

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).

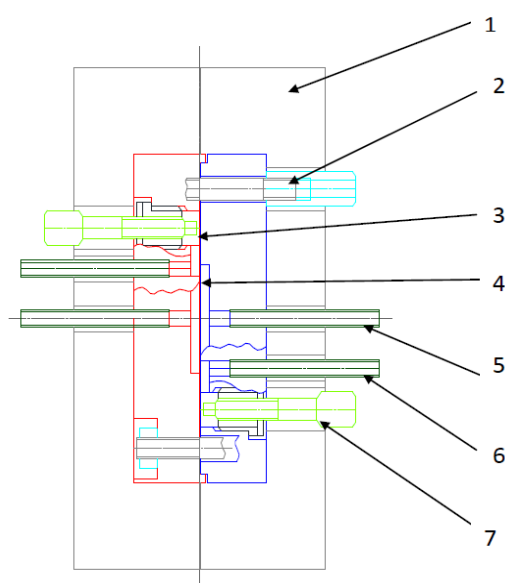


Fig. 1. Drawing of the electrochemical cell. 1 – fuel cell body, 2 - pin and collar, 3 – PEM, 4 – electrode and counter electrode, 5 - steam (H₂O) input/ output, 6 – hydrogen (H₂) input/ output, 7 - lead channel to comparison electrode

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.