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Electro-Oxidation of Methanol at Copper and Nickel Modified Clay Electrodes

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Abstract- Cu/Clay/316L and Ni/Clay/316L anodes were prepared by the electroplating of a Cu and Ni catalyst layer onto Clay/Stainless Steel plates for a direct methanol fuel cell (DMFC). The morphology and structure of the catalyst layers were analyzed by AFM and Optical microscopy. The catalyst coating layer shows an alloy character. The results show that oxides formation at the electrode surface is necessary for the methanol oxidation.

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I. Introduction

Fuel cells are efficient and environmentally acceptable conversion devices. Electric current is generated in the fuel cell by the direct electrochemical oxidation of either hydrogen (proton exchange membrane fuel cell, PEM) or methanol (Direct Methanol Fuel Cell, DMFC). The electrochemical processes that yield energy are essentially pollution free. Water formed during operation of the device is beneficial in space travel and submarines. Various applications of fuel cells range from stationary (individual homes or district schemes) or mobile (transportation as cars, buses, etc.) to mobile phones and lap top computers [1, 2]. Hydrogen is currently the only practical fuel for use in the present generation of fuel cells. The main reason for this lies in its high electrochemical reactivity compared with that of the more common fuels from which it is derived, such as hydrocarbons, alcohols, or coal. Also, its reaction mechanisms are now rather well understood [3, 4] and are characterized by the relative simplicity of its reaction steps, which lead to no side products. Pure hydrogen is attractive as a fuel, because of its high theoretical energy density, its innocuous combustion product (water), and its unlimited availability as a suitable source of energy available to decompose water. One of the disadvantages of pure hydrogen is its low density gas under normal conditions, so that storage is difficult and requires considerable excess weight with regard to that of liquid fuels. Methanol has been considered for fuel cell power generation for a number of years because it can be processed into a hydrogen-rich fuel gas fairly, easily and efficiently, by steam or auto thermal reforming. Methanol, as a liquid fuel is easily transported and stored in comparison to hydrogen gas. The methanol fuel has a superior specific energy density (6000 Wh/kg) with regard to the best rechargeable battery, lithium polymer and lithium ion polymer (600 Wh/kg) systems. This means longer conservation times using mobile phones, longer times for laptop computers' usage and more power available on these devices to support consumer demand. Another significant advantage of the direct methanol fuel cells over the rechargeable battery is their potential for instantaneous refuelling [5-7]. The performance of direct ethanol fuel cells (DEFCs) is still limited by the electrocatalysts available for ethanol oxidation, which are mostly based on expensive noble metals such as platinum or its alloys**[8-11]**. Past research on the development of DEFCs has focused mainly on the so-called PEMDEFCs that use PEM as the electrolyte, a Pt-based catalyst on the anode, and a pure Pt catalyst on the cathode **[12-13]**.

The purpose of the present work is to establish the electro oxidation of methanol on stainless steel electrodes modified with respectively, by clay and copper and/or nickel in acidic solution.

II. Experimental Section

a) *Apparatus*

Electrochemical experiments were performed using a Voltalab Potentiostat (model PGSTAT100, Eco Chemie B.V., Utrecht, The Netherlands) driven by the general purpose electrochemical systems data processing software (Voltalab master 4 software).

All the electrochemical experiments were performed in a standard one-compartment three-electrode cell. The reference electrode was SCE and the counter electrode was platinum. All electrode potentials were referred to this reference electrode. The working electrodes were copper modified kaolin/stainless steel and nickel modified /kaolin/ stainless steel.

b) *Reagents and Solutions*

All chemicals were of the highest quality. $CuSO_4$ and NiO were obtained from Merck chemicals. Deionized water was used to prepare all solution. Electrolytic solution is 0.1M H_2SO_4.

c) *Preparation of the modified electrodes*

Stainless steel (type 316L) plates were cut into rectangular strips with typical dimensions of 1 cm^2. The chemical composition of stainless steel investigated in

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this work is: (wt.%) C ≤ 0.02, Mo : 3.5-4.5, Cr: 24-26, Ni: 6-8, N ≥ 0.25, Fe remainder. Strips were abraded with SiC paper in successive grades from 400, 600 up to 1200 grit and then cleaned in distilled water and dried. The current was maintained by a galvanostat with a function generator. The anode electrode was a platinum wire, and a stainless steel electrode was used as cathode. Then, the electrodes were immersed in a glass chamber containing electrolyte of clay gel, and subjected to anodic oxidation by applying 100 mA for 6 hours. In the same way the Cu and Ni catalysts are deposited onto clay / stainless steel plate. Before each experiment, the electrode surface was activated via the cyclic voltammetry at scan rate of 500 mV/s for 20 cycles. The working electrodes (Ni-clay/stainless steel (Ni-arg-316L) and Cu-clay/stainless steel (Cu-arg-36L)) were sealed in Teflon jacket. The apparent surface area was calculated from geometrical area and the current density was referred to it.

III. Results and Discussion

a) Modified electrodes characterization

The prepared electrodes were imaged by AFM (Fig. 1) and optical microscopy (Fig. 2). The clay particles (Fig. 1-b) appear coagulated on stainless steel and their density is very important. It was observed that the powder layers exhibited a porous microstructure with micro pores, which were relatively well separated and homogeneously distributed over the surface. The films formed are continuous and not disintegrated from substrate surface.

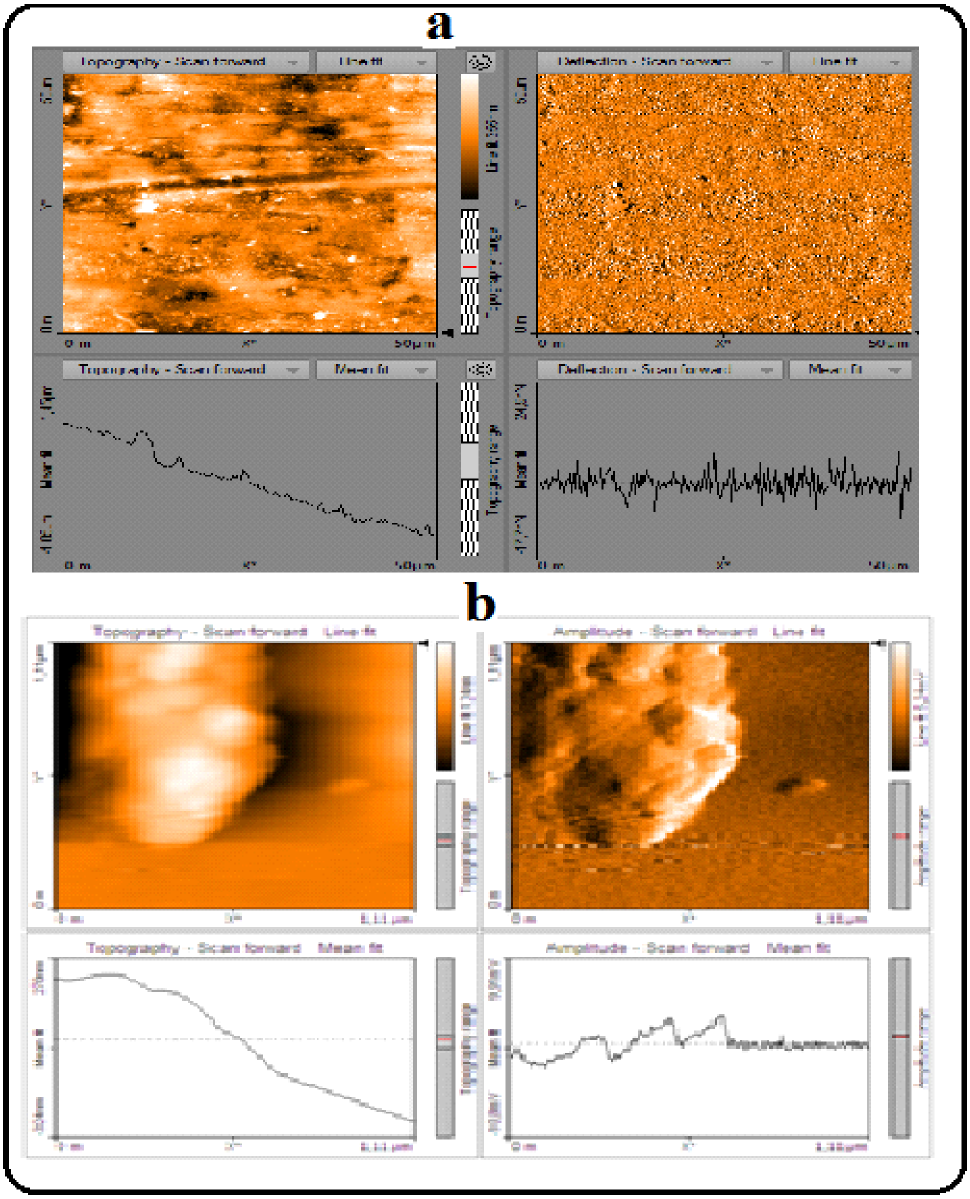

Figure 1 : Topography images of, a- stainless steel and b- clay/stainless steel

Copper is deposited electrochemically onto clay/316L surface; it forms a film continuous and porous. Copper deposit has very rough topography and it is deposited on the entire clay surface. Nickel clusters are deposited on the surface of clay/316L, they occupy sites clay conductors. Wecan observe discovered clusters of clay.

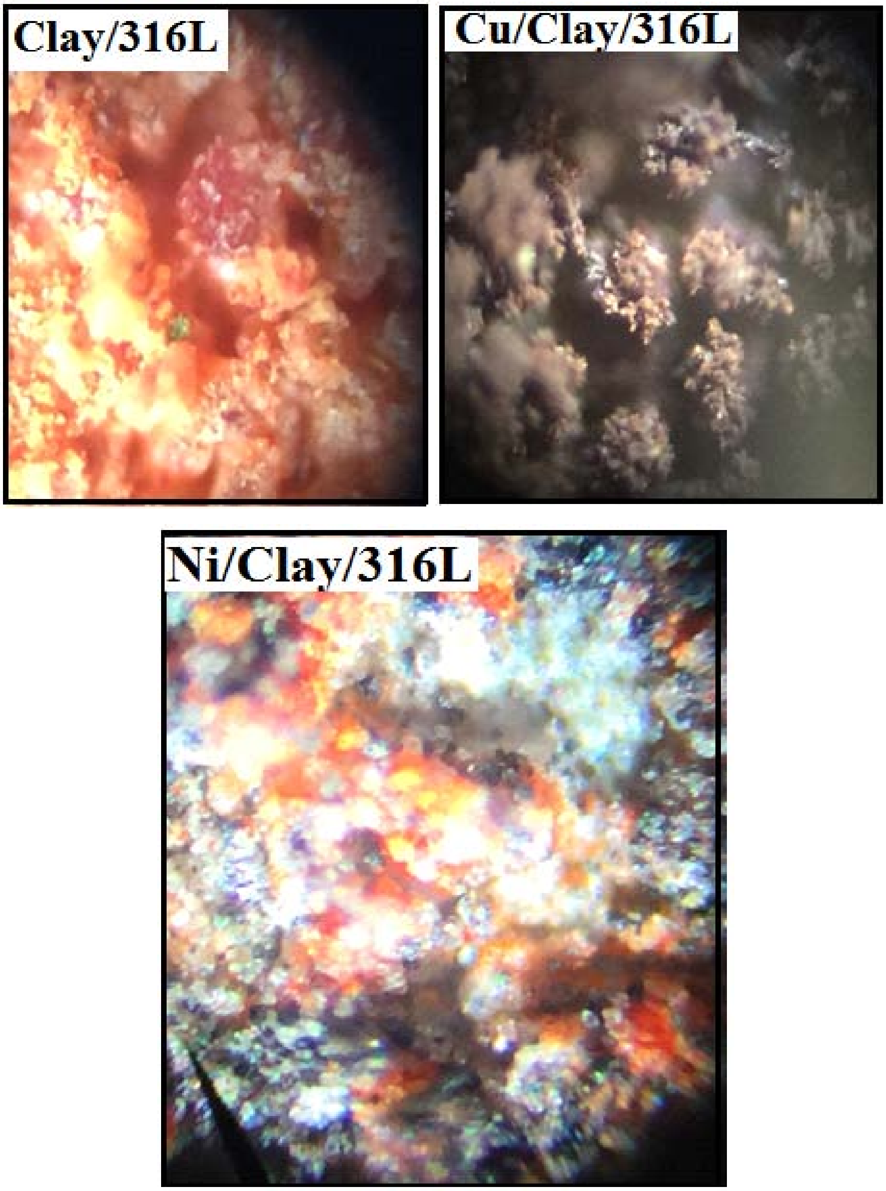

Figure 2 : Optical microscopy images

b) *Methanol oxidation*

The cyclic voltamma grams recorded respectively, for the Cu/clay/316L and Ni/clay/316L, in electrolytical solution, containing or not methanol, are shown in Figures 3 and 4. The CV was carried out to analyze the activity of the synthesized catalyst towards methanol electro oxidation in acidic media. As we can see, the presence of copper to the clay/316L surface generates elevated current densities in the presence of a small amount of methanol in the solution (Fig. 3-b). This phenomenon is confirmed by the square wave voltammetry SWV (Fig. 4). The SQW voltammetry has the advantage of increasing the sensitivity of an electrode by the cancellation of the capacitive term of the overall value of the current density. The SQW shows three peaks respectively, at -0.4 V, 0.3 V and about 1.4 V. The presence of methanol in the electrolytic solution (Fig. 4-b) increases the current density of the two peaks, 0.3V and 1.3V. These findings allow us to draw the following conclusions:

- In the absence of methanol, in the electrolytic solution, the first peak which appears on the SQW to -0.3V, corresponding to the reduction of the copper surface, while the peaks which appear successively at 0.1 and 1.4 V may correspond to the copper oxidation.

- The oxidation of methanol is encouraged by the formation of oxides on the copper surface.

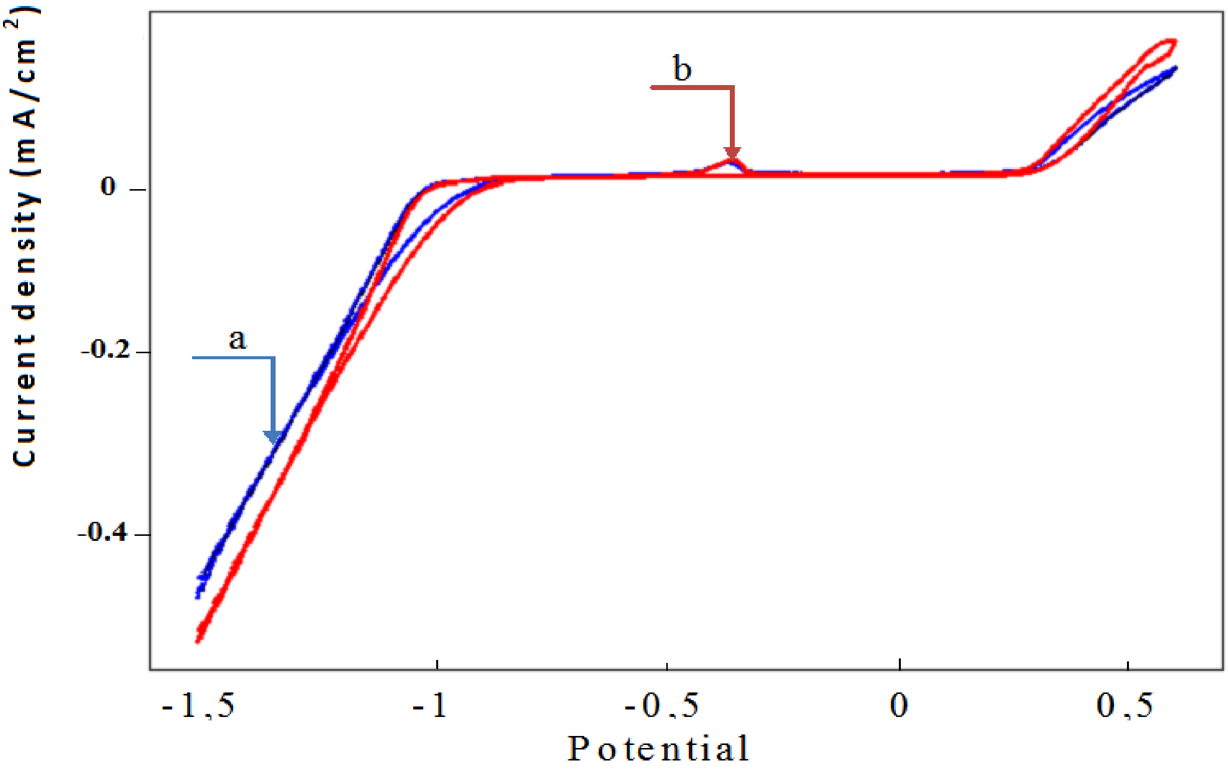

Figure 3 : Steady state cyclic voltammograms recorded for Cu/clay/316L, in 0.1M H_2SO_4 + 0.1 mmol methanol, scan rate 100mV.s^{-1}, at room temperature

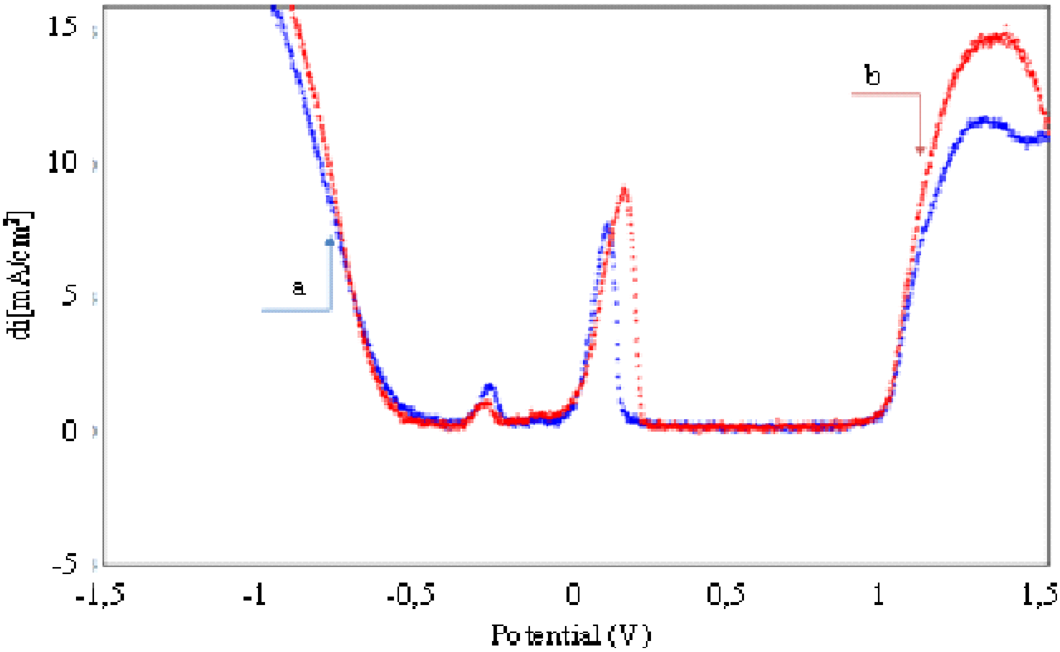

Figure 4 : SQW voltammograms recorded for Cu/clay/316L, in 0.1M H_2SO_4 + 0.1 mmol methanol

The Taffel lines recorded for the electrode Cu/Clay/316L, are represented in Figure 5. We find that the value of the equilibrium potential is shifted towards lower values in the presence of methanol in the solution, meaning that the reaction requires less energy, so (that) the reaction rate is increased.

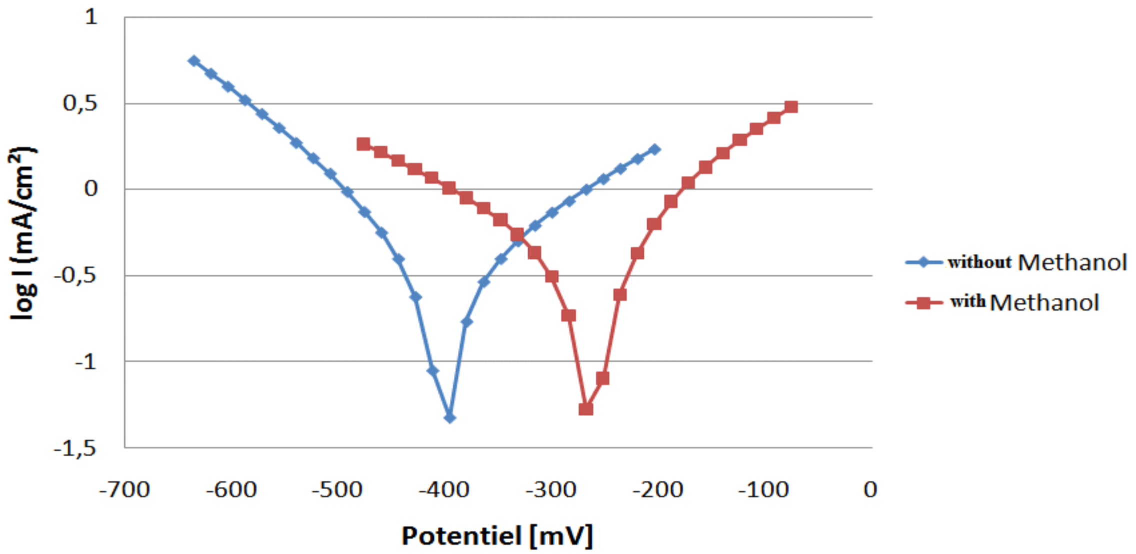

Figure 5 : Taffel lines recorded for the electrode Ni/Clay/316L, in H_2SO_4 medium containing or not methanol

Figure 6 shows the cyclic voltammograms recorded for the electrode Ni/Clay/316L, in electrolytic medium containing or not methanol. No peak is observed in the VC indicating that nickel exhibits no activity for the oxidation of methanol. On the contrary the SQW voltammetry (Fig 7) identifies a well defined peak of oxidation at 1.5V, in the presence and absence of methanol in the solution. The current density of the peak decreases in the presence of methanol, which allows concluding that nickel, has difficulty to oxidize in acidic medium, and as methanol oxidation is accelerated by the formation of oxides on the surface, hence the low activity observed in the VC.

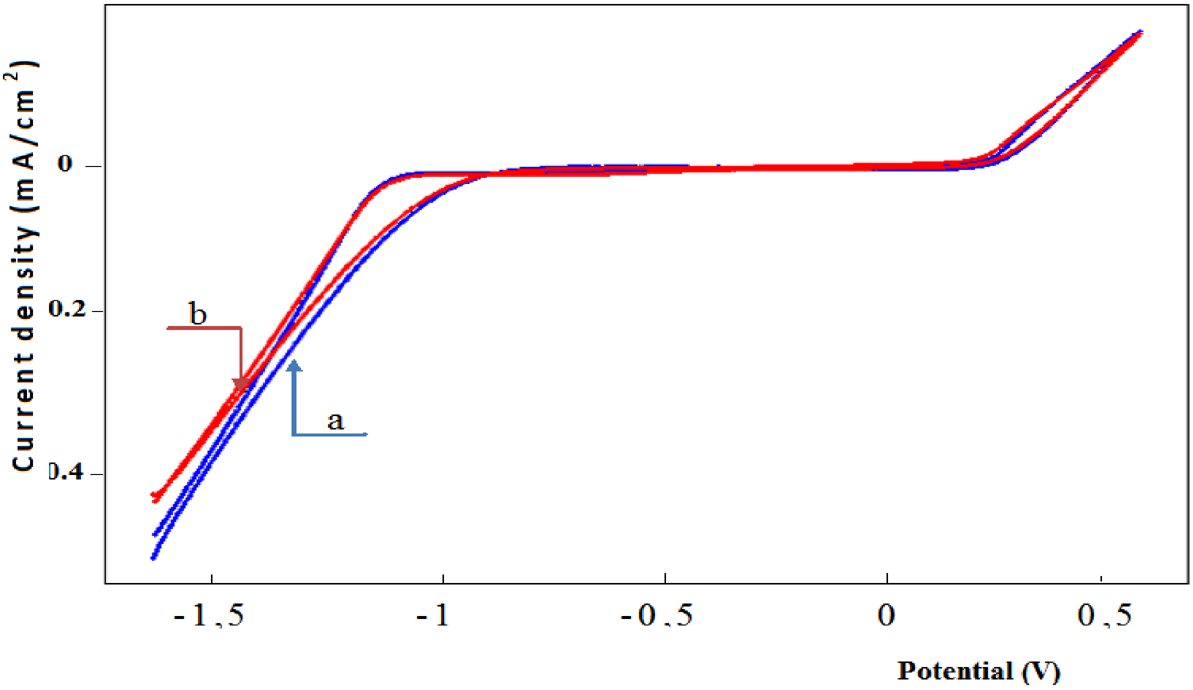

Figure 6 : cyclic voltammograms recorded for Ni/clay/316L, in 0.1M H_2SO_4 + 0.1 mmol methanol, scan rate $100mV.s^{-1}$, at room temperature

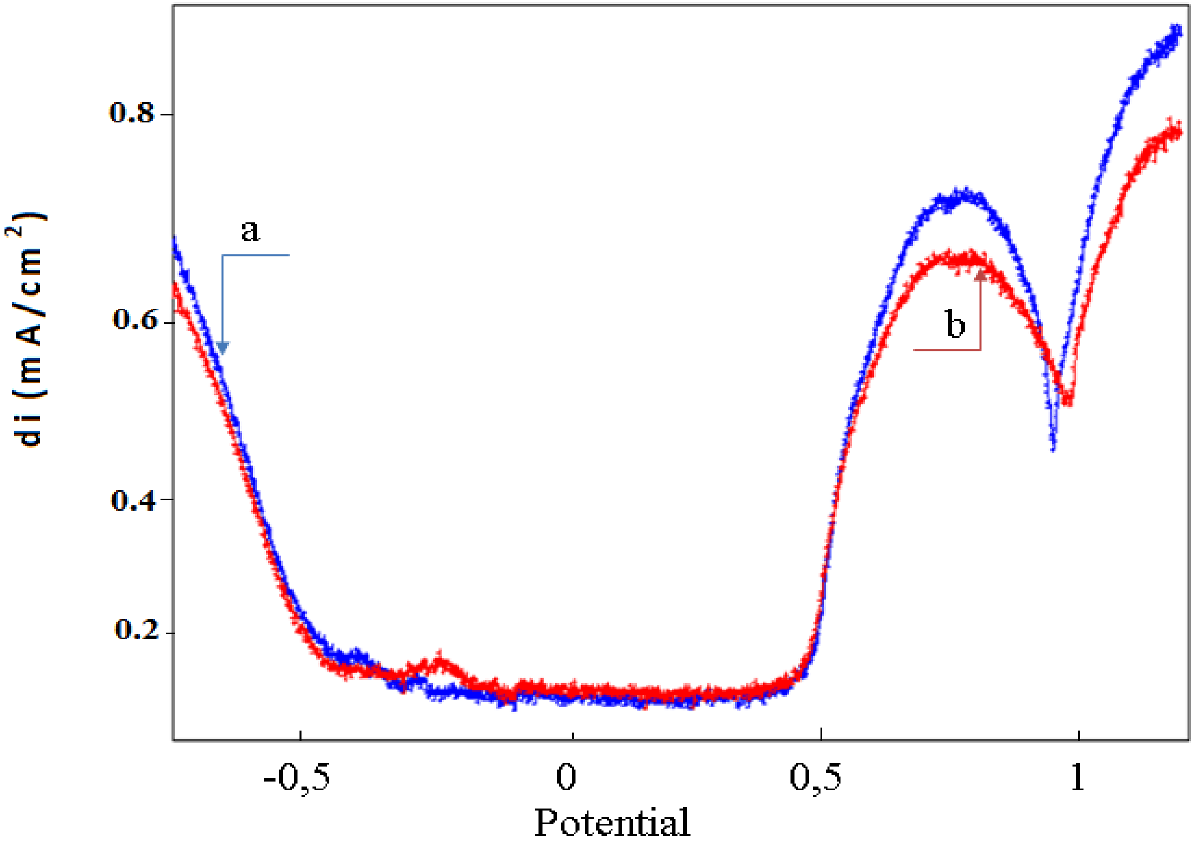

Figure 7 : SQW voltammograms recorded for Ni/clay/316L, in, a- 0.1M H_2SO_4 and b-0.1M H_2SO_4 + 0.1 mmol methanol

The EIS registered for the electrode Ni/Clay/316L, in electrolytic medium containing or not methanol (Fig. 8), we find that the diameter of the half loop decreases in the presence of methanol. In an acid medium, methanol inhibits the oxidation of the nickel surface. These results are confirmed by the drawing of straight Taffel (Fig. 9). The presence of methanol in the electrolytic medium moves the value of the potential corrosion, of the electrode Ni/Clay/316L to the highest values, and causes the decrease in the corrosion rate.

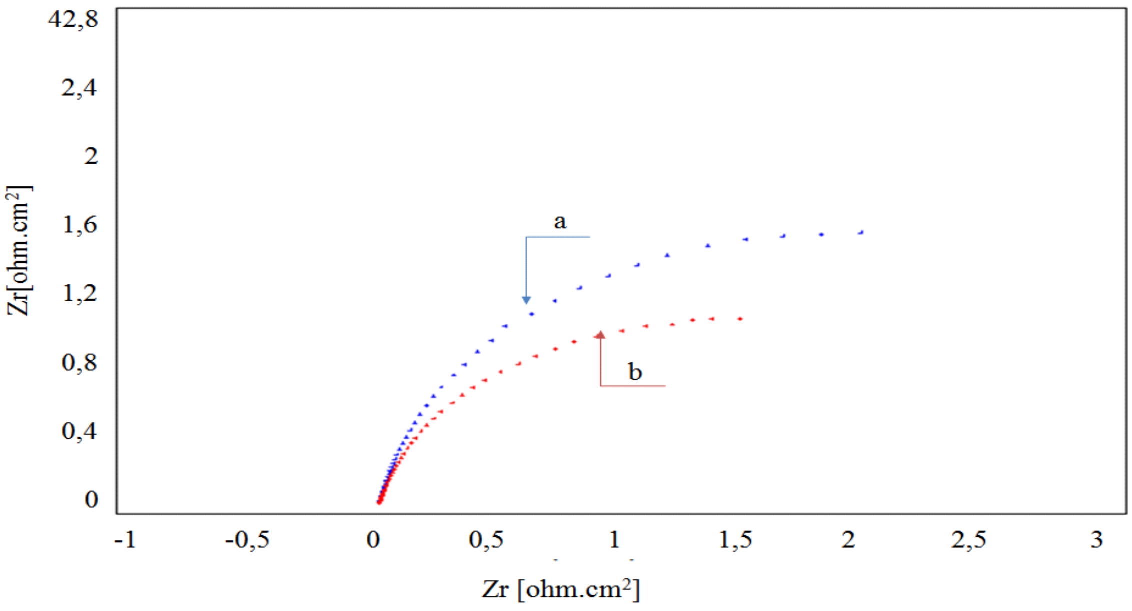

Figure 8 : EIS recorded for Ni/clay/316L, in, a- 0.1M H_2SO_4 and b-0.1M H_2SO_4 + 0.1 mmolmethanol

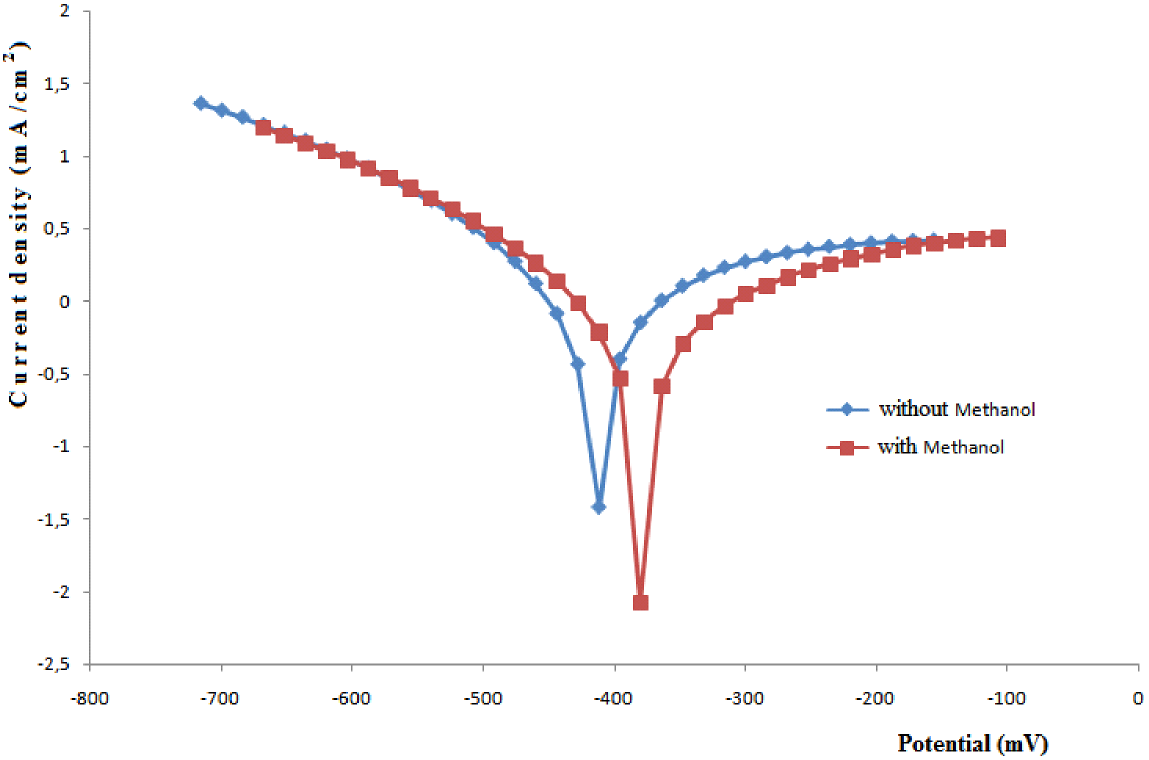

Figure 9 : Taffel lines recorded for the electrode Ni/Clay/316L, in H_2SO_4 medium containing or not methanol

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