

Parallel oxygen and chlorine evolution on $\text{Ru}_{1-x}\text{Ni}_x\text{O}_{2-y}$ nanostructured electrodes

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Abstract

Nanocrystalline materials with chemical composition corresponding to formula $\text{Ru}_{1-x}\text{Ni}_x\text{O}_{2-y}$ ($0.02 < x < 0.30$) were prepared by sol–gel approach. Substitution of Ru by Ni has a minor effect on the structural characteristics extractable from X-ray diffraction patterns. The electrocatalytic behavior of $\text{Ru}_{1-x}\text{Ni}_x\text{O}_{2-y}$ with respect to parallel oxygen (oxygen evolution reaction, OER) and chlorine (chlorine evolution reaction, CER) evolution in acidic media was studied by voltammetry combined with differential electrochemical mass spectrometry (DEMS). The DEMS data indicate a significant decrease of the over-voltage for chlorine evolution with respect to that of pure RuO_2 . The oxygen evolution is slightly hindered. The increasing Ni content affects the electrode material activity and selectivity. The overall material's activity increases with increasing Ni content. The activity of the Ru–Ni–O oxides towards Cl_2 evolution shows a distinguished maximum for material containing 10% of Ni. Further increase of Ni content results in suppression of Cl_2 evolution in favor of O_2 evolution. A model reflecting the cation–cation interactions resulting from Ni-doping is proposed to explain the observed trends in electrocatalytic behavior.

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1. Introduction

The nanostructured ruthenium dioxide represents one of the most popular electrocatalysts for both oxygen and chlorine evolution reactions [1,2]. The practically used dimensionally stable electrodes are in fact mixtures of ruthenium dioxide with titanium dioxide. Due to great similarity in structural chemistry of both ruthenium and titanium it is generally envisaged that both components form solid solutions where the oxide of the former metal acts as the active component while the later enhances the electrode stability [3]. As can be deduced from generally accepted reaction mechanism of the oxygen [3] and chlorine [1] evolution the electrocatalytic behavior of the ruthenium dioxide may be altered by convenient substitution of the Ru in the rutile structure. The literature lists several synthetic attempts to prepare substituted RuO_2 electrodes when the prepared dou-

ble oxides contained in addition to Ru also variable amounts of Ti [4], Co [5], Ce [6], V [7]. Although the information on the solid-state characterization of the prepared materials is scarce, one may generalize that conventional synthesis leads to a single phase materials in the case of iso-static substitution. In the case of hetero-static substitution the conventional synthesis usually leads to formation of multiphase system [5]. This obstacle can be avoided by use of advanced solution-based synthetic approaches like, e.g., sol–gel synthesis. The sol–gel approach was employed to prepare, e.g., single phase $\text{Ru}_{0.8}\text{Co}_{0.2}\text{O}_{2-x}$ with rutile structure and characteristic particle size ranging between 20 and 60 nm. The single phase materials in Ru–Co–O system are however meta-stable and exist only in limited temperature and composition range [8,9]. In contrast to oxides substituted with iso-static cations the hetero-statically substituted materials show significantly decreased over-voltage for chlorine evolution [9]. This paper extends the previous studies and reports the results of a study of electrocatalytic behavior of single phase nanocrystalline oxides corresponding to average composition $\text{Ru}_{1-x}\text{Ni}_x\text{O}_{2-y}$ ($0.02 < x < 0.30$). The X-ray diffraction, cyclic voltammetry and differential electrochemical mass spectrometry (DEMS) were employed to address the issue of the activity

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and selectivity of the Ru–Ni–O phases towards oxygen and chlorine evolution reactions.

2. Experimental

The ruthenium dioxide samples were prepared by procedure described previously [10]. The $\text{Ru}_{1-x}\text{Ni}_x\text{O}_{2-y}$ samples were prepared using a sol–gel approach. A starting solutions of ruthenium(III) nitrosyl nitrate (98%, Alpha Aesar) and nickel(II) nitrate hexahydrate in mixture of ethanol and propane-2-ol (1:1) (both Aldrich, ACS grade) were precipitated with aqueous solution of tetramethylammonium hydroxide (25% Alpha Aesar) [10–12]. The starting solutions containing both Ru and Ni were characterized by Ru:Ni ratio of 49:1, 19:1, 9:1, 4:1, 3:1 and 7:3. The precipitation procedure led to a formation of amorphous precursors which were aged in a PTFE lined stainless steel autoclaves at 100 °C for 40 h to facilitate the filtration process. The washed and filtered materials were treated with hydrogen peroxide (1%), dried in air and annealed at 400 °C in air for 1 h to obtain nanocrystalline materials. The crystallinity and phase purity of the prepared samples was checked using Bruker D8 advance powder X-ray diffractometer with Vantec-1 detector and Cu $K\alpha$ radiation. The particle size distribution and chemical composition of the prepared materials was determined using scanning electron microscope (SEM) (Hitachi S4800) equipped with a Nanotracer EDX detector (Thermo Electron).

The electrodes for electrochemical experiments were prepared from synthesized Ru–Ni–O materials by sedimentation of nanocrystalline powder from a water-based suspension on Ti mesh (open area 20%, Goodfellow). The duration of the deposition was adjusted to obtain the surface coverage of about 1–2 mg/cm² of active oxide. The deposited layers were later stabilized by annealing the electrodes for 20 min at 400 °C in air. The initial oxide suspensions were prepared in an ultrasound bath and contained approximately 5 g/l of ruthenium-based oxide in MilliQ quality de-ionized water. The electrochemical behavior of the prepared materials was studied by cyclic voltammetry combined with DEMS. All experiments were performed in a homemade Kel-F single compartment cell. The experiments were performed in a three-electrode arrangement controlled by a PAR 263A potentiostat. Pt and Ag/AgCl were used as an auxiliary and a reference electrode, respectively. The activity of the prepared materials in both oxygen and chlorine evolution reactions was studied in a solution containing 0.1 M HClO₄ and 0.3 M NaCl. The DEMS apparatus consisted of PrismaTM QMS200 quadrupole mass spectrometer (Balzers) connected to TSU071E turbomolecular drag pumping station (Balzers). More detailed description of the DEMS setup can be found in Ref. [10].

3. Results and discussion

The powder diffractograms of the Ru–Ni–O oxides prepared by annealing the amorphous precursors at 400 °C are shown in Fig. 1. Regardless of the actual Ni content the observed XRD patterns can be regarded as corresponding to single phase materials crystallizing in a tetragonal syngony. All the peaks in the patterns

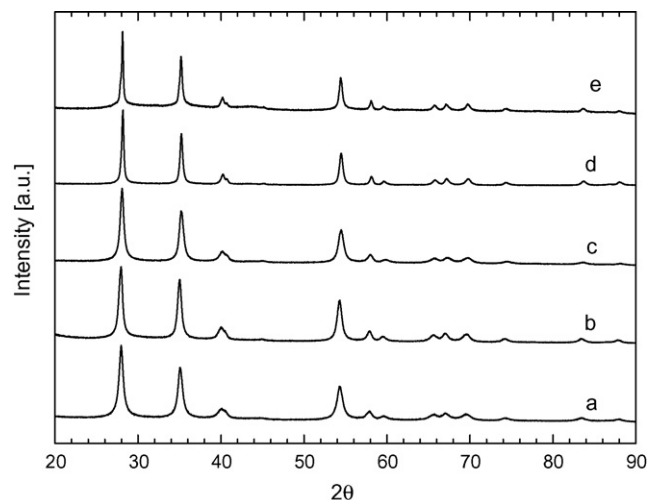


Fig. 1. Powder X-ray diffractograms of the nanocrystalline $\text{Ru}_{1-x}\text{Ni}_x\text{O}_{2-y}$ materials prepared by sol–gel approach and calcinated at 400 °C for 1 h. The actual values of the Ni content (x) are as follows: 0.02 (a), 0.05 (b), 0.10 (c), 0.20 (d) and 0.30 (e).

Table 1

The parameters of the Rietveld analysis of the X-ray diffraction patterns of $\text{Ru}_{1-x}\text{Ni}_x\text{O}_{2-y}$ oxides

x	a (Å)	c (Å)	R_p (%)	R_{wp} (%)
0.0				
0.02	4.498	3.096	8.34	10.13
0.05	4.490	3.097	6.86	8.49
0.10	4.493	3.089	7.40	9.06
0.15	4.492	3.091	7.60	9.58
0.20	4.492	3.102	5.63	7.16
0.25	4.491	3.099	8.42	11.47
0.30	4.482	3.098	4.67	5.82

can be indexed assuming a rutile structural type ($P_{42/mnm}$). The corresponding unit cell parameters resulting from the data fit are listed in Table 1. The lattice constants as well as the unit cell volume (see Fig. 2) change with the Ni content in a complex way.

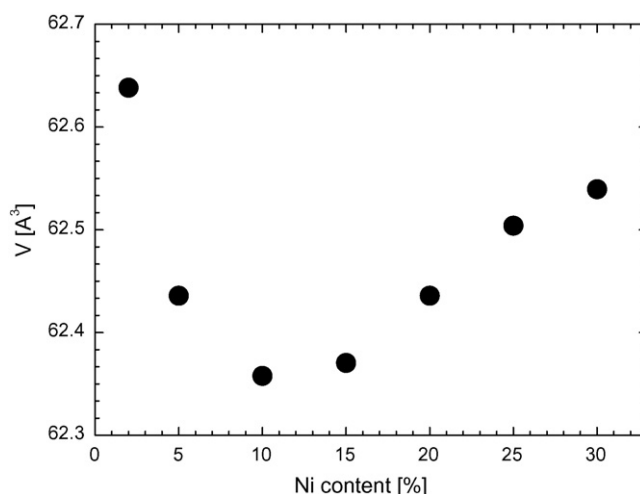


Fig. 2. The unit cell volume of the nanocrystalline $\text{Ru}_{1-x}\text{Ni}_x\text{O}_{2-y}$ oxides as a function of the Ni content.

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