doi:10.20944/preprints201808.0100.v1

Peer-reviewed version available at *Recycling* **2018**, 3, 42; doi:10.3390/recycling3030042

The new anode environmentally friendly for water electrolysis based on 430 stainless steel coated with recycled cobalt from spent lithium–ion batteries

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ABSTRACT

In this paper, a new anode environmentally friendly for hydrogen production was developed based on 430 stainless steel with an electrodeposited cobalt layer. The novelty of this work is the cobalt source once the electrodeposition bath was obtained from recycling of spent Li-ion batteries cathode with composition $LiCoO_2$. The electrodeposited cobalt behaves as supercapacitor in KOH 1M. In the linear voltammetry in KOH 1M, when the overpotential reaches 370mV, the anodic density current for 430 SS/Co is $19 mAcm^{-2}$. Thus, the anode developed in this paper achieves the double of density current with half of production cost if compared with 316SS. Moreover the anode construction described in this paper is an excellent option for Li-ion battery recycling.

Keywords: Li-ion batteries, Anode, Cobalt recycling

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1 INTRODUCTION

Renewable energy source such as hydrogen is considered crucial for a more sustainable future **[1]**. In fact, since daily processes even space exploration will depend, largely of hydrogen production within few years **[2]**. The hydrogen is considered environmentally friendly once the reaction between H_2 with O_2 molecules (forward direction in Eq.1) has only water molecules as sub-product, beyond high molar enthalpy value ($\Delta H = 285.8$ kJ/mol at 1013 mbar and 298K) **[2]**. In this context, the water electrolysis is the most attractive route among the existed processes for very pure hydrogen production (and also O_2) in large scale (inverse direction in Eq.1)**[1]**.

$$H_{2(g)} + 1/2O_{2(g)} \rightarrow H_2O_{(g)} \qquad \Delta H = 285.8 \text{ kJ/mol} \qquad \text{(Eq.1)}$$

In water electrolyses, the O_2 production is a limiting factor because the overpotential for oxygen evolution reaction (OER) is responsible for greatest source of energy loss when the electrolysis is performed in alkaline (Eq.2) or acid media (Eq.3) [**3, 4**]. However, the alkaline media is preferred because in this condition the catalysts used in water electrolysis are more active and stable [**4**]. The OER also is present in others strategic power sources such as aqueous lithium air batteries [**5**], NiMH [**3**], and Zn-air [**6**].

$$2OH^-_{(aq)} \rightarrow H_2O_{(g)} + 1/2O_{2(g)} + 2e^- \qquad \text{(Eq.2)}$$

$$2OH^-_{(aq)} \rightarrow 2H^+_{(aq)} + 1/2O_{2(g)} + 2e^- \qquad \text{(Eq.3)}$$

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Many papers are dedicated to investigate the alternative anode for OER with high efficiency [**7**]. The RuO_2 and IrO_2 are suggested as the benchmark for OER in alkaline solution [**8**]. However, these oxides have prohibitively cost for large scale application [**8**]. The commercial electrodes for water electrolyses in industrial scale must have important characteristics such as: high conductivity, high corrosion resistance, high catalytic effect for oxygen evolution reaction, moreover low cost [**9**]. For Ni foam, the current density for OER is $10mAcm^{-2}$ in η = 390mV (vs. NHE) in KOH 0.5M. When the Ni foam receives a Co layer by electroless deposition (~2.3μm) the overpotential reduces for 270mV [**10**]. This shows that a cobalt layer around 2.3μm is enough to decrease the overvoltage for OER approximately in 100mV. Although Ni anode has a good anodic behavior in OER, its cost is still high compared to the other substrates such as stainless steels. The Ni price is 8.66 US$/Kg against 1.64 US$/Kg and 0.450 US$/Kg for 316 SS and 430 SS respectively [**11**]. In this context, a special interest is devoted to stainless steel as anode for OER in alkaline solutions [**9**]. The literature revels that the 316 stainless steel (316SS) shows a density current of $10mAcm^{-2}$ in η=0.370mV in KOH 1.0 $molL^{-1}$ [**12**]. This value is similar to that found for Ni Foam in the same conditions [**12**]. This is expected since the 316 has 12% of Ni in its composition [**13**]. The 430SS has little more than 0.75% of Ni in its composition and approximately the same percentage of others alloys elements [**13**]. The low Ni content makes the 430 SS cheaper, however, also less active for OER. [**13**]. Nevertheless is possible improve the 430SS anodic properties with cobalt electrodeposition. The great advantage of this method is the possibility of cobalt recover from Li-ion batteries recycling [**14**].

Many papers describe the cobalt recycling from spent Li-ion batteries as a valuable and environmentally friendly method [**14-16**]. Moreover, very pure cobalt can be obtained by acidic dissolution of lithium cobalt oxide ($LiCoO_2$) present in spent Li-ion battery cathode [**16**]. The recycling of $LiCoO_2$ is important both economically and environmentally [**16**]. In this paper was studied the application of 430SS, coated with recycled cobalt, as anode for OER in 1M KOH solution. The cobalt used was obtained through dissolution of spent cathode of cell phones Li-ion batteries. The electrochemical characterization of this anode was accomplished through cyclic and linear voltammetry and electrochemical impedance spectroscopy (EIS).

2. EXPERIMENTAL

2.1 Preparation of cobalt electrodeposition bath

The model of Li-ion battery used in this paper was chosen based on the $LiCoO_2$ presence as cathodic material [**16**]. The Li-ion battery was manually dismantled and physically separated into their different parts: anode, cathode, steel, separators and current collectors. The cathode powder was washed with distilled water under agitation to facilitate the detachment of the active material from current collector. The active material was filtered and washed with distilled water at 40 ºC to remove possible lithium salts such as $LiPF_6$ and $LiCl_4$ and dried in air for 24 h. A mass of 250.10 g of positive electrodes was dissolved in an aqueous solution containing 470.00 mL of H_2SO_4 3.00 mol L^{-1} and 30.00 mL of H_2O_2 30 % v/v. The system was maintained under constant magnetic agitation at 80 ºC for 2 h. The pH of electrodeposition bath was maintained equal to 3.0 and the cobalt concentration was 1.00 molL^{-1}. This high concentration was chosen to increase the electrodeposition efficiency [**16**].

2.2 Electrochemical measurements

Electrochemical measurements were made using an AUTOLAB PGSTAT power supply. The working electrode was made of commercial ferritic stainless steel 430. The steel samples were prepared as rectangular foils with a geometric area of 1.00 cm^2. The auxiliary electrode, with an area of 3.75 cm^2, was made of platinum. A saturated calomel electrode (SCE) reference electrode was used. The conversion for reversible hydrogen electrode (RHE) was made using the equation 4 and, the overpotential (η) was calculated using the equation 5 [**9**] .

$$E_{(RHE)} = E_{(SCE)} + (0.059\,pH + 0.242)V \qquad \text{(Eq.4)}$$

$$\eta = E_{(SCE)} + (0.059\,pH + 0.242)V - 1.23V \qquad \text{(Eq.5)}$$

The The working electrodes were sanded with 600-grit sandpaper before each measurement and washed with distilled water. All the electrochemical measurements were performed without solution agitation, at 25 °C. The cobalt bath used in cobalt electrodeposition was obtained by acidic dissolution of spent cathode of Li-ion batteries. The Co^{+2} concentration was adjusted in 1.00mol/L. The pH chosen for cobalt electrodeposition was 4.0. The potential The potential used was -1.0V and the charge density was controlled in 3Ccm^{-2} [**9**]. The scanning electron microscope JEOL JXA model 8900 RL, equipped with an energy dispersive X-ray detector, was used for surface morphology observations and surface chemical analysis.

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3. Results and Discussion

3.1 Characterization of electrodeposited cobalt onto 430 SS

Figure 1 shows the scanning electron microscopy (SEM) of electrodeposited cobalt. The morphology of electrodeposited cobalt is commonly observed in other papers [**15,16**]. Figure 2 shows the cyclic voltammetry of 430SS with cobalt coating in KOH 1.0molL^{-1}. The first peak (A_1) is due the formation of $Co(OH)_2$ layer onto cobalt previously electrodeposited [**16**]. The peak A_2 is related to oxidation of Co^{+2} to Co^{+3} due formation of monometallic layered double hydroxides (LDH) onto electrodeposited cobalt [**17**] . The A_2 can also is related with Co_3O_4 formation [**18, 19**]. The peak A_3 is relative to electrochemical reaction related to conversion of Co^{+3} to Co^{+4} [**16**]. The formation of Co^{+4} is important because in alkaline media the OER generally involves the OH^- adsorption as first step (Eq.6). Thus, a transition metal ion with multiple valence and strong bonding power is necessary [**16**]. The equation x represent the adsorption of OH^- by charged transition metal (M^{n+}) in the hydroxide/oxide crystalline net.

$$M^{n+}_{(net)} + OH^-_{(aq)} \rightarrow MOH^{n+}_{(ads)} + e^- \qquad \text{(Eq.6)}$$

3.2 Electrochemical performance

The electrochemical interfacial process is better investigated using electrochemical impedance spectroscopy (EIS). Figure 3 and 4 compares the EIS measures of 430 stainless steel (430SS) and stainless steel with recycled metallic cobalt coating (430 SS/Co) in a KOH 1.0 molL^{-1} after cyclic voltammetry study. For EIS of 430SS (Figure 3-a) the interface is compatible with Randles circuit (Figure 3-b).

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However, for 430 SS/Co (figure 4-a) the LDH formed onto electrodeposited cobalt behaves as supercapacitor (involving the equilibrium reaction shown in the Eq.3), thus two constant-phase elements must be taking account as showed in figure 4-b [**17**].

Figure 5 compares the linear voltammetry of 430SS and 430 SS/Co in a KOH 1.0 molL^{-1}. When the overpotential reaches 370mV, the density current for 430 SS/Co is 19mAcm^{-2} against 0.80mAcm^{-2} for 430SS. The 430SS/Co exhibits the double of density current to OER if compared with 316SS [**9**] or Ni foam [**12**].

4 CONCLUSION

In this paper, a new anode for hydrogen production was developed based on 430 stainless steel with an electrodeposited cobalt layer. The novelty of this work is the cobalt source once the electrodeposition bath is obtained of acid dissolution of Li-ion batteries spent cathode. The electrodeposited cobalt in KOH 1M behaves as supercapacitor. Considering the linear voltammetry in KOH 1M, when the overpotential reaches 370mV, the anodic density current for 430 SS/Co is 19mAcm^{-2} against 0.80mAcm^{-2} for 430SS. Thus, the anode developed in this paper achieves the double of density current with half of production cost compared to 316SS. Moreover the anode construction described in this paper is a excellent option for Li-ion battery recycling.

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ACKNOWLEDGEMENTS

This work is a collaboration research project of members of the Rede Mineira de Química (RQ-MG) supported by FAPEMIG (Project: CEX - RED-00010-14) and it was supported by CNPq. The authors wish to thank the Micrograph Laboratory of the Mechanical Engineering Departament/UFSJ for the microscopy analysis.

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FIGURES CAPTIONS

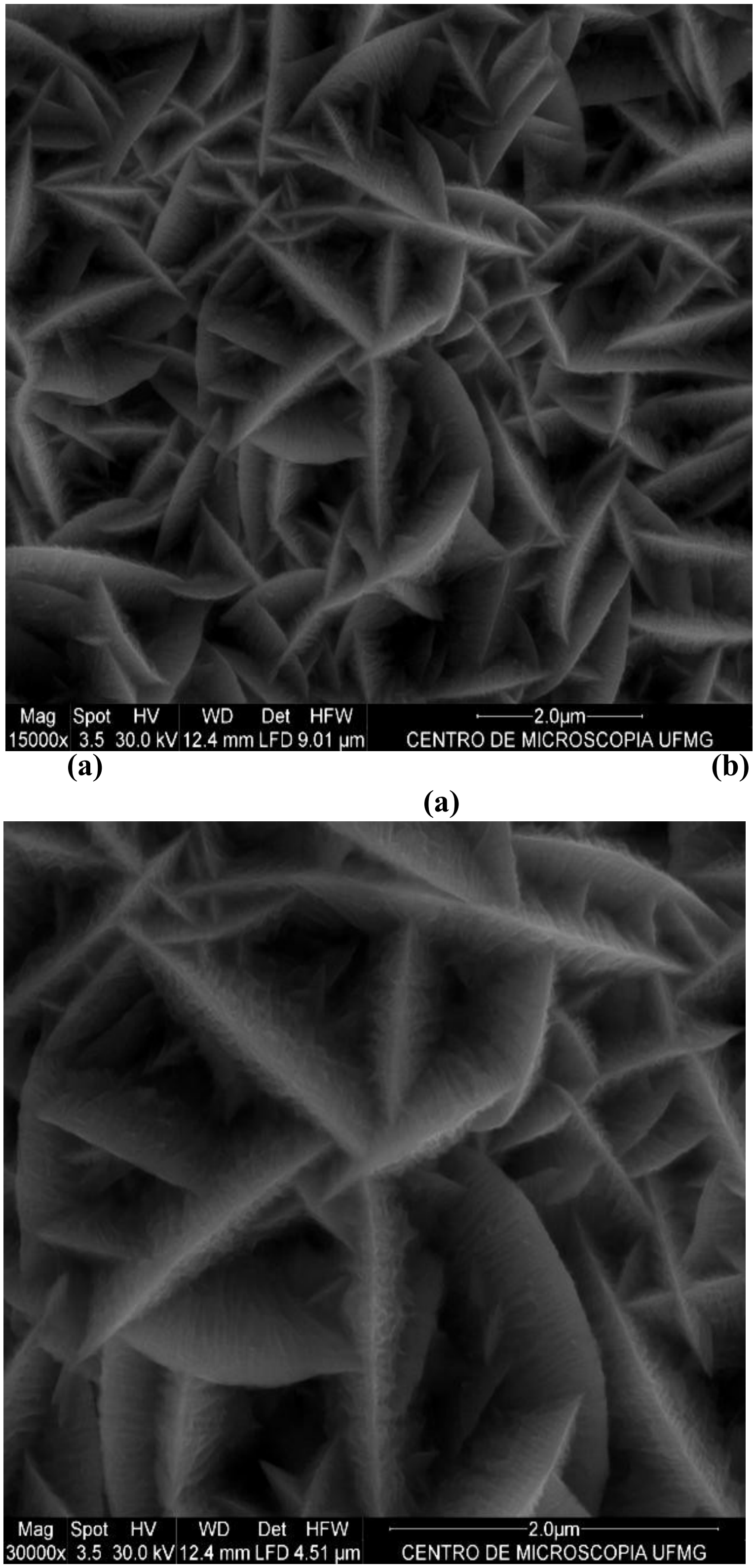
Figure 1 –SEM of electrodeposited cobalt onto 430SS with magnification 15,000x (a) and 30,000x(b).

Figure 2 –The cyclic voltammetry of 430SS and 430SS/Co in KOH $1molL^{-1}$ with different scan rate.

Figure 3 - Electrochemical impedance spectroscopy for 430SS in KOH 1M (a) and the adjusted electrical circuit (b).

Figure 4 - Electrochemical impedance spectroscopy for 430SS/Co in KOH 1M (a) and the adjusted electrical circuit (b).

Figure 5 – The linear voltammetry of 430SS and 430SS/Co in KOH $1molL^{-1}$ with scan rate equal to $1mVs^{-1}$



(a) **(b)**

(a)

(b)

Figure 1

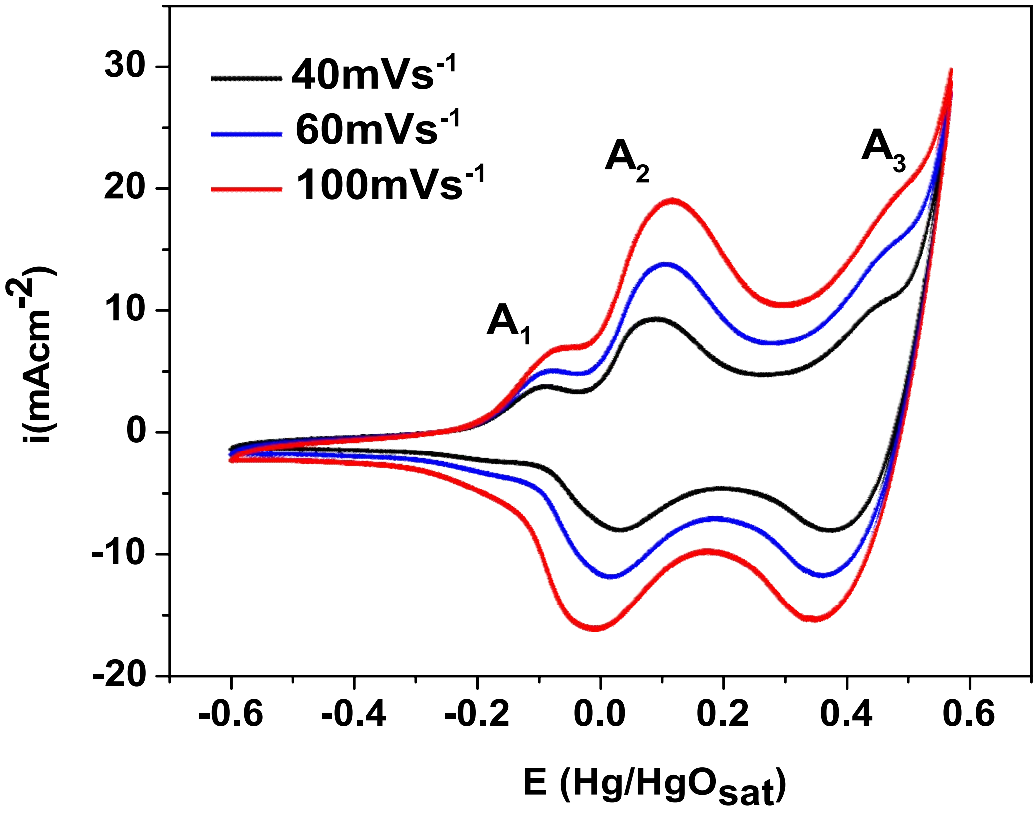
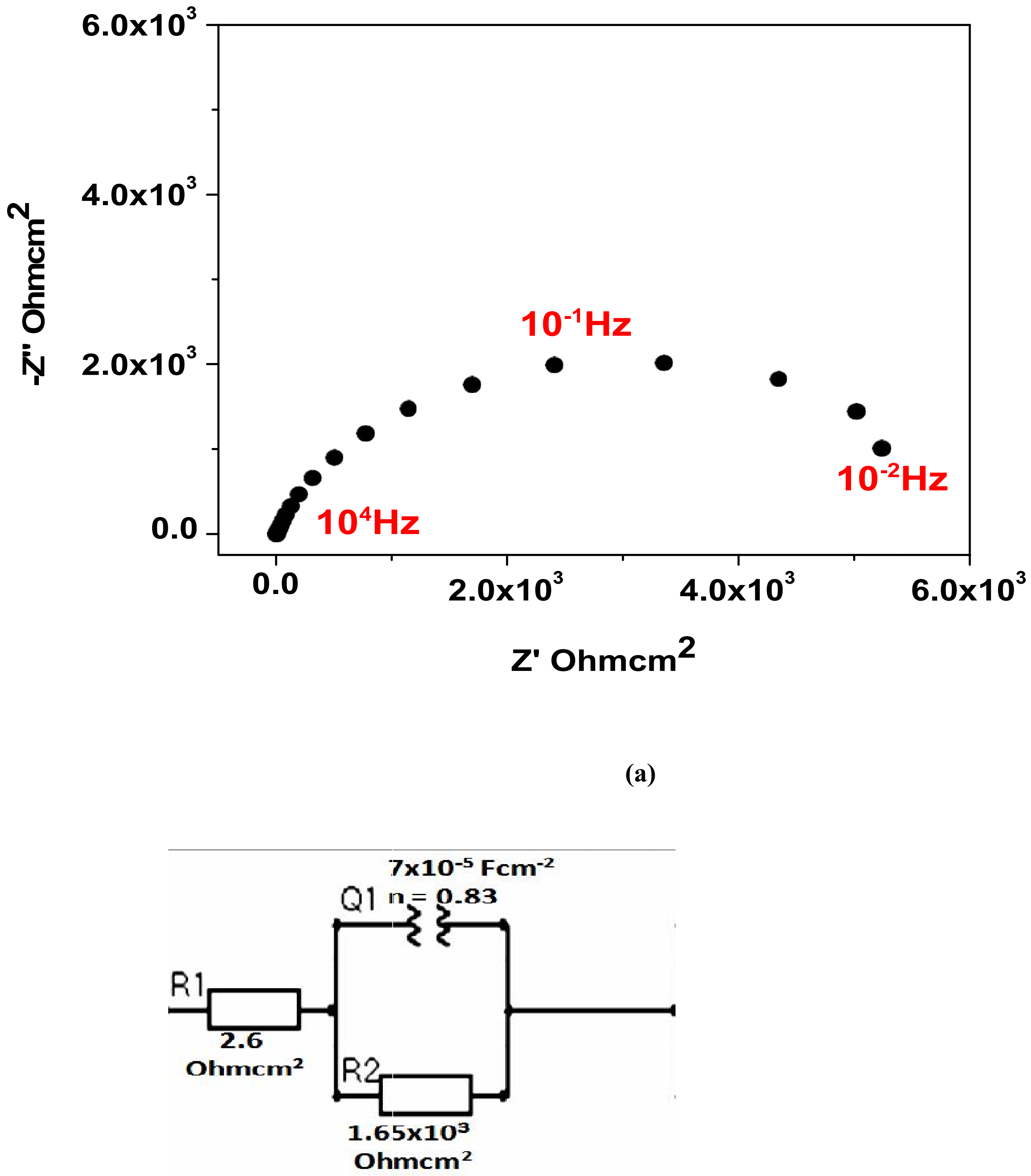

40mVs^{-1}
60mVs^{-1}
100mVs^{-1}
A$_1$
A$_2$
A$_3$
i(mAcm^{-2})
30
20
10
0
-10
-20
-0.6
-0.4
-0.2
0.0
0.2
0.4
0.6
E (Hg/HgO$_{sat}$)

Figure 2 -


6.0x10³
4.0x10³
2.0x10³
0.0
-Z'' Ohmcm2
10⁻¹Hz
10⁻²Hz
10⁴Hz
0.0
2.0x10³
4.0x10³
6.0x10³
Z' Ohmcm2
7x10⁻⁵ Fcm⁻²
Q1 n = 0.83
R1
2.6
Ohmcm²
R2
1.65x10³
Ohmcm²

(a)

(b)

Figure 3 -

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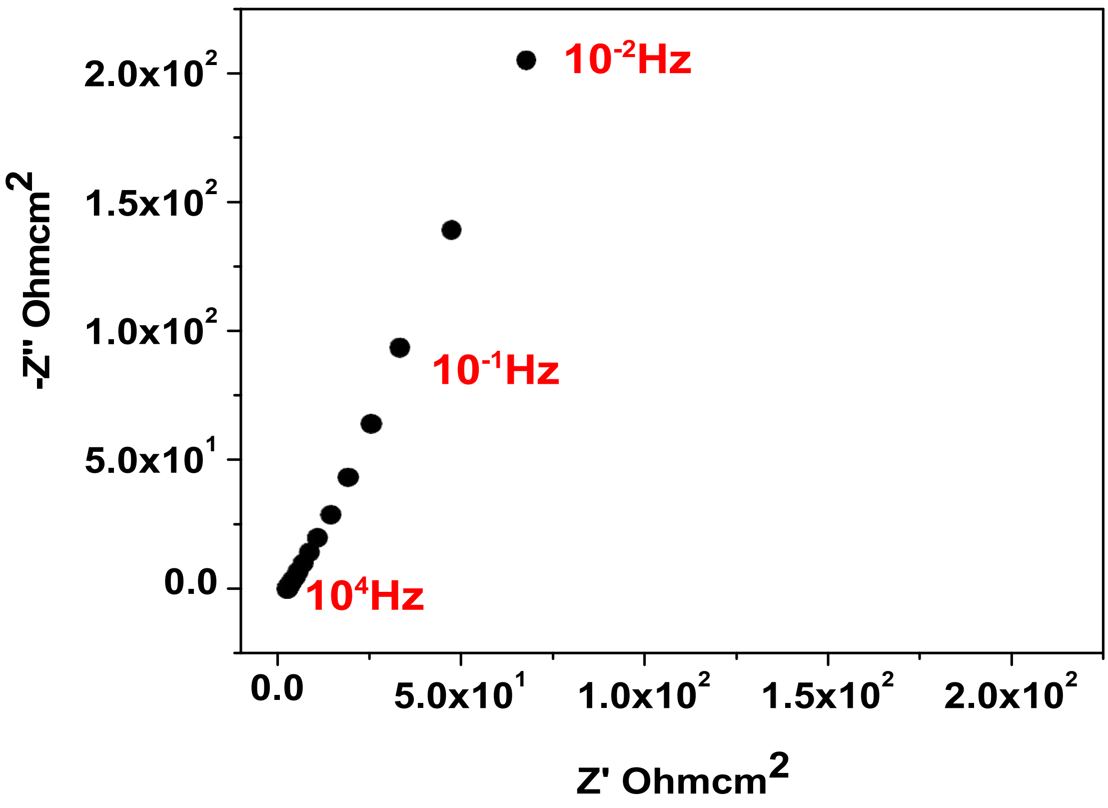
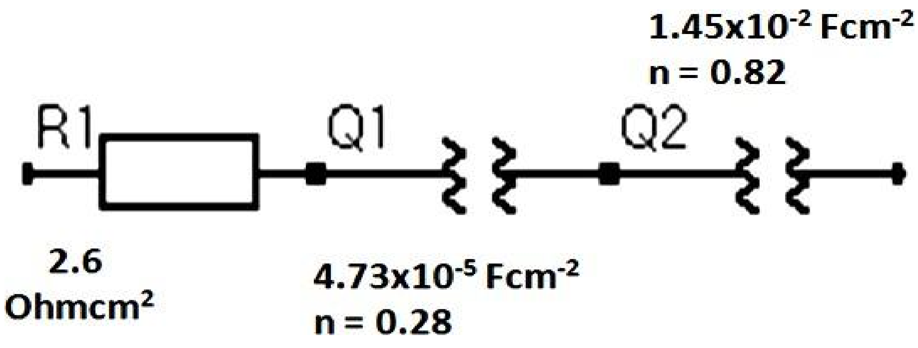


(a)



(b)

Figure 4 -

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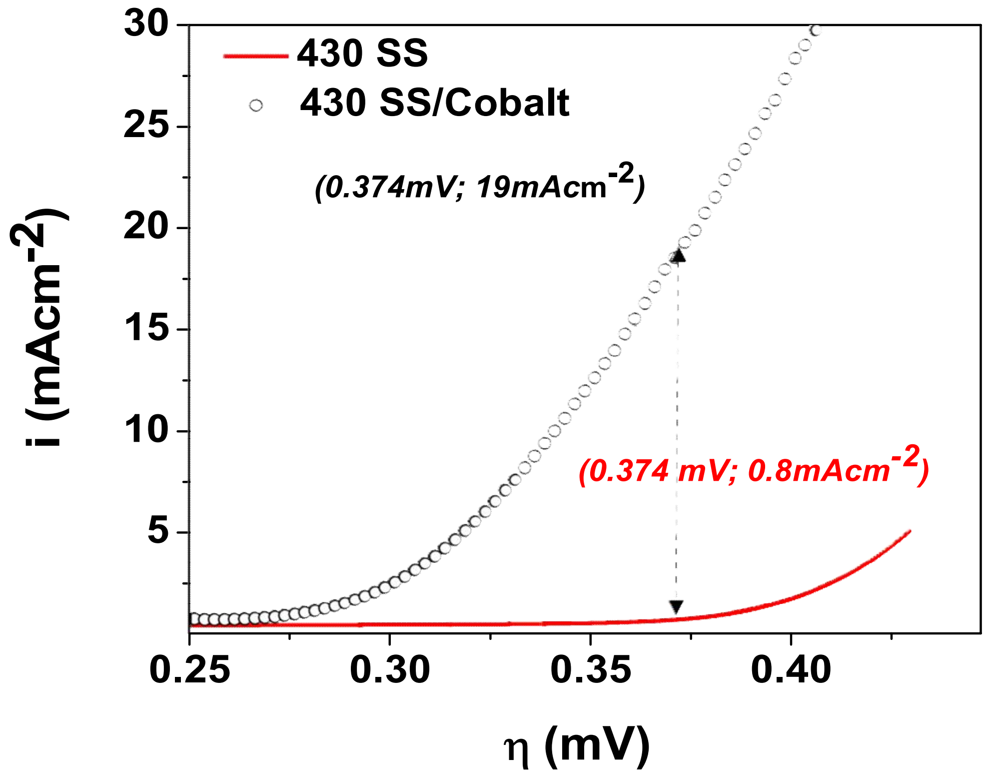

Figure 5-