Zero-Gap Chlor-Alkali Cell With Oxygen-Consuming Cathode. Hardware Effects on the Cell Operation

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Implementing oxygen-consuming cathodes in chlor-alkali membrane cells poses numerous challenges. One of drawbacks of oxygen cathodes is their susceptibility to flooding by concentrated hydroxide solution. Flooding can be minimized in zero-gap cells, where the catalyzed layer of oxygen cathode remains in an intimate contact with the membrane. In zero-gap cells there is no separate caustic compartment. Transport of both oxygen and caustic solution is managed by an efficient flow-field adjacent to non-catalyzed backing of the oxygen diffusion cathode.

While zero-gap configuration effectively reduces flooding of the cathode, the overall cell performance depends - sometimes quite substantially - on other details of the cathode compartment design.

Cathode hardware effects have been studied using zero-gap cells equipped with commercially available gas diffusion electrodes (E-TEK) with carbonsupported Pt catalyst (80% Pt, 5 mg/cm²; 20% Pt, 0.5 mg/cm²) and Asahi F4232 bi-layer membrane. Two different flow-fields of the fuel-cell type were applied, four serpentine-channel graphite flow-field machined into the current collector and LANL proprietary patterned metal flow-field. In some cells a hydrophilic spacer made of carbon cloth (Panex 30) was placed between the gas diffusion electrode and the membrane.

The cells were operated in the constant current mode at current densities from 0.2 to 1.0 A/cm^2 . The parameters monitored were: (i) the cell voltage, (ii) the cell high frequency resistance (HFR) that represents the sum of the membrane and contact resistances, (iii) caustic current efficiency, and (iv) peroxide and chloride contents in the caustic product.

The hydrophilic spacer has been found to increase HFR at low current densities (0.2 A/cm²) but substantial HFR reduction has been detected at high current densities ($\geq 0.6 \text{ A/cm}^2$).



Figure 1. Effect of the cathode hardware on HFR

The effect is attributed to changes in contact resistance between components of the electrode-membrane boundary region that exhibit electronic (electrode and spacer) and ionic (electrode binder, membrane and caustic solution) conductivity.

Elevated chloride levels in caustic were detected for cells equipped with LANL proprietary flow-field and no carbon cloth spacer (Fig.2).



Figure 2. Concentration of chloride in caustic plotted versus inverse HFR. Elevated chloride levels obtained for cells equipped with LANL flow-field are marked with vertical arrows.

The phenomenon was not accompanied by increased caustic crossover. Given different mechanisms of chloride (predominantly diffusion) and hydroxide (predominantly migration) transport through the membrane, the phenomenon most likely results from nonuniform current distribution over the membrane surface. Unsatisfactory electrical contact between the membrane and catalyzed layer of the gas diffusion electrode is considered a primary cause of the non-uniformity. Due to its different geometry, serpentine-channel graphite flowfield offers more even current distribution, but at the same time enhances generation of unwanted by-product peroxide.

The cells equipped with hydrophilic spacer and LANL proprietary flow-field exhibited best overall performance in terms of energy consumption, caustic product purity and current efficiency.

Acknowledgements

Thanks are due to Rich Varjian and Harry Burney of Dow Chemical for their technical assistance and valuable discussions.

Financial support from the Office of Industrial Technologies of the DOE is gratefully acknowledged.