

Influence of the nickel content on the electrocatalytic activity of thin nanostructured Co–Te–Ni–O films

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Abstract The influence of nickel addition in Co–Te–O catalytic films, obtained by vacuum co-evaporation of Co, Ni, and TeO₂ on electrocatalytic activity toward oxygen reactions in alkaline media has been investigated. Bifunctional gas-diffusion oxygen electrodes were prepared by direct deposition of catalyst films on gas-diffusion membranes consisting of hydrophobized carbon blacks. The method used allows the deposition of nanostructured films consisting of intertwined nanowires with high surface area. Thus, obtained electrodes with different atomic ratio $R_{(\text{Co}+\text{Ni})/\text{Te}}$ of the catalyst, fresh and thermally treated at 100 °C temperatures were electrochemically tested by means of cyclic voltammetry and steady-state voltammetry. It has been shown that the partial replacement of Co with about 30 at.% Ni leads to the increase in the film catalytic activity toward oxygen evolution reaction.

Keywords Oxygen reduction · Oxygen evolution · Electrocatalysts · Cobalt oxides · Nickel oxides

Introduction

The rechargeable metal/air, metal hydride/air batteries and regenerative fuel cells are very promising power sources [1, 2]. The battery characteristics depend mainly on the activity and stability of the bifunctional air electrode. That is the reason the bifunctional oxygen electrocatalysts to be one of the points of intensive investigation. The transition metal oxides, especially cobalt and mixed cobalt-nickel oxides, have shown promising properties as electrocatalysts for oxygen evolution (OER) [1, 3, 4] and reduction (ORR) [1, 5] reactions. It has been established that the electrocatalytic properties of these oxides vary according to their method of preparation [6]. In the numerous investigations reported in the literature, the powders of oxides have been prepared by thermal decomposition of mixed nitrates, carbonates, or hydroxides [3, 6–9], sol–gel [6, 10–12] or freeze drying methods [13]. Thin films of cobalt spinels have been prepared by chemical spray pyrolysis [4], cathodic sputtering [14], or by electrochemical methods [15, 16].

We have used a new method [17, 18] for preparing cobalt oxides films by vacuum co-deposition of Co and TeO₂ onto substrate held at room temperature. During the vacuum deposition, co-evaporated substances are mixed at an atomic level, giving the possibility of obtaining catalysts with various components in the desired proportions. It has been found that during the vacuum deposition, a chemical reaction takes place between them, resulting in the formation of CoO and of elemental Te phases [17–19]. The results obtained show that the proposed method provide a reproducible deposition of thin amorphous or nanocrystalline Co–Te–O films on different substrates, including polymer ones [18]. The films deposited on gas-diffusion membranes (GDM) possess high surface area,

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which is one of the important prerequisites for the achieving of high catalytic activity [17–19].

The study of the electrochemical behavior of the thin Co–Te–O films deposited on GDM by means of potentiodynamic and galvanostatic measurements indicate that the films can be successfully used as electrocatalysts for oxygen evolution and reduction. We have found that the films with optimal atomic ratio $R_{\text{Co/Te}} = 1.4 - 1.8$ are characterized by high mass activity, especially toward oxygen evolution reaction [19].

It is known that addition of Co to Ni oxide improves the performance of the Ni oxide cathode in the aqueous battery application [20]. Serebrennikova and Birss [21] have found an increase in charge density when cobalt is added to the Ni oxide films. On the other hand, Nicolov et al. [3] and Jasem and Tseung [22] have established that doping of Ni to cobalt spinel oxides results in creating new active sites with lower activation energy of the oxygen evolution reaction. In our previous study, we have received promising results for nickel addition to films with atomic ratio $R_{(\text{Co+Ni})/\text{Te}}$ of 0.8 [23]. This atomic ratio is lower than the optimal one found for our films [19]. In the present paper, we have focused on establishing the influence of the Ni addition on the surface morphology, structure, and electrochemical behavior of Co–Te–O films with optimal atomic ratio obtained by above mentioned method. For our investigation, we have replaced part of the Co with up to 30 at.% Ni in the films with atomic ratio $R_{(\text{Co+Ni})/\text{Te}} = 1.5$ and 0.2 mg cm^{-2} loading, which are within the optimal ranges found for the Co–Te–O films [19].

Experimental

Preparation of the catalyst and gas-diffusion electrodes

The catalytic films were prepared by thermal co-evaporation of Co by electron gun and Ni and TeO₂ from independently heated cells of Knudsen type under vacuum higher than 10^{-4} Pa. The evaporation of TeO₂ was carried out from platinum crucible while those of Co and Ni from glassy carbon ones. The condensation rates of each substance within the range $0.005\text{--}0.04 \text{ } \mu\text{g cm}^{-2} \text{ s}^{-1}$ were controlled separately during the evaporation by quartz crystal monitors. The substances were deposited on a stationary substrate placed above the crucibles. In most of the cases, a gas-diffusion membrane was used as a substrate. The membrane consists of hydrophobized carbon (45% Teflon and 55% acetylene carbon blacks) hot pressed on Ni screen in which screen serves as a current collector [24].

The system of the catalytic film condensed on the GDM represents the gas-diffusion electrode (GDE), the catalyst being the active layer, while the membrane with Ni screen inside provides the gas-supplying layer of the electrode, the

gas being supplied by diffusion. The geometric area of GDE was 1 cm^2 . The effective loading of the catalytic film was 0.2 mg cm^{-2} of geometric surface, which corresponds to a nominal film thickness of about 450 nm. All the electrodes have films with atomic ratio $R_{\text{Me/Te}} = 1.5$ where Me is (Co + Ni), Co, or Ni. Some of the gas-diffusion electrodes were heated for 3 h at $100 \text{ }^\circ\text{C}$ in air since in our previous study we have found that thermal treating at $100 \text{ }^\circ\text{C}$ leads to an increase in the voltammetric charge of the Co–Te–O films.

Characterization of the catalytic films

The amount of each condensed substances and the atomic ratios $R_{\text{Ni/Co}}$ and $R_{(\text{Ni+Co})/\text{Te}}$ at each point of the substrate were calculated from the crystal monitor data. The chemical composition of the catalyst deposited on the substrate was controlled with an X-ray microanalyzer in scanning electron microscope (SEM; JEOL Superprobe 733 with mounted System 5000-HNU).

The chemical states of the elements in the catalytic film deposited on the GDM were studied with X-ray photoelectron spectroscopy (XPS). The measurements were carried out in ultra-high vacuum chamber of the electron spectrometer ESCALAB MkII. The spectra were excited with an AlK α source with energy 1,486.6 eV. The photoelectron lines of C1s, O1s, Te3d, Co2p, and Ni2p were recorded. All spectra were calibrated using C1s line at 285.0 eV as a reference.

The structure of the films was observed by XRD-DRON-3 automatic powder diffractometer.

Electrochemical measurements

The electrochemical study was carried out by means of cyclic voltammetry and steady-state galvanostatic voltammetry using equipment consisting of potentiostat–galvanostat provided with a pulse generator (Solartron 1286 electrochemical interface).

The gas-diffusion electrodes were tested in a three-electrode cell at room temperature. The electrolyte was 20% KOH, prepared with twice-distilled water. High surface area Pt wire was used as a counter electrode. The potential was measured vs. Hg/HgO reference electrode in 20% KOH, held close to working electrode using a Luggin capillary. Cyclic voltammetry was carried out in the potential region between $-1,000$ and $+650 \text{ mV}$ vs. Hg/HgO at different sweep rates within the range of $2\text{--}20 \text{ mV s}^{-1}$. The system was deaerated by supplying Ar through the membrane and bubbling it in the electrolyte before and during cyclic measurements. The values from the galvanostatic measurements for every single point were recorded after attaining stationary conditions (usually about 2–5 min after applying the current). Cathodic polarization curves were measured under a flow of pure oxygen supplied to the air side of the electrodes.

Results and discussion

Physical properties of the catalytic film

Co2p_{3/2} and Ni2p_{3/2} XPS spectra of as-deposited films with atomic ratios $R_{Ni/Co} = 0.18$ and 0.4 are shown in Fig. 1. For comparison, the Co2p spectrum of film without Ni (Co–Te–O) and Ni2p spectrum of film without Co (Ni–Te–O), obtained by co-evaporation of Ni and TeO₂, are also given. All Co2p spectra show typical Co²⁺ state. The second peak (786.9 eV), which is shifted ~6.1 eV to higher binding energy from the first one (780.8 eV), is known as a “shake-up” satellite which

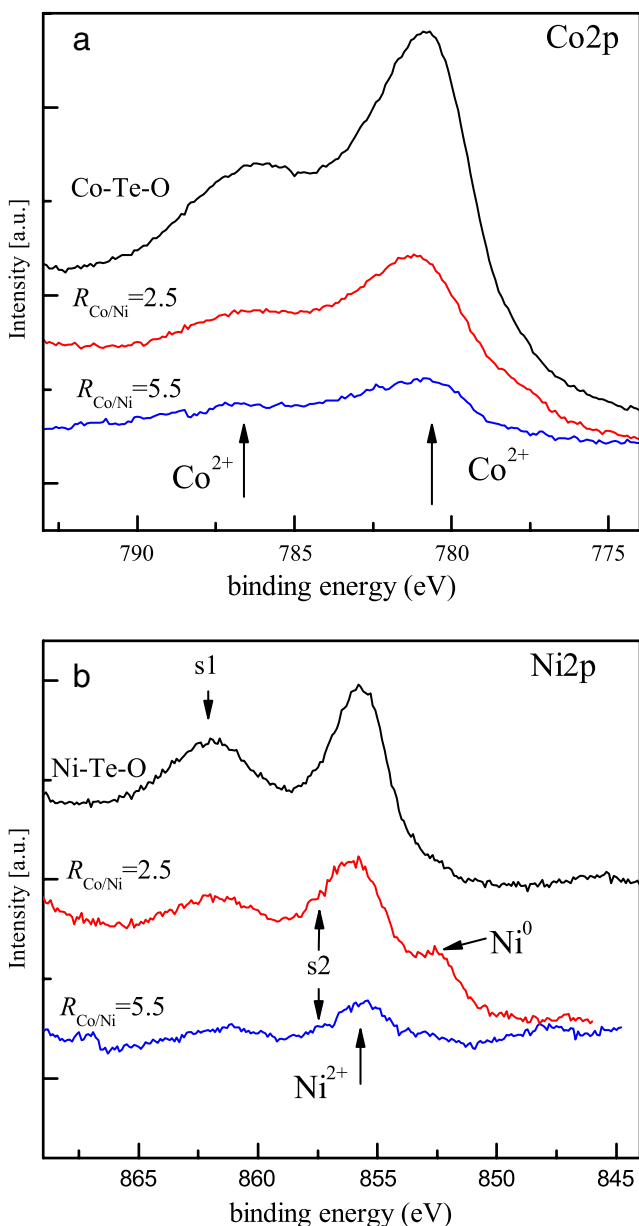


Fig. 1 Co2p_{3/2} и Ni2p_{3/2} XPS spectra from the surface of fresh films with indicated content of Ni deposited on GDM

is exclusively observed in CoO [25]. It can be seen that the nickel addition does not change the cobalt valence state. All Ni2p spectra show a presence of Ni²⁺ state with the main peak at 855.88 eV. The satellite s1 (862.00 eV) and not so well-defined satellite s2 (857.36 eV) observed at higher binding energies indicate the presence of NiO [26]. The presence of Ni²⁺ and of elemental Te found in all studied films indicate that, besides the reaction leading to CoO [19] a reaction



leading to formation of NiO also proceeds during the deposition of the films. In the film with higher content of Ni ($R_{Ni/Co} = 0.4$), additional peak of elemental Ni (852.56 eV) is also observed. The presence of Ni⁰ shows that, in this film, reaction 1 does not proceed completely during the deposition.

It was found that thermal treatment of the films at 100 °C did not cause any changes in the cobalt and nickel states. This indicates that this thermal treatment does not lead to further oxidation of elemental nickel in the films with higher content of Ni.

The SEM micrographs in Fig. 2 illustrate the surface morphology of Co–Ni–Te–O films and of bare gas-diffusion membrane for comparison. One very rough film surface, made of intertwined nanowires following the rough surface of the membrane, is seen. It should be noted that this morphology is typical for the films deposited on GDM by our method, and it does not depend on the atomic ratio $R_{Ni/Co}$, $R_{Me/Te}$, film thickness, and the thermal treatment [19].

The X-ray diffraction (XRD) spectra of the films with Ni are similar to those obtained for the Co–Te–O films. They did not show any peak which is an indication that the films are amorphous or nanocrystalline, but both the size of the crystals and their amount are too small to be detected by conventional XRD method used.

Electrochemical measurements

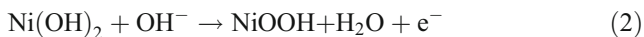
Cyclic voltammetry

Figure 3 presents the cyclic voltammograms (CV) of films with $R_{Ni/Co} = 0.18$ and 0.4 recorded at 10 mV/s. For comparison, the CVs of film without Ni (Co–Te–O) as well as without Co (Ni–Te–O) are also given. As follows from our previous investigations, GDM as well as Te and TeO₂ did not have any contribution to the peaks observed for the above mentioned films [19]. Four pairs of peaks can be seen in the figure. The peaks observed for the film without Ni (Co–Te–O) a1/c1 and a2/c2 are very broad and not well defined, but as it was discussed in detail in our previous paper, they can be associated with the following cobalt transitions: a1/c1 with CoO/CoO₂ (calculated potential at +195 mV vs. Hg/HgO) and/or Co(OH)₂/CoO₂



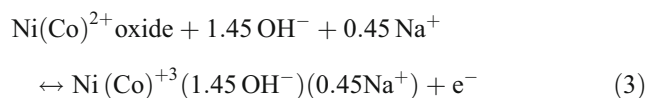
Fig. 2 SEM micrographs of **a** GDM and **b** fresh Co–Ni–Te–O film with $R_{\text{Ni/Co}}=0.4$ deposited on GDM

(+254 mV vs. Hg/HgO); a2/c2 with CoOOH/CoO₂ (+562 mV vs. Hg/HgO). The pair of peaks a3/c3 observed for film without Co (Ni–Te–O) can be associated with the Ni(II)/Ni(III) transition cited in the literature for nickel oxide and hydroxide electrodes [27–29] and described by the following equation:



It is well seen from the curves that, with increasing the Ni content in the films, the pairs of peaks a1/c1 and a2/c2 corresponding to cobalt transitions gradually decrease and disappear regardless of the high cobalt content in the films. In the same time with the nickel addition, the pair of peaks a3/c3 corresponding to Ni(II)/Ni(III) transition also disappear, but a new pair of peaks a4/c4 becomes visible. The peak a4 is observed at less positive potential (~+400 mV vs. Hg/HgO) than the peak a3 (at +525 mV vs. Hg/HgO). It

should be noted that very similar effects, i.e., low charges for pure cobalt oxide films as well as an absence of the voltammetric features connected with Co(II)/Co(III) transitions, have been observed and reported in the literature for the hydrous Co–Ni oxide films [21, 27, 28, 30, 31]. They are explained in different ways, some of which assert that only nickel is electrochemically active in the mixed Co–Ni oxide materials or that the nickel sites participate in the redox reaction with more than one electron forming Ni(IV) oxidation state. Serebrennikova and Birss [21] have explained the absence of the individual feature of Co and Ni with changes in their redox potentials and developing of a single synergistic redox potential characteristic of the mixed Ni–Co oxide materials. Based on pH dependence studies for 50:50 Ni–Co sol–gel derived films, they have proposed the following stoichiometry of the redox process:



According to us, both the weak indication for the cobalt transitions and the displacement of the characteristic peak for Ni(II)/Ni(III) transition in vacuum-deposited Co–Ni–Te–O films are the indications for the changes in the redox

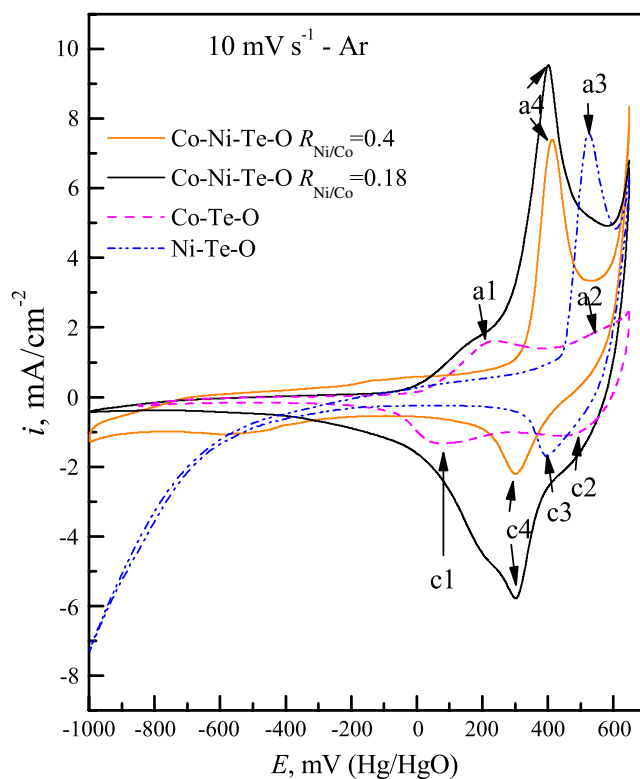


Fig. 3 Cyclic voltammograms of GDEs with fresh Co–Ni–Te–O films with indicated Ni content, fresh Co–Te–O, and Ni–Te–O films (recorded at sweep rate of 10 mV s⁻¹, 20 °C, 20% KOH)

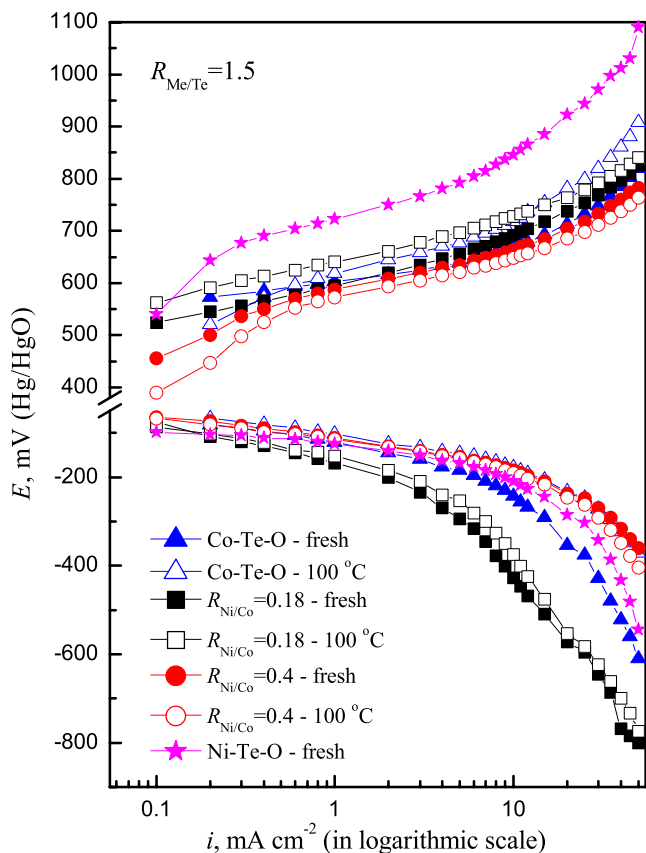


Fig. 4 Anodic and cathodic polarization curves (in logarithmic scale) of fresh and thermally treated at 100 °C GDEs with indicated nickel content (recorded at 20 °C, 20% KOH)

potentials of the Ni and Co sites and for the developing of a single synergistic redox potential, similar to those observed by Serebrennikova and Birss [21].

Steady-state measurements

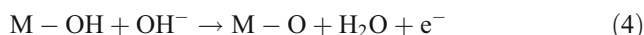
As far as the catalytic activity of cobalt and nickel oxides is known in the literature, the question arises: What is the role of Te and TeO₂ in these reactions? In our previous paper [23], we have shown that TeO₂ and Te themselves exhibit some activity, which is significantly lower, especially for Te, than that of the catalytic films.

Figure 4 shows the anodic and cathodic polarization curves in logarithmic scale of fresh and thermally treated GDEs with different nickel content in the catalytic film. It can be seen that the film without Co (Ni–Te–O) exhibits the worst activity toward OER, while the best catalytic activity to OER have the films with $R_{Ni/Co}=0.4$. It also follows from the figure that the thermal treatment does not lead to significant changes in their activity as it was observed for the GDE with Co–Te–O catalyst.

As we have already explained in our previous work [19], the precise estimation of the catalytic activity toward

oxygen reduction reaction of the films itself was difficult to be made due to the very low reproducibility of carbon gas-diffusion membrane. Nevertheless, our results did not show any tendency for improving the activity toward this reaction both with increasing the nickel content and with the thermal treating of the films.

As can be seen from Fig. 4, two linear segments, typically for OER and ORR, are observed at low and high current densities. In Table 1, the Tafel slopes of fresh and thermally treated GDEs with different nickel content in the catalytic films are given. For comparison, the Tafel slopes of GDEs without Ni or Co are also given. The Tafel slopes within the range of 73–86 mV/dec were found at the low current density region for oxygen evolution reaction of GDEs with Co–Ni–Te–O catalyst. These values are significantly higher than that of the fresh GDE with Co–Te–O films without nickel. A Tafel slope of 43 mV/dec, observed for the fresh GDEs without nickel, means that the second step in Bockris's electrochemical oxide path mechanism is the rate-determining reaction [32, 33]:



The Tafel slopes about 40 mV/dec were observed for Co–Ni spinels [34, 35], and the authors have connected the rate-determining step with Eq. 4, where according to them M is in +3 valance state. Some authors have found Tafel slopes about 60 mV/dec for Co perovskites. They have suggested that the Tafel slopes depend on the conditions of surface covering with OH⁻ [32, 33].

Keeping in mind the low reproducibility of the results obtained for oxygen reduction reaction, it should be noted that as a whole, a tendency for decreasing the Tafel slopes in the low current density was found with increasing the nickel content in the films. It should be noted that Tafel slopes within the range –59 to –67 mV/dec were found for GDEs without nickel. These values are similar to the most commonly observed ones (about –60 mV/dec) cited in the

Table 1 Tafel slopes of GDEs with indicated nickel content

GDE $R_{Me/Te}=1.5, 0.2\text{mgcm}^{-2}$		OER b (mV dec ⁻¹)	ORR b , (mV dec ⁻¹)
Co–Te–O	Fresh	43	–67
	100 °C	123	–59
$R_{Ni/Co}=0.18$	Fresh	73	–88
	100 °C	76	–67
$R_{Ni/Co}=0.4$	Fresh	82	–48
	100 °C	87	–46
Ni–Te–O	Fresh	86	–30

literature for oxide films [1]. The oxygen reduction reaction is a generally very difficult process. Two mechanisms for this reaction have been proposed in the literature: direct four-electron mechanism and mechanism with H_2O_2 formation as an intermediate compound [1]. According to the authors, the ORR mechanism for complex oxide surfaces strongly depends on the nature of the adsorption of the oxygen molecules.

Therefore, the changes in the Tafel slopes with nickel addition for both reactions could be explained with possible formation of new active sites in the catalytic films, with different nature from those in the Co–Te–O films. Probably, the OER proceeds easier due to changing in the rate-determining step or changing in the surface covering with OH^- . For ORR, the reason for changed slopes is most likely the change in the nature of the O_2 adsorption. The formation of new active sites, different in nature than the cobalt and nickel sites, is in agreement with the results obtained from the CV measurements and the formation of a single redox potential peak. As a result, there is an improvement of the catalytic activity for OER for the GDE with $R_{\text{Ni/Co}}=0.4$. However, additional investigations are needed for more precise explanation of the observed effects.

Conclusion

The results reported in the paper show that the addition of nickel in Co–Te–O catalytic films leads to significant changes in the surface redox processes and to appearing of a single peak with mixed redox potential, which is characteristic for the mixed Ni–Co oxides.

It was found also that the nanostructured Co–Ni–Te–O films with $R_{\text{Ni/Co}}=0.4$ exhibit the best catalytic activity toward oxygen evolution reaction. On the basis of our results, it can be concluded that, most probably, the active sites in the Co–Ni–Te–O films have a different nature from those in the Co–Te–O films, which leads to the changes in the process kinetic. However, a tendency for significant changes toward oxygen reduction reaction was not found. The thermal treatment also does not show significant influence on the activity of the electrodes.

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