

# Effect of Chromate Ion on the Formation of Black Film on the Cathode in Alkaline Water Electrolysis

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Alkaline water electrolysis is a major industrial electrochemical process for the production of hydrogen. Nickel anode and nickel/mild steel cathodes are usually used with sodium hydroxide (20%) or potassium hydroxide (~28%) as electrolyte. During the continuous operation of these industrial cells time dependent voltage increase is observed due to carbonation of the electrolyte, clogging of the pores of the asbestos diaphragms and a black film formation on the cathodes. Experiments were carried out to prevent the film formation by the addition of chromate. The effect of cathode current density and the concentration of the chromate on the formation of the film was evaluated and reported in this paper. Chromate ion was found to inhibit the film formation in the concentration range of 0.1 to 0.2 g/l and the film was not observed even after 1000 hrs of operation at the operating conditions of the industrial water electrolyses.

*Key words:* Water electrolysis, cathodes, chromate addition

## Introduction

Hydrogen has been produced commercially by alkaline water electrolysis for over 100 years [1]. Efforts are made to improve the current and voltage efficiencies of the electrolyser through different approaches, such as, improved cell designs, modified/new separator materials and introduction of new electrolysis concepts etc. Stable and reliable performance is a major requirement for industrial conditions. The escalation of cell voltage with time has been observed in many of the alkaline water electrolyzers. Contributions to this time dependent voltage effects have been ascribed mainly to the deterioration of electrocatalytic activity of the electrodes, specifically on the cathode and as a consequence, the energy consumption increases [2]. The time dependence of the hydrogen overpotential was related to gas bubbling, which affects the steady-state conditions at the electrode – electrolyte interface, the deposition of impurities on the cathode [3] or adsorption of atomic hydrogen [4]. The increase in overpotential results in raising the cell voltage by more than 200 mV and hence a decrease in energy efficiency by 15% over a period of one to two years. The formation of a black film has also been observed on the cathodes in cells under continuous operation and remedial measures for removing this film have also been reported [5].

We have investigated this to avoid the formation of black film by the addition of chromate in alkaline water electrolysis and the results are presented in this paper.

## Experimental

A laboratory scale undivided cell was assembled with a 500 ml glass beaker fitted with suitable PVC cover. The anode was a nickel sheet (9 x 6 x 0.1 cm) and the cathodes were from mild steel, stainless steel and nickel of the same size. The electrodes were inserted through the lids and positioned at an inter electrode distance of 1.0 cm. The sodium hydroxide electrolyte was prepared from LR grade chemical and distilled water and the other chemicals were of AR grade. The temperature of the electrolyte was maintained at 338 K by keeping the cell in a thermostat. D.C. current was supplied from a rectifier (25 A, 0 – 12V).

## Results and discussion

The alkaline electrolytes are known to absorb carbon dioxide from the atmosphere and in the industrial cells, the carbonate content increases to about 4% over a period of two years. So, to study the effect of carbonate content in the sodium hydroxide

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electrolyte, the experiments were carried out at 338 K with the addition of carbonate (0.5 – 4.0%) and without carbonate in the electrolyte and the results are presented in Fig.1. From the figure it is clear that the cell voltage increased by about 200 to 250 mV when the carbonate content is 4% irrespective of the cathode employed. Carbonation of the electrolyte by about 1% leads to a decrease of hydroxide content by 0.8% and at 4% carbonate concentration the hydroxide is reduced to about 17%. The cell mud collected from one of the industries, on analysis was found to contain predominantly carbonate, which must be due to the precipitation of the carbonate that occurs above 6% sodium carbonate in the hydroxide electrolyte.

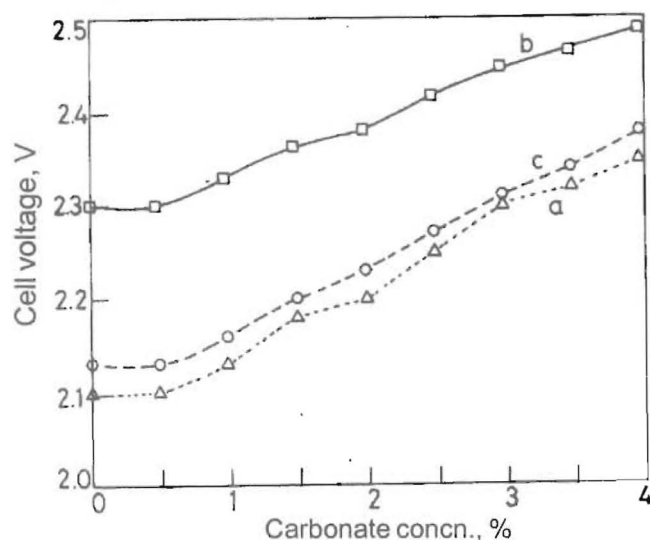


Fig.1: Effect of carbonate content on the cell voltage with different cathode materials.

a). Mild steel, b). stainless steel and c). nickel.

Conditions:

Electrolyte	17% Sodium Hydroxide,
Temperature of the electrolyte	338 K
Anode	Nickel
Current density	5 A dm <sup>-2</sup>
Current passed	2.7 A

The formation of the black film was observed with both mild steel and nickel, but it was more pronounced with mild steel than nickel. With stainless steel, the film was not observed within the set duration of the electrolysis. The film formation was found to depend on the carbonate content on visual observation of the cathode at various intervals with different concentration of carbonate. In the absence of

carbonate the black film appears in about 6 hours but it occurs within about 4 hours at 4% carbonate content in the electrolyte.

The black film on nickel turns to a green color on keeping outside the cell. Similar observation was also reported and the film was found to be  $\text{Ni}_2\text{O}_3 \cdot 10\text{H}_2\text{O}$  [2]. Another report indicates the presence of both nickel and iron on nickel cathodes [6]. The iron contamination was due to the presence of iron impurity in the alkali used or from the container/piping etc. Iron content below 0.03 ppm does not produce any significant effect and at above 3 ppm level, the deposition was found to be initiated. The black film on mild steel cathode, collected from the industry was examined by X-ray diffraction (JEOL 8030) as shown in Fig.2. The composition of the film corresponds to that of iron as well as to nickel-iron (Kamacite). The deposition of iron/ nickel-iron either on mild steel or nickel actually reduces the overpotential because of its roughness and increased surface area. Only with activated cathodes that exhibit lower hydrogen over potentials than bare nickel or mild steel, the iron deposit affects by increasing the overpotential slightly [7].

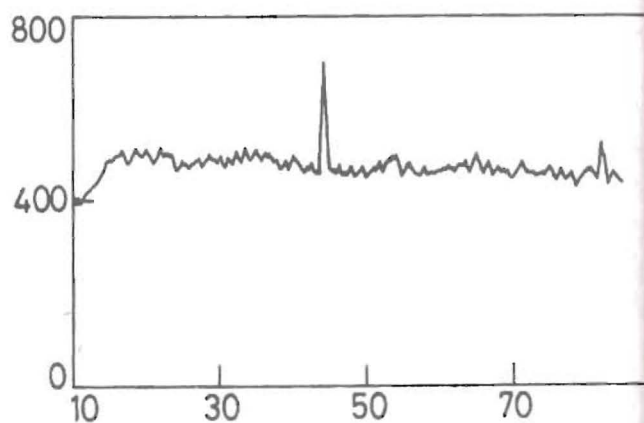


Fig. 2 : XRD pattern of the black deposit.

The formation of the film by the deposition of iron or nickel or both, though may be useful in enhancing the catalytic activity of the cathode, has been found to increase in thickness and peels off periodically contaminating the electrolyte and the diaphragm. This may deteriorate the performance of



the diaphragm. The discoloration of the electrolyte and the black cell mud affects the cleanliness and aesthetics of the plant environment. The film formation has to be prevented without affecting much the operational procedures and scheme.

Chromate was added at various levels from 0.1 to 1.2 g/l. After 32 hours of the cell operation of the cell at 65°C, it was found that the black film was completely absent at all concentrations above 0.1 g/l. Figure 3 shows the dependence of the cell voltage on chromate content. A significant improvement in cell voltage was observed with and without chromate and chromate addition as low as 0.1 g/l has been found to retard the formation of black film. Chromate addition in the electrolysis of sodium chloride to chlorate is well reported [8]. The chromate is added to the chlorate electrolyte in the concentration range of 2–7 g/l. This has been found to be beneficial in more than one mode, such as, (i) decreasing the reduction of  $\text{ClO}^-$  and  $\text{ClO}_3^-$ , (ii) offering buffer action in the range of pH 7.0, (iii) increasing the efficiency of cathodic hydrogen evolution and thus reducing the oxygen content in the exit gas and (iv) reducing the corrosion of steel parts. The chromate has been found to get reduced at the cathode and deposited as a thin porous layer of  $\text{Cr}(\text{OH})_3$  [10]. This surface film formation generates the necessary effect of minimizing the  $\text{ClO}^-$  reduction only at a chromate concentration of above 0.3 g/l. and is not effective below 0.08 gpl. The  $\text{Cr}(\text{OH})_3$  film has been found to be porous only to permeate hydroxyl and hydrogen ions and impermeable to larger ions, such as,  $\text{ClO}^-$ ,  $\text{ClO}_3^-$ ,  $\text{O}_2$  etc and other reaction intermediates. In the present instance, the reduction  $\text{Fe}(\text{OH})_3 \rightarrow \text{Fe}(\text{OH})_2$  and similarly those of nickel and other impurities that contribute to the film, must be prevented in the same manner as the ions in chlorate cell and thus the formation of the black film is avoided. It seems that a lower concentration of chromate (0.1 g/l) is sufficient to prevent the black film formation as against ~5 g/l in chlorate electrolysis. But, in the case of the industrial cells the requirement of the chromate may be slightly more, about 0.2 g/l, since most of the electrolyzers are fabricated out of steel and a portion of the chromate may get deposited on these structures.

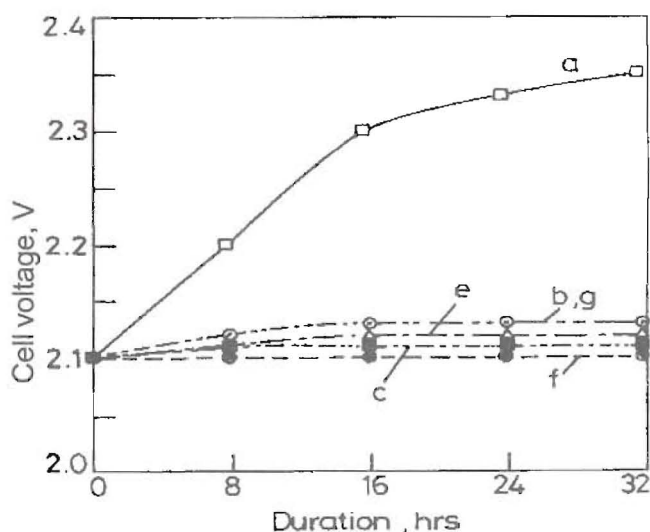


Fig. 3. Effect of chromate concentration in the electrolyte on the cell voltage.

(a) without chromate, (b) 0.1 g/l. (c) 0.3 g/l, (d) 0.6 g/l, (e) 0.9 g/l and (f) 1.2 g/l.

Since the addition of chromate does not affect in any way the activity of the anode, cell voltage was taken as indicative of the changes occurring at the cathode. The cell voltage shows a slight increase at all concentrations of the chromate and after the initial increase becomes stable. This must be due to the resistance offered by the  $\text{Cr}(\text{OH})_3$  film itself which grows faster in the initial period of the electrolysis and thereafter slows down. The average thickness of the  $\text{Cr}(\text{OH})_{\text{film}}$  was found to be of the order of  $5 \mu\Omega \cdot \text{m}^2$  that gives rise to a voltage drop of 0.15 V at  $3 \text{ kA} \cdot \text{m}^2$  [9,10]. The thickness of the film must be increasing slightly with the chromate concentration with a corresponding increase in its resistance and so is the higher cell voltage as the chromate content increases. The formation of the film depends on factors such as the cathode potential and duration. The fall in the cell voltage on the addition of chromate must be due to the changed kinetics of the HER in presence of the  $\text{Cr}(\text{OH})_3$  film. Earlier study found a decrease in cathode potential in presence of chromate in chlorate solution. But in hydroxide solution this effect on HER has been found to depend on the substrate. In view of the observed decrease in cell voltage in the present set of experiments in sodium hydroxide, it seems, further investigations are needed to understand the effect of chromium hydroxide film in modifying the catalytic activity.

The suitability of the chromate addition was evaluated and no black film was observed over a period of 1000 hours of continuous operation at a chromate concentration of 0.1 g/l in 17% NaOH at a current density of 10  $\text{Adm}^{-2}$ .

## Conclusion

The production of hydrogen by alkaline water electrolysis becomes less energy efficient due to the carbonation of the electrolyte, which has been found to increase the cell voltage by 200 to 250 mV at 4% carbonate concentration. The black film formation is accelerated with the increase in carbonate concentration in the electrolyte. The black film, as examined in mud sample from actual water electrolysis plant, was identified to be of Ni-Fe deposit of Kamacite type and this is not likely to be the cause for the voltage charge with time. Addition of chromate below 0.1 to 0.2 g/l has been found to completely avoid the black film formation on the cathode as evidenced from operating for over 1000 hours.

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