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Review paper

THE DEVELOPMENT OF MODERN LOW TEMPERATURE FUEL CELLS

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Abstract

Classification of fuel cells is presented. Progress in low temperature fuel cells fueled by hydrogen, methanol and formic acid is discussed and the possible future use of fuel cells is indicated. Ethanol is a special fuel because it is available from renewable environmentally friendly sources and its oxidation product (CO_2) can be transformed by photosynthesis to ethanol. The design of the anode catalyst for electrochemical ethanol oxidation in the Direct Ethanol Fuel Cell (DEFC) is described in some detail.

Key words: *low temperature fuel cell; anode catalyst; Direct ethanol fuel cell*

INTRODUCTION

Fuel cells are almost ideal energy converters. The conversion of chemical energy to electrical energy has the general scheme:

$$\text{Fuel} + O_2 \rightarrow \text{electric energy}$$

In fuel cells this takes place without the limitations of the Carnot heat cycle. Thus, they are more efficient in extracting energy from a fuel than conventional generators. Fuel cells can bi classified according to their operating temperature [1-3], as shown in Figure 1.

Progress in developing low-temperature cells is discussed in this work. The best-known low temperature fuel cell, the hydrogen fuel cell, is presented in Figure 2.

For example a car fitted with the most common hydrogen fuel cell (Fig.3) needs only 8 kilograms of hydrogen for 500 kilometers distance, compared to a classic car consuming 20-30 liters of gasoline or diesel fuel. This is an important achievement. If a cell is fed by pure hydrogen (produced in the photochemical process) it produces also a clean product - water, i. e. no adverse effects on the environment are produced.

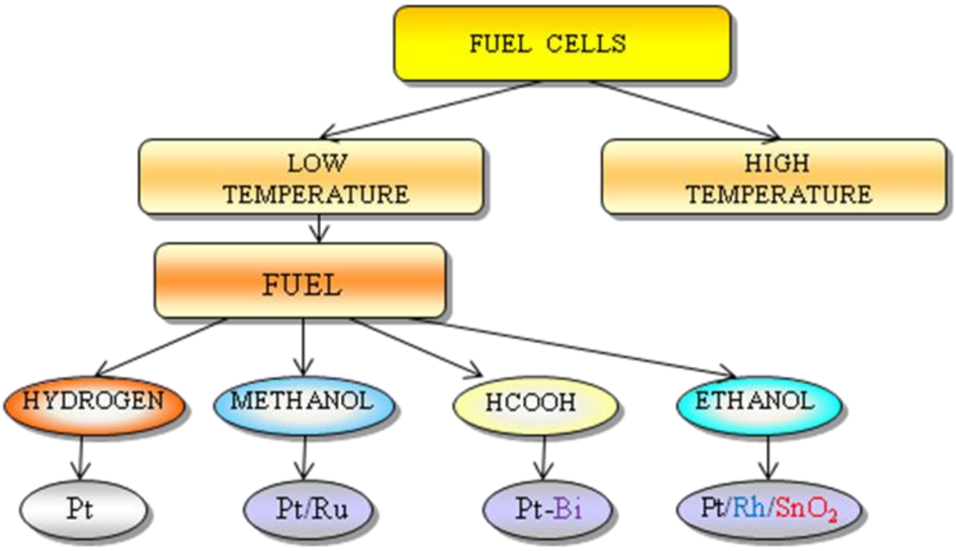


Figure 1. The classification of fuel cells with fuels and catalysts for low-temperature type indicated.

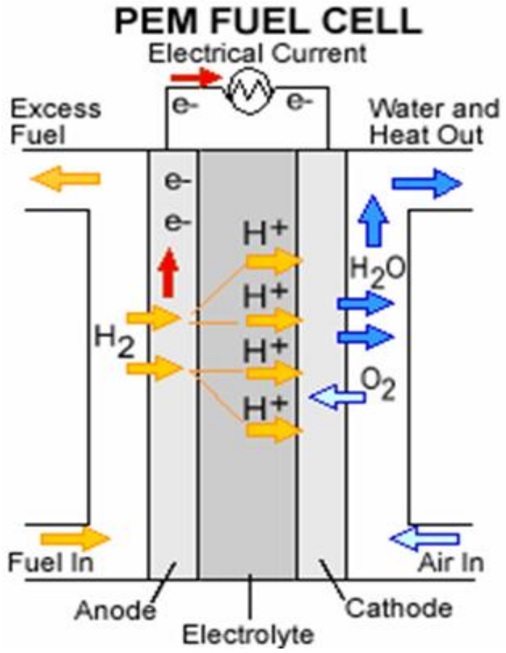


Figure 2.Schematics of proton exchange membrane fuel cell (PEMFC) (from: http://z.about.com/d/alternativefuels/1/0/H/9/-/-/fcell_diagram).

Difficulties with storage and distribution of hydrogen restrict the use of these cells, and requires further development of cells based on methanol, formic acid and recently ethanol. These cells produce nothing beside energy, water and carbon dioxide. Other advantageous features of fuel cells are continuous silent work in comparison with steam and wind generators.

Figure 3. An example of car with fuel cells: GM Sequel.

HYDROGEN CELLS

Platinum is typically used at the anode and cathode of a hydrogen fuel cell. These fuel cells have been used in military and space applications for more than 30 years. In these applications, the price is a not primary issue. More recent constructions are fitted with a platinum/ruthenium anode allowing the use of hydrogen containing carbon monoxide from petrochemical processes [2-26]. Recent developments seek to eliminate platinum, substituting palladium or tungsten carbide dotted with palladium at the anode.

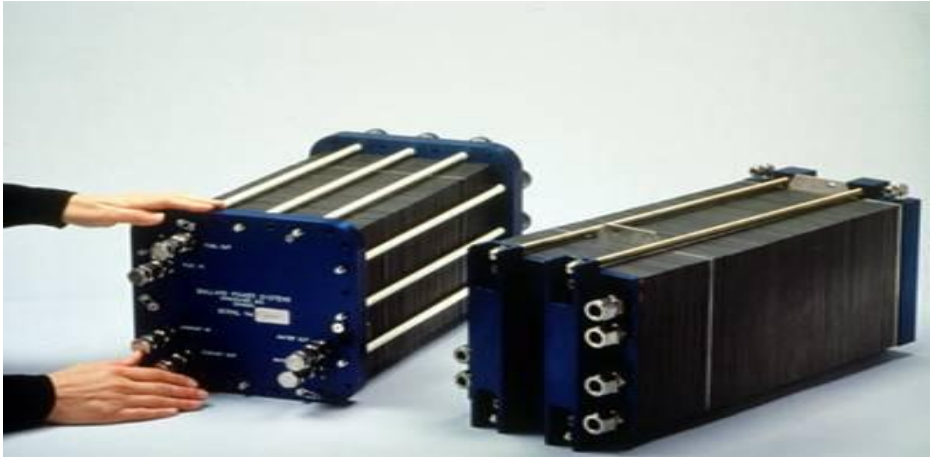


Figure 4. An example of a commercial hydrogen fuel cell.

The cell is constructed in a manner similar to a filter press. Individual units are connected in series giving the battery a desired voltage.

DIRECT METHANOL FUEL CELL

Carbon monoxide is an intermediate product of methanol oxidation in the Direct Methanol Fuel Cell (Fig. 5). It poisons platinum contained in the anode. For this reason platinum modified with a second metal is a component of an anode. Ruthenium is most commonly used as this second metal.

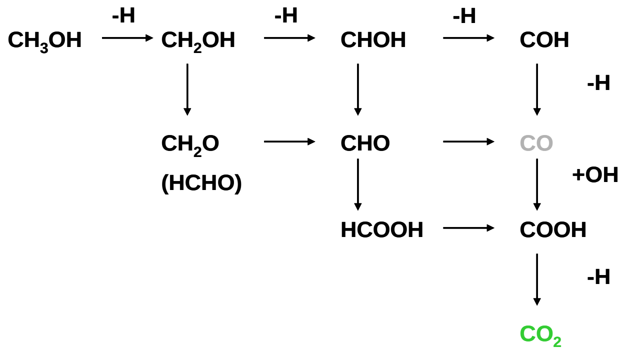
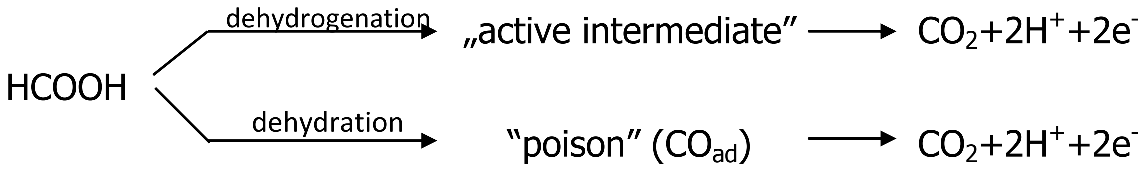


Figure 5. Oxidation of methanol

The aim of present works is preparation of catalysts which avoid the formation of CO on Pt sites and minimization of catalyst particle size both on cathode and anode material [11-26]. These advances could improve efficiency of energy conversion and lower the total costs. Methanol-based fuel cells can be used in cars and mobile electrical devices such as cell phones or laptops. However due to methanol's poisonous properties distribution of this type of cell is limited.

FORMIC ACID FUEL CELLS

Platinum is the base component of anode material. However, other catalysts containing additional components besides platinum are under development [27-45] because platinum can be deactivated by the intermediate products of formic acid oxidation (Fig. 6).

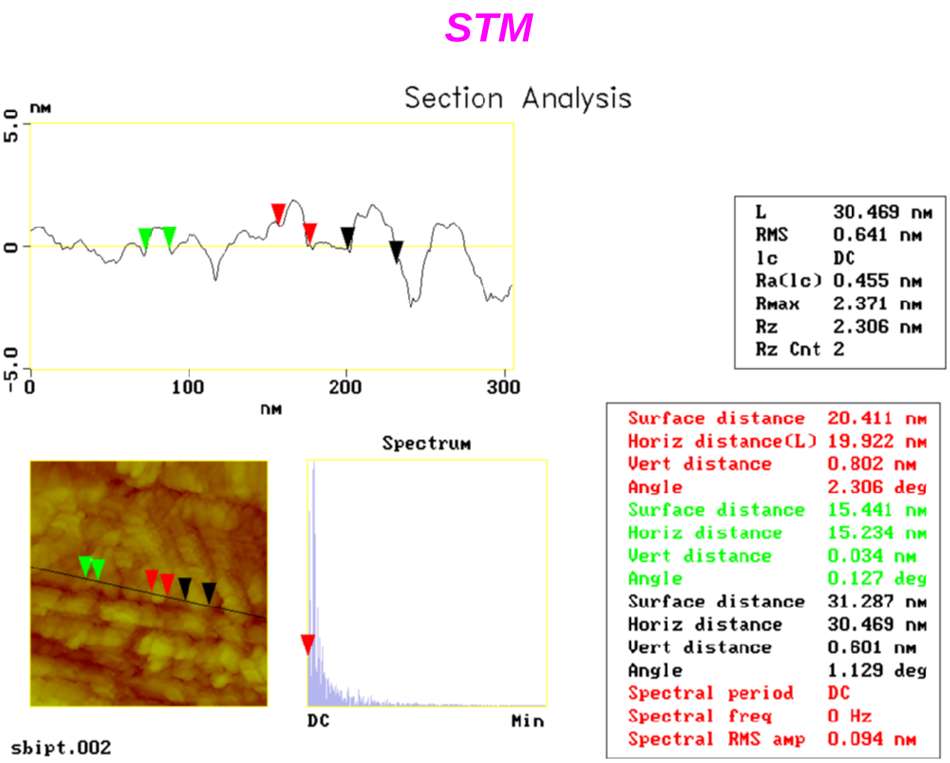


$$HCOOH \rightleftarrows HCOOH_{ads}$$
$$HCOOH_{ads} \rightarrow HCOO_{ads} + H^+ + e^-$$
$$HCOO_{ads} \rightleftarrows CO_2 + H^+ + e^-$$
$$j = 2F k_2' (1-\theta_p) c_{HCOOH}^{0.5} \exp\left(\frac{0.5FE}{RT}\right)$$

Figure 6. Mechanism of formic acid oxidation on platinum

Oxidation of formic acid goes in two independent ways. Both of them lead to carbon dioxide, but intermediate product CO_{ads} poisons the surface of the electrode. One additional metal which prevents the deactivation of the electrode is bismuth [44-46]. Surface topography of Pt-Bi catalyst is presented in figure 7.

Pt-Bi catalyst grains of 10-30 nm size clearly can be seen on the presented image. Small particle size and satisfactory current densities of formic acid oxidation point to the prospective use of this fuel in a fuel cell operating at limited oxygen pressures.



L	30.469 nm
RMS	0.641 nm
lc	DC
Ra(lc)	0.455 nm
Rmax	2.371 nm
Rz	2.306 nm
Rz Cnt	2

Surface distance	20.411 nm
Horiz distance(L)	19.922 nm
Vert distance	0.802 nm
Angle	2.306 deg
Surface distance	15.441 nm
Horiz distance	15.234 nm
Vert distance	0.034 nm
Angle	0.127 deg
Surface distance	31.287 nm
Horiz distance	30.469 nm
Vert distance	0.601 nm
Angle	1.129 deg
Spectral period	DC
Spectral freq	0 Hz
Spectral RMS amp	0.094 nm

Figure 7. An STM image of Pt-Bi electrode surface

DIRECT ETHANOL FUEL CELLS

Ethanol is the best prospective fuel for fuel cells because is environmentally friendly. This fuel is non-toxic and can be produced from renewable sources. Its distribution does not require the construction of new, expensive equipment. Ethanol has a high energy density. From one molecule of ethanol one can get 12 electrons. Reactions going on in Direct Ethanol Fuel Cell (DEFC) are given:

Anode reaction: $C_2H_5OH + 3\ H_2O \rightarrow 2\ CO_2 + 12\ H^+ + 12\ e^-$

Cathode reaction: $3\ O_2 + 12\ H^+ + 12\ e^- \rightarrow 6\ H_2O$

Summary reaction: $C_2H_5OH + 3\ O_2 \rightarrow 2\ CO_2 + 3\ H_2O$

At present, intensive work is under way to develop an efficient catalyst for the electrochemical oxidation of ethanol [47-58]. The catalyst must be trifunctional due to the necessity of breaking the C-C bonds in a molecule of ethanol. The Brookhaven National Laboratory in the USA developed the anode catalyst consisting of Pt, Rh, and SnO_2 [52, 55, 57, 58]. The Adzic method [54] was used for the creation of the Rh layer partially covering the surface of platinum. The method of preparing trifunctional Pt/Rh/SnO_2 catalyst for electrochemical oxidation of ethanol is shown in Figure 8.

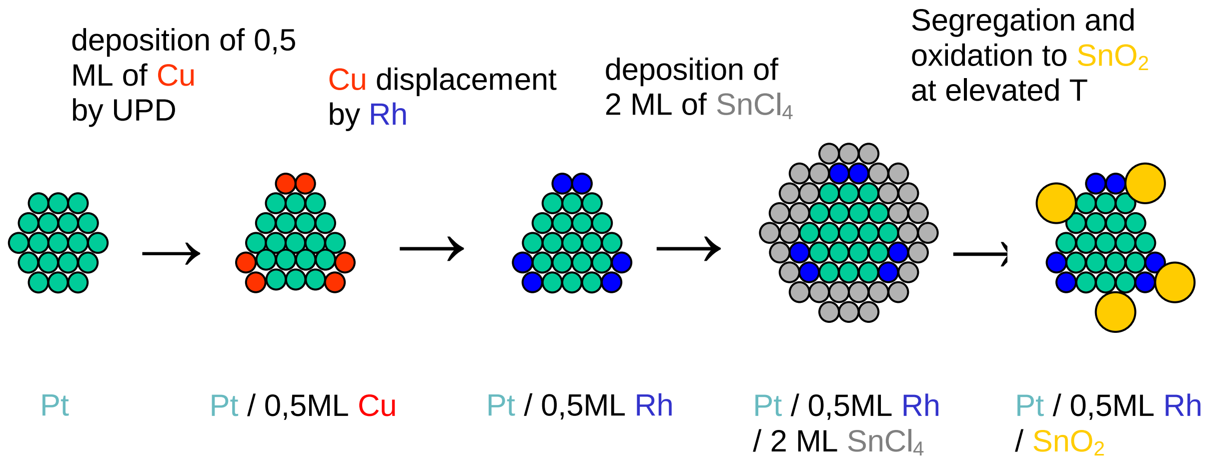


Figure 8. Scheme of ternary catalyst preparation including: electrochemical creation of 0.5 Cu monolayer on Pt nanoparticle; conversion of Cu to Rh through the process of chemical exchange; deposit on the surface of Pt-Rh grains "2 monolayers" of $SnCl_4$*; thermal oxidation of* $SnCl_4$ *to* SnO_2

The size of platinum nanoparticles deposited on activated carbon (Vulcan 72) was determined using XRD technique (Fig. 9) and the Scherrer equation. The average size of Pt nanoparticles was determined from the size of a symmetrical peak half-width (220). It is equal to: 2.9-3.1 nm.

The average Pt/Rh/SnO_2 nanoparticle size determined using the same technique is 3-5 nm. The optimal amount of SnO_2 nanoparticles present on the surface of platinum was determined in the electrochemical experiments (Fig. 10).

The largest ethanol oxidation currents were recorded for the Pt electrode surface coated with SnO_2 in an amount of 1-2 monolayers (ML).The reaction products formed during the process of electrochemical oxidation of ethanol was verified by IRRAS technique [52, 55, 57]. This technique allows registration of the infrared spectra of chemical compounds existing on the anode surface during the electrochemical process running at a given potential (Fig. 11).

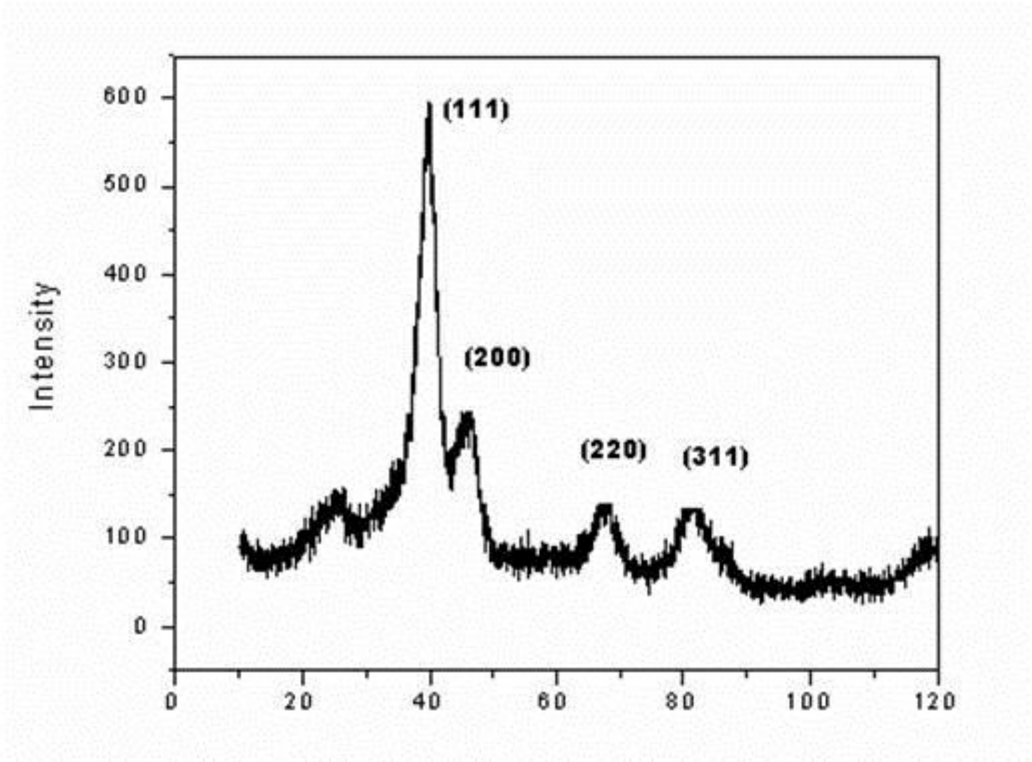


Figure 9. The XRD pattern for the platinum particles deposited on amorphous carbon (Vulcan 72)

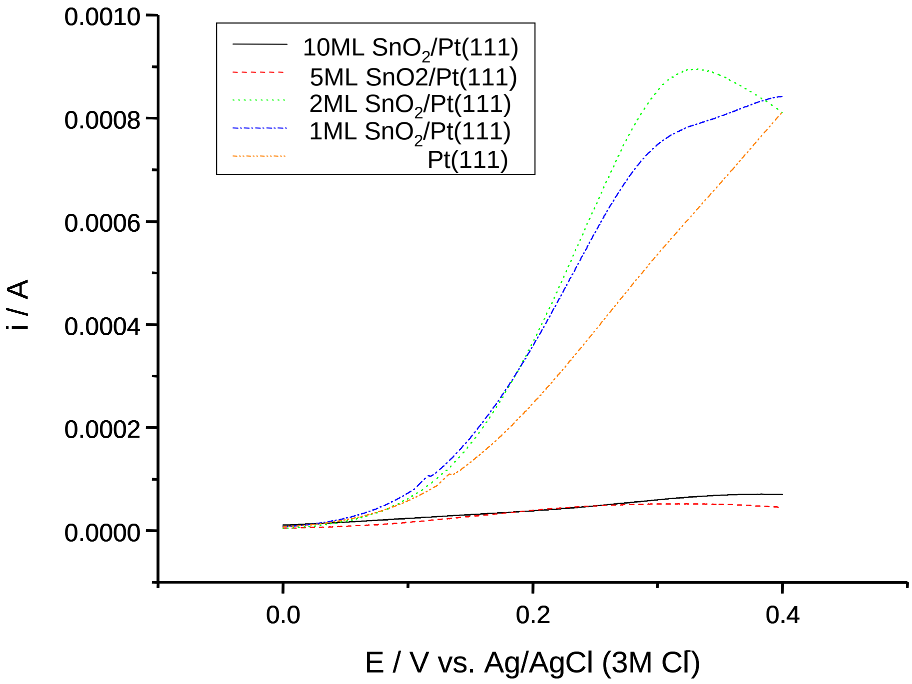


Figure 10. Optimization of present amount of SnO_2 on the surface of Pt favorable for efficient oxidation of ethanol: ethanol oxidation currents versus the electrode potential for various tin dioxide coverages of Pt

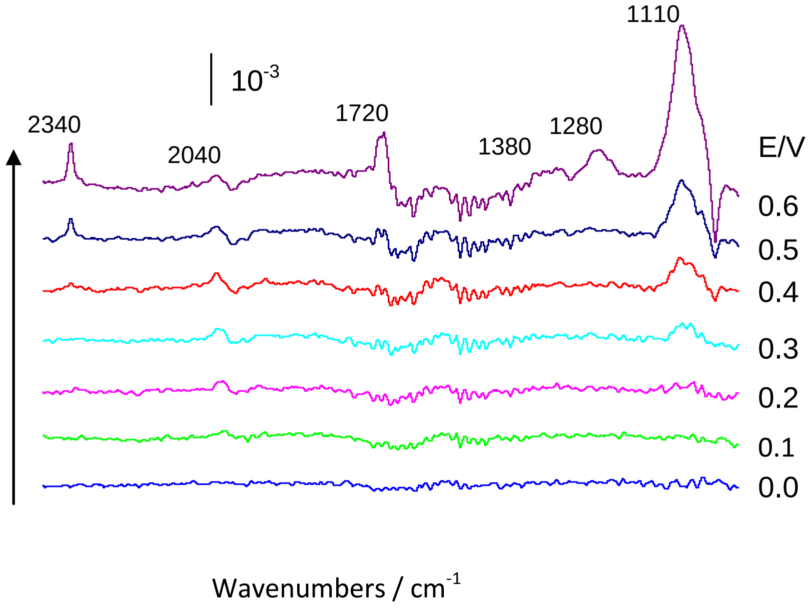


Figure 11. IRRAS spectra recorded during the oxidation of ethanol on the (2 ML) SnO_2/Pt (111) electrode. Solution contains 0.1 M $HClO_4$ + 0.1 M ethanol. Spectra normalized to the spectrum recorded at the potential -0.05 V

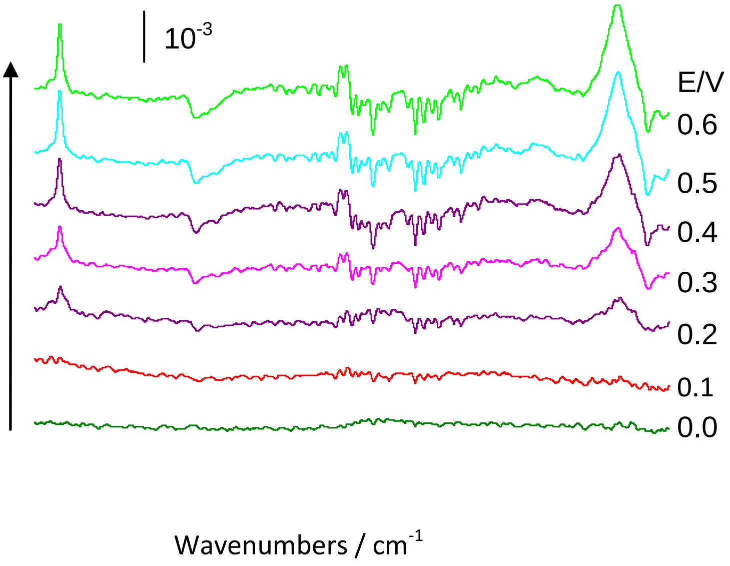


Figure 12. IRRAS spectra recorded during the oxidation of ethanol on the (2ML)SnO_2/Rh(0.5 ML)/Pt(111) electrode. Solution contains 0.1 M $HClO_4$ + 0.1 M ethanol. Spectra normalized to the spectrum recorded at the potential -0.05 V

The presented spectra indicate that starting from the potential of 0.4 V, the characteristic CO_2 peak appears at a wavelength of 2340 cm-^{1}. Thus, oxidation of ethanol to CO_2 starts at this potential. But for electrodes containing Pt, SnO_2 and Rh (Fig. 12) the process of CO_2 formation begins at potential 0.2 V. This indicates that the presence of Rh on the surface of platinum enhance ethanol oxidation.

Comparison of the ethanol oxidation activity for a catalyst containing 20% Pt nanoparticles covered by 0.5 Rh monolayer and 2 ML of SnO_2 with a commercial catalysts containing 20% Pt-Ru nanoparticles is shown in Figure 13.

Comparison of ethanol oxidation currents recorded for the new catalyst and the commercial catalyst indicates that the new catalyst is much more active. The rate of ethanol oxidation for the new catalyst is about one order of magnitude greater (at 0,2 V) than the rate registered for the commercial catalyst.

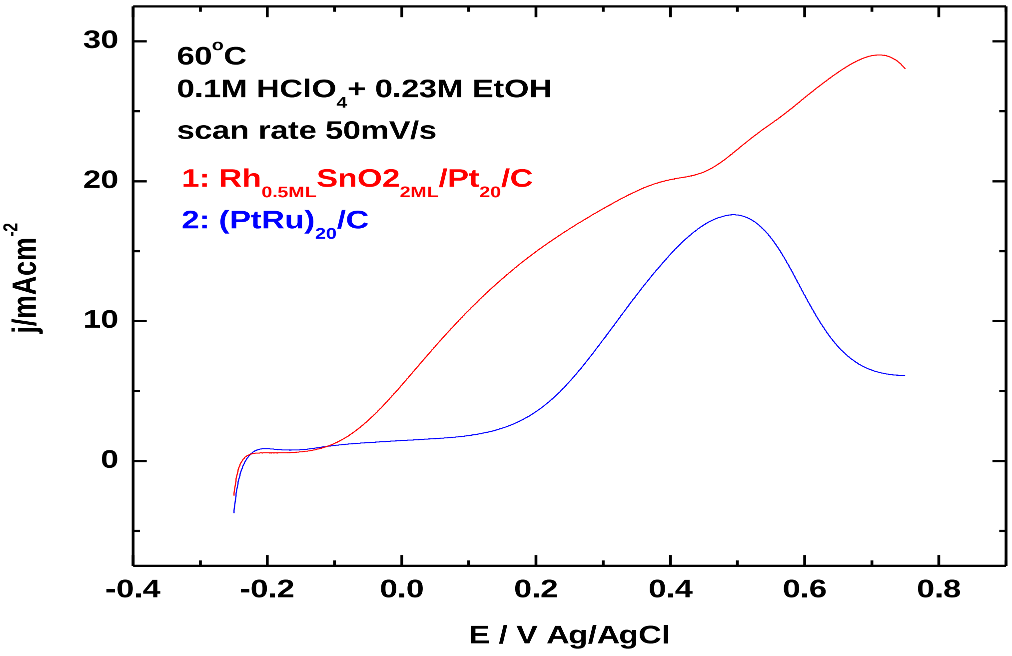


Figure 13. Ethanol oxidation currents versus electrode potential

1. - for catalyst containing on active carbon 20% Pt nanoparticles covered by 0.5 Rh monolayer and 2 ML of SnO_2 *(denoted as* $(Rh_{(0,5ML)},SnO_{2(2ML)}/Pt_{20\%}/C)$*,*

2. - for commercial catalysts containing 20% Pt-Ru nanoparticles at activated carbon.

CONCLUSIONS

- Hydrogen, methanol, formic acid and ethanol are effective fuels for fuel cells, but it should be noted that only ethanol is now produced from renewable sources.
- The main component of the anode catalyst in acidic fuel cells is platinum modified by another metal (Ru, Bi, Rh).
- Ethanol oxidation on Pt is enhanced by modifying the surface with Rh.
  Further enhancement can be achieved by the addition of SnO_2.
- Spliting of the C-C bonds in the ethanol oxidation was verified by the detection of CO_2 in the IRRAS spectra.
- Catalyst: Pt / 0.5 ML Rh / SnO_2 is a promising material for the anode in DEFC.

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