



INSTITUTIONEN FÖR KEMI OCH MOLEKYLÄRBIOLOGI

# **Selectivity in the Chlorate Process: Hydrogen Evolution and Hypochlorite Reduction on Chromium Oxide/Hydroxide**

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# Abstract

Production of chlorate is dependent of using sodium dichromate as a component in the electrolyte. Dichromate provides selectivity by forming a Cr(III) oxide-like film on the cathodes. Without dichromate, unwanted cathodic reactions dominate instead of the hydrogen evolution reaction (HER), and chlorate is not produced. However, Cr(VI) is a hazardous element and must be replaced in the process with a less harmful compound for environmental and safety reasons. Removing Cr(VI) from the chlorate process has proven to be challenging, and no replacement element or material has been found.

This thesis presents experimental and theoretical results leading to a mechanism that explains the selectivity between the unwanted reactions and the HER. The mechanism also supports previous findings regarding the Cr(III) film formed in situ on chlorate cathodes.

The approach in this work was to ex situ electrodeposit two structures, Cr(OH)<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub>, as pure films. These ex situ-formed films could then be characterized prior to investigating their electrochemical performance relevant to the chlorate process.

The morphology of the films were analysed by scanning electron microscopy, revealing clear differences. The Cr(OH)<sub>3</sub> film was thin and rough, while the Cr<sub>2</sub>O<sub>3</sub> film was composed of plate-shaped crystallites with approximately 1 μm in length. The molecular structure was investigated by Raman spectroscopy. This was, to some extent, challenging by the discovery that Cr(OH)<sub>3</sub> converts to Cr<sub>2</sub>O<sub>3</sub> at high laser energies. Still, the spectra collected with lower laser power clearly showed Raman signatures related to Cr(OH)<sub>3</sub>.

Electrochemical investigations showed that hypochlorite reduction was blocked on both surfaces, Cr(OH)<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub>, indicating that the blocking effect is related to Cr(III) and not to the films' molecular structure or morphology. This reaction was also completely hindered by the Cr(OH)<sub>3</sub> deposited on more active electrodes towards hypochlorite reduction, as Fe or Au.

In contrast, the HER could still proceed on both Cr(III) films. Interestingly, on Cr<sub>2</sub>O<sub>3</sub> the electrode activity was enhanced towards the HER, while Cr(OH)<sub>3</sub> displayed the opposite effect. These results show that the HER take place on the Cr-film, which must be taken in to account in the selective mechanism.

The blocking mechanism was first rationalized in the context of surface charge of Cr(III) oxide-like films and their p-type semiconducting properties. These properties may somewhat hinder the reduction of hypochlorite, but cannot give the full explanation for the selectivity. Further insights about the mechanism were given using DFT calculations and the complete selectivity mechanism was determined. Cr-sites cannot be reformed during hypochlorite reduction, and are irreversibly blocked by OH. Thus, the reduction of hypochlorite is blocked by OH groups strongly binding to the surface. The HER, however, can readily proceed at the OH covered surfaces.

Key words: sodium chlorate, hydrogen, sodium dichromate, hypochlorite, HER, mild steel electrodes, Cr<sub>2</sub>O<sub>3</sub>, Cr(OH)<sub>3</sub>