

Oxygen-Depolarized Cathode for Aqueous Hydrochloric Acid Electrolysis: Part II - E.S. De Castro, Y.-M. Tsou, R.J. Allen (De Nora North America, Inc., E-TEK division), G.N. Martelli, and F. Federico (De Nora Technologie Elettrochimiche)

A membrane electrolysis cell can be employed to recover chlorine from aqueous solutions of hydrochloric acid. The electrochemical evolution of hydrogen at the cathode poses restraints on the plant construction and engineering in order to meet safety requirements. For chlorine recovery to be feasible, the energy consumed in the electrolysis cell must also be favorable. While stable long-lived anodes employing electrocatalytic coatings are well developed for chlorine evolution, the cathode half as outlined above is a limitation for the process.

One solution is to replace the gas-evolving cathode with an oxygen consuming or oxygen depolarized cathode (1). Oxygen, enriched air, or air can be fed to the cathode whereby water is the reduction product. In addition to eliminating the production of hydrogen, the oxygen reduction is expected to lead to more favorable cell voltages. A successful gas diffusion electrode would provide a catalyst and electrode structure that is stable over the normal operating activities of an industrial electrochemical plant.

Typical operating conditions consist of an aqueous solution of hydrochloric acid having a maximum concentration of 20% and a maximum temperature of 60°C. The gas diffusion electrode and catalyst also have to withstand exposure to the corrosive hydrochloric acid/chlorine solution during both scheduled and uncontrolled plant shutdowns. As we will show, platinum is not stable under typical shutdown regimens. Although platinum is generally recognized as a superior oxygen reduction catalyst, some have also noted that halide ions including chloride poison the oxygen reduction reactions on this catalyst (2). Thus, one challenge for this program was to identify a catalyst that performs as well or better than platinum without platinum's instability in this acid media.

We initially found that a carbon-supported form of rhodium is especially stable to solutions of chlorine-saturated hydrochloric acid (1). When incorporated in the ELAT®, this catalyst exhibits similar oxygen reduction performance when compared to platinum. However, unlike platinum, gas diffusion electrodes incorporating this new rhodium catalyst maintain their performance after transient interruption of power or oxygen to the electrochemical cell. Using this novel rhodium-rhodium oxide catalyst in small lab cell tests, we had reported 100 day operation at 3 kA/m² and an additional 60 days on line at 4.5 kA/m². Operating at the higher current density shows only a 10 mV cell voltage loss over this period.

While performing adequately in demonstration programs, the rhodium-rhodium oxide catalyst posed two challenges that made practical implementation difficult. One was the need to "activate" the catalyst with reducing media in order to maintain a ratio of metal-to-metal oxide. The other was an inability to reproduce the best results found using the metal-metal oxide system.

An exploration on the causes for the variation in the

rhodium-rhodium oxide system led to the discovery of a new supported rhodium sulfide catalyst (3). Rhodium sulfide retains all the positive attributes of rhodium-rhodium oxide such as stability during uncontrolled shutdowns, good oxygen reduction kinetics, and tolerance to typical trace organics found in the feed stream while eliminating the need to adjust the ratio of metal-to-metal oxide.

Rhodium sulfide incorporated in the ELAT gas diffusion electrodes has successfully passed all the stages of commercialization: from initial testing in a pilot electrolyzer (four-cell, 4 m²) to qualification of all manufacturing processes (repetitive large scale catalyst synthesis, production of machine made gas diffusion electrodes within product specification, and large format cathode membrane electrode assembly) at a Demonstration Electrolyzer (76 cells, 228 m²) scale, to final commercial fulfillment and start up of a two electrolyzer plants in Brunsbüttel, Germany in October 2003.

By using a new rhodium sulfide catalyst, we demonstrated the use of an oxygen-depolarized cathode as a viable route to lowering the cell voltage for recovery of chlorine from aqueous solutions of HCl.

REFERENCES

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