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Full Paper

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Electrochemical and atomic force microscopy study of natural phosphate modified steel

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ABSTRACT

This article describes the preparation and characterization of some anodes, destined to direct ethanol and methanol fuel cells. These electrodes were prepared by electrodeposition of natural phosphate (NP) and/or kaolin into a perforated stainless steel plates. Ac impedance spectroscopy, cyclic voltammetry and other electrochemical methods were investigated alongside characterization to determine the influence of the presence of NP and kaolin on the anodic surface corrosion resistance. AFM was used to image the surface topography and morphology of modified electrodes. © 2015 Trade Science Inc. - INDIA

INTRODUCTION

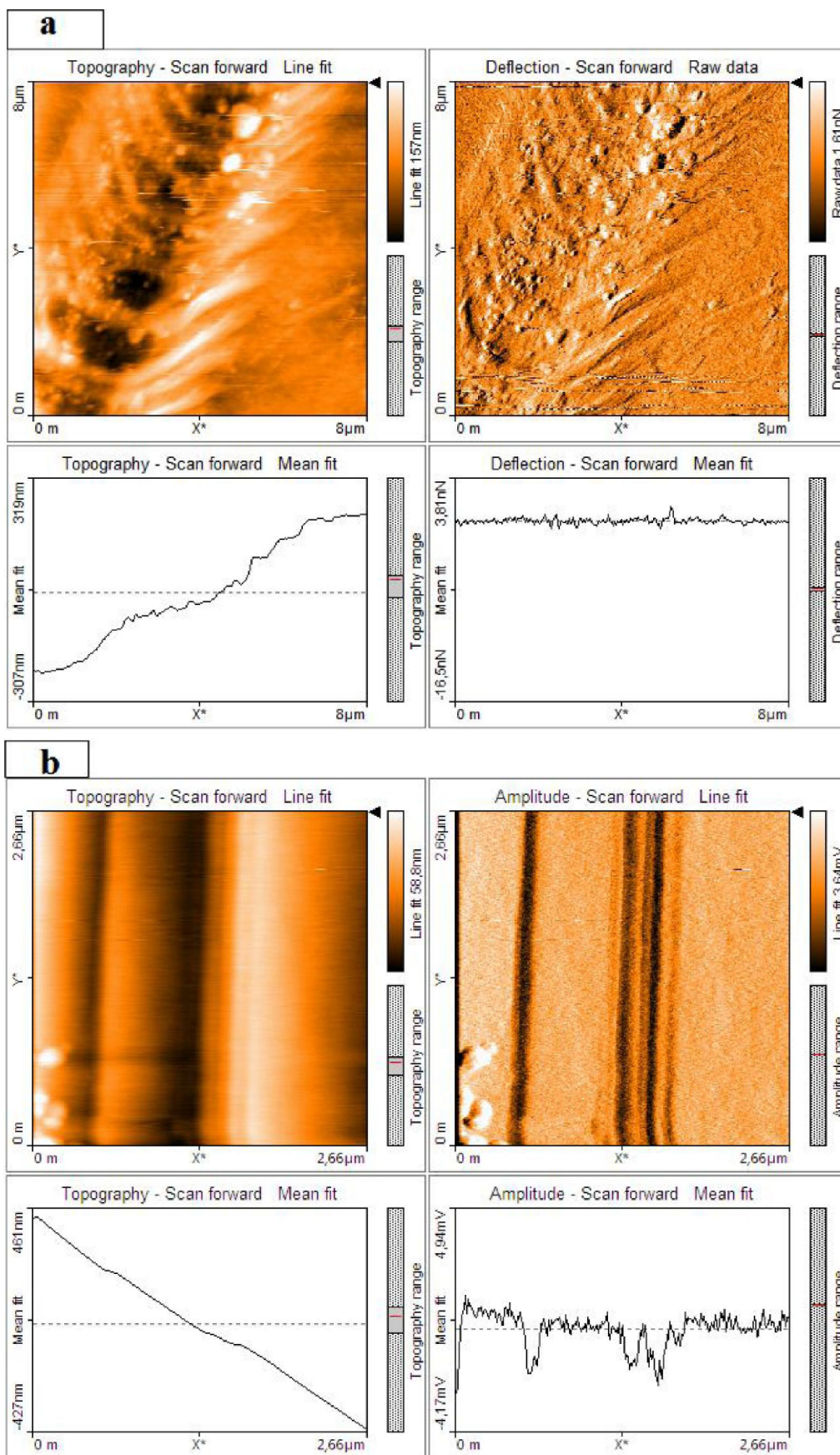
The use of the methanol and ethanol fuel cells is limited by the poor anode performance and counteract the poisoning effects at the cathode due to the methanol cross-over^[1, 2]. In the electro oxidation of methanol and ethanol the electrode material is clearly an important parameter where a high efficient electro catalyst is needed.

The use of Pt alone is limited by the adsorption of several incompletely oxidized intermediates^[3, 4] which provoke deactivation of platinum surface. For this reason, there are several studies investigating modified Pt, for methanol and ethanol electro oxidation, such, Pt-Ru^[5], Pt-Pb^[6], Pt-Ni and Pt-Ru-Ni^[7].

In this work we propose to coat stainless steel surfaces with another catalyst material as a natural phosphate and kaolin phases in order to form satisfactory modified electrodes for eventually methanol

or ethanol fuel cells route. To fulfill the purpose of strong adhesion of natural phosphate and kaolin on stainless steel, coating by electrochemical technique is interesting as a simple technique and can be achieved at room temperature. Based upon the solubility product constant of natural phosphate and kaolin at 25°C, it can be estimated that both the matrices can be easily deposited on stainless steel substrate by electrochemical methods.

The morphological study was investigated by the atomic force microscopy (AFM). Firstly, scanning tunneling microscopy (STM)^[8, 9] constituted a relatively new family of microscopy that can measure surface morphology. In STM the electrical current caused by the tunneling of electron through the tip and sample is used to maintain the distance between them. STM requires that the sample surface be conductive, AFM^[10] was developed in 1986 to measure insulating surfaces. AFM has since developed very



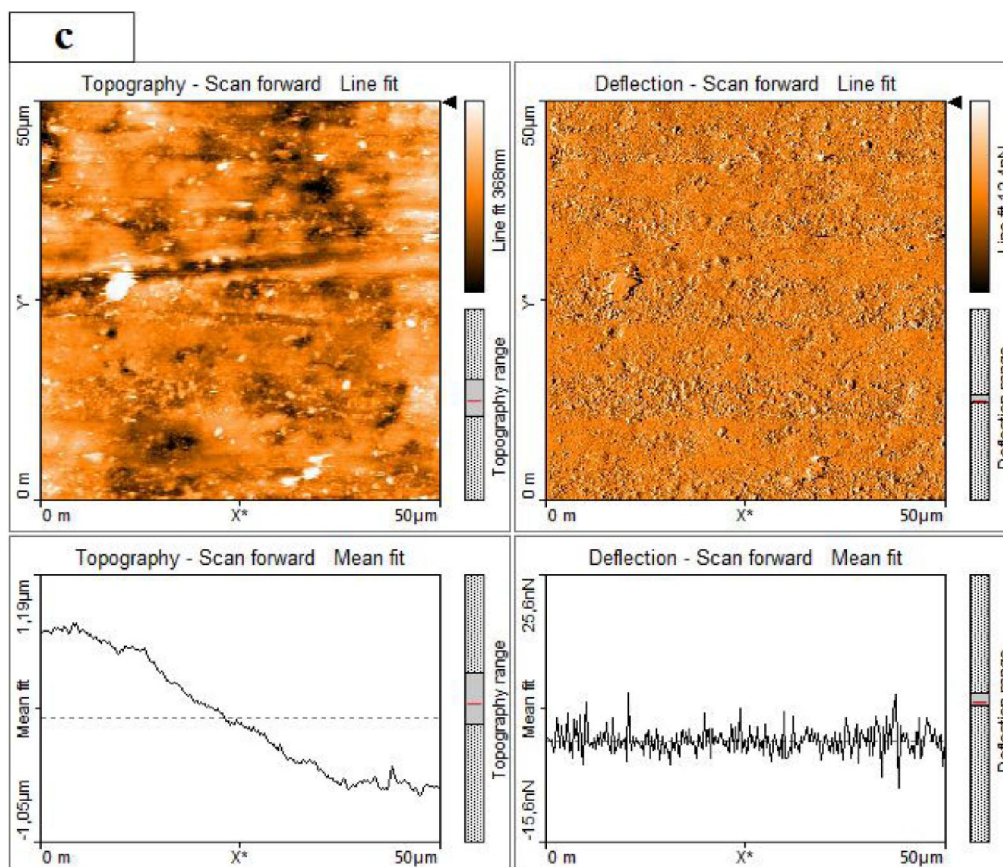


Figure 1 : Typical AFM images of electrodeposited films into stainless steel plates; (a) NP-316L electrode, (b) Arg-316L electrode and (c) stainless steel plate

rapidly and has found various applications in many fields, it provides a real space three dimensional image of a surface through the detection of an interaction between a sharp mechanical tip and the surface features.

EXPERIMENTAL

Reagent

A Natural Phosphate (NP) used in this work was obtained in the Khouribga region (Morocco)^[11]. Prior to use, this material was treated by techniques involving attrition, sifting, calcinations (900 °C), and washing. Kaolin was obtained in the north of Cameroun region.

Sample preparation

Stainless steel (type 316L) plate was cut into rectangular strips with typical dimensions of 1 cm². The chemical composition of stainless steel investigated in 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 natural phosphate and/or kaolin gels, and subjected to anodic oxidation by applying 100 mA for 6 hours.

Modified electrodes characterization

The Atomic force microscopy AFM, in dynamic mode was used to image the electrodeposited film, which was scanned in air. Dynamic mode is an oscillating cantilever method of imaging, the cantilever is driven at high frequencies and the surface is monitored by changes in the amplitude. A FlexFM microscope from Nanosurf (Swissland) with com-

mercial sharpened tips attached to rectangular beams was used in this work. The dynamic mode was immediately used to observe the topography (morphology) of samples after making deposition.

Electrochemical experiments were carried out with a Voltalab potentiostat (model PGSTAT 100, Eco Chemie B. V., Utrecht, The Netherlands) driven by the general purpose electrochemical systems data processing software (voltalab master 4 software). The electrochemical cell was configured to work with three electrodes, using NP and/or kaolin modified stainless steel as the working, platinum plate for counter, and saturated calomel (SCE) as reference electrodes. Impedance measurements were made in the frequency range between 10 mHz and 100 KHz with five points per decade at the corrosion potential. A sine wave with 10 mV amplitude was used to perturb the system. The Nyquist diagrams obtained were automatically controlled by computer programs. The electrolytical solution used (0.1 M HCl) was prepared from distilled and deionised water. All tests were performed at 25 °C.

RESULTS AND DISCUSSION

Modified electrodes

AFM images obtained of preparing electrodes

are shown in Figures 1(a), 1(b) and 1(c), corresponding respectively to NP modified stainless steel (NP-316L), kaolin modified stainless steel (Arg-316L) and stainless steel (316L) electrodes, accompanied curves represent an analysis of the roughness of each thin film X^* represents the horizontal momentum position. It was observed in the both cases (NP-316L and Arg-316L) 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 continued and not disintegrated from substrate surface. From the many AFM images we collected on the NP and kaolin films, the apparent size of the fibers ranges from 0.665 μm (for kaolin) to 4 μm (for NP). The network structure of the thin films (NP and kaolin) had been formed by electrodeposition into stainless steel plates.

As shown in Figure 2 on the NP-316L electrode, the cyclic voltammograms recorded respectively for stainless steel (curve a) and NP-316L (curve b) electrodes in HCl (0.1 M) solution, demonstrated two different behaviours. In the absence of NP film, the work electrode shows an anodic peak at positive potentials, which probably corresponds to the surface oxidation. In the presence of NP film, the anodic peak shifts to a low positive potential values.

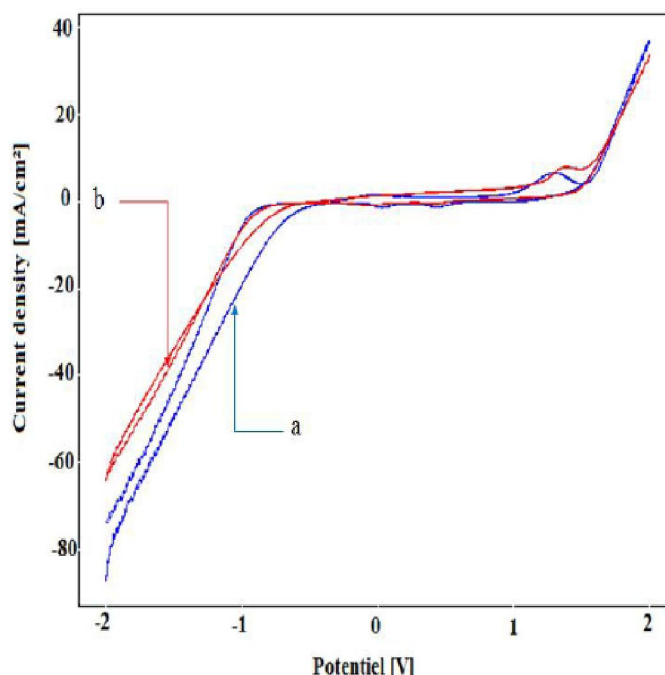


Figure 2 : Cyclic voltammograms of-a- stainless steel electrode, -b- NP-316L, in HCl (0.1 M) at 50 mV/s

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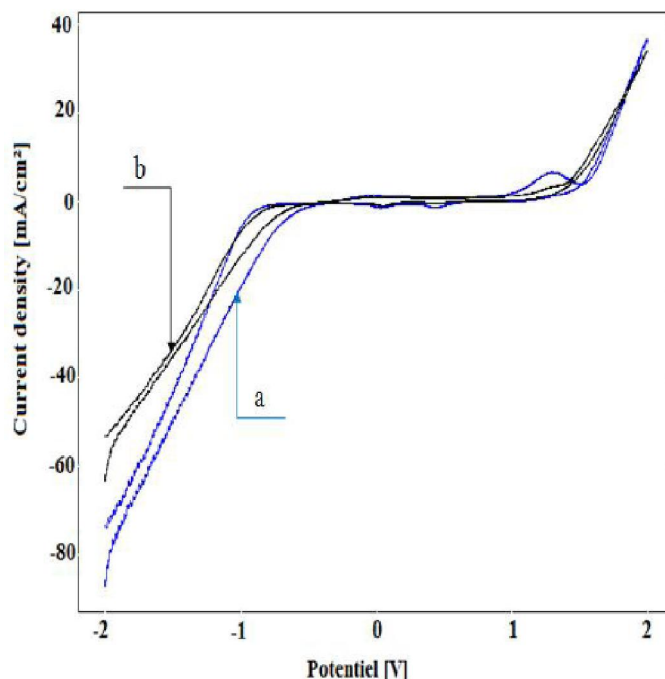


Figure 3 : Cyclic voltammograms of-a- stainless steel electrode, -b- Arg-316L, in HCl (0.1 M) at 50 mV/s

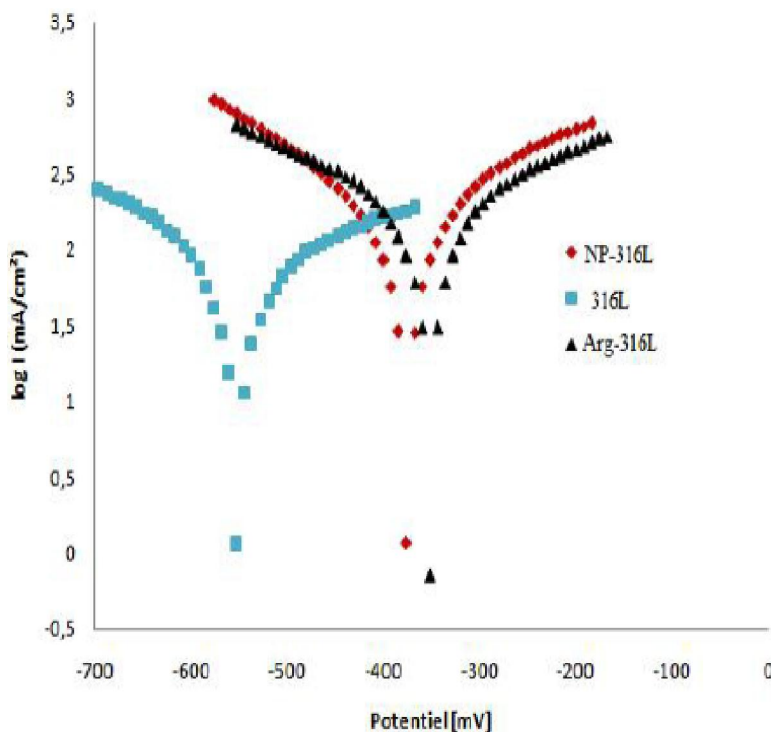


Figure 4 : Polarization curves recorded for prepared electrodes and stainless steel, in 0.1 M HCl

Figure 3 illustrated the obtained voltammogram, from the kaolin modified steel electrode (Arg-316L), in 0.1 M HCl solution. In the absence of kaolin film, the work electrode shows an anodic peak at positive potentials (curve a), corresponds to the surface oxidation. In the presence of kaolin film (curve

b), the anodic peak disappears. The change of the CVs shapes (Figures 2 and 3), before and after modification, is a major sign that stainless steel electrode was, effectively, modified, respectively, with NP and kaolin layers.

Figure 3 shows the potentiodynamic polariza-

TABLE 1: Summary of electrochemical parameters for the studied electrodes in 0.1 M HCl solution

Echantillon	E(i=0) mV	R _p ohm.cm ²	I _{Corr} μA/cm ²	β _a mV	β _c mV
316 L	-550,2	697,94	61,6089	348,7	-224,6
NP- 316L	-376,2	278,64	134,5001	253,7	-228,6
Ag- 316L	-350,9	295,26	160,0161	329,2	-325,4

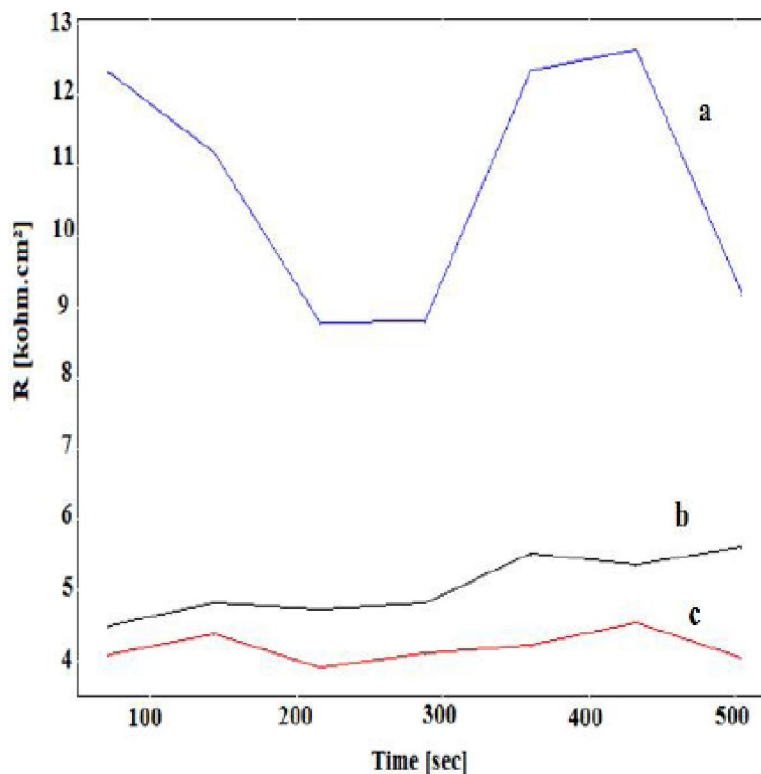


Figure 5 : Evolution of polarization resistance with time. a- stainless steel, b- Arg-316L electrode and c- NP-316L

tion behaviour in the Tafel region given recorded respectively at prepared electrodes, in 0.1M HCl solutions. The corrosion parameters such as corrosion potential (E_{corr}), corrosion current density (I_{corr}) and Tafel constants (B_a and B_c) derived from these figures are given in TABLE 1.

We find that the initial electrode is more resistant to corrosion than NP-316L and Arg-NP electrodes. However the addition of a thin powder layers, respectively NP and kaolin to stainless steel, weakens the surface of the stainless steel.

Figure 5 shows the evolution of polarization resistance versus time. The polarization resistance monitoring is an effective electrochemical method of measuring corrosion. The electrical resistance of any conductor is given by Ohm's Law: $R = V/I$,

where R is the effective instantaneous resistance, V is the applied voltage, and I is the instantaneous current between electrodes. If the electrodes are corroding at a high rate with the metal ions passing easily into solution, a small potential applied between the electrodes will produce a high current, and there will be low polarization resistance. This corresponds to high corrosion rate.

A strong resistance is recorded by stainless steel (curve a). The kaolin deposited onto the substrate undergoes a strong dissolution in the electrolytic medium (curve b), but it behaves better than NP-316L electrode (curve c).

Figure 6 shows the possibility of developing pitting corrosion in the studied solution. The likelihood of developing a pitting corrosion is higher in the

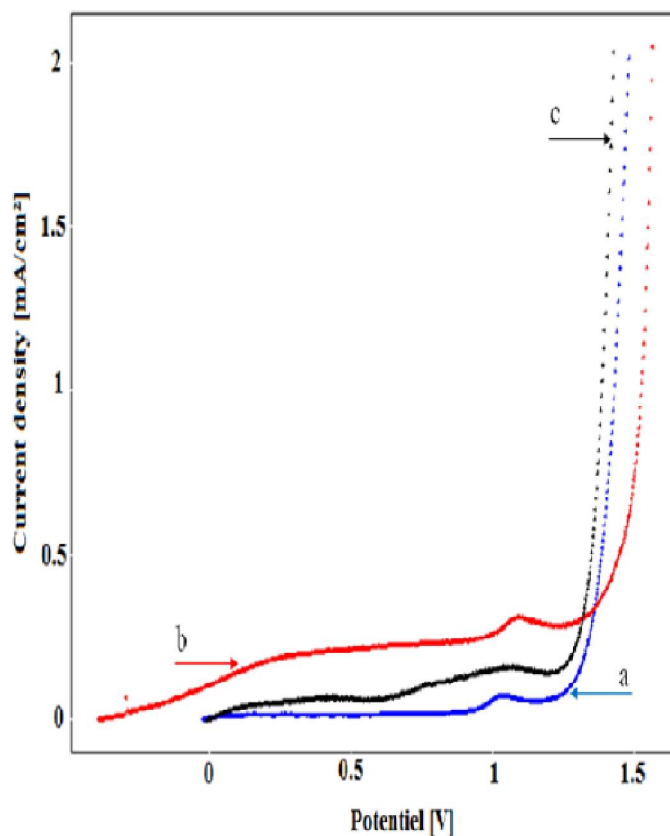


Figure 6 : Pitting corrosion possibility for, a- stainless steel, b- NP-316L and c- Arg-316L in 0.1 M HCl solution case of Arg-31L electrode. The NP coating electrode is protected against this type of corrosion.

CONCLUSION

New electrodes were fabricated and corrosion resistance in electrolytic medium was tested. The corrosion resistance of these electrodes is acceptable; they are candidates' four methanol and ethanol fuel cells. NP and kaolin deposited into stainless steel surface form porous films.

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