Electrocatalytic oxidation-reduction reactions of metal-hydride alloys with teflon-carbon additives

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Model metal hydride (MH) electrodes for fast screening of MH alloys electrochemical performance have been developed in a former work of ours. The effect of additives (teflonized blacks or carbons) on the electrodes character-istics has been demonstrated. An attempt to explain this effect and to create a physical model of the reactions taking place in the MH electrodes has been done in the present study. Our working hypothesis is that simultaneous reactions of carbon oxidation and reduction of MH oxides are taking place thus creating spread out micro-galvanic elements.

The additivity principle has been applied in order to explain and to prove the electrochemical mechanism of the process. Partial polarization curves have been measured in order to demonstrate the possibility of working hypothesis. An original approach for quantitative estimation of the rate of the general reaction has been developed and applied by measuring: (i) X-ray diffraction and Impedance Spectroscopy for explanation of additives effect; and (ii) Real galvanic element between carbon free MH electrode and electrode with teflonized carbon blacks only is constructed and tested to prove the working hypothesis.
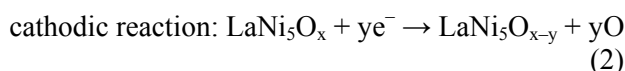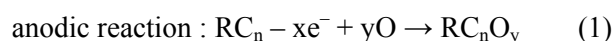
Key words: Metal hydride electrode, fast screening method.

INTRODUCTION

The fast electrochemical screening of different MH alloys is an effective tool in the development of Ni-MH batteries. Straightforward model electrodes for preparation and testing have been developed in a former work of ours [1]. The electrodes consist of MH alloys particles and teflonized blacks or carbons used as additives (binding agents) [2]. The effect of additives on the electrochemical perform-ance of the electrodes has been mentioned. The electrodes with teflonized Vulcan XC-72 have demonstrated a much better performance compared to the electrodes with teflonized blacks (Acethylene black) or teflonized carbons (Norit NK). The MH electrodes with teflonized Vulcan XC-72 are reaching their theo-retical capacity after two cycles and remain stable with time. One possible explanation of such an effect is the reaction between the MH alloy and the carbon blacks leading to reduction of the alloy surface oxides. It is known that the $LaNi_5$ particles are partially oxidized during electrode preparation. The purpose of the first several cycles is the reduc-tion of these oxides. Then the reaction of hydriding-dehydriding progresses rapidly, i.e. following a number of cycles the electrode capacity reaches a plateau [3, 4].

Our hypothesis is that oxidation-reduction reactions on spread micro galvanic elements are taking place. Such reactions are well known in the literature [5–9]. Due to the thermodynamical redox potentials differences of $LaNi_5$ oxides (mainly NiOx), $E_0 = 1.59$ V, and carbon, $E_0 = 0.50$ V, galvanic elements are created within the electrode pores. The nickel oxides on the MH particles surface are reduced and the carbon in the teflonized carbon blacks is oxidized. The partial reactions are possibly the following:

$$\text{anodic reaction}: RC_n - xe^- + yO \rightarrow RC_nO_y \qquad (1)$$

$$\text{cathodic reaction}: LaNi_5O_x + ye^- \rightarrow LaNi_5O_{x-y} + yO \qquad (2)$$

Most probably these are mainly nickel oxides reduction reactions, for example: $NiO_2 \leftrightarrow Ni(OH)_2$.

Possible physical model of such scattered micro-galvanic elements is schematically illustrated in Figure 1. It shows the structure of an electrode com-prising the teflonized blacks fibres and bonded to them particles of metal-hydride alloy. Metal alloy particles and carbon in teflonized blacks have direct electronic contact. Within the electrode pores the metal and carbon particles realize an ionic (elec-trolytic) bond through the electrolyte, thus providing the necessary conditions for creation of galvanic element ($LaNi_5O_x$-C). The mixed electrode potential is established. The surface oxides reduction reaction (left side) proceeds on metal alloy particles, while

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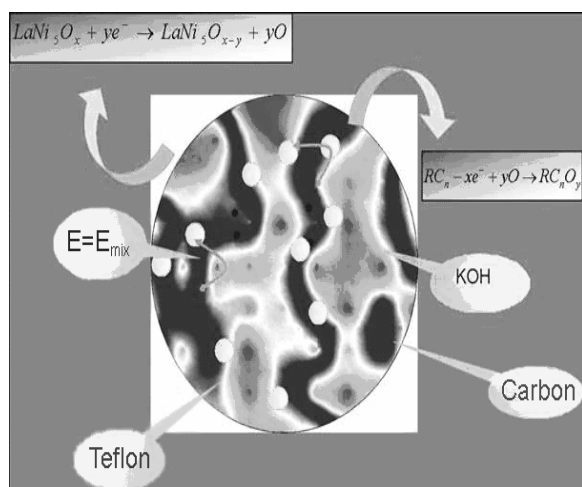the oxidation reaction proceeds on carbon particles (right side).

Fig. 1. Physical model of carbon-teflon electrode with spread micro-galvanic elements for electrocatalytic reactions of mMe:Ni:Co reduction and carbon oxidation in KOH electrolyte.

In the classical case of application of additivity principle [5, 6] there is an independent method to measure the rate of the overall reaction. In our case we cannot measure analytically the rate of carbon oxidation or metal oxides reduction. Following methods have been applied for independent estimation of the rate of the overall reaction: (i) X-ray analysis; (ii) Electrochemical Impedance Spectroscopy; and (iii) measurement of the current of real galvanic element between carbon free MH electrode and electrode with teflonized carbon blacks only.

EXPERIMENTAL

Standard metal hydride alloy produced by "Traibacher" with composition La:mMe:Ni:Co = 33:57:10% has been used for the MH electrodes preparation. The grain sizes of the supplied alloy are near 2 mm, grownd down to 0.063 mm. Three teflonized carbons (blacks) are tested: Vulcan XC-72, Acetylene black and Norit NK.

The Vulcan XC-72 carbon blacks are manufactured by "Cabot Corp.", USA. They have an active surface area of near 200 m^2/g. Their structure and composition are not disclosed by the company, however it has been confirmed that they have high electrochemical activity and are utilized for batteries and fuel cells electrode preparation worldwide. The Acetylene black are virtually pure carbon. They are produced by acetylene burning in oxygen free environment and virtually have no functional groups. Their surface area is close to 60–70 m^2/g. The Norit NK is an active carbon manufactured by "Norit Co." and utilized primarily for medical purposes. Its

surface area is approximately 600 m^2/g, while its structure and composition are proprietary for the company.

The electrodes are prepared from a mixture of metal alloy and teflonized carbons (TC) in weight proportion of 60:40. The mixture is pressed onto a current collector formed from a nickel mesh at room temperature and pressure of 200 atm. The optimization of the ratio between the MH alloy and the teflonized carbons in parallel with the preparation procedure is described in our former work [3]. The geometrical area of the electrodes is either 1 cm^2 or 5 cm^2.

The electrochemical measurements are conducted in a three-electrode cell at room temperature. The counter electrode is a nickel plate, the reference electrode being Hg/HgO. The electrolyte is 8 M KOH. The Impedance Spectroscopy is carried out on an Autolab PGSTAT30/2 with an auxiliary FRA 2 (Frequency Response Analyzer). The measurements are performed under potentiostatic control with sine signal amplitude of 10 mV at an operating temperature of 20°C. The measured frequency span is from 0.1 kHz to 1 MHz. The X-ray measurements are carried out on a Philips APD-15 apparatus with copper luminous Cu Kα, λ = 1.54178 Å and graphite monochromator. A "Tacussel Electronique" BI-PAD Galvanostat/Potentiostat type is used for the electrochemical tests. All presented results reflect the average value of a minimum of three measured electrodes.

EXPERIMENTAL RESULTS

Oxidation-reduction reactions partial curves

The partial curves are plotted under galvanostatic control conditions. For the carbon oxidation anodic partial curves 1 cm^2 electrodes have been used prepared only with teflonized Vulcan XC-72, Acetylene black or Norik NK. MH alloy plus teflon powder electrodes have been utilized for the surface oxides reduction cathodic partial curves.

The partial curves are presented in Fig. 2. It is evident that the two partial curves intersect and the cross point's co-ordinates give the mixed current (i_m) and the mixed potential (E_m) values. It is apparent that the partial curves for the three additives bear similarity. All intersects with the reduction partial curve lay within its negative domain $(E_P)_κ < (E_P)_{Me}$, hence there are grounds for a $LaNi_5O_x$-C micro-galvanic element emergence.

Figure 3 presents the details on large scale. The partial curves for oxidation of Vulcan XC-72 and reduction of MH alloy plus teflon powder are not shown. The cross point corresponds to a mixed

current i_m = 0.12 mA·cm^{-2} and a mixed potential of E_m= 205 mV. The Figure 3 illustrates the potential deviation as well, which is close to ±10 mV. Such potential deviation is quite normal for porous electrodes with highly developed surface. Consequently the calculated value for the current is approximate and close to i_m ~ 0.1 mA·cm^{-2}. Additionally, Figure 3 presents the open circuit potential for an electrode containing LaNi$_5$ and teflonized Vulcan XC-72. This potential varies within the range of 160–220 mV and we have concluded that there is a good agreement for the calculated from the partial curves and the measured on the real electrode open circuit potentials. This has supported our belief that the proposed mechanism for oxidation-reduction reactions on micro-galvanic elements is really taking place.
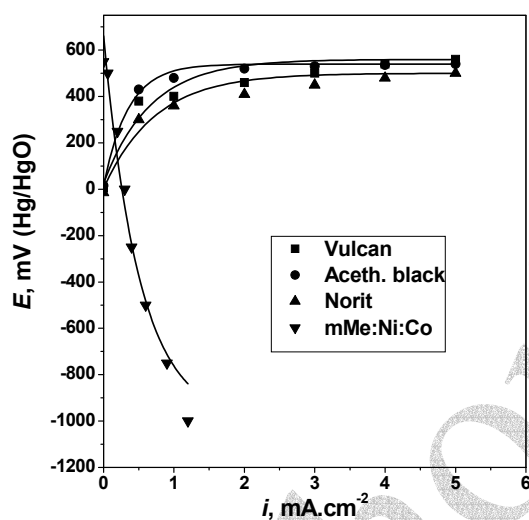

Fig. 2. Partial curves for reduction of mMe:Ni:Co - ▼ and oxidation of teflonized Vulcan XC-72, acetylene black and Norit NK.

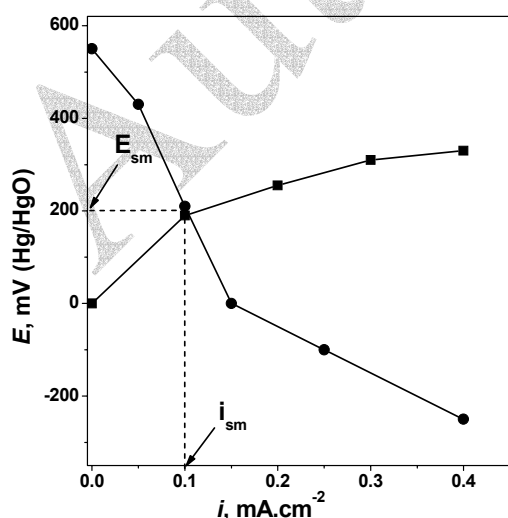Fig. 3. Partial curves for reduction of mMe:Ni:Co +PTFE (●) and oxidation of teflonized Vulcan XC-72 (■).

X-ray analysis

Two types of electrodes have been analyzed – the first one prepared from teflonized Vulcan XC-72 and LaNi$_5$, and the second one produced from teflonized Acetylene black and LaNi$_5$. The analysis has been conducted on dry prepared electrodes and after they have been submerged in 8 M KOH for 15 hours. Our concept for this kind of experiment is that during the time of electrodes soaking wet in the electrolyte, a micro-galvanic element of the LaNi$_5$O$_x$-C type will be created. This will, probably, result in LaNi$_5$ surface oxides reduction.

Figure 4 depicts the X-ray analysis of dry and soaked in 8M KOH for 15 hours electrodes prepared with a Vulcan XC-72 additive: the curve 1 - dry electrode corresponds to the non-soaked electrode, while curve 2 is for the soaked electrode. The peaks belonging to the NiO$_x$ are denoted by "(2)", indicating that on the surface there are predominantly NiO$_x$. The peaks at 2θ = 44° correspond to the LaNi$_5$O$_x$ (Figure 4, 5). The intensity of the dry electrode is higher. This change however is not substantial to support our belief for visible reduction of the surface oxides that would back up our working hypothesis. The same is true for the peaks at 2θ = 52° and 77° belonging to the NiO$_x$.
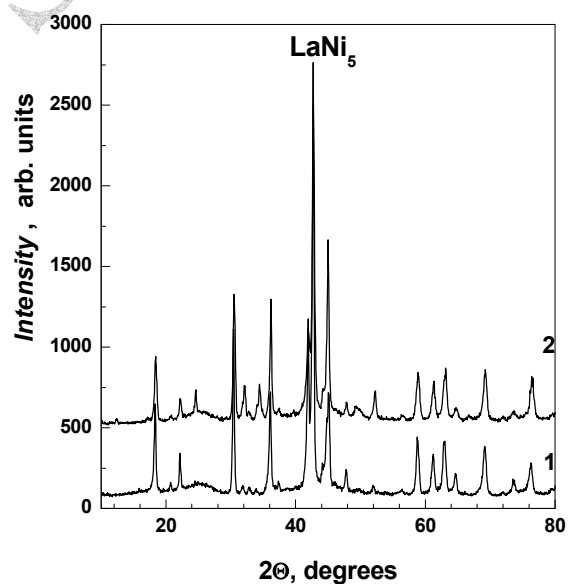

Fig. 4. X-ray diffraction pattern measured for dry and soaked mMe:Ni:Co electrodes; T = 25ºC; 8 M KOH; additive: teflonized Vulcan XC-72; 1 - dry electrode; 2- soaked electrode; time of wetting 15 hours.

X-ray diffraction pattern (pictures the X-ray analysis) of electrodes prepared with teflonized Acetylene black and LaNi$_5$ (Figure 5) bearing similarity to X-ray diffraction pattern in Figure 4, though the difference between the soaked and non-soaked electrode is practically absent.
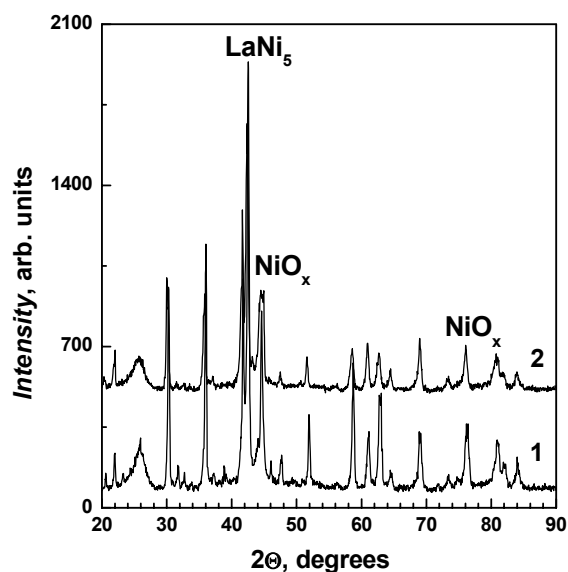
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Fig. 5. X-ray diffraction pattern measured for dry and soaked mMe:Ni:Co electrodes; T = 25ºC; 8 M KOH; additive: teflonized Acetylene black;   1- dry electrode; 2 - soaked electrode; time of wetting -15 hours.

Electrochemical impedance measurements

According to our working hypothesis, the micro-galvanic elements ($LaNi_5O_x$-C) are created as soon as the electrodes are wetted and the oxidation-reduction reactions proceed until the reagents depletion, i.e. up to their chemical potential equalization. For these reasons the impedance measurements have been initiated immediately after the electrodes submergence. Figures 6, 7 and 8 depict the impedance spectra for 1 cm^2 electrodes prepared correspondingly with additives of Vulcan XC-72, Acetylene black and Norit NK. The electrolyte resistance of the three diagrams is uniform and close to R_L–0.5 Ω, which serves to demonstrate the good reproducibility of the results [10]. The electrochemical impedance spectra of the electrodes containing teflonized blacks, Figures 6 and 7 correspondingly for Vulcan XC-72 and Acetylene black follow an analogous pattern, which validates the fundamental similarity of the reactions [11]. Two processes are distinguished which occur at high and low frequency zones. The steep slope indicates the reactions capacitive nature with emphasized transport hindrances. The CPE (Constant Phase Element) existence suggests the presence of reduction products and particles that are not prone to dissolution. The low frequency zone represents a well-shaped semicircle, which is indicative of a reaction. Quantitatively, the reaction resistance for the Vulcan XC-72, Figure 6, is much lower compared to that for the Acetylene black electrodes, Figure 7. The ideal circle distortion makes us believe that more than a single process occurs,

possibly a number of mixed (corrosion) reactions with closely spaced time constants. The curves traces, supported by basic corrosion considerations, lead us to the conclusion that the carbon oxidation is the hindered reaction.
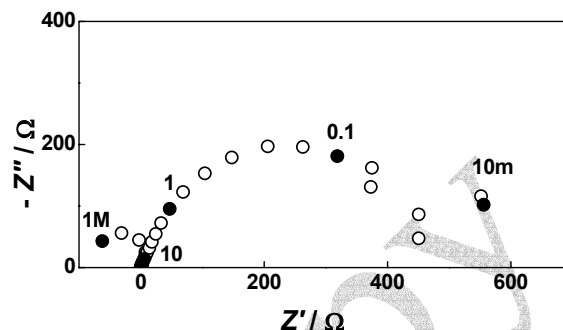

Fig. 6. Electrochemical impedance spectroscopy of mMe:Ni:Co electrode with additive teflonized Vulcan XC-72.
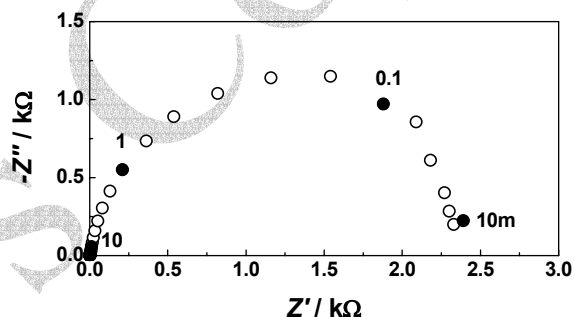

Fig. 7. Electrochemical impedance spectroscopy of mMe:Ni:Co electrode with additive teflonized Acetylene black.
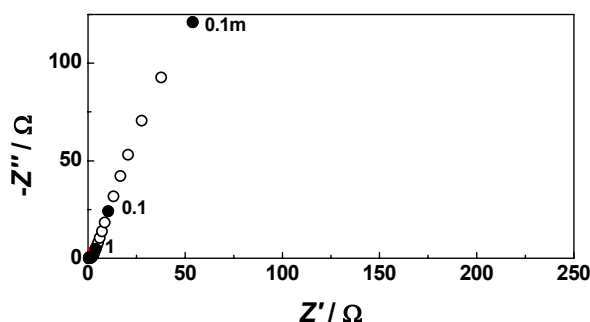

Fig. 8. Electrochemical impedance spectroscopy of mMe:Ni:Co electrode with additive teflonized Norit NK.

The electrodes prepared with the Norit NK have electrochemical impedance diagram again displayed within two zones, low- and high-frequency ones. It is worth mentioning that the low frequency zone is characterized by a very high resistance and it is rate determining for the process. This is most probably due to the carbon (Norit NK) presence whose crystal structure oxidation is considerably hindered.

The electrochemical impedance measurements lead us to the following conclusions: the reaction

resistance is lower than that for the electrodes with teflonized blacks (being lowest for Vulcan XC-72), where in all probability more than a single mixed (corrosion) reaction occurs and the rate determining step is the carbon oxidation reaction.

Practical LaNi₅Oₓ-C galvanic element preparation and corresponding measurements

Aiming to prove our working hypothesis we have prepared a real $LaNi_5O_x$-C galvanic element. The electrodes have geometrical surface area of S = 5 cm^2. The anode consists of teflonized Vulcan (50 $mg \cdot cm^{-2}$) only. The cathode is made of 100 $mg \cdot cm^{-2}$ MH alloy + 12 $mg \cdot cm^{-2}$ teflon powder. The cathode teflon powder content has been optimized in advance within the range of 10 to 15 $mg \cdot cm^{-2}$. The electrodes were mounted in a cell filled with 8 M KOH electrolyte. The current of the real galvanic element was measured by short-circuiting it *via* an ampermeter, while the cell voltage was measured with a voltmeter. The galvanic element block diagram is shown in Figure 9. The current and voltage measurements have been started immediately after the electrodes were submersion into the electrolyte.
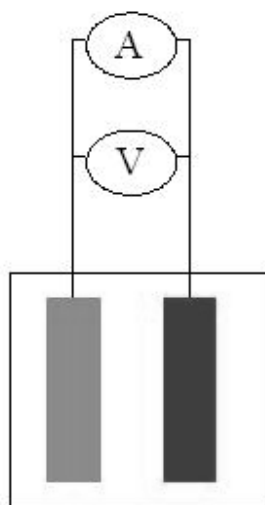

Fig. 9. Scheme of galvanic element; A- anode; B- cathode; ampermeter; voltmeter.

Figure 10 illustrates the relationships of short-circuit current *vs* time for galvanic elements comprising a MH alloy cathode and anodes made of teflonized Vulcan XC-72 (■) and teflonized Acetylene black (●). The galvanic element voltage is not shown in the figure, but it varied within the range from U = 24 mV to U = 0 mV for the time of the experiments. The plots reveal that the galvanic element comprising the Vulcan XC-72 anode supplies much higher currents compared to the Acetylene black anode. It seems that Vulcan XC-72 holds functional groups that are easier to oxidize [12]. For

clarity the current-time relationship for the Acetilene black galvanic element is shown in the inset. It is apparent that the teflonized Vulcan XC-72 element demonstrates higher initial current densities approximating $i = 0.03$ $mA \cdot cm^{-2}$. This value of the current density is in a good agreement (within the same order of magnitude) with that calculated from the partial curves i_m value of $i = 0.1$ $mA \cdot cm^{-2}$ (see Figure 3). The calculated and measured potential and current values agreement, finding its proof in Figures 2, 3 and 10, serve to verify the progress of oxidation-reduction reactions on micro-galvanic elements, which makes us believe that our working hypothesis has been substantiated.
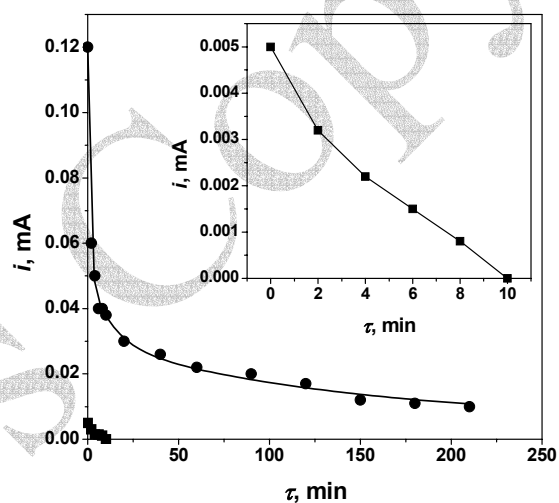

Fig.10. Dependence of galvanic element's short circueted-current from time; cathode mMe:Ni:Co + PTFE; anodes: teflonized Vulcan XC-72 (■) and teflonized Acetylene black (●).

CONCLUSIONS

An explanation of teflonized Vulcan XC-72 additive effect on the electrochemical behaviour of MH electrodes has been given. The working hypothesis for creation of scattered micro-galvanic elements, where reduction of $LaNi_5$ surface oxides and oxidation of carbon takes place, has been proven. It has been illustrated that the oxidation of Vulcan XC-72 is much faster than oxidation of Norit NK and acetylene blacks. The anodic reaction facilitation is most probably due to the fact that the Vulcan XC-72 possesses more RC_n functional groups.

The use of teflonized carbons/blacks in MH electrodes results in enhancement of the hydriding-dehydriding reaction rate and maintains the mMe(Co, Ni, Al) alloys in reduced state. One possible effect that may find its commercial application would be to lower the operation temperature and the pressure of the hydriding-dehydriding reactions on high capacity hydrogen containing MH alloys.

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ВЛИЯНИЕ НА ВЪГЛЕН-ТЕФЛОНОВАТА СТРУКТУРА ВЪРХУ ЕЛЕКТРОКАТАЛИТИЧНИ ОКИСЛИТЕЛНО-РЕДУКЦИОННИ РЕАКЦИИ НА МЕТАЛ-ХИДРИДНИ СПЛАВИ

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(Резюме)

В предишна наша работа са разработени моделни метал-хидридни (МХ) електроди за бързо електрохимично охарактеризиране на МХ сплави. Изследван е ефектът на добавките (тефлонизирани сажди или въглени) върху характеристиките на електродите. В настоящото изследване е направен опит да се обясни този ефект и да се създаде физичен модел на системата. Нашата работна хипотеза е, че в моделните МХ електроди с добавки от тефлонизирани сажди или въглени едновременно протичат реакциите на окисление на въглените и редукция на МХ сплави върху разпръснати микрогалванични елементи. Приложен е адитивния принцип, за да се обясни и докаже електрохимичния механизъм на процеса. Измерени са парциалните поляризационни криви за да се покаже възможността за протичане на указаните реакции. Разработен е оригинален подход за количествена оценка на скоростта на общата реакция чрез измерване на: (i) рентгенова дифракция и електрохимична импедансна спектроскопия; и (ii) създаден, конструиран и тестван е реален галваничен елемент между електроди само от тефлонизирани въглени (сажди) и електроди само с МХ сплав с което е доказана работната ни хипотеза.