



Corrosion of ruthenium dioxide based cathodes in alkaline medium caused by reverse currents



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ABSTRACT

A reverse current obtained during power shutdowns in industrial processes, such as chlor-alkali production or alkaline water electrolysis, is deleterious for hydrogen evolving ruthenium dioxide (RuO₂) based cathodes. It has been observed that RuO₂ coatings after a power shutdown, necessary for e.g. maintenance, are severely damaged unless polarization rectifiers are employed. In this work we show why these types of cathodes are sensitive to reverse currents, i.e. anodic currents, after hydrogen evolution. RuO₂ coatings deposited on nickel substrates were subjected to different electrochemical treatments such as hydrogen evolution, oxygen evolution, or reverse currents in 8 M NaOH at 90 °C. Polarity inversion was introduced after hydrogen evolution to simulate the effect of reverse currents. Because of chemical interaction with hydrogen, a significant amount of the RuO₂ coating was transformed into hydroxylated species during cathodic polarization. Our study shows that these hydroxylated phases are highly sensitive to electrochemical corrosion during anodic polarization after extended hydrogen evolution.

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1. Introduction

Ruthenium dioxide (RuO₂) or mixtures of RuO₂ and other metal oxides (TiO₂, IrO₂ etc.), deposited on a titanium (Ti) support, have successfully been used as catalytic and durable coatings for decades in different industrial processes such as chlorine or oxygen gas production. These types of electrodes are often referred to as dimensionally stable anodes (DSA[®]). RuO₂-based coatings have also found practical applications as a catalyst for hydrogen evolution in chlor-alkali production and alkaline water electrolysis [1]. RuO₂ is then usually deposited on nickel (Ni) substrates because of higher corrosion resistance of Ni, compare to e.g. Ti, in highly concentrated alkaline electrolyte at elevated temperatures.

The most challenging drawback for RuO₂-based cathodes is not activity or duration for hydrogen evolution but reverse currents at power shutdowns. For example, when the chlor-alkali process is interrupted, e.g. for maintenance, a reverse current will flow in the electrochemical cell caused by the change in equilibrium, i.e. hypochlorite and other active chlorine species close to the anode

surface starts to reduce. As a consequence the RuO₂-based coating on the cathode starts to degrade, which is suggested being caused by oxidation [1–3]. By introducing polarization rectifiers, the effect of reverse currents can be minimized. A cathodic potential is then applied large enough to protect the RuO₂ catalyst from anodic dissolution during a power shutdown [2].

Although several authors have reported loss of catalyst material as an effect of reverse currents [3–6], the long-term stability of RuO₂-based coatings has not been well studied. In the previous studies reverse current was introduced by polarity inversion, i.e. repetitive cycling of the current or potential between the hydrogen and oxygen evolution reaction or by applying an anodic current after extensive hydrogen evolution. Furthermore, different investigations have shown substantial changes in RuO₂ and other mixed oxides after hydrogen evolution. For example, increased voltammetric charge and activation of the catalyst was found with cyclic voltammetry [7–9]. It was suggested that wetting of active sites or hydroxylation of RuO₂ caused the activation process. Studies with X-ray diffraction (XRD) showed an expansion of the RuO₂ crystal lattice caused by hydrogen absorption into the rutile structure while exposed to hydrogen evolution in acidic medium [10]. In addition, other XRD studies have found irreversible decrease and shift of the rutile diffraction peaks for RuO₂ exposed to an alkaline

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electrolyte [3,11]. Roughening of the electrode surface area caused by strong hydrogen evolution has also been reported from studies using atomic force microscopy [12] and scanning electron microscopy [13]. All of these studies indicate that RuO₂ is unstable during hydrogen evolution.

According to thermodynamics, RuO₂ exposed to an alkaline electrolyte suggests being reduced to metallic ruthenium during hydrogen evolution [14,15], however, several authors have in the past used X-ray photoelectron spectroscopy (XPS) with the conclusion that metallic ruthenium does not form [8,16,17]. In contradiction to earlier conclusions, we have in a recent work showed that metallic ruthenium, in fact, is formed during hydrogen evolution in an alkaline electrolyte and at high current density [18]. The study further shows that the RuO₂ coating, prior to metallic Ru formation, is subjected to a transformation into ruthenium oxyhydroxide (RuO(OH)₂). Earlier, authors have suggested that RuO₂ is partly reduced through hydration or hydroxylation during hydrogen evolution [3,9,11,16], although never studied in detail. Our detailed material characterization support hydroxylation, however not through a reduction process but instead via a nonelectrochemical process induced by hydrogen incorporation into the RuO₂ rutile crystal structure [18].

The influence of reverse currents on the stability of the formed RuO(OH)₂ has, to our best knowledge, never been studied in detail before. Therefore, we have applied several material characterization techniques, such as scanning electron microscopy (SEM), X-ray diffraction (XRD), and X-ray fluorescence (XRF), to study the corrosion behavior of RuO₂-based coatings in a strong alkaline environment after different electrochemical treatments. The sample treatments include the hydrogen evolution reaction (HER), the oxygen evolution reaction (OER), and in addition a sequence of alternating HER and OER for the effect of reverse currents. Understanding the corrosion mechanism for RuO₂-based cathodes during working conditions, such as hydrogen evolution in alkaline environment, is important before further improvements of the activity and stability of said coatings can be developed.

2. Experimental section

2.1. Electrode preparation

The spin coating technique was implemented to assure that reproducible samples were obtained [19,20]. Nickel disks (Ni-201) with a diameter of 25 mm and thickness of 1 mm were used as substrates. Prior to coating, the disks were blasted with Al₂O₃ particles (diameter: 50–75 μm). After the blasting pre-treatment the disks were ultrasonically cleaned in Milli-Q water for 10 min at 30 °C and finally rinsed with acetone.

A coating solution containing 0.60 M Ru in 1-propanol was prepared by dissolving 7.450 g RuCl₃ × nH₂O (40.27 wt-% Ru, Heraeus) to a final volume of 50 ml in 1-propanol (Fischer Scientific). 100 μl of the coating solution was applied to cover the Ni surface and left for 2.5 min. A uniform distribution of coating solution over the Ni substrate was then obtained through a spin coater from Micro Systems Ltd for 30 s with a rotation speed of 4500 rpm. The electrodes were then left to dry in air for 5 min, followed by additional 5 min at 80 °C. Thermal decomposition of RuCl₃ to RuO₂ was performed at 500 °C for 12 min. The solution application, drying and calcination procedure was repeated until four layers of RuO₂ were deposited on each Ni disk. The heat treatment at 500 °C was prolonged to be one hour during the last coating cycle. With this method, RuO₂-coated Ni electrodes were obtained with a final metal loading of 4.54 ± 0.17 g Ru m⁻². Prior to each electrochemical measurement, the electrode was cut to a size of 3.1 cm² and attached to a conductor; a 25 cm long Ni rod (diam. 1.5 mm) welded to the top end of the electrode.

2.2. Electrode characterization

The microstructure of the coating surfaces was studied using a LEO 1550 SEM and a SIGMA HV FEG-SEM, both systems from Zeiss, operated at 20 kV accelerator voltages. The latter was used to acquire high-resolution images of the electrode surface. A Versa 3D DualBeam microscope from FEI was used for cross-section images. Prior to ion beam milling, platinum was deposited on the electrode surface.

The electrochemical experiments required that a current feeder had to be welded on top of each RuO₂-coated Ni electrode. When the current feeders were removed after the electrochemical tests the top of the electrodes were slightly damaged, e.g. through removal of small part of the coating/substrate. Direct weight measurements, to determine the coating loss, were therefore not appropriate. Instead X-ray fluorescence measurements were performed using the portable element analyzer NITON XLT898 from Thermo Scientific. The intensity of the Ru K_α peak was correlated to the coating amount obtained in mass Ru per area (g Ru m⁻²) using six calibration samples with varying amount of coating layers of RuO₂ deposited on Ni substrates prepared using the spin coating technique as described earlier. For the calibration samples the amount of coating, in mass Ru per area, is determined through the actual weight of the RuO₂ coating. An uncoated Ni disk was used as a blank. The Ru content of the electrodes was determined through the average of four XRF measurements at random selected spots before and after each electrochemical test using the calibration curve. Coating loss was calculated in weight-% Ru after each electrochemical test.

X-ray diffraction analysis was performed with an Xpert XRD system from Panalytical using Ni-filtered Cu K_α radiation. Symmetric θ-2θ scans were performed using normal Bragg-Brentano geometry. The sample preparation described in section 2.1 generates coatings that are built up by nanoparticles (see Fig. 1d) and the average particle size could be determined through the Scherrer equation [21,22] using the full width of half maximum (fwhm) and the shape factor K = 0.9 for the RuO₂ (110) reflection.

2.3. Electrochemical measurements

The electrochemical measurements were performed in 8 M NaOH at 90.0 ± 0.2 °C using an electrochemical cell with a three-electrode configuration where the RuO₂/Ni sample, a Ni-mesh, and a standard calomel electrode (sat. KCl) from Radiometer Copenhagen were used as a working electrode, a counter electrode, and a reference electrode, respectively. The working and counter electrodes were placed at a distance of forty mm from each other while the reference electrode was placed in an external compartment, which was connected via a tube to a Luggin capillary. The tip of the capillary was placed two mm from the surface of the working electrode to minimize the effect from the IR-drop in the electrolyte, but not too close to disturb the current distribution. No further IR-correction was used during the experiments. The electrochemical cell was prepared with a newly made sample and filled with fresh electrolyte prior to each electrochemical test. The electrolyte was prepared from NaOH pellets (reagent analytical grade, Scharlau) dissolved in Milli-Q water and was stirred continuously during each experiment. Although NaOH of analytical grade was used, impurities in the NaOH pellets (mainly Pb and Fe) were released into the electrolyte and some of it was deposited on the electrode surface during cathodic polarization. However, reducing the amount of impurities did not have any influence on the corrosion process during polarity inversion. Analytical grade NaOH pellets, without additional purification, were therefore used for the electrochemical experiments

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