Zn(Ta₁₋ₓNbₓ)₂O₆ nanomaterials. Synthesis, characterization and corrosion behaviour

MIHAELA BIRDEANU[1,2]*, GHEORGHE FAGADAR-COSMA[2], IULIANA SEBARCHIEVICI[1], AUREL-VALENTIN BIRDEANU[3], BOGDAN TARANU[1], IOAN TARANU[1] and EUGENIA FAGADAR-COSMA[4]

[1]National Institute for Research and Development in Electrochemistry and Condensed Matter, 1 Plautius Andronescu Street, 300224 Timisoara, Romania, [2]Politehnica University of Timisoara, Vasile Parvan Ave.6, 300223-Timisoara, Romania, [3]National R&D Institute for Welding and Material Testing – ISIM Timişoara, 20 M. Viteazu Ave., 300222, Timisoara, Romania and [4]Institute of Chemistry Timisoara of Romanian Academy, 24 M. Viteazu Ave, 300223-Timisoara, Romania

EXPERIMENTAL DETAILS

Method for corrosion testing

Powder samples of $Zn(Ta_{1-x}Nb_x)_2O_6$ (where x = 1, 0.5, 0.1, 0.05 and 0) were dissolved in a 1 M H_2SO_4 (96–98 % Merck) solution for 1 h, at room temperature, the resulting solutions were used for treatment of OL surface.

Before each experiment, the electrode surface was mechanically polished to a mirror-like surface finish using emery paper of different grades, rinsed with double distilled water, degreased with ethanol and then immediately immersed in the treatment solutions. Thereby, passive layers containing the nanomaterials were formed on the surface of the OL electrodes. The immersion time for each experiment was 5 min at room temperature. After immersion, the modified electrode was rinsed with water and transferred as rapidly as possible into the electrochemical cell for corrosion testing. In each case, the open circuit potential was monitored for 30 min before the recording of polarization curves. Control samples were subjected to the same procedure except for the final step (treatment with the pseudo-binary oxides solutions).

A disk of carbon steel (OL) containing: 0.12–0.18 % C, 0.10–0.35 % Si, 0.70–1.10 % Mn, 0.03 % P, 0.07–0.13 % S and 98.21–98.98 % Fe was employed as the working electrode. The OL was mounted into a Teflon body used for ensuring a good electrical contact and an active constant surface of 0.28 cm².

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* Corresponding author. E-mail: mihaelabirdeanu@gmail.com

Cell description

The experiments were performed in a three-electrode cell using an OL working electrode, a saturated calomel electrode (SCE) as the reference electrode and a platinum wire as the counter electrode. The electrolyte solution was 0.1 M Na_2SO_4. All potentials reported in this article were referenced to the standard hydrogen electrode (SHE).

The potentiodynamic polarization measurements were performed by sweeping the potential between –1.3 and 0.2 V at a scan rate (v) of 1 mV s^{-1}.

The potentiodynamic polarization curves were analyzed using VoltaMaster 4, v.7.09, software. This software performed the Tafel fitting and calculated the values of the corrosion potential (E_{corr}), corrosion current density (i_{corr}) and corrosion rate (v_{corr}) in μm per year.

The degree of inhibition efficiency *IE* (%) was calculated based on the equation:

$$IE\% = 100\left(1 - \frac{i_{corr}}{i_{corr}^0}\right) \qquad (S1)$$

where, i_{corr}^0 and i_{corr} are the values of corrosion current density in the absence and in the presence of $Zn(Ta_{1-x}Nb_x)_2O_6$ (where x = 1, 0.5, 0.1, 0.05 and 0) nanomaterials, respectively.

EDAX ANALYSIS

The results of the EDAX analysis of the samples are presented in Fig. S-1a––e. The EDAX analysis certified the initial mole ratios between Zn, Nb and Ta (the lines corresponding to Zn, Ta, Nb and O were identified). In the 8.5–10.5 keV energy range, the K-lines of O and Zn are well defined and were used for the quantitative analysis. In the range between 5 and 9 keV, the energy L-lines of Ta and Nb were identified.

OPTICAL PROPERTIES

The diffuse reflectance spectra of all the nanomaterials in the UV–Vis λ region 230–650 nm are presented in Fig. S-2.

OPEN CIRCUIT POTENTIAL (OCP)

OCP or free potential provides preliminary information on the nature of processes occurring at the interface protective film/electrolyte. It is a qualitative indicator of the state of corrosion of a metal substrate in an electrolytic medium and it also helps to determine the immersion time required to establish the steady state. The OCP *versus* time (t) measurements (Fig. S-3) were recorded in 0.1 M Na_2SO_4 electrolyte solution over 30 min.
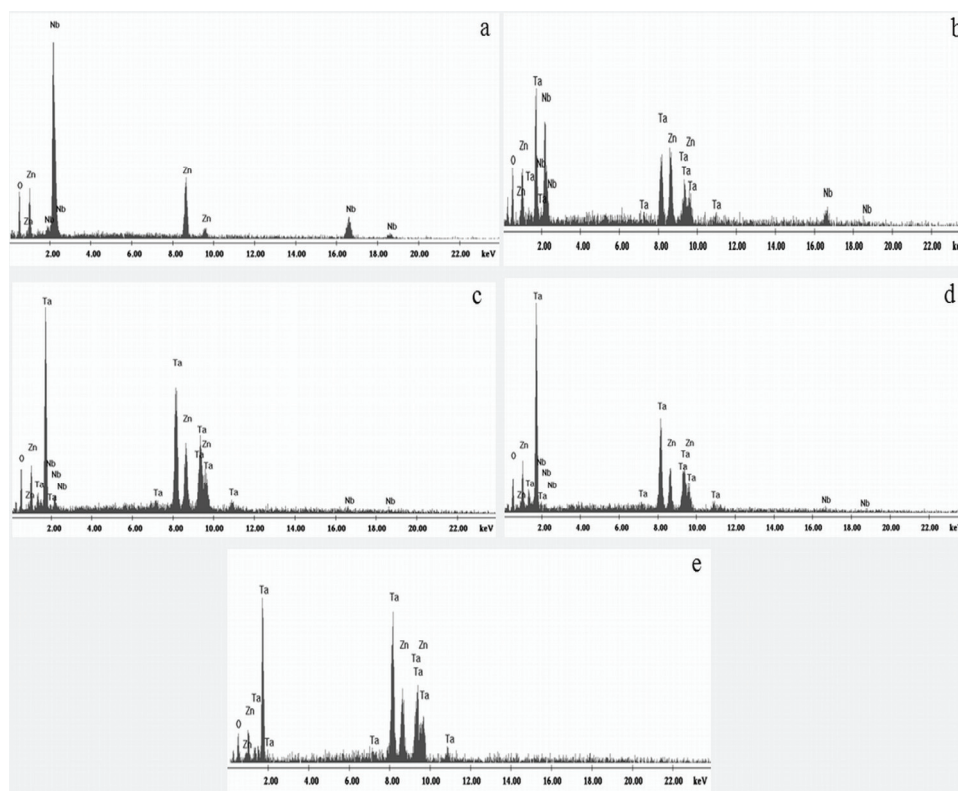
Fig. S-1. The EDAX of: a) $ZnNb_2O_6$, b) $Zn(Ta_{0.5}Nb_{0.5})_2O_6$, c) $Zn(Ta_{0.9}Nb_{0.1})_2O_6$, d) $Zn(Ta_{0.95}Nb_{0.05})_2O_6$ and e) $ZnTa_2O_6$.
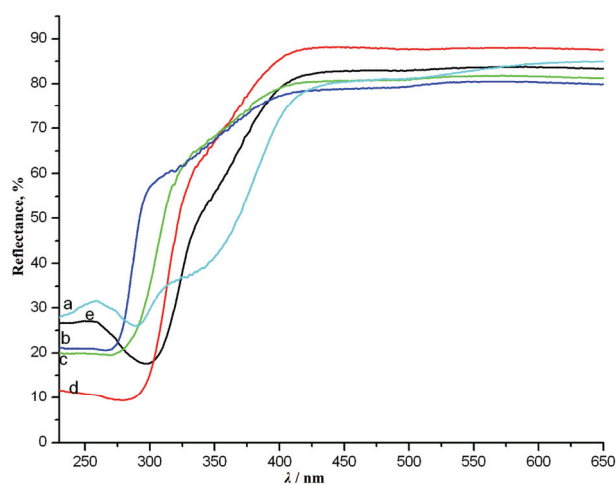

Fig. S-2. Diffuse reflectance spectra of: a) $ZnNb_2O_6$, b) $ZnTa_2O_6$, c) $Zn(Ta_{0.95}Nb_{0.05})_2O_6$, d) $Zn(Ta_{0.9}Nb_{0.1})_2O_6$ and e) $Zn(Ta_{0.5}Nb_{0.5})_2O_6$.
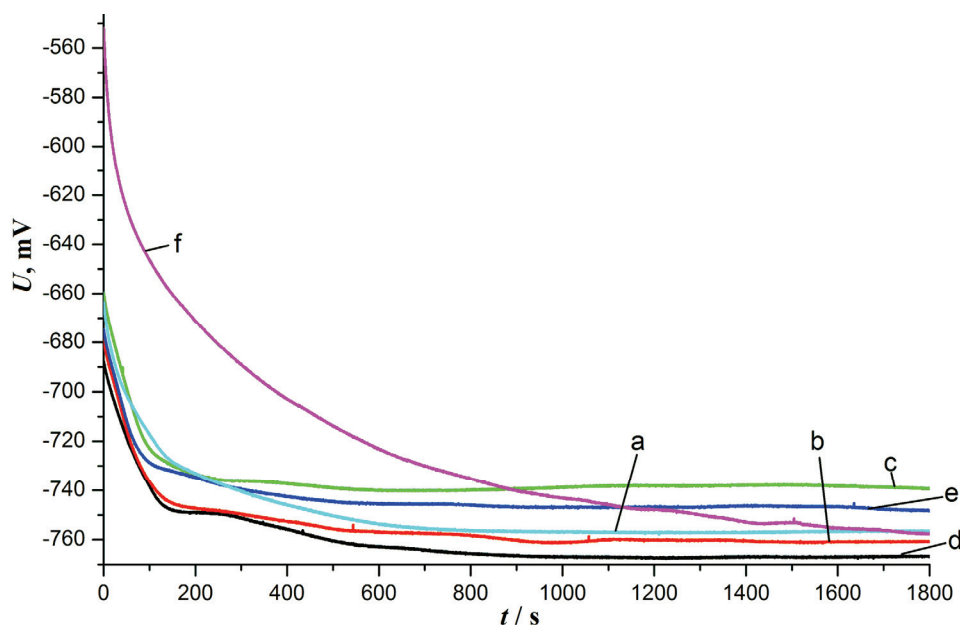
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Fig. S-3. Evolution of the open circuit potential with time for the investigated electrodes in 0.1M Na_2SO_4 electrolyte solution for: a) $ZnTa_2O_6$, b) $Zn(Ta_{0.95}Nb_{0.05})_2O_6$, c) $Zn(Ta_{0.9}Nb_{0.1})_2O_6$, d) $Zn(Ta_{0.5}Nb_{0.5})_2O_6$, e) $ZnNb_2O_6$ and f) OL.

An initial analysis of these curves showed that in all cases, an exposure time of 30 min leads to a shift in free potential towards more negative values. Comparing the OCP profiles obtained for the treated electrodes with those obtained for the untreated electrode, it could be observed that the latter showed a stronger decrease in potential until it reached the same value as that of $ZnTa_2O_6$, (after 30 min). The covered OL (abrupt decrease of the OCP) has a protective oxide film that improves its corrosion resistance. The uncovered OL reaches the steady-state slower. After 30 min exposure time, the free potential value of the $ZnNb_2O_6$ electrode showed the smallest decrease (Δ_{OCP} = 73 mV) and that of the $Zn(Ta_{0.9}Nb_{0.1})_2O_6$ electrode was shifted towards more positive potentials, showing a different stability and the protective behaviour of the tested materials.