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Voltametric behaviour of Ti_nO_{2n-1} ceramic electrodes close to the hydrogen evolution reaction

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Voltammetric behaviour close to the hydrogen evolution reaction has been studied on metallic conducting oxides from Ti_nO_{2n-1} series with $n = 4$–6. The Ti_4O_7, Ti_5O_9 and Ti_6O_{11} ceramic electrodes were prepared by the reduction of TiO_2 compacts with hydrogen. The current–voltage curves (i, E) were obtained by the potentiodynamic method in aqueous solutions. The electrochemical reaction which occurs in the cathodic potential region is discussed in terms of proton insertion into the Ti_nO_{2n-1} structure. The influence of the porosity of the ceramic electrodes on the electrochemical reaction taking place in this potential region was examined using electrodes of different pore size distributions (different values of roughness factor, r). The influence of the degree of reduction of titanium oxide (n in Ti_nO_{2n-1}) on the electrolytic activity for the hydrogen evolution reaction on these oxides was examined.

Introduction

New technologies have permitted the development of new types of electrode consisting of a metallic substrate and a ceramic coating, or more recently, new ceramic materials with high electronic conductivity. Ceramic electrodes can be made to have a high degree of resistance to the electrolyte and to electrolysis products. Although oxide electrodes were introduced 25 years ago as electrocatalysts for anodic gas-evolving reactions, industry has recently shown [1, 2] increasing interest in their cathodic performance due to their high surface area which reduces the hydrogen overpotential. Apart from its direct electrolytic production, hydrogen evolution is the cathode reaction accompanying, in particular, chlorine formation and, in general, most anodic processes occurring in aqueous media.

Hydrogen evolution on oxides is a very interesting process from the fundamental point of view, since all existing theories normally assume a pure metal surface as the substrate. Basic research on cathodic behaviour of oxides is practically non existent, except for a few papers dealing with hydrogen evolution on RuO_2 [3–6], IrO_2 [7] and $LaNiO_3$ [8]. The electrochemical reactions which occur on TiO_2 in the cathodic potential region are discussed in several papers [9–14]. In most of these studies, the semiconductor characteristics of the oxide film were not taken into account but three different points of view were considered: (i) a dual-barrier model to explain the charge transfer reactions [13]; (ii) the existence of a film of absorbed oxy-hydroxy species [14]; and (iii) the presence of a three-dimensional oxide film. Semi-conducting titanium oxide films cannot be compared simply to metallic conducting Magnéli phases.

In the Ti–O system between the limits of $TiO_{1.75}$ and $TiO_{1.90}$ a homologous series of 'Magnéli phases' with the formula Ti_nO_{2n-1} is formed with n taking values from 4 to 10, in which crystallographic shear planes lie upon (1 2 1) planes. The existence of these plane defects is responsible for the high electrical conductivity at room temperature. At room temperature only three oxides i.e. Ti_4O_7, Ti_5O_9 and Ti_6O_{11} exhibit metallic behaviour and around 150 K metal to semiconductor transitions have been observed for these oxides [15]. Considerable attention has been focussed on the magnetic [16–18] and electrical properties [19–21] of Ti_4O_7 and a detailed X-ray study of its structure has been reported [22]. The unique combination of high electrical conductivity and high chemical stability should be more pronounced for the first two oxides from the Ti_nO_{2n-1} series, i.e. Ti_4O_7 and Ti_5O_9.

In recent years, Ti_nO_{2n-1} has attracted attention as a possible electrode material and/or substrate for electrocatalysts in diverse technological applications. Applications of Ti_nO_{2n-1} as an electrode material have been covered by several patents [23–26]. On the other hand, few papers described laboratory studies of its fundamental electrochemistry [27–32].

The majority of studies have been done on both bare and metal coated (lead, palladium, platinum) commercial Ebonex electrodes. In all cases, the cyclic voltammograms for the Ebonex ceramic electrodes showed substantial charging currents. In addition, there were a number of broad and poorly defined peaks for the oxidation and reduction which extended over much of the potential ranges; their position and magnitude depended on several experimental parameters, including the electrolyte medium, the history and pretreatment of the surface, potential range and the direction of scan. Ebonex

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ceramic electrodes showed relatively large overpotentials for the generation of oxygen and hydrogen.

In this paper we report studies of the cathodic behaviour of Magnéli phases using ceramic Ti_nO_{2n-1} electrodes prepared in this laboratory [33]. In the first part of the work on hydrogen evolution on substoichiometric titanium oxides, the voltametric behaviour was investigated during cathodic reaction with the aim of gaining insight into the response of the oxide surface to the cathodic polarization. The effect of pore size distribution of the ceramic material and the effect of the degree of reduction of titanium oxide on the hydrogen evolution reaction are discussed in the second part of this paper.

2. Experimental details

2.1. *Preparation of electrodes*

The Ti_nO_{2n-1} ceramic electrodes were prepared starting from a commercial pigment TiO_2. In order to minimize the capillary forces in the powders the mixture of water+isopropanol (1 : 1) was added and then, after drying, 5 wt% PEO solution was added as a binder. The powders were compacted in a uniaxial press under 200 kg cm^{-2} pressure into disc-shaped compacts of 44 mm diameter and 5 mm thickness. The discs were sintered in air at 1050 °C for one day and, after removing the oxygen from the furnace, hydrogen was used for the reduction. Four hours and 1050 °C was enough to obtain monophasic Ti_4O_7 electrodes. For the higher oxides a shorter reduction time was used.

The ceramic materials were characterized by the apparent density, pore size distribution, resistivity, powder X-ray diffractometry and thermogravimetry. The pore size distribution was determined by a mercury porosimeter (Carlo–Erba). Voltammetric experiments were done using a monophasic ceramic material. Identification of oxide was carried out with an X-ray (FeK$_\alpha$-radiation) diffractometer (DRON-2). Patterns were compared with those listed in ASTM X-ray data files. In addition, thermal analysis measurements were performed to confirm the oxide concerned. The degree of reduction (n in the Ti_nO_{2n-1} formula) was determined from weight gain while heating samples in air up to 1000 °C. Thermogravimetric measurements were made with a Derivatograph 1000–1500 °C (M.O.M. Budapest) thermal analyser.

2.2. *Voltametric experiments*

The experimental results of the ceramic electrodes were obtained by employing the voltammetric technique. Experiments were carried out at room temperature in a three-electrode, two-compartment cell. The counter electrode was a platinum net. The reference electrode was a saturated calomel electrode (SCE), to which all potential values are referred. The SCE was immersed near the working electrode via a Luggin capillary.

The following equipment was used: a potentiostat type EP-20A (ELPO), a linear sweep generator type EG-20 (ELPO), an X–Y recorder type Endim 620.02 (VEB Messapparatenwerk Schlatheim). The voltammetric experiments were done in various electrolytes (0.1 M H_2SO_4, 10 wt% H_2SO_4, 0.1 M Na_2SO_4, 0.9 M KOH aqueous solutions). All solutions were prepared from analytical grade reagents and doubly distilled water.

A sharpened titanium bar was used as a holder and electrical contact to the working electrode. The back and sides of the electrode were insulated using a coating of chlorinated rubber lacquer. Only the working surface (0.8 cm^2) was exposed to the solution. The working electrode was immersed in the solution for 15 min before the voltammograms were started in order to avoid undefined effects which may arise from the soaking of a ceramic electrode. In the second part of the experiments all voltammograms were obtained after complete scanning of the voltage range until the electrode was stabilized and the curves were reproducible. The current densities were calculated from the geometrical surface (S_g) in contact with the electrolyte.

3. Results and discussion

Figure 1 shows the voltammetric curves at 1 mV s^{-1} recorded first in the potential range of 0.4 to 1.2 V vs SCE and then by moving the lower limit of the potential range by 200 mV steps down to −0.8 V. It is interesting to note that the lower limit affects the

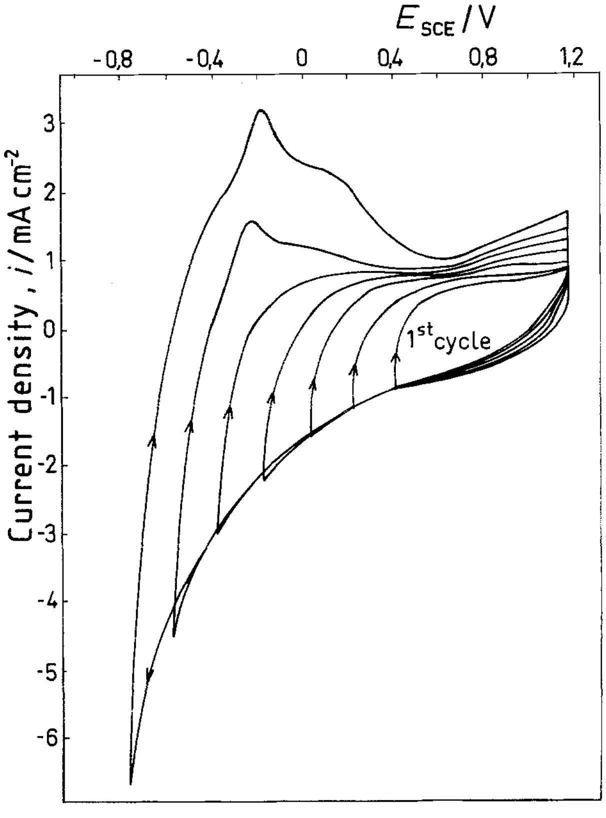

Fig. 1. Voltammetric curves at 1 mV s^{-1} of a Ti_4O_7 electrode in 0.1 M H_2SO_4 between E and 1.2 V vs SCE. E was varied between 0.4 V (curve 1) and −0.8 V in 0.2 V steps.

anodic current over the whole potential range while the cathodic current remains substantially reproducible in the range 0.4 to 1.2 V. The reduction is partly irreversible in the sense that the excess charge spent between +0.4 *V* and the lower limit is recovered over all the potential range up to 1.2 V. This indicates a high degree of heterogeneity of the surface. At 1.2 V the reoxidation process is complete and the fact that the curves are superimposable between 0.8 and 0.3 V during the negative scan is a clear indication that the original state of the surface of Ti_4O_7 has been totally recovered.

The charge injected between 0.4 V and the lower limit is recovered at higher potentials. This fact suggests that the surface species formed cathodically on the oxide undergo some ageing during the residual scan before current reversal. it is possible that the intermediates are partially soluble in the oxide and cannot be regarded simply as adsorbed species. After exceeding −0.4V of the lower limit of the potential range in the returning scan at −0.2V a well defined anodic current peak appears. This anodic peak can be correlated to the exactly determined form of intermediates.

The cyclic voltammograms which contain the potential range for the hydrogen evolution reaction on the Ti_4O_7 electrode are presented in Fig. 2. The anodic sweep was restricted to potentials more negative than oxygen evolution. As can be seen, a cathodic peak at −0.5V vs SCE appears in the first cathodic sweep. In the second and successive sweeps the position of this peak is shifted to more negative potentials and the overpotential for hydrogen evolution is gradually reduced. After multiple sweeps the cathodic peak completely disappears and the evolution of hydrogen takes place at a more positive potential. In the positive potential sweep the voltammograms show two well defined anodic peaks at about −0.4V and about −0.2V. The first, small anodic current peak can be attributed to the oxidation reaction of the adsorbed hydrogen. It is interesting to note that the cathodic curves are superimposable in the range +0.75 to −0.2 V. This indicates that the original state of the surface of Ti_4O_7 has been totally recovered, as in the first experiment. At more negative potentials the cathodic curves undergo some change when the electrode is cycled up to disappearance of the cathodic current peak. The coupled anodic peak at −0.2 V remains at the same potential during successive sweeps and the anodic current density increases. On the basis of these results a hypothesis can be proposed that the cathodic peak, which disappears when the electrode is cycled with the simultaneous moving of the hydrogen overpotential, can be correlated to the insertion of a proton into the channels of the Ti_4O_7 structure. The coupled anodic peak at −0.2 V can be correlated to the deinsertion process. The insertion can be written as follows:

$$Ti_nO_{2n-1} + xH^+ + xe^- \rightleftharpoons H_xTi_nO_{2n-1} \qquad (1)$$

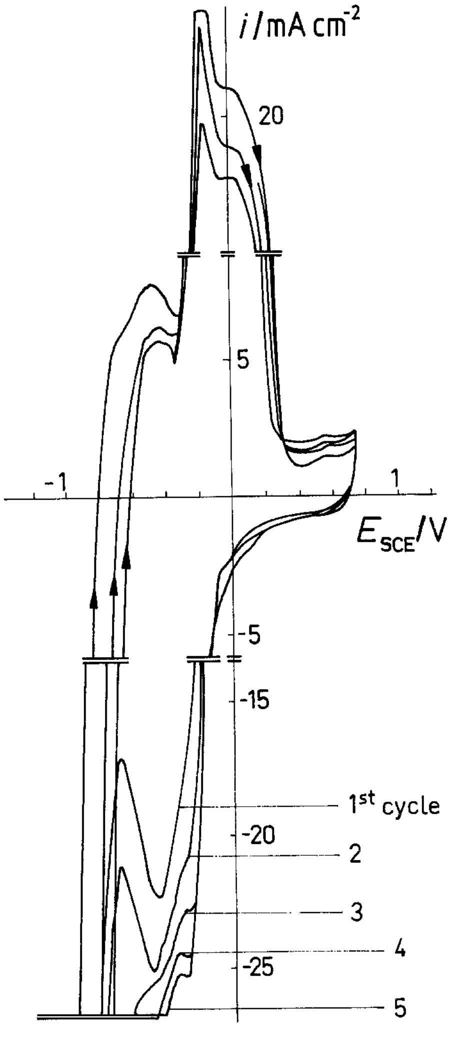

Fig. 2. Cyclic voltammogram (i, E) at 10 mV s^{-1} of a Ti_4O_7 electrode in the 10 wt % H_2SO_4 solution between −1.6 and +0.75V vs SCE.

There is a large decrease in the hydrogen overpotential on the Ti_4O_7 electrode due to the shift of the Fermi level after the insertion of hydrogen. The structure of Magnéli phases is capable of inserting small ions into the channels which lie along the *c*-direction [34]. The probable incorporation of proton ions into the titanium oxide film has already been reported by Torresi *et al.* [11, 12]. The insertion process explains the reproducible reoxidation of the surface and the shift of the beginning of hydrogen evolution.

In the second set of experiments the influence of the porosity of the ceramic electrodes on the electrochemical reaction was examined. The most informative *in situ* characterization of oxide electrodes can be obtained by cyclic voltammetry in a solution of an inert electrolyte in a potential range where the solvent is not electrochemically decomposed. The voltammetric charge q^* is proportional to the number of surface active sites, thus providing a relative measure of the electrochemically active surface area [35, 36]. This kind of information is very useful since a crucial problem when comparing different materials or different preparations is the separation of electronic

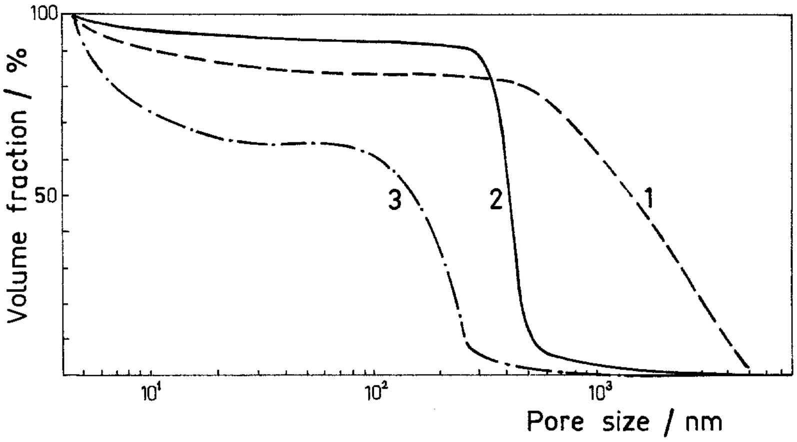

Fig. 3. Pore size distributions of the investigated Ti_4O_7 ceramic electrodes (1, 2, 3).

factors from geometric ones (i.e. the normalization of the activity to the unit of true surface area).

The surface areas of the electrodes were estimated using cyclic voltammetry. The measurements were made for each electrode in the potential region between the hydrogen and oxygen evolution reactions at sweep rates of 1 to 20 mV s^{-1}. Cyclic voltammograms (not shown in the Figure), limited to the potential range 0.2 to 0.5 V, where the anodic and cathodic currents were equal in magnitude and the capacitative current was linear with the sweep rate, were employed to obtain a crude estimate of the surface areas of each electrode. Assuming a double-layer capacitance of 6×10^{-5} F cm^{-2} [37, 38] for a smooth surface of oxide, it was also possible to determine the roughness factors. The scattering of the values of r for the investigated electrodes was in the range of 0.33×10^4 to 3.0×10^4.

Figure 3 illustrates the pore size distributions of three electrodes with the same values of resistivity (0.8 mΩ cm) and the same degree of reduction (100% Ti_4O_7). For the electrodes given in Fig. 3 the values of r were: (1) 1×10^4; (2) 3×10^4 and (3) 0.33×10^4, respectively. Comparative cyclic voltammograms of the 1, 2 and 3 electrodes in the limited potential range of 0.2 to 1.8 V are shown in Fig. 4.

In Fig. 5 some of the voltammograms obtained for Ti_4O_7 ceramic electrodes (1, 2 and 3) are shown. The voltammograms were recorded after the electrodes were stabilized and the curves were reproducible. As can be seen the differences of the shape of the voltammograms are very significant. The differences arise from difficulties for proton exchange along pores, cracks and grain boundaries. When Figs 3, 4 and 5 are compared it may be concluded that the

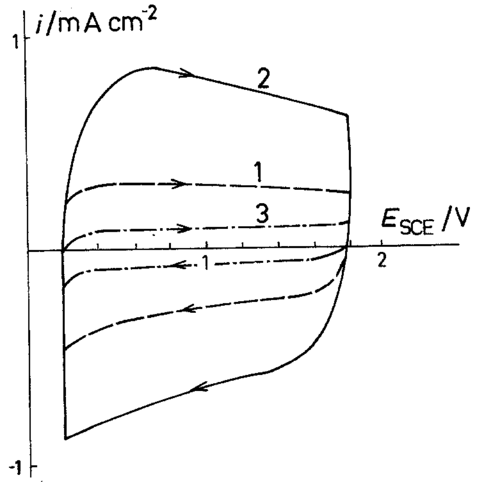

Fig. 4. Comparative cyclovoltammograms at 10 mV s^{-1} in the 0.1 M Na_2SO_4 solution for Ti_4O_7 electrodes (1, 2, 3) with various pore size distribution in the capacitative region.

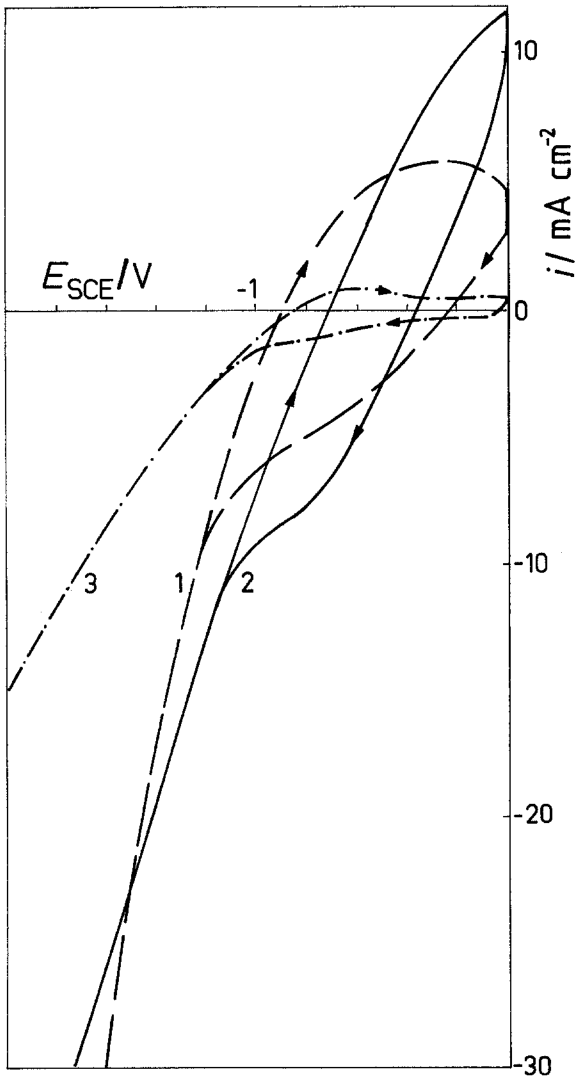

Fig. 5. Comparative cyclovoltammograms at 10 mV s^{-1} in the 10 wt % H_2SO_4 solution for Ti_4O_7 electrodes (1, 2, 3) with various pore size distribution in the hydrogen evolution region.

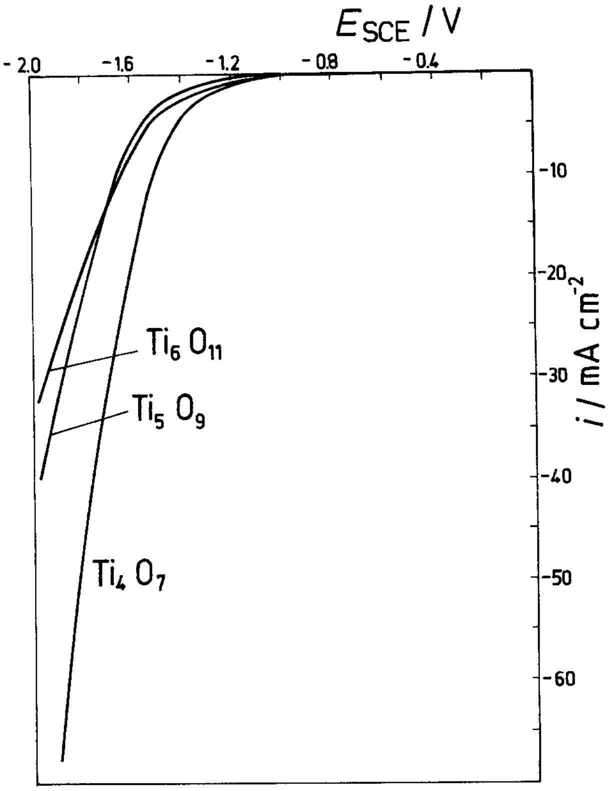

Fig. 6. Cathodic polarization curves (i, E) of the Ti_4O_7, Ti_5O_9 and Ti_6O_{11} electrodes in the 0.9 M KOH solution.

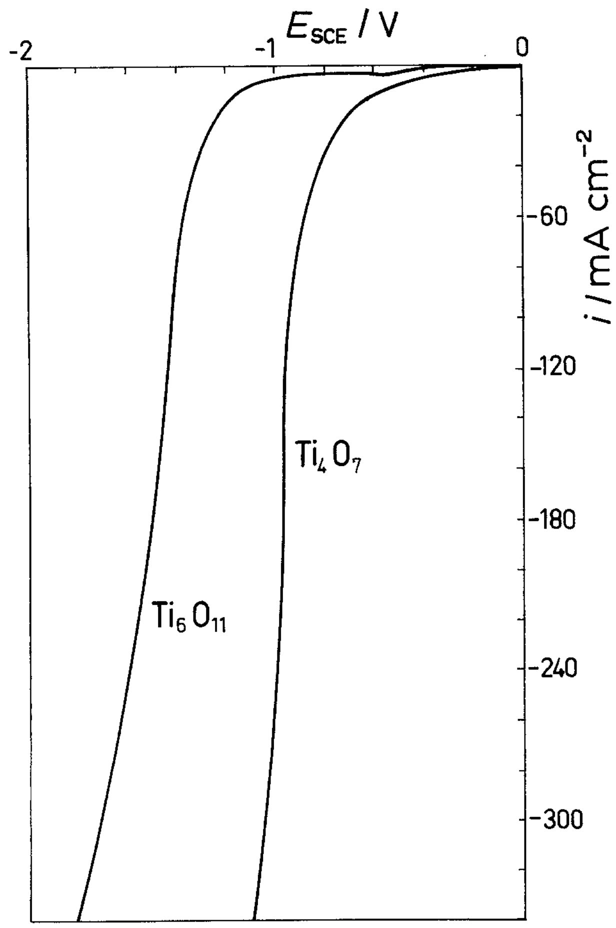

Fig. 7. Cathodic polarization curves (i, E) of the Ti_4O_7 and Ti_6O_{11} electrodes in the 10 wt % H_2SO_4 solution.

small pores (approximately less than 300 nm) do not participate in the hydrogen evolution reaction on ceramic electrodes or their electroactivity is very limited. The most reproducible results and the biggest current densities can be obtained on the ceramic electrodes which are characterized by a large number of large pores (electrode 1).

A qualitative comparison of electrocatalytic activity of the Magnéli phases, the composition of which are: Ti_4O_7, Ti_5O_9 and Ti_6O_{11} is given by the polarization curves (i, E) in Fig. 6 and Fig. 7. These experiments were performed on the monophasic ceramic electrodes which are characterized by approximately equal values of the roughness factor (r about 1.7×10^4). The cathodic polarization curves were recorded after the electrodes were stabilized and the curves were reproducible. The experiments were performed in alkaline (0.9 M KOH) and acid (10 wt % H_2SO_4) solution.

As expected, the electrocatalytic activity of the substoichiometric titanium oxides strongly depends on the degree of reduction of the oxide. The influence of n in the formula Ti_nO_{2n-1} is more apparent in the acid than in the basic solution.

4. Conclusion

It has been found that the degrees of reduction of substoichiometric titanium oxides do not change after a long time of hydrogen evolution in both acid and basic solution. This indicates that the reaction involves only the very surface of the oxide and the lattice is never modified. The reasons for this are to be sought in the metallic conductivity of Magnéli phases: since no electric field penetrates into the crystal, ionic motion necessary for bulk reduction is prevented.

The voltammetric behaviour of Magnéli phase ceramic electrodes during anodic polarization and in the capacity region in aqueous electrolytes will be reported in later papers.

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