Effects of Operating Conditions on Selected Performance Characteristics of Oxygen-Depolarized Chlor-Alkali Cell

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Chlor-alkali industry consumes around 2% of the electrical energy produced in the United States. One of suggested ways of improving energy efficiency of chlor-alkali electrolysis is replacement of hydrogen-evolving cells by oxygen/air-depolarized cells (Fig.1). Desired cathodic reaction in such cells is 4e$^-$ reduction of oxygen:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad (1)$$

Hypothetical energy savings resulting from employing reaction 1 approach around 30% at a current density of 3-4 kA/m^2 that is commonly applied in state-of-the-art hydrogen evolving membrane cells.

Unfortunately, reduction of oxygen is frequently incomplete and generates unwanted by-product peroxide:

$$O_2 + H_2O + 2e^- \rightarrow OH^- + HO_2^- \quad (2)$$

Under unfavorable conditions reaction 2 can produce sufficiently high concentration of peroxide in the caustic soda solution to cause precipitation of solid sodium peroxide even at high temperatures (90^{o}C) typical for chlor-alkali electrolysis:

$$OH^- + HO_2^- + 2Na^+ \rightarrow Na_2O_2 + H_2O \quad (3)$$

Precipitation of the peroxide inside the cell causes serious caustic/oxygen flow maintenance problems and can also lead to an irreversible damage of the gas diffusion cathode.

Effects of cell operating conditions on peroxide generation rate were studied using 50 cm^2 zero-gap oxygen-fed chlor-alkali cells. The cells were equipped with commercially available (E-TEK) carbon supported platinum gas diffusion electrodes.

Relative quantity of peroxide generated was found to increase with current density (0-10 kA/m^2) for both low (0.5 mg/cm^2) and high (5.0 mg/cm^2) Pt catalyst loadings. Similarly, a noticeable increase in the peroxide generation rate was observed upon increase of the salt brine concentration (Figure 2).

The latter result demonstrated that water activity at the reaction site is an important factor affecting peroxide generation. Less effective transport of water through the membrane during electrolysis of more concentrated brine solutions promotes reaction that requires less water, i.e., peroxide generation reaction (eq. 2). However, humidification of oxygen stream was found rather ineffective as a way of reducing peroxide concentration. This indicates that most of the humidification water does not reach the reaction site.

Slight increase of the caustic current efficiency upon increase of the brine concentration was also observed. The effect is due to decreased swelling of the membrane at higher brine concentrations as documented by an increase of the membrane resistance.

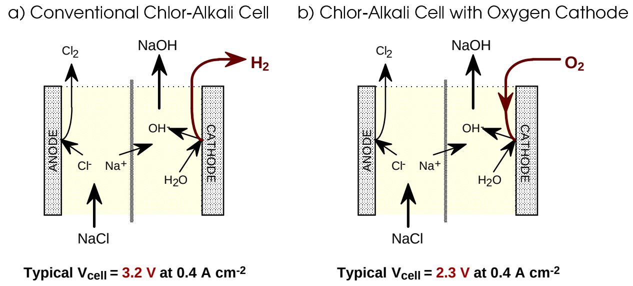

Figure 1: 30% lowering in cell voltage and, hence, 30% lowering in energy consumption per unit product is achieved in chlor-alkali cells by replacing the hydrogen-evolving cathode by an oxygen-consuming cathode.

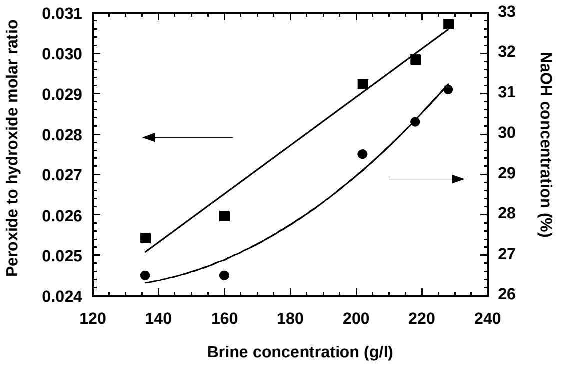

Figure 2: Effect of NaCl brine concentration on peroxide generation and caustic soda concentration.