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CARBON NANOTUBES AS SUPPORT FOR CO/TiO₂ ELECTROCATALYSTS FOR HYDROGEN EVOLUTION

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Abstract:

The aim of this work was to apply multiwalled carbon nanotubes (MWCNTs) as a catalyst support in composite Co/TiO₂/C electrocatalysts for hydrogen evolution. In order to elucidate the effect of MWCNTs, corresponding catalysts deposited on traditional carbon material Vulcan XC-72 were prepared as well.

Structural characterization was performed by SEM, IR and XPS method. It is shown that intrinsic catalytic activity of catalysts deposited on both MWCNTs and Vulcan XC-72 are almost the same.

It was shown that the surface area of the catalysts deposited on MWCNTs is twice higher than the one on classical Vulcan XC-72 substrate.

Electrochemical characterization was performed by cyclic voltammetry and steady-state galvanostatic methods in alkaline solution (3,5 M KOH). Introduction of MWCNTs was shown to increase considerably catalyst's activity. The overpotential (at $i = 20 \text{ mA}\cdot\text{cm}^{-2}$) is for 45 mV lower than corresponding one with Vulcan XC-72.

These results are valuable per se and also are good indicators for further improvement of this type of catalysts.

Key words: composite catalyst, multiwalled carbon nanotubes (MWCNTs), hydrogen evolution reaction (HER), Co, TiO₂

1. INTRODUCTION

One of the most important fields of modern electrocatalysis is engineering of new electrode materials for hydrogen evolution and fuel cells. Electrode materials should be *i*) catalytically active, *ii*) chemically and mechanically stable and *iii*) inexpensive. The composite materials based on mixture of metal from the right side of the transition series (hyper *d*) and metal (or its compound) from the left side of transition series (hypo *d*) appear as effective to satisfy the above criteria. Physical background of hypo-hyper *d*-electrocatalysts has given by Brewer's valence-bond theory^[1] and electrochemically interpreted by Jakšić^[2].

In our previous papers^[3,4] hypo-hyper *d*-electrocatalysts containing amorphous TiO₂ as a hypo *d*-phase and non-platinum metals (Ni, Co or CoNi) as a hyper *d*-phase were structurally and electrochemically characterized. The catalyst based on Co has been shown as the most active one, but we believe that this is not its highest performance.

It is well known that there are two approaches to improve the catalysts: *i*) increase of intrinsic activity by rising of interaction between hypo and hyper *d*-phases and *ii*) developing of real surface area of the electrode.

In the previous works^[3,4], the effect of increasing of hypo-hyper *d*-interaction was studied involving anatase instead amorphous TiO₂ as a hypo phase. The aim of this work is to determine the effect of developing catalyst's surface area by employing multiwalled carbon nanotubes (MWCNTs) as a carbon substrate instead Vulcan XC-72.

Iijima's discovery in 1991^[5] has initiated intensive research on carbon nanotubes (CNTs). Their unique and superior physical, mechanical and electrical properties allow wide range of application as e.g. hydrogen or energy storage, electrode material in electrochemical capacitors, field emission electron source, fillers in polymer composites etc. The extraordinary conductivity, mechanical stability and inner geometry make as well CNTs promising material as catalyst support replacing traditionally carbon blacks.

2. EXPERIMENTAL

The catalysts were prepared by sol-gel procedure described elsewhere^[3,6]. Two catalysts of the same composition (10%Co + 18%TiO₂) were prepared, but on different carbon substrate (MWCNTs and Vulcan XC-72, resp.). The first one was deposited on Vulcan XC-72 as a catalyst support, while the second one on multiwalled carbon nanotubes (MWCNTs). Structural analysis was performed by scanning electron microscopy (SEM), x-ray photoelectron spectroscopy (XPS) and Fourier transformed infrared spectroscopy (FTIR).

The real vs. geometric surface area ratio was determined by cyclic voltammetry as described elsewhere^[4]. Polarization characteristics were measured by steady-state galvanostatic method using gas-diffusion working electrodes^[4] in alkaline solution (3,5 M KOH). Reference electrode was Hg/HgO, while as counter electrode platinum wire was used.

3. RESULTS AND DISCUSSION

In Fig 1, SEM photographies of both catalysts are shown. The catalyst's particles deposited onto Vulcan XC-72 are of a spherical shape and grouped in clusters sized of 100-200 nm, so that good adherence was achieved. There is a number of holes between the aggregates on the catalyst's surface, higher specific surface area, and consequently higher catalytic activity is created due to these features.

The catalyst's particles grafted on MWCNTs are grouped in smaller clusters than those on Vulcan XC-72. This causes holes between particles to appear. Due to intrinsic geometrical features of MWCNTs (empty cylinders with higher developed surface area as compared to the spherical particles of Vulcan XC-72), they possess inner holes so that inner porosity of MWCNTs is considerably higher than the one of Vulcan XC-72. This is important for better dispersion of other catalyst's components of the on the surface, especially of active catalytic centers – metallic particles.

SEM analysis is not able to give any information on the nature of bonding (mechanical or chemical) of different particles into the catalyst's clusters. This information can be obtained by further spectroscopic investigation, by e.g. infrared spectroscopy or X-ray photoelectron spectroscopy (XPS), as shown below.

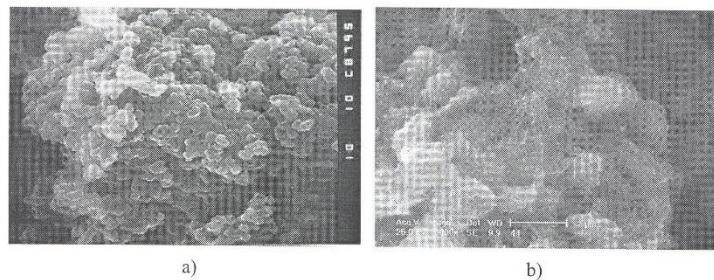


Fig. 1. SEM photographs of the catalyst deposited on a) Vulcan XC-72 and b) MWCNTs

In Fig.2 XPS spectra of Ti and Co are given. The values of binding energy on maximum of the $Ti2p_{1/2}$ and $Ti2p_{3/2}$ peaks correspond to existence of TiO_2 on the catalyst's surface (Fig. 2a). The maximum of $Ti2p_{1/2}$ corresponds to the table value of TiO_2 , while the value of $Ti2p_{3/2}$ peak is for 0,1 eV different from the table one (458,9 eV vs. 459,0 eV), what suggests that interaction between TiO_2 phase with metallic phase exists. The difference between the maxima is almost equal to the standard energy of binding of TiO_2 ($\approx 5,7$ eV).

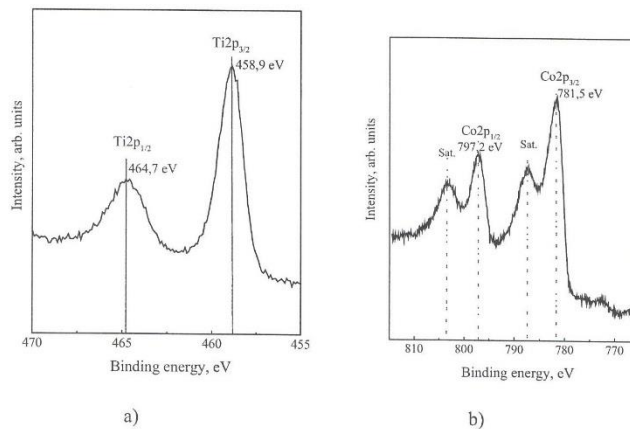


Fig. 2. XPS spectra of a) Ti^{4+} ($Ti2p_{1/2}$ and $Ti2p_{3/2}$) and b) Co^{2+} ($Co2p_{1/2}$ and $Co2p_{3/2}$), taken at the catalyst's surface

The values of maxima of $Co2p_{1/2}$ and $Co2p_{3/2}$ peaks (797,2 and 781,5 eV) indicate existence of cobalt as $Co(OH)_2$ phase on the catalyst' surface. The peaks are spread and with

low intensity, what suggest that amount of cobalt into elemental state is considerably lower than in valence state (Co^{2+}). Based on the determined values of the binding energies (Fig. 2), it is very probable that, next to $\text{Co}(\text{OH})_2$, Co^{2+} also exists in small amount of CoO and CoTiO_3 . This is supported with the satellite peaks on 787,3 and 803,3 eV, which is a consequence of paramagnetism of CoO phase.

XPS analysis also indicates that some interaction between the hypo and hyper d -components takes place.

On the FTIR spectra of investigated catalysts the only band of interest originates by TiO_2 ^[7]. To determine hypo-hyper d -interaction one has to compare values of maximum of TiO_2 band incorporated in the electrocatalysts and maximum of the band from pure TiO_2 obtained in identical conditions as that in electrocatalyst. The shift of the maximum value is almost the same for both compared catalysts. This shift is 55 to 57 cm^{-1} related to the maximum of pure TiO_2 (Table 1). So, it shows that there is an intrinsic interaction between hypo oxide and hyper d -metallic phase into the catalysts. The level of hypo-hyper d -interaction is the same in both investigated systems.

Table 1. Change of wave number, double layer capacity, C_{dl} and ratio of real vs. geometrical surface area, S_R/S_G

Catalyst	Δ wave number/ cm^{-1}	$C_{dl}/\text{mF}\cdot\text{cm}^{-2}$	S_R/S_G
10%Co + 18%TiO ₂ + Vulcan XC-72	57	153,7	2560
10%Co + 18%TiO ₂ + MWCNTs	55	396,00	6600

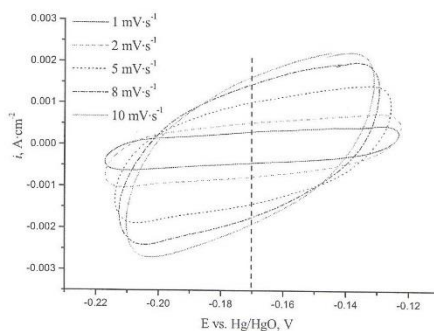


Fig. 3. Cyclic voltammograms in the potential region of double layer charging for different scan rates (10%Co + 18%TiO₂ + Vulcan XC-72)

Substitution of Vulcan XC-72 with MWCNTs as carbon substrate results in a decrease of HER overpotential for as much as 40 mV. This increase of the catalytic activity is results only of more developed surface area of the catalyst deposited on MWCNTs. Hypo-hyper *d*-interaction is the same in both systems, so there is no improvement in intrinsic activity. The higher activity for hydrogen evolution is a result first of all of the nature of carbon nanotubes (their inner structure, surface area and conductive characteristics). The high developed surface area enables better dispersion of active catalytic centers across the catalyst's surface. Also, extra-conductive properties enable easier electron exchange with hydrogen protons, what intensifies formation of adsorbed hydrogen atoms and further hydrogen molecules. On the other side, its high inter- and trans-particle porosity as well as its geometry (empty cylinders), does facilitates the escape of hydrogen molecules from catalyst's surface.

The effect of substitution of Vulcan XC-72 with MWCNTs in case of Co-based catalysts is not so pronounced as in case of Ni-based ones where the decrease of the overpotential for HER is even more than 120 mV^[9]. This is due to very small particles of cobalt (lower than 2 nm)^[3] as a active catalytic centers, so their dispersion in the on the Vulcan substrate is very high.

4. CONCLUSION

At least three main conclusions could be drawn:

- 1) Applying the modified sol-gel procedure provides production of catalysts that exhibit pronounced synergetic effect for the hydrogen evolution reaction.
- 2) This effect is due to both high developed surface area as result of obtained nanostructured components of the catalysts and the strong metal-support interaction between hypo and hyper *d*- electronic phases, which is equal for both investigated systems.
- 3) Using MWCNTs as carbon substrate instead Vulcan XC-72 creates an increased catalytic activity, as a result of higher developed surface area as well as better dispersion of active catalytic centers over the catalyst's surface.

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