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# Sol-gel-deposited cobalt and nickel oxide as an oxygen evolution catalyst in alkaline media

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## ABSTRACT

Catalysts based on cobalt and nickel oxide were investigated as anode material for oxygen evolution reaction (OER) for an alkaline anion exchange water electrolyser. The catalysts have been prepared on stainless steel non-woven fabrics as electro-catalytic materials by sol-gel deposition [1,2]. Thin films were deposited by dip-coating multi step process to increase the thickness of the thin film and then sintered at different temperatures for 1 h. Electrochemical studies are carried out to test the catalytic activity for the OER in alkaline media. Surface morphology and composition of the catalysts were analyzed by scanning electron microscopy and energy dispersive analysis of X-ray. Polarization curves prepared in a half-cell setup with 1 M KOH electrolyte at room temperature reveal a 400 mV difference between the developed CoNi oxide catalysts [3]. The catalysts with the best electrochemical properties will be tested in an experimental anion exchange membrane electrolysis cell under real conditions.

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## Introduction

The electrolysis electrochemically converts water to oxygen and hydrogen by means of electricity. Hydrogen can therefore be used as a storage medium and also it can re-generate electric power in a fuel cell. In this manner a decentralized electric energy can be stored and transported on the established transport paths.

One of the most established electrolyzing technique is the Alkaline Electrolyzer with liquid KOH solution as the electrolyte. To combine the positive properties of Alkaline Electrolysis and those of Proton Exchange Membrane Electrolysis an Alkaline Anion Exchange Membrane Water Electrolyser (AAEMWE) has been developed. The KOH electrolyte was

changed to a solid polymer electrolyte with anion exchange abilities, whereby the reaction mechanisms remain the same [4–7].

This makes it more environmentally friendly and compact in design. The low corrosive environment at AAEMWE makes it possible to use cheaper material for the bipolar plates and non-noble materials for the catalyzer as well [8].

Energy efficiency of electrolysis may be improved by increasing the H<sub>2</sub> and O<sub>2</sub> production. In the present study cobalt and nickel oxides were applied as anode catalysts for the oxygen evolution reaction (OER). A reduction of the over-potential for OER could be obtained through developing of a new type of current collectors – substrates with a porous surface covered with multiple component non-precious metal catalysts [2,9,10]. Ni- and Co-based mixed oxides could be

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created by the sol–gel method, where organometallic precursors are thermally decomposed [1]. The sol–gel process allows the production of nanoscale mixed oxide coatings using simple reagents and not expensive equipment [3].

## Experimental

### Experimental setup

The surface morphologies of the anode separators were investigated by EDS-analysis, X-Ray fluorescence spectrometer (XDAL, Helmut Fischer GmbH & Co. KG) and scanning electron microscopy (SEM) with a Leo Supra 55VP microscope from Carl Zeiss AG.

The electrodes with a geometrical surface of about 2 cm<sup>2</sup> were tested for OER in 1 M KOH (p.A., Sigma Aldrich) in classical 3-electrode electrochemical cells using Electrochemical Workstation VMP3B-20 (Bio-Logic SAS). Saturated calomel electrode was used as reference electrode (RE), Ti–Pt mesh as counter electrode (CE). The experiments were carried out under galvanostatic steady-state condition. Before starting the measurements the electrode surface was polarized for  $t = 30$  min by applying a relatively high ( $I = 200$  mA) cathodic current [9]. After this pre-conditioning that the measurements started at 200 mA and the current was lowered stepwise to 0.5 mA. Five measurements were performed with each electrode. After each experiment the electrode was relaxed  $t = 30$  min at OCP. Then it was polarized for  $t = 3$  min at  $I = 200$  mA. The average of five polarization curves is shown in this article.

### Materials

Stainless steel (316L/1.4404) non-woven fabrics PACOPOR ST AL3 (VS) from PACO PAUL GmbH & Co. KG were used as anode substrates.

To get as close as possible to the desired mixed oxide NiCo<sub>2</sub>O<sub>4</sub>, the work focused on the mixing molar-ratios Co:Ni of 2:1 and 2:2. In order to achieve a better comparability coated electrodes were also investigated with nickel oxide and cobalt oxide only. For the sol–gel coating cobalt and nickel acetylacetonates (from Chempur) were dissolved in the desired mixing ratio in an ethanol-glacial acetic acid solution (ethanol/acetic acid = 3:2) and stirred for a few hours until the powder was dissolved completely. Based on positive experience with isopropanol as a solvent, individual experiments were also conducted with this solution. The solutions are summarized in Table 1 and are hereinafter abbreviated with the here described names.

After rinsing with water and ethanol the anode substrate was dipped into the solution and then pulled out with 1 mm/s using a dip coater (RDC21-K from BUNGARD-Elektronik GmbH&Co KG). After 10 min stay at room temperature, the sample was dried for 15 min at 200 °C. The whole procedure was repeated from 1 to 6 times. In the end the sample was sintered at 400 °C, 600 °C or 800 °C for 1 h in Standard Tube Furnace Type SR (A) from GERO Hochtemperaturöfen GmbH & Co. KG.

**Table 1 – Metal ion concentration of the solutions with solvents.**

Solution	Co <sup>3+</sup> [mol/l]	Ni <sup>2+</sup> [mol/l]	Solvent
T	0.2	0.1	Ethanol
U	0.2	0.2	Ethanol
V	0.2		Ethanol
Tt	0.1	0.05	Ethanol
X	0.1	0.05	Isopropanol
Y		0.1	Ethanol
Z		0.1	Isopropanol

## Results and discussion

### Analysis

A verification of the cobalt content was performed by X-ray fluorescence analysis and EDS-analysis. In almost all samples and with both analyses, cobalt could be detected on the surface. To determine the nickel content is difficult, since nickel is present in the base material, a nickel peak is therefore always measured. With the X-ray fluorescence analysis it was possible to quantitatively measure an increase in the nickel content, which did not derive from the base material, but from the coating. It can also be seen when two EDS-spectra, one from an uncoated substrate and one from a coated substrate, were put on top of each other. Cobalt and nickel peaks are clearly visible, see Fig. 1.

There was a correlation between the coating frequency and the cobalt and nickel content in the coating layer. If the coating was repeated more often, more cobalt was determined on the fibers. The cobalt content increased by around 10 times, when the sample was coated three times instead of once. However, it cannot be said that an increase of the coating repetitions leads to a constantly increasing cobalt content. The cobalt content increased just around 10 percent, when the sample was coated six times instead of three times.

The cobalt content of the samples with calcination temperatures of 400 °C and 600 °C is almost identical. However, with increasing temperatures the oxygen content increased. Samples which were annealed at 800 °C changed their mechanical properties fundamentally. The material transformation from austenite to martensitic steel has started, accompanied by a strong oxidation.

### Images and graphics

Fig. 2 shows SEM-images from the uncoated substrate. The substrate has a compact, but non-closed surface, which makes it ideal for use as a gas filter. Even at a low magnification, see Fig. 2a), the fine and disordered fibers can be seen. The edge length of the fibers could be measured by means of SEM, they are about 25 microns. The surface of the fibers is smooth. Some grain boundaries are visible.

Fig. 3 shows typical SEM-images of the coating. It is T-solution coated sample with annealing temperature at 400 °C for 1 h. The difference in distribution is due to the coating repetition. The sample, shown on Image 3a), was coated 1 times, the sample on image 3b) 6 times. Although we used the BS detector, no color differences between base material and

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