# Studies of the initial oxidation of cobalt in alkaline solutions using scanning electrochemical microscope

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**Abstract.** Scanning electrochemical microscopy and atomic force microscopy were used together with cyclic voltammetry and rotating ring disc experiments to study the initial oxidation of cobalt in alkaline solution. The results show that the mechanism of cobalt oxidation involves a solid state path as well as dissolution combined with precipitation. In the concentration region studied, 0.1–1 M NaOH, the solid state path seems to predominate.

The AFM images clearly show a three-dimensional growth mechanism and that the initial oxidation starts at active sites at the surface.

Metal oxide and hydroxide films are of practical interest because of their electrocatalytic properties, photochemical activity and charge storage capabilities. Electrochemically generated films are generally more active and it is therefore of great interest to study the initial oxidation mechanism. Two main questions are stressed in many film-forming systems: first, whether the reaction proceeds through a solid state route or by a dissolution/precipitation path, and second, whether the film growth is two- or three-dimensional. In the dissolution/precipitation route, soluble species are formed and can be detected, for example, by conventional rotating ring disc electrode (RRDE) measurements, provided that the precipitation reaction is not too fast. The film growth is generally inhomogeneous and three-dimensional. In this work, the initial oxidation of cobalt in alkaline solution was investigated with these questions in mind. Scanning electrochemical microscopy (SECM) and atomic force microscopy (AFM) were used together with cyclic voltammetry and RRDE. Most spectroscopic and diffraction techniques only provide information averaged over macroscopic regions of the electrode surface. This is in contrast with scanning probe methods (SPMs) such as atomic force microscopy (AFM), where the electrode surface can be studied with nanometer to atomic resolution, ex situ or in situ. The high spatial resolution of the surface is of interest because structural and chemical inhomogeneities can have a significant influence on the local mechanism of electrochemical reactions on the electrode. Thus,

by performing AFM measurements one gets topographical information about the electrode surface. Furthermore, AFM reveals whether small oxide particles have formed on the electrode surface where other techniques, such as X-ray grazing angle measurements, fail to detect them. AFM can be used to image both conducting and nonconducting samples. SECM was used to detect soluble species formed during the oxidation process. By keeping the tip at constant potential during the polarization of the cobalt sample, these experiments resemble the RRDE measurements. However, the tip electrode can be located close to the surface and more short-lived species can be detected.

The results show that soluble species can be detected by RRDE and SECM when the oxidation takes place in 1 M NaOH. Preliminary results show that a larger fraction of soluble species can be detected by SECM. In 0.1 M NaOH the detection of soluble species failed, which indicates that the oxidation proceeds through a solid state route. The AFM images clearly show three-dimensional growth on specific active sites.

## 1 Experimental

In electrochemical experiments with potentiostatic control, as in the SECM and RRDE techniques used here, the potential of the sample (working electrode) under consideration is controlled relative to the potential of a reference electrode with known potential through which no current flows. Instead, the current is drawn between the sample and a so-called counter electrode.

Figure 1 shows a block diagram of the SECM apparatus. The SECM is based on faradaic currents that flow between the tip and the sample, not on tunnelling currents as in electrochemical variants of STM. An advantage with SECM is that it gives chemical information, in contrast with most other SPMs. The resolution of the SECM is limited by the size of the tip and may ultimately be down to 10 nm. The theory, instrumentation and applications of SECM instruments have been reviewed by Bard et al. [1]. A Macintosh computer (PowerMac 6100) with an NB-DIO-24 digital interface card
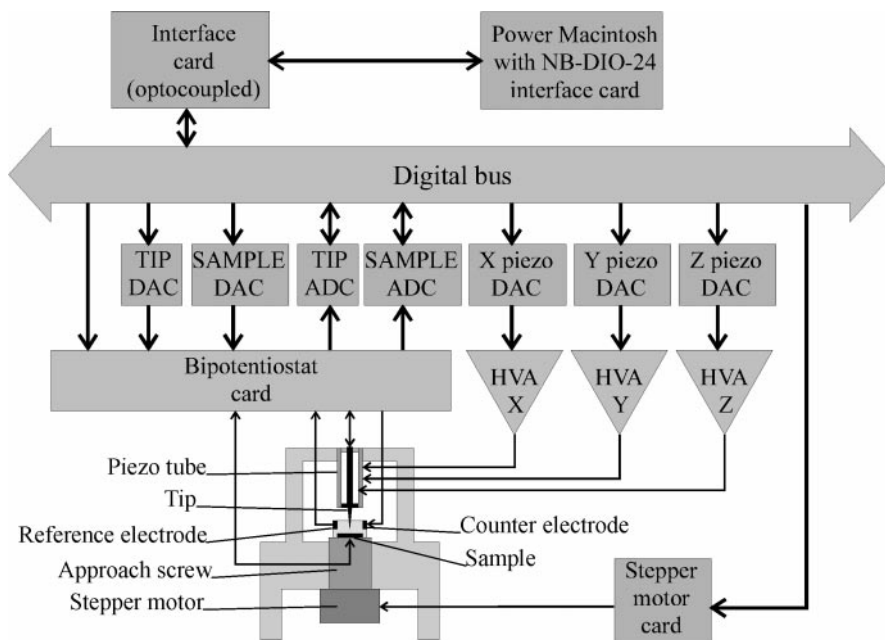
**Fig. 1.** Schematic block diagram of the SECM instrument, where DAC, ADC and HVA denote digital-analog converter, analog-digital converter and high-voltage amplifier, respectively

(National Instruments) connected to a home-built electronic box was used to generate the desired potential waveform applied to the electrochemical cell. The digital signals generated were converted by the home-built digital-to-analogue converter and applied to the bipotentiostat. The resulting current is converted to a voltage, which in turn is digitized by an analogue to digital converter before it enters the computer again. An optical coupling between the computer and the rest of the SECM was used in order to eliminate any electronic noise from the computer. The bipotentiostat is based on the well-known circuit described by Bard et al. [2]. The bipotentiostat has a noise and ripple level less than 20 pA and signal bandwidth of 30 kHz. The maximum current output is 250 mA and the maximum voltage output is 10 V. The bipotentiostat can also be operated as a galvanostat. The whole SECM system is completely automated and controlled through the computer. All DAC, ADC and interface cards have 16 bit resolution. "LabView" software from National Instruments was used for integration data acquisition, control analysis and presentation of the system.

The mechanical parts of the electrochemical scanning microscope were custom-built, with a stepping motor for coarse vertical displacement of the electrochemical cell, giving a minimum step of 80 nm and a speed of 245 steps/s. Fine motion between the sample and the Pt tip was achieved by using a 2" long piezo tube for x, y and z deflection. For some of the experiments the bending mode of the piezo tube was used for the z-motion to increase the maximum range from $8\,\mu m$ to $200\,\mu m$.

The electrochemical cell was custom-built for the SECM apparatus. The cell has a maximum volume of 2 ml and is made of a Teflon bottom, which also serves as the sample holder, and a Pyrex glass wall. Samples, conducting and non-conducting, 5 mm in diameter, can be used. The electrical connections between the sample and electrical leads are made by silver epoxy glue. The counter electrode is made of platinum sheet. With this cell construction the sample is easily removed from the cell for further ex situ examination. The reference electrode was made of silver wire coated with silver chloride mounted in a glass tube filled with saturated sodium chloride solution. The junction between the reference electrode and the rest of the cell was made of ceramic plug. Platinum microelectrode tips with diameters ranging from 9 to $150\,\mu m$ were sealed in glass tubes and made flat by wet grinding on 4000 mesh silicon carbide paper. The SECM was operated in the so called collection mode, where the tip was kept at constant potential during polarization of the sample [3]. The stepping motor had a maximum speed of 245 steps/s and thus provided 1 mm displacement/1200 steps.

The cobalt substrate was polarized between $-1.2$ and $-0.3$ V vs. Ag/AgCl in 0.1 M NaOH nitrogen-saturated solution. The sweep was initiated at $-1.2$ V and reversed at $-0.3$ V and finally terminated at $-1.2$ V. The tip was kept at constant distance and potential, $E_T = -1$ V. After the polarization of the cobalt, the sample was carefully washed with doubly distilled water and dried before the AFM measurements. The Pt tip was removed from the solution and stripped in 1 M $NaClO_4$, pH = 4 solution.

The RRDE experiments were performed using an EG & G PAR model 366 Bipotentiostat interfaced through an HP multimeter and connected to an HP 85/86 microcomputer for control and data analysis. The computer programs were developed and written in BASIC.

A conventional single-compartment cell (Methrom 150 ml), with specially designed lid, was used.

The RRDE was made of a cobalt disc, 0.5 cm in diameter, and a platinum ring of 99.99% purity (Johnson & Matthey). The electrode was moulded and insulated in epoxy resin with an insulating gap of 0.02 cm. The RRDE dimensions were $R_1 = 0.25$, $R_2 = 0.27$ and $R_3 = 0.37$ cm. The collector efficiency was calculated as $N = 0.456$, according to Albery et al. [4].

Prior to the experiments the electrodes were wet ground with 1200, 2400 and 4000 mesh carborundum paper (Struers) followed by cleaning in ethanol in an ultrasonic bath for 5 min and finally being rinsed with doubly distilled water before im-

mersion in the cell. The reference electrode was a saturated calomel electrode ($E = 236$ mV vs. nhe) and platinum gauze was used as the counter electrode.

Solutions were prepared from Merck reagents of ultra pure quality and de-aerated with nitrogen prior to the experiments.

The rotation speed of the RRDE unit was kept constant at 1600 r.p.m. The Pt-ring electrode was activated before each sweep by switching the electrode potential between $-1$ and 1 V. During the sweep the ring potential was held at $-1$ V, ensuring diffusion-controlled conditions.

All experiments were carried out at room temperature.

After polarization measurements the working electrode was immediately removed from the solution and thoroughly washed with doubly distilled water and dried before the ex situ measurements.

The grazing angle X-ray diffraction measurements were conducted with a Siemens D5000 diffractometer equipped with an appropriate computer and software for instrumental control and data processing. The incident angle was set to 0.3.

The AFM measurements were conducted in air at room temperature, using the NanoScope III AFM (Digital Instruments) in contact mode. The AFM images were generated by maintaining a constant force between the tip and the sample.

## 2 Results and discussion

### 2.1 RRDE

Rotating ring disc measurements were conducted in 1 M and 0.1 M NaOH. The disc was polarized from $-1.2$ V to $-0.3$ V and back. The ring potential ($-1$ V) was chosen so that the reduction of Co(aq) formed during the oxidation of the disc proceeded under diffusion control. In Fig. 2 the disc and the ring currents are plotted for the positive-going sweep. As the cobalt disc is oxidized, cobalt hydroxide is subsequently formed on the surface either by a solid state path (2) or by precipitation from soluble species (scheme I, path 3). If soluble intermediates participate in the reaction sequence it will be possible to register that on the ring electrode. Soluble products were detected on the ring in the potential region -800 to $-600$ mV. The ring current show a sloping tendency because, at the negative potential used, $-1$ V, the reduction of cobalt ions takes place in parallel with hydrogen evolution. The maximum fraction of soluble cobalt species formed was calculated from the ratio between the ring and disc currents at
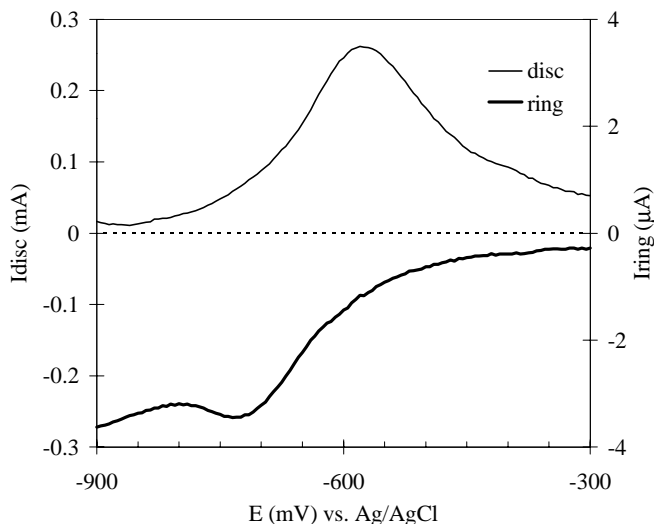


**Fig. 2.** RRDE measurements. Sweep rate 25 mV/s and rotation speed 1600 r.p.m. Ring potential $-1$ V

constant potential ($-725$ mV) according to (1).

$$Co(aq) = \frac{i_r}{N\, i_d} \times 100 \qquad (1)$$

where $N$ is the collector efficiency and $i_r$ and $i_d$ are the ring and disc currents, respectively. Only about 3% soluble species could be detected. From these measurements one can conclude that the reaction takes place mainly along the solid state path (scheme I, path 2). Soluble species could not be detected on the negative-going scan, i.e. during the reduction of cobalt hydroxide. At lower concentrations, 0.1 M, no soluble species could be detected on the ring, indicating a solid state mechanism.

### 2.2 SECM

Measurements in the high-concentration range confirmed the RRDE results, i.e. soluble products could be detected during oxidation of cobalt but were lacking in the reduction of the cobalt hydroxide formed.

In order to quantify the measurements the theoretical ratio between the tip and the disc currents must be determined. Experiments were therefore made in acid solution, where the only oxidation product is $Co^{2+}$. With a tip size of 150 μm the factor between the tip and the sample currents was about $6 \times 10^{-4}$. By using this value for measurements in alkaline
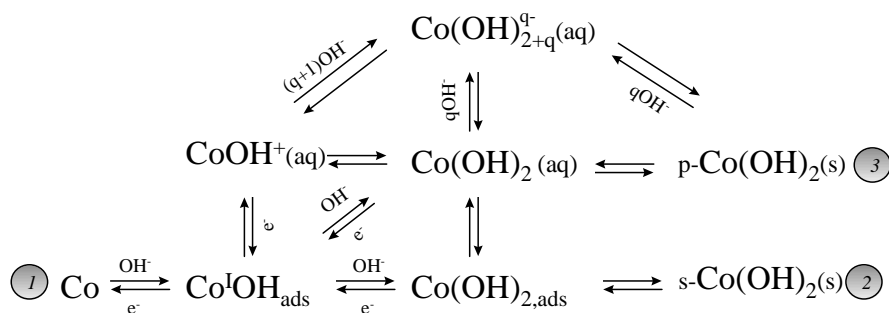


**Scheme I**. Schematic mechanism for the anodic dissolution of cobalt in alkaline solution. p: precipitated; s: formed by solid state reaction

solution we find that a much larger fraction of the reaction proceeds through the dissolution/precipitation path (scheme I, path 3) than revealed from the RRDE measurements. This indicates that the precipitation rate is so fast that most of the soluble species are unable to escape to the bulk solution.

In Fig. 3, SECM measurements in 0.1 M NaOH are shown. The sample was polarized and the tip potential was constant at $-1$ V. On the positive-going scan the sample is oxidized, but no soluble species could be detected on the tip, in agreement with the RRDE results. In the negative-going scan, where the cobalt hydroxide is reduced, the tip current shows a corresponding peak current. However, this current is positive and is probably due to a capacitive coupling between the sample and the tip as the tip approaches the surface [5]. At long distances the peak disappears. It can therefore be concluded that the process in 0.1 M solution can be looked upon as a solid state reaction.

## 2.3 AFM

The amount of hydroxide formed by the polarization of cobalt in 0.1 M NaOH corresponds to about four monolayers, calculated from the reduction charge (Fig. 3). AFM images of the surface show that the hydroxide is inhomogeneously distributed. In Fig. 4 an AFM image of an area with a high density of cobalt hydroxide particles is shown. The particles have lateral diameters of 170–280 nm and the height varies from
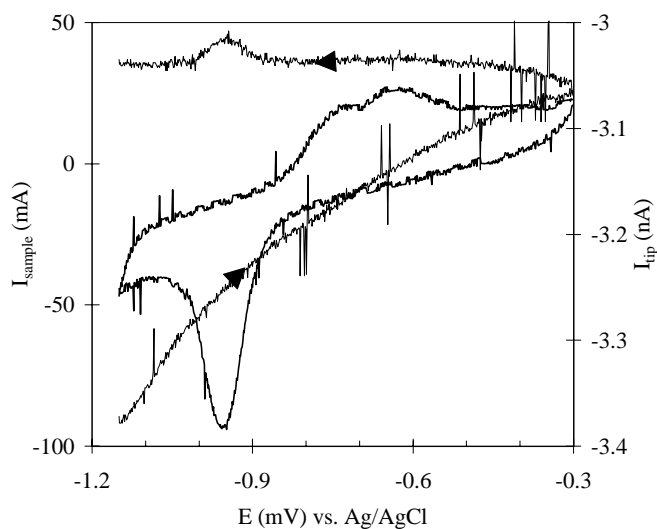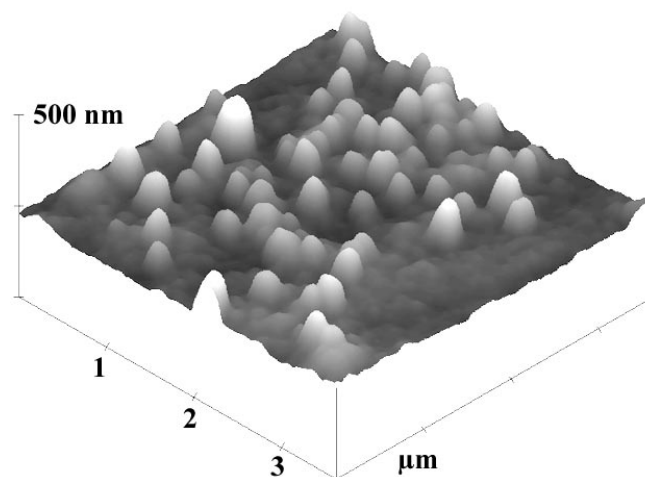


**Fig. 4.** AFM image of cobalt polarized in 0.1 M NaOH solution

40 to 210 nm. The largest particles are probably created as a result of a coalescence of smaller particles. Small pits were observed close to the particles. These pits are not symmetrical around the particles, as was found for pits in aluminum [6].

The AFM results clearly show that the growth mechanism is three-dimensional and that the oxidation starts at highly active sites. AFM images on samples polarized in 1 M solutions show a complete hydroxide layer [7].

## 3 Conclusions

The mechanism of cobalt oxidation in alkaline solution involve a solid state path as well as dissolution combined with precipitation. In the concentration region studied, 0.1–1 M NaOH, the solid state path seems to predominate.

The growth mechanism is three-dimensional and the initial oxidation starts at active sites at the surface.



**Fig. 3.** SECM measurements in 0.1 M NaOH. Sweep rate 25 mV/s. Tip potential $-1$ V. The curve with the arrows originates from the tip current

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