed in various concentrations of nitric acid (ranging from 30% to 40%v/v) at room temperature. Etching of copper was performed. Substrates were rinsed with DI water again. Upon cooling, substrates prepared in this manner were a dark yellow in color, due to the high concentration of gold.

Table.1. Specifications for Etching

Sl. No.	Etchant	Etching Concentration	Time (min)
1	Nitric acid	30%	20
2	Nitric acid	40%	20

3. MATHEMATICAL MODELING POROUS IMPEDANCE IN THE FREQUENCY DOMAIN

The porous impedance (Z_p) models the porosity of the supercapacitor electrodes. Due to this porosity, the real part of the impedance increases with decreasing frequency and the full capacitance of the device is only available for dc conditions.

$$Z_p(j\omega) = \frac{\tau}{C}\frac{\coth\sqrt{j\omega\tau}}{\sqrt{j\omega\tau}} \quad (1)$$

The Eq.(1) gives the mathematical expression for porous impedance in frequency domain ($Z_p(j\omega)$). This expression has only two independent parameters (C, τ),where C is the capacitance value of RC circuit and τ defines the time constant which means, that including L and R, only four parameters have to be extracted from the measured spectra. General expression for porous impedance is denoted as $G(j\omega)$. This is used to identify the parameters value. Buller [17] shows a suitable way for the inverse transformation of Z_p which is given in Eq.(2).

$$G(j\omega) = \frac{k_1}{\sqrt{j\omega}}\coth\frac{k_2}{k_1}\sqrt{j\omega} \quad (2)$$

where, k_1 and k_2 are the coefficients. Comparing the coefficients of Eq.(1) and Eq.(2) leads to,

$$k_1 = \frac{\sqrt{\tau}}{C}$$

$$k_2 = \frac{\tau}{C}$$

Take inverse transform for Eq.(2). Now the equation becomes,

$$\frac{k_1}{\sqrt{j\omega}} \coth \frac{k_2}{k_1}\sqrt{j\omega} \leftrightarrow \frac{k_1^2}{k_2} + \frac{2k_1^2}{k_2}\sum_{n=1}^{\infty} e^{\left(-n^2\pi^2 k_1^2/k_2^2\right)t}. \quad (3)$$

Here, we use the RC circuit to model the first branch. Number of parallel branches used is represented by the variable '*n*' in the above equation. The general impulse response of RC parallel circuit in frequency and time domain is given below,

$$\frac{R}{(1+ j\omega RC)} \leftrightarrow \frac{1}{C} e^{(-t/RC)} \quad (4)$$

$$R = \frac{2k_2}{n^2\pi^2}$$

$$C = \frac{k_2}{2k_1}$$

Apply k_1 and k_2 values in above *R* (Resistance) and *C* (Capacitance) equations. Resistance and capacitance values become,

$$R = \frac{2\tau}{Cn^2\pi^2}$$

$$C = \frac{C}{2}$$

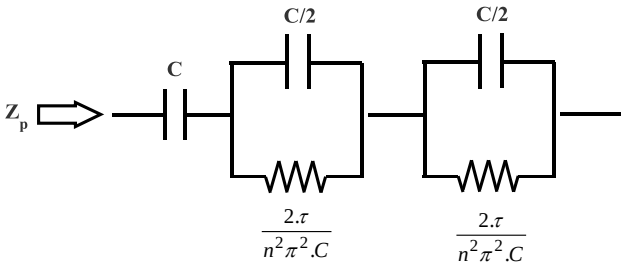

Fig.1. RC Equivalent Circuit for Nanoporous Electrode

The Fig.1 illustrated the RC equivalent circuit for nanoporous electrode. First, number of branches must be chosen as a compromise between the required accuracy and the consequent complexity. The branches represent the supercapacitor's behaviour over a long time scale. Thus, to model the phenomena that acquire at different times, their time constants should be quite different.

After a fast charge all of the energy is stored in the first branch. Then leaving the supercapacitor in an open circuit causes the energy to be redistributed in the parallel branches. At low frequency, resistance represented by the real part of the equation and the capacitance represented by the imaginary part of the equation.

4. RESULTS AND DISCUSSIONS

4.1 ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY ANALYSIS

Electrochemical Impedance Spectroscopy (EIS) is an effective method which is used to characterize and improve the performance. All electrochemical experiments were performed using CHI 600 series Electrochemical Analyzer/Workstation. Distilled water was used for the solution preparation. A conventional three-electrode system was employed. It consists of Gold wafer as working electrode, an Ag (saturated KCl) as a reference and platinum wire as counter electrode. 0.1M Na_2SO_4 electrolyte was used. Nyquist plot obtained in EIS and equivalent circuit of the substrate were given in the Fig.2 and Fig.3.

A depressed semicircle is observed at high frequencies, attributed to the charge transfer resistance and the double layer charging of the electrode surface, followed by an inclined straight line, characteristic of the Warburg region. The obtained circuit is similar to Randles type equivalent circuit, where the double layer capacitance as well as the diffusion impedance within the pores of the electrode material is represented by constant phase elements [24].

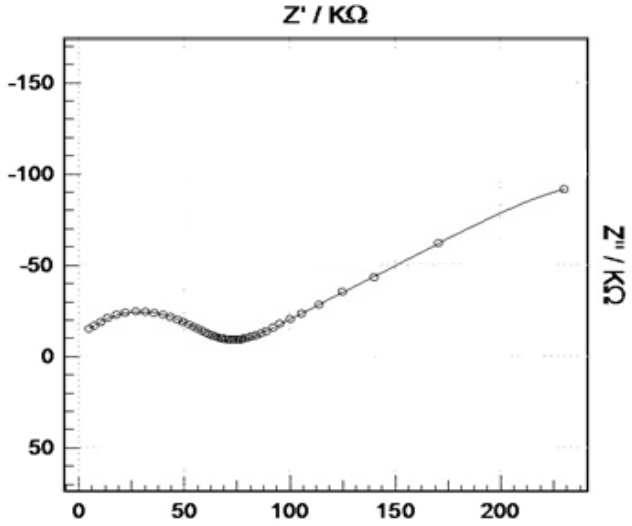

Fig. 2. Nyquist Plot of Impedance Spectra

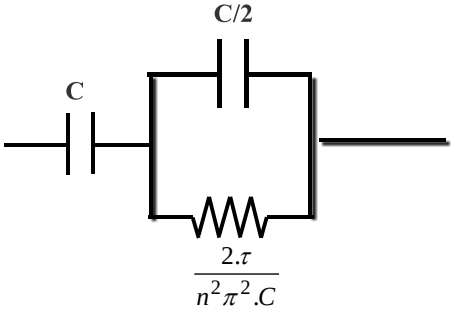

Fig.3. Obtained Equivalent Circuit

4.2 SEM CHARACTERISATION

SEM is used to determine the surface morphology. SEM is capable of producing high resolution images of a sample surface.

Surface morphology of the gold substrate is shown in Fig.4. A 15kV electron beam was used to capture this SEM image. Here, magnification rate is 7,000X. Black dots in the figure represent defects in the metal wafer. After etching process both SEM and FESEM characterisation were taken. For supercapacitor electrode fabrication, large numbers of small size pores are preferable. If the size of the pore increases, capacitance value of the electrode will decrease [14].

To obtain the good capacitance value, etching was performed in different concentrations. Pore structure and pore size can be compared by using the corresponding SEM characterisation results.

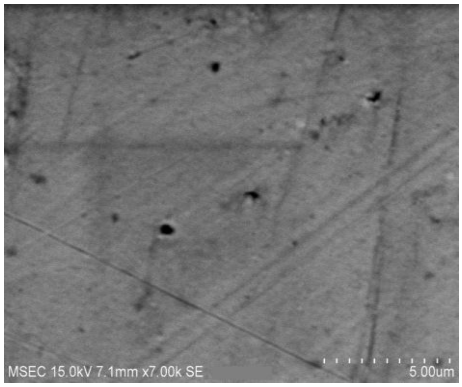

Fig.4. SEM Image of Plain Gold Wafer

The Fig.5 is the SEM characterisation of gold substrate (current collector) after 30% etching. 55,000X magnification rate was used to get the nano porous structure. By using this scale, we can approximately calculate the pore size. These pores are used to hold more charge carriers. Fig.6. shows the etched substrate for 40% concentration. This nano porous structure has more pores while comparing to the 30% concentration. Size of the nano pores can be approximately calculated. 200 nm scale is used to measure the nano pore's size. It can hold more charge carriers in the porous structure.

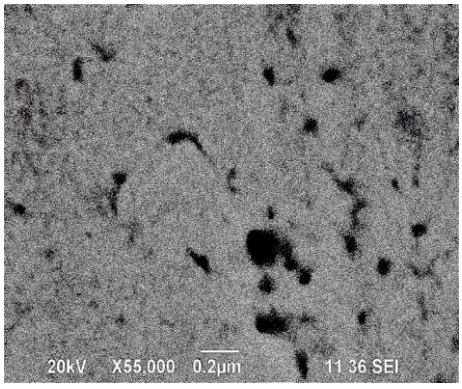

Fig. 5. SEM Image of Gold Substrate after Etching 30% Concentration

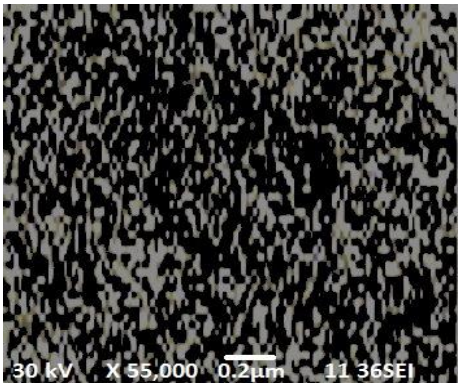

Fig.6. SEM Characterisation of Gold Wafer After 40% Etching

4.3 FESEM CHARACTERISATION

FESEM is a very useful tool for high resolution surface imaging in the fields of nano materials science. FESEM uses narrower beam. It provides 6 times better resolution than SEM. The Fig.7 and Fig.8 presents the FESEM characterisation of etching substrate.

A 20kV electron beam was used to perform this characterisation. Other specifications like magnification rate, height and width of the beam, pixel size were determined from the FESEM image. While comparing with SEM, FESEM gives more information. Here, magnification rate is very high.

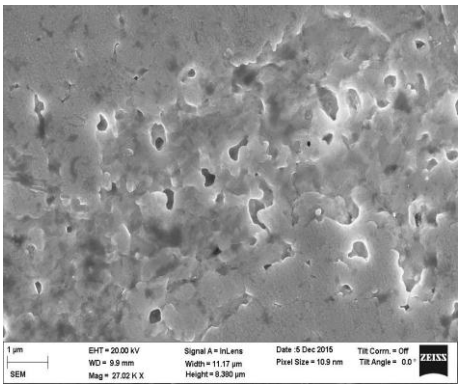

Fig.7. FESEM Image of Gold Substrate after Etching 30% Concentration

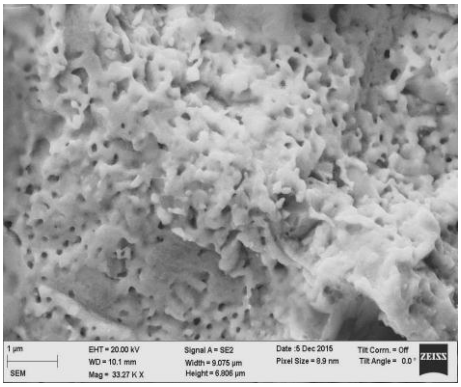

Fig.8. FESEM Image of Gold Substrate after Etching 40% Concentration

4.4 EDAX ANALYSIS

Energy Dispersive X-ray Spectroscopy is based on the recognition of characteristic X-rays emitted of an element as a result of the de-excitation of interior electron holes produced by a high energy electron beam. The Fig.9 shows the EDAX spectrum of porous substrate. A spectrum consists of all the characteristic X-rays emitted by the elements present in the sample. X axis denotes the energy of electron beam. High energy rays provide accurate compositions. Y axis represents the count value.

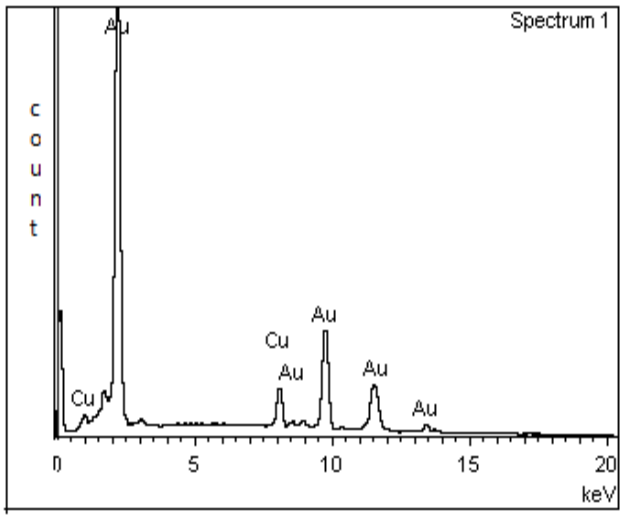

Fig.9. EDAX spectra

Count represents the number of emitted characteristics X-rays. From the above spectrum elemental compositions can be calculated. While varying the energy value, count value is varied. The obtained compositions of the etched substance are listed in Table.2. Porous substance has both the copper and gold metals. Approximate concentration, weight and atomic weight were obtained from the EDAX result.

Table.2. EDAX Results

Element	Approximate Concentration	Weight	Atomic %
Cu	72.77	14.04	33.71
Au	355.32	85.97	77.39
Total	100		

5. CONCLUSION AND FUTURE WORK

Supercapacitor's superior characteristics open up new ways to power micro sources development. Nano porous current collector was prepared by dealloying (etching) the binary Au:Cu alloy. This porous gold is a promising material to store more electrical charge carriers. Surface analysis was done by SEM, FESEM and EDAX. Mathematical modelling of nano porous electrode was derived and EIS analysis was performed. One of the major intentions it has become so popular in recent years is that it can be simply, swiftly and reproducibly made from readily available sources. Various hybrid electrodes with nanoporous current collector can be developed for further enhancement of specific capacitance and electrical stability in future.

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