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Studies of Aliphatic Alcohol Oxidation Using Cyclic Voltammetry

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Abstract: Some aspects on aliphatic alcohols electro oxidation are presented, in order to establish the effect of various base electrolytes and different concentrations. The experiments involve to most used alcohols, like methanol, ethanol, propanol and buthanol, using cyclic voltammetry, rigorously established temperature and cleaned electrodes after each test, to minimize the variables.

Keywords: electrooxidation, fuel cell, aliphatic alcohol.

1. Introduction

Alcohol oxidation and alcohols, used as fuels is a very becoming issue, in order to find the best conditions for their usage in the automotive industry.

The global reaction, totalizing the reactions at the anode and the cathode; that takes place when the alcohols are oxidized, are as follows:

Anode:
$C_xH_yO + (2x-1)H_2O \rightarrow xCO_2 + nH^+ + ne^-$
$n = 4x + y - 2$
Cathode:
$1/2O_2 + 2H^+ + 2e^- \rightarrow H_2O$
Global reaction:
$C_xH_yO + (x + y/4 – ½) O_2 \rightarrow x CO_2 + y/2 H_2O$

These studies are meant to contribute to the oxidation process optimization. Cyclic voltammetry is a type of potentiodynamic electrochemical measurement, where a certain voltage is applied to a working electrode placed in electrolyte and current flowing at the working electrode is plotted versus the applied voltage to give the cyclic voltammogram. Cyclic voltammetry can be used to study the electrochemical properties of species in solution as well as at the electrode/electrolyte interface.

At the moment a single type of electrode was used, but different alcohols.

2. Experimental

2.1. The experimental apparatus

To study the electrooxidation of aliphatic C1-C4 alcohols, cyclic voltammetry was employed, using platinum (Pt) electrode and both acid and base based electrolytes. The apparatus for the experiments, a potentiostat model PGZ 301 Dynamic EIS Voltammetry - Radiometer Copenhagen, with VoltaMaster 4 software, is presented in figure 1.

The electrochemical cell, (BEC/EDI X51V001) is equipped with working electrode, wire-like platinum, of 0.04 cm^2 active surface; counter electrode, plate shape platinum, with 1 cm^2 active surface and a reference electrode, standard calomel electrode, SCE.

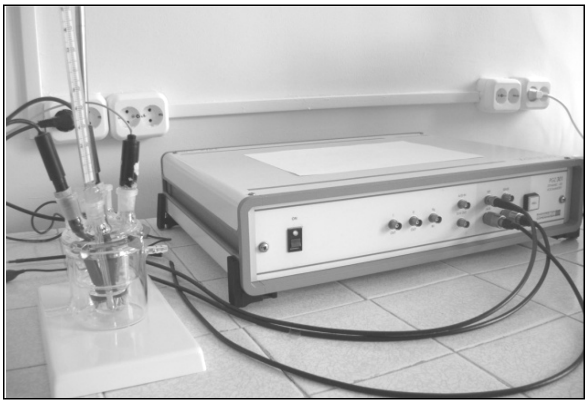

Figure 1. The experimental apparatus

2.2. Working conditions

Different electrolytes were used: NaOH (Fluka) 0.5M, Na_2CO_3 (Fluka) 0.5M, $NaHCO_3$ (Fluka) 0.5M and H_2SO_4 (Merck) 0.5M. For dilution ultra pure water was available, from a Millipore Simplicity 185 apparatus, with UV Photo-Oxidation lamp. The electrooxidation process of methanol, ethanol, n-propanol, 2-propanol and n-butanol have been studied at a constant 24°C, scan rate of 100 mV/s and 100 mA sensibility. To ensure the experimental data's accuracy, the working electrode was pre-polarized in diluted sulfuric acid, for 0-1800 mV potential range, before each measurement.

3. Results and discussions

The electrooxidation of methanol, in base type electrolyte, presented as cyclic voltammograms can be viewed in figures 2, 3 and 4.

The methanol's electrooxidation takes place most favorably in Na_2CO_3 0.5M electrolyte, at pH = 11, according to figure 5, where the anodic currents of the highest peaks are presented at different pH values.

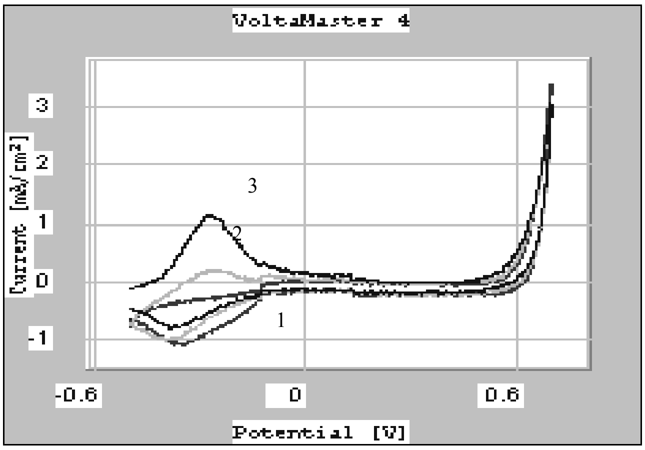

Figure 2. Cyclic voltammograms of methanol oxidation 0.25M(2) and 0.5M (3). Base electrolyte NaOH 0.5M (1) at pH=13

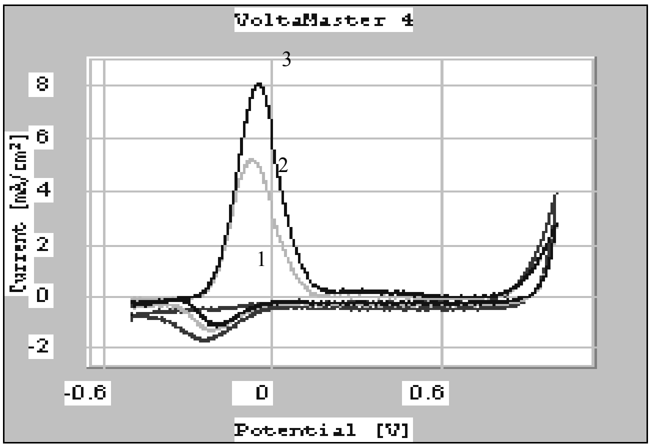

Figure 3. Cyclic voltammograms of methanol oxidation 0.25M(2) and 0.5M(3). Base electrolyte Na_2CO_3 0.5M (1) at pH=11

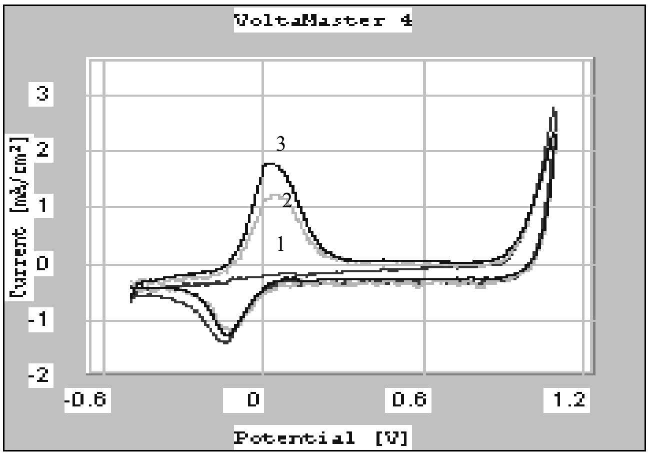

Figure 4. Cyclic voltammograms of methanol oxidation 0.25M(2) and 0.5M (3). Base electrolyte $NaHCO_3$ 0.5M (1) at pH=9

According to figure 6, two current plateaus can be seen, at 1.27 V and 1.50 V potentials, and the current density associated with them, increases as the alcohols concentration increase.

The influence of concentration and electrolyte type, for the electrooxidation of ethanol, is presented in figure 8.

The electrooxidation of ethanol in acid electrolyte, figure 7, two plateaus appear almost at same potentials, but the current densities associated with them are higher, than for methanol. Both for methanol and ethanol, two reduction plateaus appear, at the second pass, (cathodic side); more clear in case of methanol's oxidation.

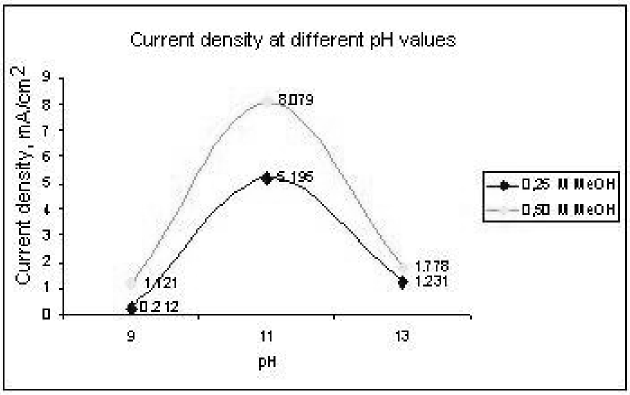

Figure 5. Current densities at different pH values

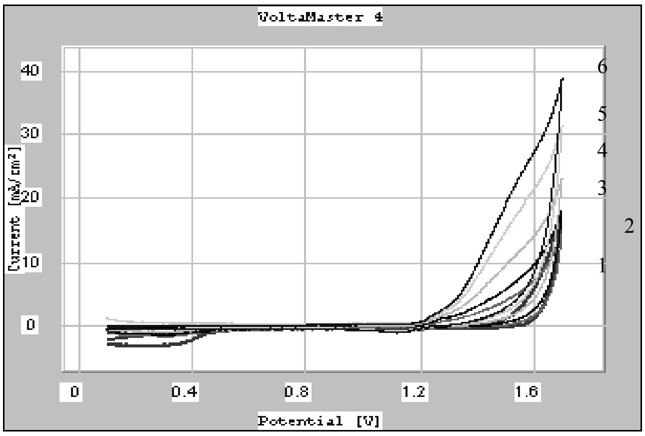

Figure 6. Cyclic voltammograms of methanol oxidation 0.125M(2); 0.2M(3); 1M(4); 1.5M(5); 2M(6). Base electrolyte H_2SO_4 0.5M (1)

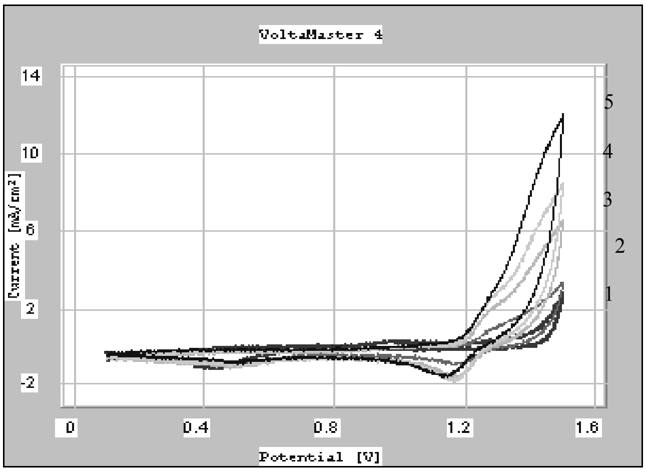

Figure 7. Cyclic voltammograms of ethanol oxidation 0.04M(2); 0.1M(3); 0.2M(4); 0.7M(5). Base electrolyte H_2SO_4 0.5M (1)

For the electrooxidation of ethanol, in Na_2CO_3 0.5 M and $NaHCO_3$ 0.5M electrolyte, presented in figures 9 and 10, a decrease of current density can be observed in $NaHCO_3$ electrolyte, although the voltamogramm's form are similar.

Electrooxidation of n-propanol and 2- propanol was studied only acid electrolyte, H_2SO_4 0.5M. The resulted voltamograms, are presented in figures 11 and 12. The process's partial reversibility, in both cases, can be observed, proven by reduction peaks on the voltamograms return side. The current densities associated with the peaks, are higher for the n-alcohols than any other alcohols.

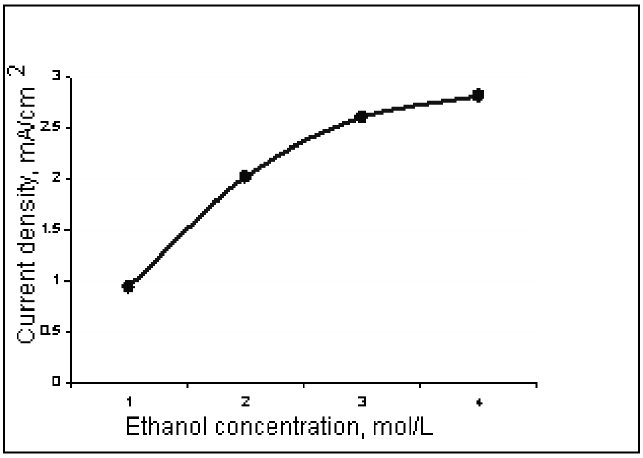

Figure 8. Current density values at different concentrations of ethanol. Base electrolyte, H_2SO_4 0.5M

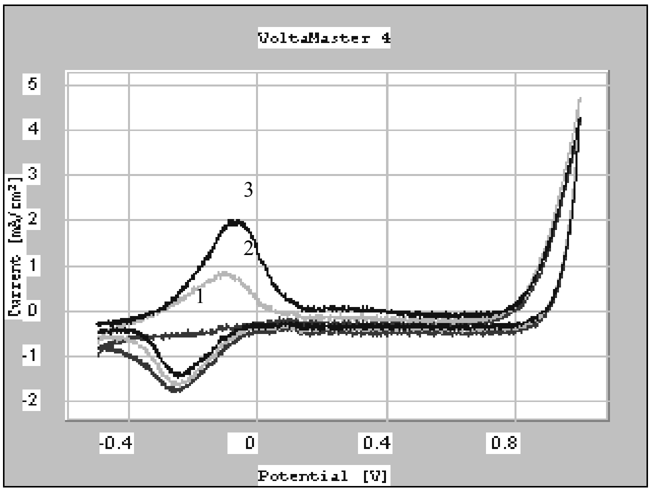

Figure 9. Cyclic voltammograms of ethanol oxidation, 0.2M(2) and 0.35M (3). Base electrolyte Na_2CO_3 0.5M (1) at pH=11

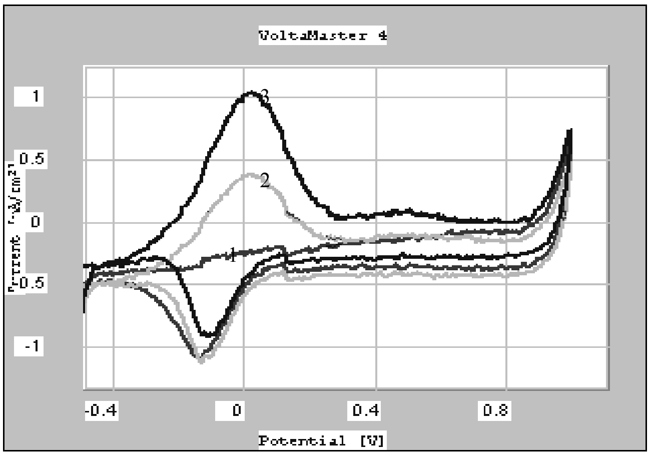

Figure 10. Cyclic voltammograms of ethanol oxidation 0.2M(2); 0.35M (3). Base electrolyte Na_2CO_3 0.5M(1) at

The n-buthanol's electrooxidation was studied in acid electrolyte, H_2SO_4 0.5M, shown in figure 13. The oxidation peaks, at around 1.4 - 1.6 V, are better shaped, and the corresponding current density in higher, as the alcohol's concentration increase.

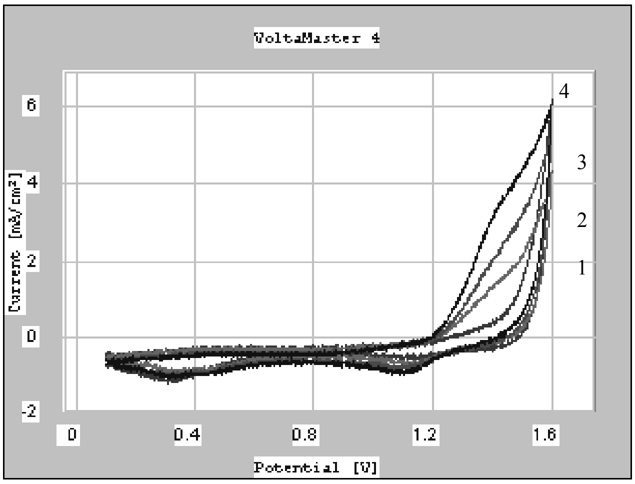

Figure 11. Cyclic voltammograms of n-propanol oxidation, 0.1M(2), 0.2M(3), 0.3M(4). Base electrolyte H_2SO_4 0.5M (1)

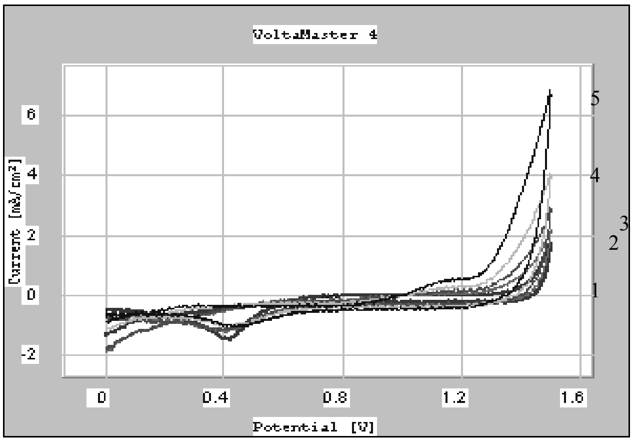

Figure 12. Cyclic voltammograms of 2-propanol oxidation 0.1M(2), 0.2M(3), 0.3M(4), 0.8M(5). Base electrolyte H_2SO_4 0.5M (1)

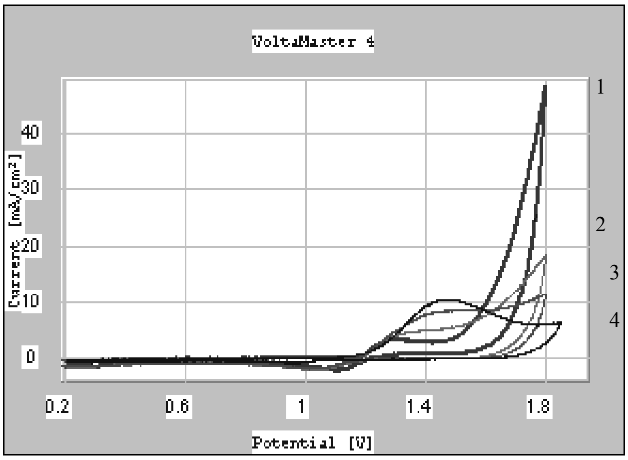

Figure 13. Cyclic voltammograms of n-buthanol oxidation 0.05M(2), 0.2M(3), 1M(4). Base electrolyte H_2SO_4 0.5M (1)

4. Conclusions

As a general conclusion, and most importantly also, regardless of the alcohols C-chain and base electrolyte type, the increasing alcohol concentration results in higher current density values. Of course, for each alcohol , the maximum current density was achieved working in different electrolytes and at different pH values. The optimal conditions for methanol electrooxidation were -0.05 V potential, pH=11, and current density of 8.079 mA/cm^2.

High values of current density are also obtained by electrooxidation of ethanol (7.057 mA/cm^2) and buthanol (8.644 mA/cm^2), at 1.44 V potential, but only in acid electrolyte. The current density values for the electrooxidation of methanol and propanol in acid electrolyte, are smaller than values for alcohols with pair number of C atom in the structure (ethanol and buthanol), measured at the same potential.

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