

UNIVERSITY OF PARDUBICE
Faculty of Chemical Technology
Department of Theory and Technology of Explosives

**NEW TRENDS IN RESEARCH
OF ENERGETIC MATERIALS**

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Pardubice, Czech Republic

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PROCEEDINGS
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*intended as a meeting of students, postgraduate students, university
teachers and young research and development workers concerned
from the whole world*

SOPHISTICATED ELECTROCATALYSTS FOR ECONOMICAL PRODUCTION OF HYDROGEN PART B: ELECTROCHEMICAL CHARACTERIZATION

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Abstract

Electrochemical characterization of composite hypo-hyper d- electrocatalysts for hydrogen evolution reaction (HER) was performed using cyclic voltammetry and steady-state galvanostatic method.

Cyclic voltammograms are without any pronounced peaks corresponding to some surface processes, typically for porous electrodes.

The influence of the temperature on electrocatalytic activity was studied. The catalysts with support treated on 480°C are more active than those on 250°C. The overpotential difference ($\eta_{250^\circ\text{C}} - \eta_{480^\circ\text{C}}$) for hydrogen evolution at 60 mA·cm⁻² is 15 mV for Co based electrocatalyst and even 60 mV for Ni based. Comparing the electrocatalytic activity of the catalysts with different hyper d-metallic phase, one can conclude that the activity decreases in the sequence: Co > CoNi > Ni. Evidence is produced that the investigated non-precious catalysts show significant synergetic effect. These results are valuable per se and also as indicators for further improvement of non-platinum hypo-hyper d-catalysts.

Key words: hypo-hyper d- catalyst, hydrogen evolution reaction (HER), Co, CoNi, Ni and porous electrodes

1. INTRODUCTION

The search for new, sophisticated and less expensive materials for electrocatalysis with pronounced synergetic characteristics, (i.e. high current density at overpotential near 0) is one of the most actual field of contemporary electrochemistry. Significant synergetic effect can be achieved by combining the metals of the opposite sides of transition series, i.e. metals with empty or partially filled *d*- orbitals, thus being bad catalysts and metals with internally paired *d*- electrons, thus being good catalysts for hydrogen evolution reaction (HER) ^[1]. These materials are named hypo-hyper *d*- electrocatalysts, some of them even exceed the catalytic activity of individual precious metals.

There is an analogy between the hypo-hyper *d*- electronic compound stability and electrocatalytic activity, in which Laves phases of high symmetry and extra stability have the highest activity for hydrogen evolution. This is confirmed for non-precious hypo-hyper *d*- combinations as MoFe₃, WFe₃ ^[1], LaCo₅, LaNi₅ ^[2] etc.

Depending on the applied preparation procedure, the crystallinity of the catalysts can vary from amorphous up to high crystalline. Hypo-hyper *d*-components can be in metallic (zero valence state) or in higher valence state as oxide, sulfide, phosphide etc. Depending on

the state of the hypo and hyper *d*- phases, these catalysts can be divided into 5 groups, as shown in table 1 [3].

Table 1. Grouping of hypo-hyper *d*- intermetallic electrocatalysts

Type of hypo-hyper <i>d</i> - electrocatalyst	Examples
I Intermetallic catalysts	Mo-Co, MoPt ₃ , MoNi ₃ , MoFe ₃ , LaCo ₅ , Ti _{1-x} Ni _x (Tiney Ni), Ni-Co-Mo, Ni-Zr, Co-Zr, etc.
II Sulfides, Phosphides	Ni-W-S, Ni-W-P, Fe-Ni-P etc.
III Catalysts based on Raney Ni	Ni-Al-Ti, Ni-Al-Mo, Ni-Al-Cr, Ni-Zn-Ti, Ni-Zn-Mo etc.
IV Mixed Oxides	TiO ₂ -RuO ₂ , TiO ₂ -IrO ₂ , Ru _x Ti _{1-x} O ₂ , RuO ₂ -IrO ₂ etc.
V Hypo Oxide – Hyper metal	Pt-TiO ₂ , Pt-Ru-WO ₃ , Ni-V ₂ O ₅ etc.

The aim of this work was to obtain and electrochemically characterize non-platinum nanostructured hypo-hyper *d*- electrocatalysts. The hypo component is oxide phase – TiO₂, thermally treated on 250 and 480°C, thus resulting in transformation of the TiO₂ from amorphous into anatase structure. The hyper *d*-phase is in metallic state – Co, Ni or CoNi.

2. EXPERIMENTAL

Catalysts prepared by the procedure described elsewhere [4], where further transformed into porous gas-diffusion electrodes. Pressing at 300 kg·cm⁻² on 300°C [5] was employed, so that a two layer electrode consisting of acetylene's carbon black + PTFE as a substrate and a top layer of catalyst + PTFE mixture (See Fig. 1).

Electrochemical cell used for testing is shown in Fig. 2. The counter electrode was a spiral shaped platinum wire, the reference – Hg/HgO, while the electrolyte was a solution of 3,5 M KOH (p.a., Merck) in deionized ultrapurified water. During the electrochemical testing, the solution in the cathodic area was purged with hydrogen.

The measurements were performed by AMEL electrochemical line (Function Generator AMEL 568, Potentiostat/Galvanostat 2053 and software package SOFTASSIST 2.0).

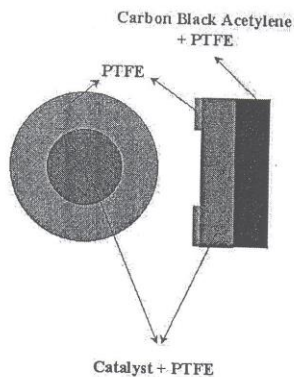


Fig 1. Cross section of three phase gas-diffusion porous electrode

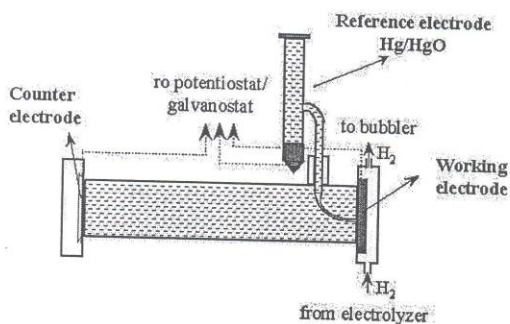


Fig 2. Electrochemical cell used for the electrochemical characterization

3. RESULTS AND DISCUSSION

In Fig. 3, cyclic voltammograms of the investigated electrodes are shown. Generally, the voltammograms of the catalysts containing TiO_2 as anatase (thermally treated at 480°C), show more intensive surface processes as well as electrode reactions. Hydrogen evolution (A) occurs at lower potential on the catalyst thermally treated at 480°C for all investigated systems. Also the oxygen evolution reaction is more intensive and occurs at lower potentials for the same systems. This is due to achievement of stronger metal-support d -interaction, when TiO_2 is in crystalline form^[6,7]. Ni system shows less intensive peaks for the surface processes as Ni to Ni^{2+} transition (B) and corresponding reduction peak (D) (Fig. 3a). The systems in Fig. 3b and c, show pronounced peaks of surface processes due to presence of Co. The peak F represents transition of elemental Co to Co^{2+} , peak B transition of Co^{2+} to Co^{3+} and oxygen evolution, while peak C oxygen evolution reaction. D and E are corresponding peaks of oxygen reduction and metal oxide reduction.

catalyst, -290 mV for CoNi based and -425 mV for Ni based. Comparing the activity of the catalysts with the same hyper *d*-metallic phase with different form of TiO₂, it is obvious that the catalysts containing anatase are more active than those containing non-crystalline TiO₂, except for CoNi based system where the activities are almost the same. For instance, for Co based catalysts this difference at 60 mA·cm⁻² is 15 mV, for CoNi based 0 mV and even 60 mV for Ni based. As mentioned above, the stronger metal-support interaction is achieved between crystalline TiO₂ and the hyper *d*-metallic phase. Otherwise, hyper *d*-metallic component gives the prevailing catalytic activity, while hypo *d*-electronic phase contributes to the overall synergetic effect of such composite electrocatalyst by so called Strong Metal Support Interaction (SMSI) [6,7]. The hypo-oxide phase is not only a support, but also active and significant part of the catalyst, which provides the second, bifunctional role. Thus, TiO₂ is a component that improves the catalytic activity in this case.

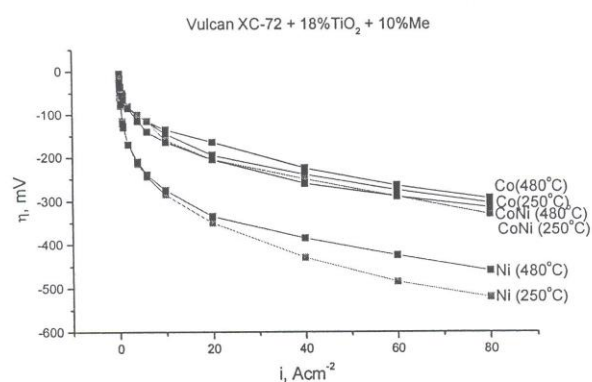


Fig 4. Polarization curves of the investigated catalysts for hydrogen evolution in alkaline solution

4. CONCLUSION

As main conclusion of the electrochemical investigations one can mention that:

- 1) Applying the modified sol-gel procedure we produced catalysts that exhibit pronounced synergetic effect for the hydrogen evolution reaction. Among the 6 prepared and tested hypo oxide-hyper metal *d*-catalysts, the most active were those with Co and CoNi phases.
- 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.
- 3) Thermal treatment of the metal support (hypo oxide *d*-phase) at 480°C where anatase crystalline TiO₂ was obtained, contribute to stronger metal-support interaction as result the higher electrocatalytic activity was achieved.