

Co and W alloys as catalysts for evolution of H_2 at elevated temperatures

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Cathodes for evolution of H_2 were prepared by electrochemical deposition of Co and W on Ni or Ti. The morphology and the microstructure of the electrodes were characterized by scanning electron microscopy and X-ray diffraction and the electro-catalytic efficiency was evaluated based on steady-state polarization curves, Tafel plots and electrochemical impedance spectroscopy. It was shown that the electro-catalytic activity of the prepared electrodes is dependent on the morphology and microstructure of the Co and W deposits. Similar to Pt, the catalyst has a low charge transfer resistance, high exchange current density and electro-catalytic activity, with respect to HER.

Keywords: Tungsten, cobalt, catalysts, hydrogen evolution, PEM, HER.

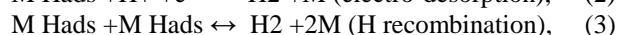
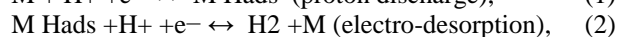
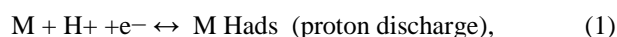
INTRODUCTION

There is a need to find stable and cheap electrocatalysts for the PEM cell with low overpotentials [1]. However, except for noble metals such as Pt, Rh, Re, Pd, Ir, most other less-noble pure metals have a much lower activity in the HER [2]. The ability of a metal to catalyze the HER is measured by the exchange current density, which is the rate of hydrogen evolution per surface area at the equilibrium electrode potential. Different metals have different exchange current densities. While a four-fold increase in current density was observed for Pt-Ru supported on double-walled carbon nanotubes as high-performance anode catalysts [3], these materials are still expensive to produce and the search is on developing inexpensive non-precious metal materials. Platinum loadings as low as 0.014 mg/cm² have been reported using novel sputtering methods [4] and as a consequence the cost of the catalyst is no longer the major barrier to the commercialization of PEM fuel cells. It was first demonstrated in 1964 that transition metal porphyrins, namely cobalt phthalocyanine (CoPc) could act as oxygen reduction reaction (ORR) electrocatalysts in alkaline conditions [5]. Very high power densities have been achieved at low temperatures in both dual-chamber and single-chamber fuel cells using Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} as the cathode [6]. The attempts to design a material that would approach the electrochemical activity of

noble metals have lead in the past to 3d transition metal-based binary alloys of Ni- or Co [7]. Long-term performance durability tests in an H_2 -air fuel cell with Co-PPY-C composite material as the cathode catalyst have demonstrated a high power density in the past [8]. More recently a kinetic study of electron transfer reactions of H_2 -evolving Co-diglyoxime catalysts suggested that the covalent linking of two Co-hydride complexes could substantially increase the rate of H_2 production by decreasing the volume required for diffusional collisions at modest overpotentials [9]. The three principal routes to follow in order to deal with slow reaction rates are: using novel catalysts, raising the temperature and increasing the electrode area. Overall research has focused on: the intrinsic nature of the reaction, the electrode composition, the surface morphology, the electronic properties and electrochemical activation treatments.

THEORY AND EXPERIMENT

The hydrogen evolution reaction (HER) proceeds on a metallic electrode M via three mechanisms [1]:



Mechanisms (1) and (2) require the formation and cleavage of M Hads bonds and the HER rate is determined by the strength of proton adsorption bonding to the metal surface. Thus, the maximum rate of hydrogen evolution can be expected at intermediate values of M Hads bond strengths, resulting in the well known ‘volcano curve’ [2].

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The view has been that the combination of two transition metals would result in an enhanced HER electrocatalytic activity. Indeed, the Tafel and EIS results presented in [7] showed that alloying Ni with left-hand side transition metals (Fe, Mo, W) yielded an increased electrocatalytic activity in the HER when compared to pure Ni. These results demonstrated that the design of high-activity HER electrocatalysts could be based on the increase of both active surface area and intrinsic activity of the material. While the former can be achieved by a proper choice of material and synthesis method an increase in the intrinsic activity can be achieved by a proper combination of left- and right-hand side transition metals [7]. It has been generalized that the intrinsic catalytic activity for the HER can be related to the electronic structure of metals. The theory of transition metal-based alloys has been discussed by Jaksic [10] on the basis of the Engel–Brewer valence-bond theory, as a generalized Lewis acid–base reaction model [11]. The assumption is that the elements Mo and W have partially or half-filled d-orbitals and interact with the internally paired d-electrons of transition metals, such as Ni, Pd, Pt, Co. As a result the strength of bonding is changed and leads to increased intermetallic stability. Another theory of the HER on bimetallic catalysts has been postulated by Ezaki et al. [12]. The concept of Ezaki was based on experiments involving the assessment of the hydrogen overpotential and its interpretation using electronic structure calculations [13]. Co and CoW alloys have been electrodeposited under potentiostatic conditions in a commercial three-electrode cell (Co as the anode and SCE as the reference electrode) with EG&G PAR – Versastatt, SoftCorr 352. Copper plate, nickel foam, titanium felt and carbon felt have been used as substrates. The electrolytes contain CoSO₄·7H₂O, CoCl₂·H₂O and H₃BO₃ for Co films and CoSO₄·7H₂O, Na₂WO₄·2H₂O as a complexation agent for CoW alloys. The potential is kept at -0.8V (vs.SCE) for Co films and -0.9, -1.0, -1.1, -1.2, -1.3V (vs.SCE) for CoW alloys on copper plate substrates at a temperature of 40°C and 70°C, respectively. X-ray fluorescence analysis has been employed to determine the cobalt and tungsten distribution in the coatings. A scanning electron microscope - JEOL JSM 6390 with INCA Oxford has been applied for examining the surface morphology and specific distribution of the elements. Electrochemical measurements have been conducted in order to evaluate the electro-catalytic activity of the developed catalysts. A standard three-electrode cell with a liquid electrolyte has been used for cyclic

voltammetry and galvanostatic curves in an alkaline solution, C_{KOH}= 1M.l⁻¹. The electrodes have a working area of S=1 cm². The reference electrode for a liquid electrolyte was an H₂ electrode, “Gascatel”. A “Solartron” electrochemical interface was used for conducting cyclic voltammetry, steady-state galvanostatic curves and long-term tests. Measurements with solid acid and Nafion membranes were conducted in a cell similar to standard fuel cells. A drawing of the cell is shown in Fig. 1. It has Ti plates between which an MEA has been tested. The working electrode was a Co and W catalyst deposited on titanium or carbon felt. The counter electrode was a standard Pt on carbon paper fuel cell electrode (E-Tek), working with hydrogen as the anode (hydrogen oxidation).

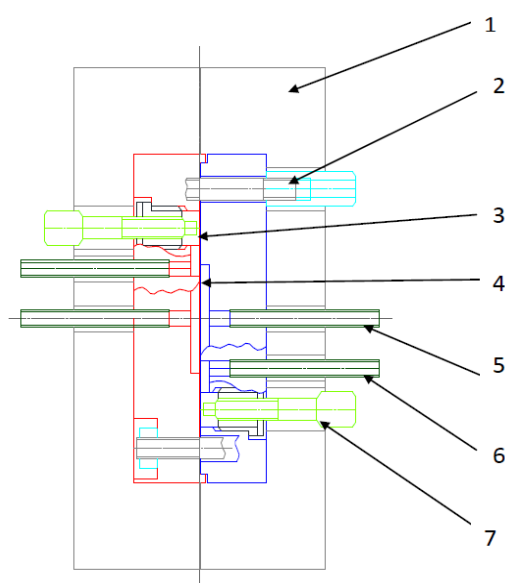


Fig. 1. Drawing of the electrochemical cell. 1 – fuel cell body, 2 - pin and collar, 3 – PEM, 4 – electrode and counter electrode, 5 - steam (H₂O) input/ output, 6 – hydrogen (H₂) input/ output, 7 - lead channel to comparison electrode

RESULTS AND DISCUSSION

The results show that under -0.9 and -1.0V (vs. SCE) the alloy contents almost equals the amount of Co and W. The amount of W decreases when the potential shifts to more negative values (Table 1). This is the reason to choose -1.0 and -1.2V potential regimes of deposition for the next experiments on nickel foam, Ti and C – felt, which correspond to the relations Co/W as 50 wt. % to 50 wt. % and 70 wt. % to 30 wt. %, respectively. The decrease in the amount of tungsten when shifting the potential towards more negative values is probably due to an increase in hydrogen evolution on the electrode, which is catalyzed by the presence of tungsten.

Table 1. The element contents in the alloy under different potential conditions on the copper plate substrate.

	-0.9 V	-1.0 V	-1.1 V	-1.2 V	-1.3 V
Co, wt%	53	50	66	70	76
W, wt%	47	50	34	30	24
Thickness, μm	0.2	0.3	0.4	0.2	0.2

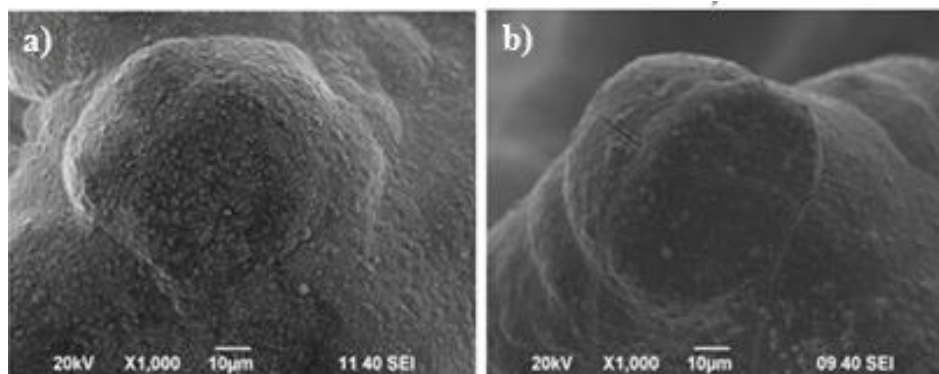


Fig. 2. SEM pictures of deposited Co-W films on Ni-foam at cell voltages: -1.0 V (a) and -1.2 V (b)

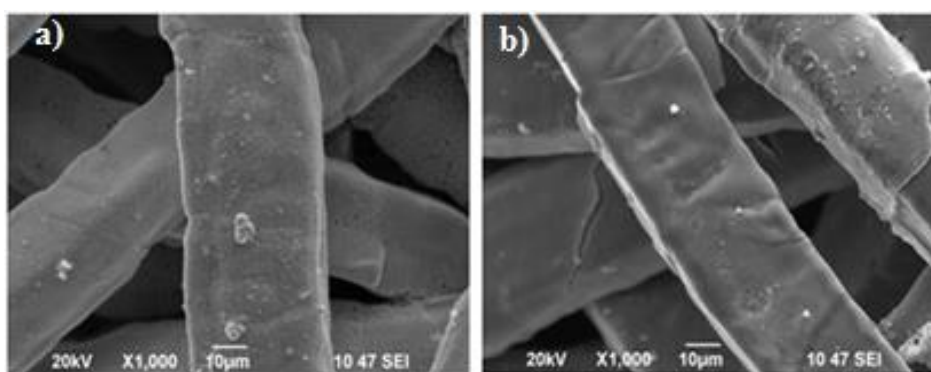


Fig. 3. SEM pictures of deposited Co-W films on Ti-felt at cell voltages: -1.0 V (a) and -1.2 V (b)

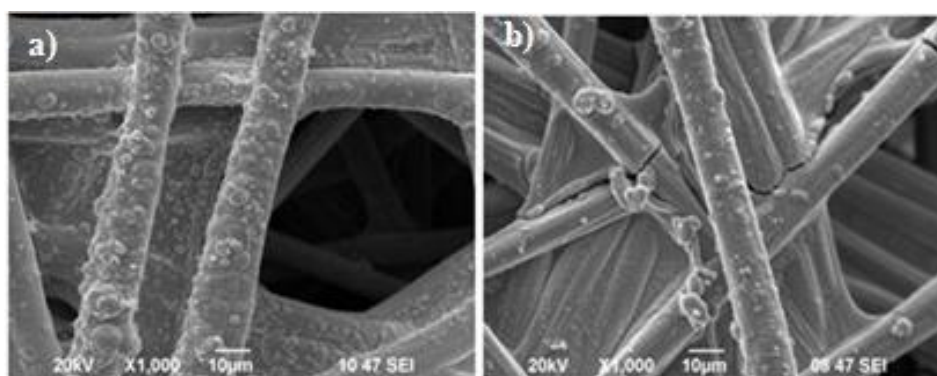


Fig. 4. SEM pictures of deposited Co-W films on C-felt at cell voltages: -1.0 V (a) and -1.2 V (b)

Table 2. The element contents in the alloy under different potential conditions on copper plate, Ti felt and carbon paper substrate.

Support	Cu plate		Ti felt			Carbon paper	
Cell potential (V)	-1.0	-1.1	-1.0	-1.1	-1.2	-1.0	-1.2

Co, wt %	44	43	47	42	80	50	86
W, wt %	53	47	47	52	20	45	11
Oxygen, wt %	3	10	6	6	0	5	3

Table 3. Composition of electrochemically tested electrodes.

No	Support	Anode	Co, wt %	W, wt %	O ₂ , wt %	Cell voltage (V)
1	Cu plate	Pt, Ti	68.5	31.5	-	1.0
2	Cu plate	Co	55.0	45.0	-	1.0
3	Ti felt	Co	55.0	45.0	-	1.0
4	Ti felt	Co	47.0	47.0	6	1.0
5	Ti felt	Co	42.0	52.0	6	1.1
6	Ti felt	Co	42.0	52.0	6	1.1

The morphology of the deposited Co and W films is seen on the pictures shown in Figures 2, 3 and 4. The coatings are characterized by cracks at the more negative potential and poor adhesion to the substrate, but they possess a fine crystalline structure. A large amount of tungsten is measured by point EDX analysis as recorded at the convex part of the surface in contrast to the inner (recesses) one, wherein cobalt is prevailing. The probable cause for the disjoint distribution is mass transfer.

The compositions of the deposited alloys shown in the pictures above are as presented in Table 2. From the pictures and alloy compositions it is clear that under a higher cell voltage the Co percentage increases. The deposited film is stable and equally covers the support for Cu and Ti. For carbon paper the coverage is rougher.

The cyclic voltammograms of selected electrodes are presented in Fig.5. The electrolysis conditions and composition of electrodes are as presented in Table 3.

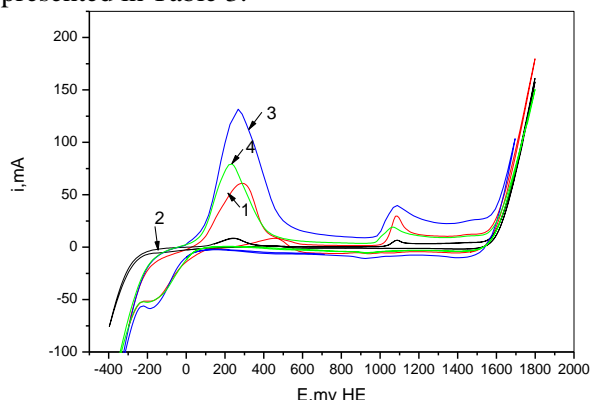


Fig. 5. Cyclic voltammo curves for all tested electrodes with compositions as in Table 3. At 20 mv/s the dependence curves for electrodes 1, 2, 3 and 4 are shown as indicated.

From Fig.5 it is clear that with the increase of tungsten in the alloy, the peaks intensity increases too. The hydrogen evolution starts at lower potentials for electrodes 3 and 4, where the tungsten

percentage is higher. Obviously tungsten is responsible for the higher catalytic activity of the alloys. The galvanostatic VA curves shown in Fig. 6 confirm the relationship between the percentage of tungsten and the catalytic activity of the electrodes.

A comparison between Pt on carbon paper (E-tek), Ti felt and the best of our electrodes, No. 5 is presented in Fig.7. The results show an excellent activity of the Co-W alloys prepared by electrochemical deposition. This is observed for the Tafel slopes shown in Fig. 8. They are identical for Pt and Co-W and equal to $b=34-36$ mV/dec, which corresponds to the Tafel mechanism of hydrogen evolution.

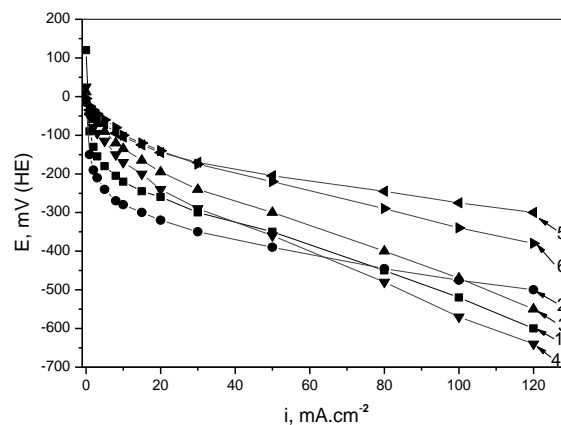


Fig.6. Galvanostatic VA curves for all electrodes with compositions as in Table 3; electrolyte, 20 % KOH. Dependence curves for electrodes: 1- ■, 2-●, 3 - ▲, 4 - ▼, 5 - ◀ and 6 - ▶, are shown as indicated.

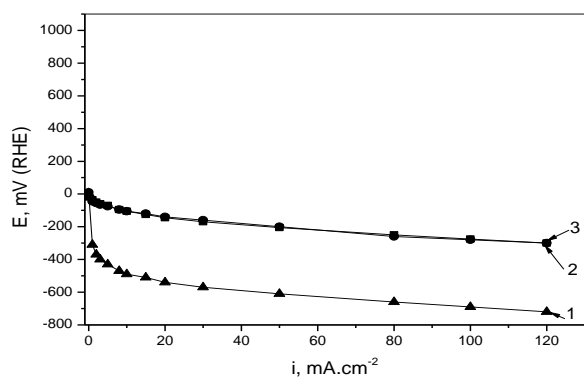


Fig. 7. Galvanostatic VA curves for the best electrode composition; electrolyte 20 % KOH. Dependence curves for electrodes: 1-▲Ti mr., 2-●Pt, 3-■ electrode-No. 5, are shown as indicated.

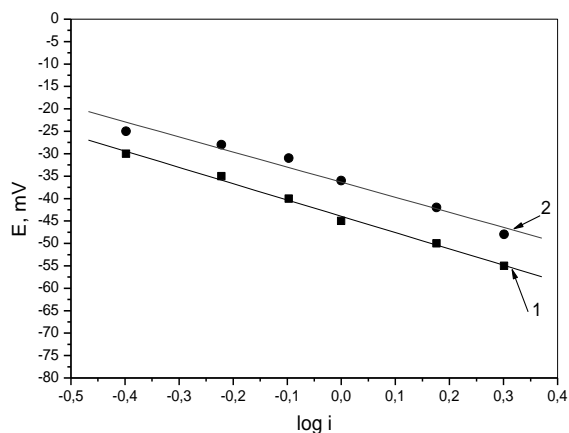
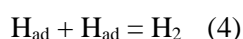


Fig. 8. Tafel relationships derived from Fig.7. 1-■ Pt (b = -36mV), 2 - ● electrode No. 5 (b = -34mV).

Based on the value of $b=33$ mV we may conclude that the hydrogen evolution reaction on our catalyst follows Tafel's mechanism in accordance with the reaction:



The best composition of a Co-W alloy was deposited on Ti felt, producing an electrode with a geometrical area of 4 cm². The electrodes were tested in an electrochemical cell at temperatures of 20 and 60°C with a Nafion membrane. The counter electrode was a Pt/C fuel cell electrode from "E-Tek" working with hydrogen as the anode. The results in KOH (kinetically favored) and acid electrolyte (Nafion) are similar, which shows again the excellent activity of the developed catalyst.

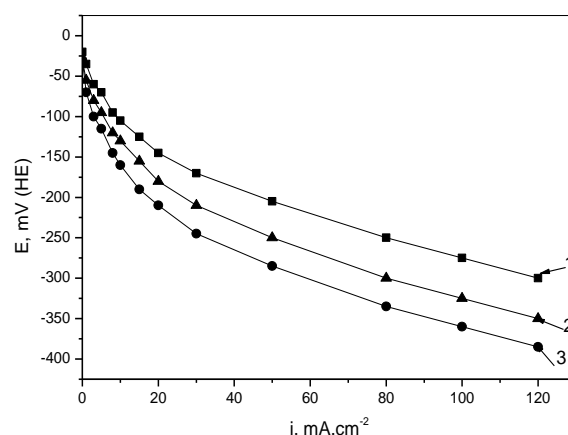


Fig. 9. Galvanostatic VA curves for an electrode with a composition as electrode No. 5 in different electrolytes: 1-■ 20%KOH, 25 °C; 2-▲ PEM 60°C; 3-● PEM 20°C.

CONCLUSIONS

The kinetic parameters, indicative of a high HER activity, were determined using linear polarization. The results presented clearly demonstrate that tungsten causes an increase in the electrocatalytic activity probably due to the modified electron density of states at the Fermi level dependent on the variation of the Co/W content ratio. Our studies also indicate an improvement in the electrocatalytic activity for a high W content. The decrease in the amount of tungsten for different Co/W content ratios and shift of the potential towards more negative values is probably due to an increase in hydrogen evolution on the electrode, which is catalyzed by the presence of tungsten. Hydrogen evolution starts at lower potentials where the tungsten percentage is lower. A fuel cell power density of 450 mW cm⁻² has been reported for pyrolyzed binary FeCo-N/C complexes [14] while for pyrolyzed FeCo-PANI/C the values are 550 and 560 mW cm⁻² [15]. In the future we need to seek out innovative synthesis methods to produce self-supported, active, high surface area, stable non-precious metal catalysts.

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Co/W СПЛАВИ КАТО КАТАЛИЗАТОРИ ЗА ПОЛУЧАВАНЕ НА H₂ ПРИ ВИСОКИ ТЕМПЕРАТУРИ

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(Резюме)

Изследвани са Co/W сплави като катализатори за получаване на H₂. Co/W сплави са нанесени електрохимично върху Ni или Ti подложка. Морфологията и микроструктурата на електродите са характеризирани с помощта на сканиращ електронен микроскоп и рентгенова дифракция. Електрокаталитичната активност бе определена с помощта на поляризационни криви, Тафелови наклони и електрохимична импедансна спектроскопия. Показано е, че електрокаталитичната активност на изработените електроди зависи от морфологията и микроструктурата на нанесения слой от Co и W. Подобно на Pt, катализатора има ниско съпротивление на пренос на заряд, висока плътност на обменния ток и електрокаталитична активност по отношение на HER.

