

# FINAL PROJECT REPORT – D5.2

## Executive Summary



Grant Agreement number: 227004

Project acronym: NEW ED

Project title: Advanced bipolar membrane processes for highly saline waste streams

Funding Scheme: Collaborative project

Period covered: from 1st June 2009 to 30th November 2012

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New ED aimed at closing industrial water cycles and reducing the amount of waste water streams with highly concentrated salt loads stemming from a broad range of industrial production processes by exploiting the waste components (salts) and transforming them to valuable products. This goal was to be achieved by developing new bipolar membranes for electro dialysis (ED), a new membrane module concept and by integrating this new technology into relevant production processes.

The key feature of the innovative new bipolar membranes is a nano- to micro-porous and at the same time ion conducting intermediate layer, through which water is convectively transported from the side into the transition layer of the membrane. This technique decouples the requirement of the ion-conductive layers to have high selectivity and high water permeability at the same time. It also enables the bipolar membranes to treat highly-concentrated industrial brines by applying higher current densities.

The project was performed by a consortium of five partners. The consortium includes three RTD partners: RWTH Aachen University, University of Twente and Ben-Gurion University, focusing on new membrane materials as well as alternative membrane and module design. FuMA-Tech as an industrial partner and technology provider with great experience in electrochemical membrane processes and ion-exchange membrane technology steers technological development and exploitation of the outcomes of New ED in close cooperation with the RTD partners. In addition, Bayer MaterialScience, a large end-user was part of the consortium, to demonstrate and test the products developed within New ED.

Four manufacturing approaches were investigated to develop the new type of bipolar membranes, with convective instead of diffusive water transport to the transition layer of bipolar membranes.

- *The corrugated membrane approach:* Parallel micro-sized channels are embossed into the contact surfaces of the ion exchanger sheets later forming the bipolar membrane to create a network of interconnecting channels between the sheets. The channels are fed with water supplied from the outside in a closed system.
- *The sulpho-chlorination approach:* A nano- to micro-porous polymeric material is made ion conductive by sulphonation or sulpho-chlorination and is placed between the two sheets forming the bipolar membrane.
- *The ion-conductive fleece and ion-exchange resins approach:* The intermediate layer is formed by an ion-conductive fleece or by a structured bed of ion exchange resins.
- *The layer-by-layer approach:* Polyelectrolytes are applied in a layer-by-layer fashion to the materials forming the interconnecting layer. They are used as catalysts or to improve the conductivity in the interconnecting space. This promising approach was not projected in the DOW (added to the program) and will be followed up after the completion of the project.

The corrugated membrane approach was found to be the most promising technology for water supply to the interface. Corrugated membrane preparation was adapted to existing methods and technology and channels of reproducible dimensions well below 100 micrometer were formed on the surfaces of the membrane sheets using stainless steel molds. Sheets were manufactured in sizes sufficient for industrial stacks. The lamination of the layers into a permanently bonded bipolar membrane was optimized for smaller scale industrial sized membranes. Currently, as a result, these laminated bipolar membranes show a significantly increased limiting current density compared to commercial membranes. Some optimization in the lamination technique still seems possible as loosely bonded bipolar membranes resulted in lower

stack resistances than the best commercial bipolar membrane available, indicating that energy consumption of BP-electrodialysis processes can be reduced further.

The new membrane and module concept was tested with a salt stream from a Bayer polycarbonate production. The data generated in the experiments in the New ED project show that the long term operability of the new membranes needs improvement and that in terms of energy efficiency, high current density electro-dialysis cannot yet successfully compete with electrolysis, which is the alternative presently preferred by Bayer. Electrolysis consumes about 0.08 kWh/mole converted. To reach this value, an electrolysis unit would have to reach over 60% current efficiency and a voltage drop per repeat unit of 2 Volt or less. These values can be reached, but only at current densities below 1000 A/m<sup>2</sup>.

Significant optimization measures are required until the application of bipolar membranes becomes economically feasible at higher current densities. Therefore, long-term pilot tests were not carried out. For the same reason, detailed economic as well as ecological evaluations were not conducted.

Parallel to the experiments aimed at offering solutions for high volume / low cost applications, intensive work was conducted to investigate the option of using the new membranes in low volume niche applications. The case studied was the use of three chamber bipolar ED in the production of itaconic acid, an organic acid seen as an attractive intermediate for the manufacturing of chemicals and bio-fuels from renewable resources. A pilot plant with 10 repeat units was used and numerous operating parameters were varied. Up to now, the high resistance of the anion exchange membranes for the itaconate ions prevents high current densities. Unless this problem can be solved by better suited anion exchange membranes, the advantages of the new bipolar membranes cannot be sufficiently utilized.

Summarizing the possible applications of the new technology, a careful selection taking into account the boundary conditions seems to be crucial. Medium to larger volume inorganic salt separations are suitable, if cheap alternatives (emission as waste water, electrolysis units existing in the vicinity) are ruled out and if the products in spite of only moderate concentration and purity can be used in existing processes. Organic salt separations must be carefully investigated with respect to the permeability of the anion exchange membranes for the ions produced and/or the need to employ anion membranes (Are 2 chamber set-ups possible?).

### **Project management**

The project suffered from the considerable difficulties encountered in WP1 and WP3 and from the retraction of the end-user Prayon. With considerable additional effort of the remaining partners and assisted by a cost neutral extension granted by the EU, nevertheless all tasks could be finished.