Performance of the Falling Film Chlor-Alkali Cell equipped with Carbon-free Oxygen Depolarized Cathode

G.N. Martelli^{*, a}, E. Reduzzi^a, A. Calderara^a, C.Urgeghe^b
(a) De Nora Tecnologie Elettrochimiche SrL Gruppo DeNora
Via Bistolfi, 35 – 20134 Milan, Italy
*e-mail: <u>nicola.martelli@denora.it</u>
(b): Dipartimento di Chimica, Università di Ferrara, Ferrara, Italy

The use of Gas Diffusion Electrodes was introduced in the early 1980s as a feasible technological approach for the reduction of power consumption in the Chlor-Alkali process.

This result can be achieved by substituting the traditional cathodic reaction :

 $2H_2O + 2e = H_2 + 2 OH^- \qquad (1) \qquad E^\circ = -0.828 V$ with the following one :

 $2H_2O + O_2 + 4e = 4 OH^{-1}$ (2) $E^{\circ} = +0.401 V$ where , with the combined use of gas consuming electrodes (called for this particular application Oxygen Depolarized Cathodes : **ODC**) and oxygen gas as reactant , hydroxil ions are produced without producing hydrogen , resulting in a significative energy saving (a practical reduction of the power consumption of about 30% vs. the traditional process is easily attainable in a short term operation).

The results of a joint research program , presently ongoing in this field between Gruppo DeNora and UHDE GmbH will be presented .

The type of structure used in an early stage of development was the so-called **ESNS** type electrode, manufactured by *E-TEK Inc.*, now *E-TEK* Division of **DeNora North America**, Inc., Somerset, NJ.

The original structure , based on a silver catalyst particles supported on active carbon (Vulcan XC-72), has been intensively tested in the "gas pocket" configuration, and subsequently modified, searching for practical solutions to the known phenomena of deactivation :

- Electrode flooding, due to progressive loss of hydrophobicity, and intrusion of the catholyte into the electrode's pores, also favored by the differential pressure existing between the gas side and the liquid side of the electrode.
- Progressive corrosion of both carbonaceous components and silver catalyst, followed by silver redistribution

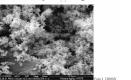
Sensitivity to uncontrolled shut-down

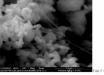
All these reasons suggested to concentrate the attention to a different type of electrode design , based on a **carbonfree catalyst** , that is an evolution of the past ESNS configuration .

The catalyst presently used is based on a mixture of micronized silver particles and PTFE binder .

The manufacture of the catalyst is rather critical, and requires an accurate control of the production parameters. The scaled-up procedure is today suitable for the production of reproducible catalyst batches of 1 kg size.

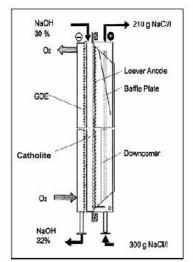
The Ag particles show a very uniform size distribution , and contain a limited amount of Hg (lower than 5%) that is introduced to increase their stability to corrosion , as demonstrated by RDE analysis of the catalyst powder . The average particle size is in the range from 10 to 50 nm as detected by XRD analysis . Typical SEM images of the catalyst are given below :



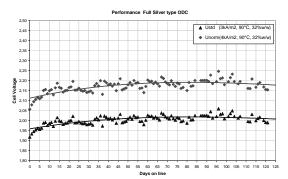


The catalyst is incorporated into a gas diffusion electrode structure, that contains a Ag net used to support the catalyst mass and distribute the current. The construction of the electrode is simple, and no structural differences exist at the moment between the gas and the liquid side.

This electrode structure is presently under long term test, at the Gersthofen (DE) test facility, using the Falling Film Chlor-Alkali cell design, schematically described below:



Some results obtained to date , in an experimental cell having an active surface of 0.16 m^2 , representing a full-height section of an industrial electrolizer , are given in the following graph :



The most important achievement of this type of configuration is the stability of the system also during uncontrolled shut-down , providing that the cell is protected with a polarization rectifier . Some results of the systematic approach used to understand the behavior of the system during various possible conditions occurring during shut down will be discussed , including some interpretation of the operating data , mainly during the first days of cell operation .

Some economical considerations will be finally given , including a comparison with an alternative approach to recover energy , that foresees the use of the hydrogen produced by the traditional Chlor-Alkali process as fuel for PEMFC stacks .