

EVALUATION ON THE ELECTRO-ELECTRODIALYSIS TO CONCENTRATE HI FROM HI/H₂O/I₂ MIXTURE IN S-I THERMOCHEMICAL CYCLE USING NEW ELECTRODE

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INTRODUCTION

ENEA, the Italian National Agency for New Technologies, Energy and the Environment, is involved in a R&D program on thermochemical water-splitting cycles to be coupled with solar-thermal power plants. This project is being carried out in the framework of an integrated national program dealing with the sustainable hydrogen production and storage. The sulfur-iodine (S-I) process was selected as one of the thermochemical cycles to be investigated.

The establishment of an efficient scheme for separating HI from HI_x (HI-H₂O-I₂ mixture) in S-I cycle, is a critical process step left open to further study. In fact, HI_x solution has a HI molarity of ca. 4 mol/L, and an usual distillation column results in a distillate of HI with azeotropic (7.5 mol/L) concentration by a large thermal burden. Extractive distillation with phosphoric acid and reactive distillation under pressurized condition have so far been proposed to avoid the problem (O'Keefe *et al*, 1982; Roth & Knoche, 1989). More recently, electro dialysis has been proposed (Onuki *et al*, 2001; Hwang *et al*, 2003; Kasahara *et al*, 2004).

Our experimental survey of the electro dialysis route is here presented. HI concentration by electro dialysis was examined using commercial cationic exchange membranes and a titanium-based electrode. Results obtained are discussed.

RESULTS AND DISCUSSION.

In figure 1 the experimental set up is schematized. Iodine is reduced in the cathodic element, and the HI is oxidized at the anode. The electro dialysis cell (type: ED-64-002, PCA-Polymerchemie Altmeier Gmb) is connected with two tanks (anodic and cathodic, 35 cm³ each) initially containing the same feed HI-H₂O-I₂ solution. Two peristaltic pumps (Gislon mod. Minipuls 2) allow continuous recirculation of the mixture. A pc-controlled potentiostat (type: Ecochemie mod. Autolab PGSTAT30) applies the required cell voltage; the resulting current density is monitored. The cell, entirely made of polypropilene, has titanium-based home-made electrodes with 75 x 75 mm active area. The gap between electrodes is ca. 1.3 mm. The used Nafion™ 115 cation exchange membrane has about 64 cm² active area and a nominal 0.125 mm thickness.

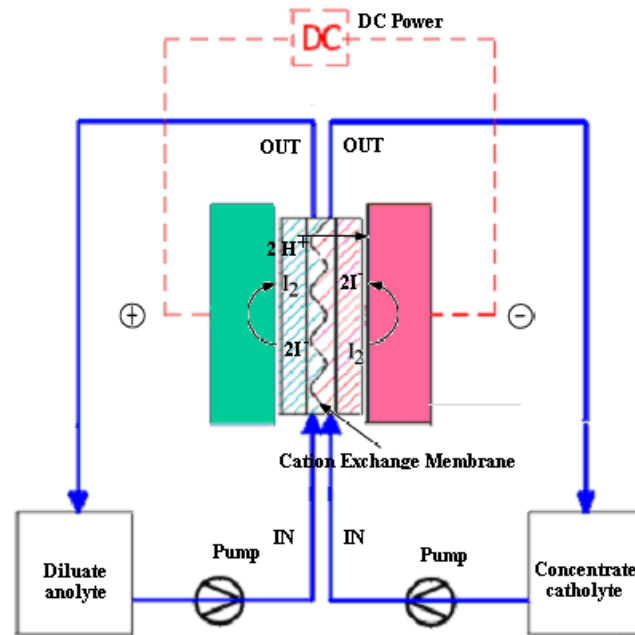


Fig. 1: Scheme of the electrodiolysis experimental set up.

Preliminary tests at constant voltage in the 0.1÷1 V range were carried out using an initial HI/H₂O feed solution at [HI] = ca. 0.2 mol/L. Resulting current density values obtained are reported in figure 2: current density initially increased up to ca. 0.4 mA/cm² by increasing the voltage at 0.3 V; further increase of cell voltage resulted in current density decrease. These obtained current density values are rather low.

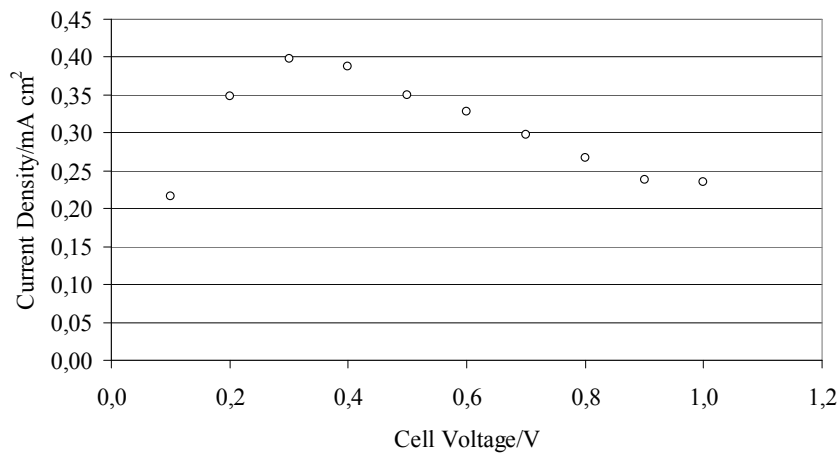
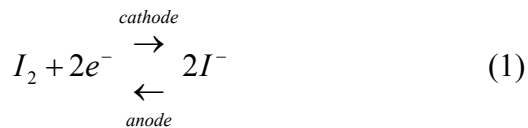


Fig. 2: Polarization trend with [HI] = 0.2 mol/L feed solution at 25°C.

Since current density is due to the redox reactions



the low current density can be partly due to the low reactants concentration but, more reasonably, to the low reaction kinetic rates on the titanium-based electrodes. Hence, more consideration has been given to the electrodic material specifications.

Some cyclic voltammetry measurements were carried out at $0 \div 1.0$ V (100 mV/s scanning rate) using a feed HI_x mixture with $[HI] = 0.2$ mol/L and $[I_2] = 0.1$ mol/L. In figure 3 the results of the titanium electrodes are compared with those obtained with a platinum electrode under the same operative conditions. From these results it is possible to conclude that platinum is a much more efficient catalyst than titanium in the I_2/HI redox reaction, leading to current densities the order of $10 \div 20$ mA/cm². While the titanium electrode led to an overvoltage of ca. 0.33 V, this value is practically zero when the platinum electrode was used.

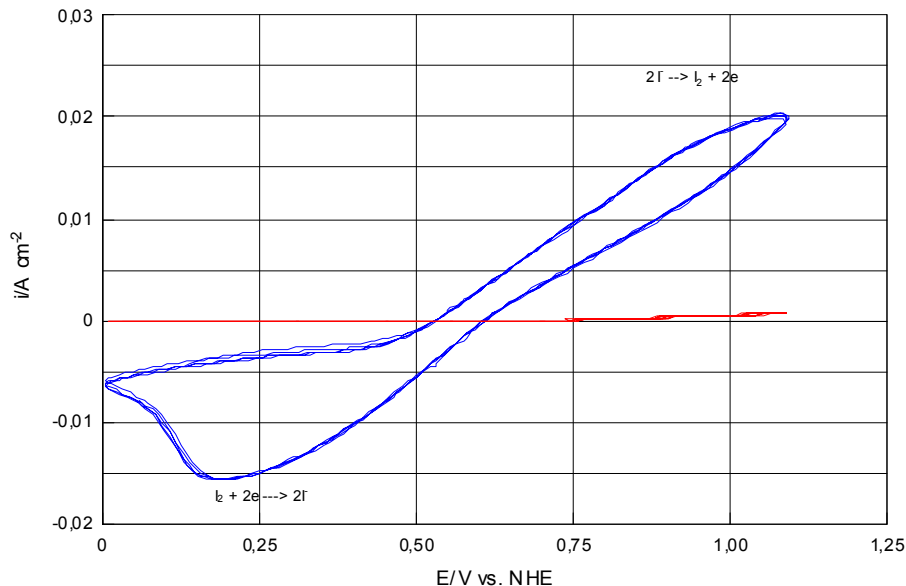


Fig. 3: Cyclic voltammetry (100 mV/s) on titanium (red) and platinum (blue) electrodes with $[HI] = 0.2$ mol/L and $[I_2] = 0.1$ mol/L feed solution at 25°C.

In order to improve current density and reaction kinetics, rhodium deposition on titanium electrode surface was considered. A microporous titanium oxide film (obtained by anodic oxidation) was electrochemically coated with a small amount of this noble metal. We estimated about 3.2 mg/cm² of rhodium deposition on the electrode surface, corresponding to 3-4 μm of thickness. In figure 4 the behavior of this Ti/TiO₂/Rh electrode is compared with a platinum and a glassy carbon electrode. It is noteworthy that with the Ti/TiO₂/Rh electrode the current density is almost doubled.

CONCLUSIONS.

Our preliminary experimental results on the electro dialysis of $HI-H_2O-I_2$ mixtures evidenced that low reaction rates and current density are mainly ascribable to the

electrode material. Titanium-based electrodes coated with rhodium by electrodeposition showed catalytic activity higher than platinum electrodes, and the same order of glassy carbon electrodes even at very low rhodium content.

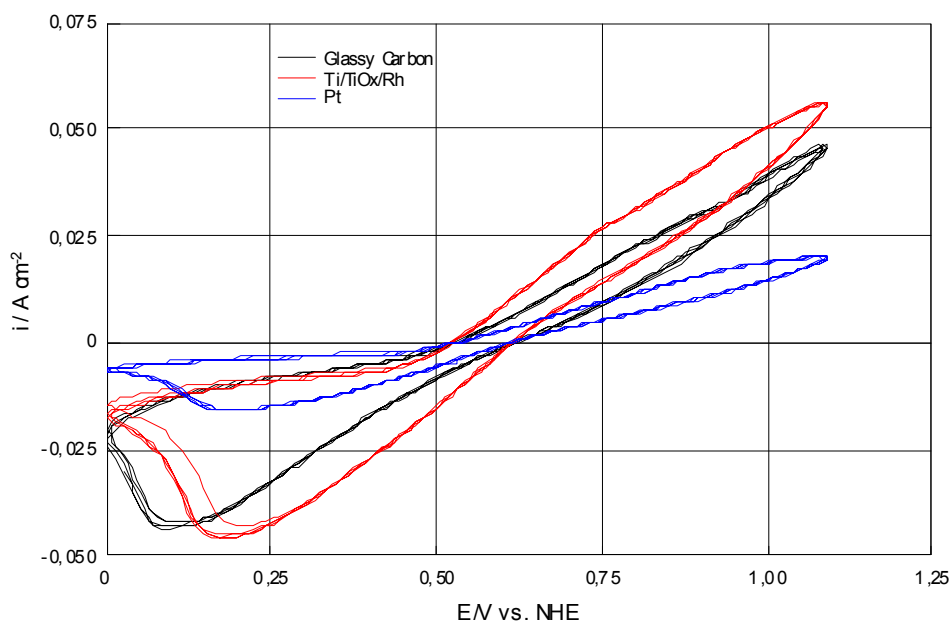


Fig. 4: Cyclic voltammery (100 mV/s) on different electrodes: Ti/TiO₂/Rh 8.4 mg/cm² (red), platinum (blue) and glassy carbon (black) with [HI] = 0.2 mol/L and [I₂] = 0.1 mol/L feed solution at 25°C.

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BRIEF BIOGRAPHY OF PRESENTER

Giampaolo Caputo is a chemical engineer graduated at the University of Rome “La Sapienza”. From 2004 he works as researcher at the ENEA (the Italian National Agency for New Technologies, Energy and the Environment) at the Casaccia research centre in Rome, working for the “Solar Thermodynamic Project”, with research on thermochemical hydrogen production powered by high temperature solar heat. The activity is mainly focused in the development of the sulfur-iodine thermochemical water-splitting cycle and solar-powered reforming of reformable compounds. He published papers on international journals, five patent applications. He also participated to National and International programs on High Temperature Hydrogen Production.