CATALYST WITH A CARRIER SYNTHESISED BY SOL-GEL FOR FUEL CELLS

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Introduction

Methanol is one of the most promising fuels for fuel cells, especially if it can be oxidized directly and completely to carbon dioxide. The low cost and the functionality of Direct Methanol Fuel Cells (DMFC) are the reasons why they are competitive to other cells. Of particular interest is the choice of a catalyst which would satisfy certain requirement, would be cheap and resistant to deactivation. The activity of heterogeneous catalysts is determined by the type of surface, crystal structure, and the particle size. The most important condition of high activity of catalyst is high surface area and the small size of particle. One of the most common catalytic materials is platinum so the aim of this study was to check the possibility of using the Pt catalyst supported on Al_2O_3, $Al_2O_3 – SnO_2$ in the methanol cell. In the systems Pt/Al_2O_3 and $Pt/Al_2O_3 – SnO_2$, metal phase is deposited on a carrier synthesized by the sol-gel method [1,2]. We have studied the effect of use the platinum catalyst (Pt/ Al_2O_3 and Pt/ $Al_2O_3 – SnO_2$) on methanol oxidation during cyclic voltammetry.

Experimental

1. Preparation

The non – modifidied support (Al_2O_3) and the binary composition ($Al_2O_3 – SnO_2$ with a molar ratio between 1:0.1 and 1:0.2) was synthesised by the sol – gel method worked out at our laboratory[1,2]. As a precursor we used aluminium isopropanol, tin (IV) acetate and acetic acid was applied as a moderator of the rates of hydrolysis and condensation (regulation of pH). The encapsulated solvents were removed from the gel by evaporative drying. Then the samples were heated at 373 K for 6 hours.

Platinum was introduced by impregnation (1% of platinum in ratio to weight of support). The source of platinum was the solution of hexachloroplatinum acid. The catalysts with platinum was reduced by termoprogrammed reduction in the hydrogen atmosphere. Table 1 presents symbols of samples.

2. Characterization of catalysts

2.1. The X-ray powder diffraction patterns of samples were taken on a PW 1130/90 diffractometer (Philips), with Ni filtered Cu K_α radiation. The positions of reflections were calculated by APD Philips program.

2.2. The degree of metal dispersion was determined by the hydrogen chemisorption

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measurements carried out on the ASAP, model 2010 V2.00 Micrometrics using 200-300 mg of materials with the grain size fraction between 0.1 – 0.2 mm.

2.3. Cyclic voltammetry measurements were carried out by using potentiostat/galvanostat 9131 ATLAS 91, in the range of potential from -1.7 V to +1.7 V. The sweep rate was 200 mV/min.

The working electrode was “foaming” nickel with catalysts in form of gel (introduced by impregnation), the counter electrode was graphite and the reference electrode was Hg/Hg_2Cl_2 electrode. The electrolyte was 0.01M KOH. Methanol (0.5 M) was added to the electrolyte by the portion (10 cm^3). The kinetics studies of methanol oxidation was performed by using five types of the electrodes: Ni, Al_g/Ni, Pt - Al_g /Ni, Sn_g 0.1/Ni, Pt - Sn_g 0.1/Ni, Sn_g 0.2/Ni, Pt - Sn_g 0.2/Ni.

Table 1 *Names of samples*

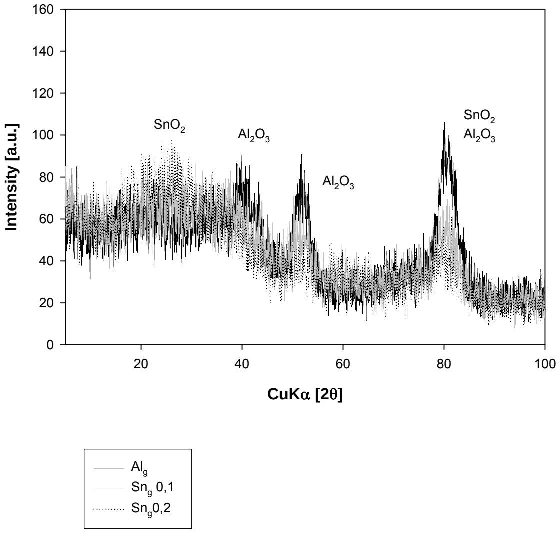
Sample	Molar ratio Al_2O_3-SnO_2
Al_g	1 : 0
Sn_g 0.1	1: 0.1
Sn_g 0.2	1 : 0.2

Results and discussion

1. XRD results

The XRD analysis of the catalysts has shown that sol – gel method allows obtain the high-temperature γ-Al_2O_3 phase, which shows the best catalytic activity. For the binary gel composition we have observed the reflexes assigned to the SnO_2 crystal phases. In the case of metal systems the reflexes corresponding to Pt are weak this could suggest that we have small groups of platinum on the surface of supports and/or low their concentration.

Fig. 1 and Fig. 2 present the XRD diffraction patterns of the supports and catalysts with different supports.



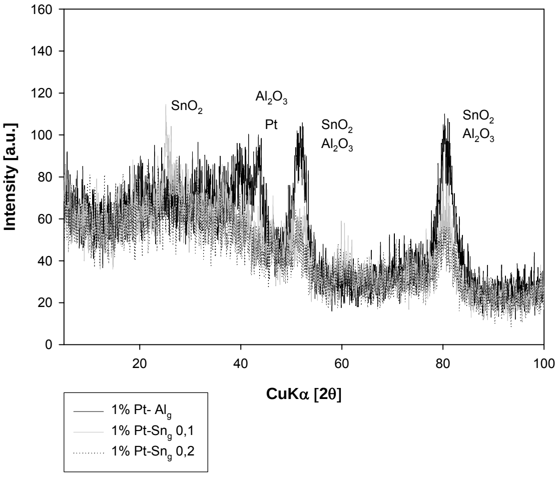


Fig. 1 *(left) XRD spectra of gel samples: Al_2O_3 and binary systems after calcination in air atmosphere for 6 hours at 500^0C.*

Fig. 2 *(right) XRD spectra of platinum samples with Al_2O_3 and binary systems as the supports after thermo-programmed reduction in hydrogen atmosphere.*

2. *Degree of metal dispersion*

The results of hydrogen chemisorption indicate that in comparison with the standard carriers of the same kind the gel carriers permit a much higher degree of metallic phase dispersion both in unary and binary systems. It should be noted that the highest degree of platinum dispersion degree was observed for the aluminum support. We suppose that this is related to the high homogeneity of hydroxyl groups on the surface Al_2O_3 produced by sol – gel method. The higher homogeneity of surface implies a better homogeneity of the metal precursor phase bond to the support as a consequence a high degree of metal dispersion.

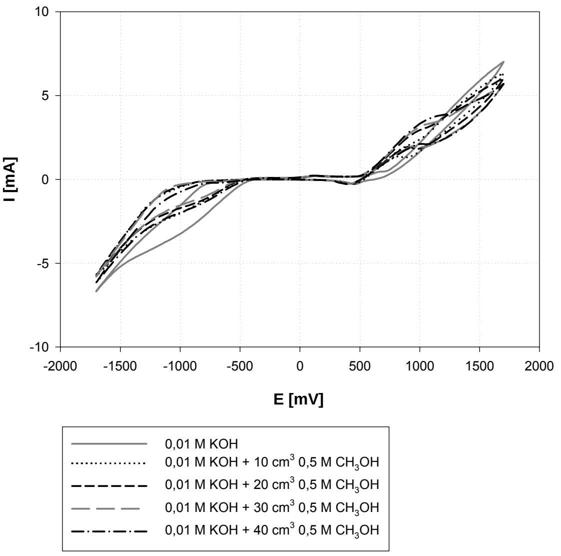
Table 2 presents a comparison of degree of platinum dispersion standards and gel supports.

Table 2 *A comparison of degree of platinum dispersion (precursor of Pt – $H_2PtCl_{6\ aq.\ sol.}$, 1% w/w Pt) for gel and standard supports Al_2O_3-SnO_2.*

Sample	Degree of Pt (H/Pt) for standard supports	Degree of Pt (H/Pt) for gel supports
Al_g	0.4	1.1
Sn_g 0.01	0.2	0.8
Sn_g 0.05	0.1	0.573
Sn_g 0.10	0.013	0.3
Sn_g 0.20	0.008	0.1

3. *Cyclic voltammetry measurements*

The aim of the study was to determine to the effect of methanol addition on the voltammetry of particular catalysts. Because of the different chemical composition of the electrode, our cyclic voltammograms differed from those reported in [3-5].



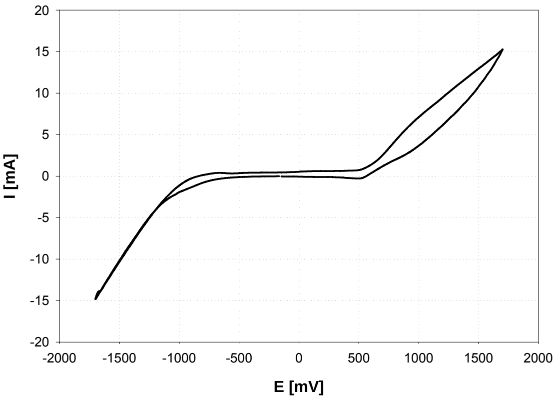


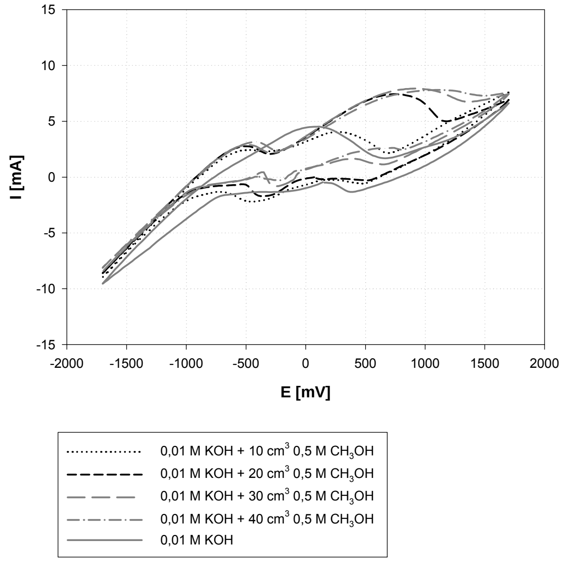
Fig. 3 *(left) The cyclovoltammograms of pure Ni at ambient temperature.*

Fig. 4 *(right)The cyclovoltammograms of Al_g/Ni at ambient temperature.*

Fig. 3 – 5 show the cyclovoltammograms of Ni electrode, Ni electrode with Al_g, Pt - Al_g/Ni in 0,01M KOH solution recorded at ambient temperature. Fig. 6 – 8 show the cyclovoltammograms of Ni electrode, Ni electrode with Al_2O_3, Pt - Al_2O_3/Ni in 0,01M KOH solution recorded at 65^{0}C.

The voltammograms for cells with Ni electrode are the references for study of the influence of the catalysts on methanol oxidation.

In the case of Al_2O_3 (Fig. 4) we don't observe changes in the kinetics of methanol oxidation during the methanol addition, which means that support (Al_g) does not influence the cell work.



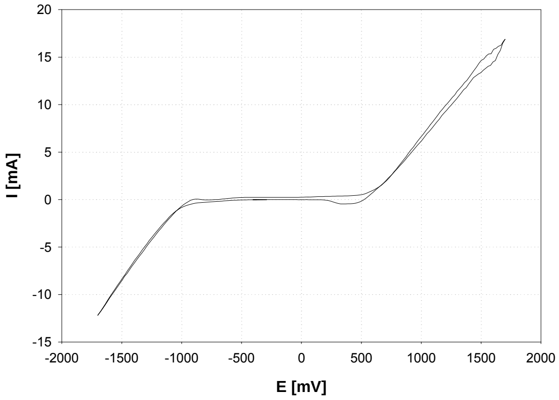
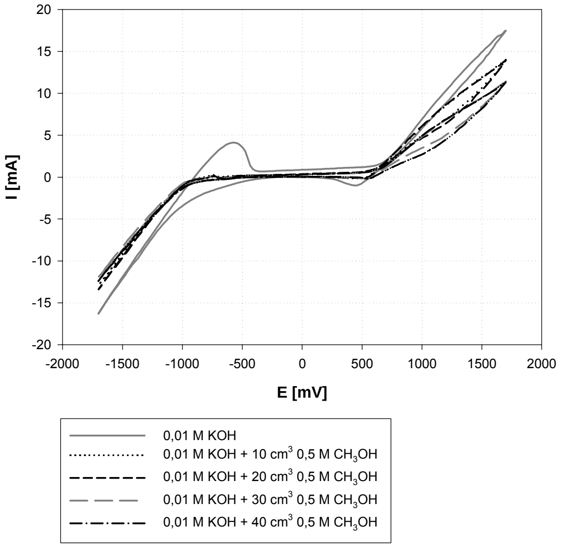


Fig. 5 *(left) The cyclovoltammograms of 1% Pt-Al_g/Ni at ambient temperature.*

Fig. 6 *(right)The cyclovoltammograms of pure Ni at 65^{0}C.*



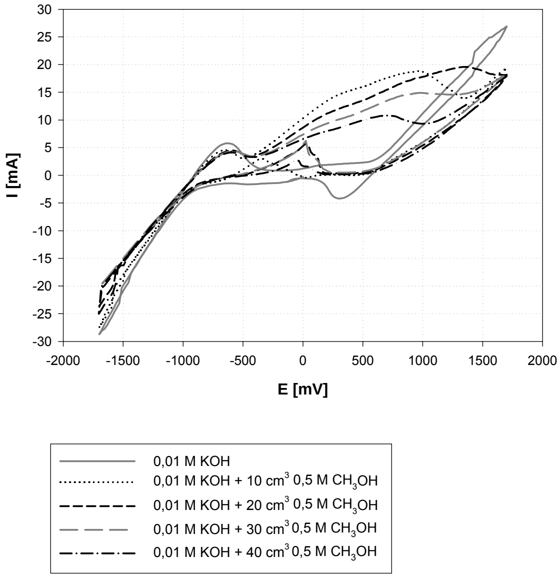


Fig. 7 *(left)The cyclovoltammograms of Al_g/Ni at 65^{0}C.*

Fig. 8 *(right) The cyclovoltammograms of 1% Pt-Al_g/Ni at 65^{0}C.*

The cyclovoltammograms of the system Pt - Al_g (Fig. 5) revealed an anodic peak at 250 mV, for the cell working at ambient temperature and at 65^0C (Fig. 8). This peak is shifted towards higher potentials with a growing concentration of methanol and can suggest that platinum takes part in methanol oxidation. The other peaks probably corresponded to $Ni(OH)_2$, NiO(OH) produced during the work of the electrode. The anodic peak at – 625 mV on Fig. 7 can be caused by changes induced by higher temperature. At 65^0C Al_g did not influence on electrooxidation of methanol because we did not observe the peak at 250 mV which is typical of Pt.

The results for binary catalysts are not shown because of their unstability in the alkaline media. Sintering the electrodes with catalytic materials didn't give satisfy results.

Conclusions

Cyclic voltammetry method is one of the best method to estimate the activity of catalysts and cells. The results of our study have shown a significant influence of Pt - Al_2O_3 on the kinetics of the methanol oxidation, although the mechanism of their performance is not known yet. The results obtained by investigation of the methanol oxidation on platinum catalysts have shown that the degree of platinum dispersion is high in comparison to that on commercial supports. Thus the method proposed can be recommended as one of the best of producing these catalysts.

References

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