Nickel - wolfram modified carbon fibers - CVA, SEM and IS investigation

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The possibility of the creation and application of an electrocatalytically active material on the basis of modified carbon fibers – electrolytically deposited nickel-wolfram was investigated. Non-oxidized and oxidized by a specific procedure carbon fibers were used. Trough this procedure a significant quantity of -COOH groups is formed on the carbon surface [1]. The nickel-wolfram alloys, which have different structure and varying wolfram concision, were deposited from three different electrolytes. The kinetic of the deposition on the carbon substrates was examined by CVA. Probes obtained in potentiodynamic way (after running the cathodic part in the area of potentials from 0 to –1.8 V vs. SCE) were investigated by SEM. The SEM micrograph in Fig. 1 shows a characteristic growth (of a corn cob type) with clearly distinct globular Ni-W crystallites.

Carbon fibers which were previously pretreated at various potentials in a Ni-W electrolyte solution were studied in a buffer solution which did not contain any Ni-W salts. An interesting effect was observed. At potentials –0.2 V and –0.9 V, i.e. lower than the deposition potential (-1.1 V) characteristic peaks attributed to a Ni-W dissolution process were obtained (Fig 2). Such reaction is not observed in the case of non-oxidized fibers. This fact is attributed to an ion-exchange process which takes place on the –COOH groups at a definite potential value.

The electrocatalytic activity of the prepared systems was studied by means of impedance spectroscopic measurements for the hydrogen evolution reaction in aqueous H_2SO_4 solutions. The lower the velocity of the Ni-W deposition is, the lower the R_{ct} value is (Table 1). The Rct values for the Ni-W-modified oxidized fibers are significantly lower in comparison with the corresponding values for the Ni-W-modified non-oxidized fibers, indicating stronger electrocatalytic efficiency.

References

[1] A. D. Jannakoudakis, P. D. Jannakoudakis, E. Theodoridou and J. O. Besenhard, J. Appl. Electrochem., 20 (1990) 619.

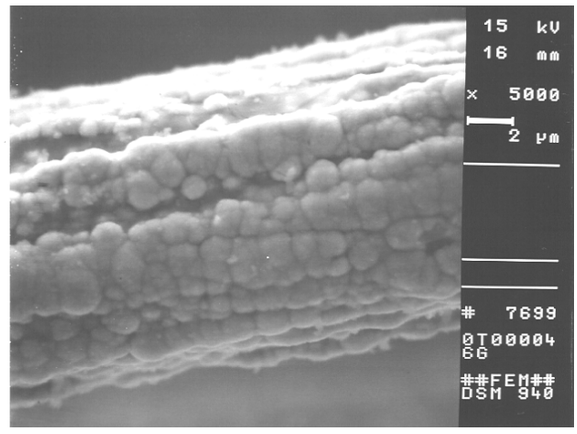

Fig. 1. SEM-micrograph of Ni-W-modified oxidized carbon fibers (electrolyte: $Ni(NH_2SO_3)_2$ 80 g/L Ni, $NiCl_2$ 10 g/L, $NaWO_4$ 10 g/L, Na citrate 30 g/L, H_3BO_3 36 g/L, υ = 2 mVs^{-1}).

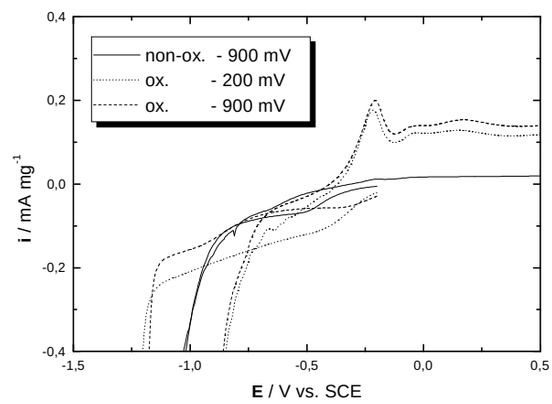

Fig. 2. Cyclic voltammograms (in pure buffer solution, pH=4) of non-oxidized and oxidized carbon fibers pretreated previously in the Ni-W electrolyte solution at various potentials, υ = 2 mVs^{-1}).

υ (mVs^{-1})	R_{ct} (Ωmg^{-1})	
	Non-oxidized	**Oxidized**
50	11.5	5
10	8.4	3
2	5.1	1.5

Table 1. Ni-W-modified carbon fibers ($NaWO_4$ 10g/L)