**Nanostructured Ni–Fe alloy electrodes for seawater electrolyzer.**

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**1.Introduction**

The climate change, caused by the increase of greenhouse gas emissions (GHGs), has incited governments and societies to change their environmental policies in favor of more sustainable method for energy generation and consumption [1]. Furthermore, there is a growing interest in reducing pollution in all transportation fields, in particular for naval transport that is one of the fastest growing sector in terms of GHGs, and also improve comfort by avoiding acoustic emissions inside ports and harbors [2].[3]

The renewable resources are considered a viable opportunity also for the carbonization of all transportation fields, although the difficulty of storing the surplus of produced energy still represents a fundamental problem to solve. In such regard, hydrogen can play a key role since it can be used as an energy vector. Hydrogen is a clean energy source, during its conversion into electricity, no toxic or polluting substances are emitted. Converting electricity into hydrogen and using hydrogen as energy carrier may be a technical and economically interesting option. In fact, hydrogen is currently receiving significant attention as energy carrier in many country roadmaps and studies, especially if short-term storage (weeks) is required.

Hydrogen [4] can be cleanly generated by means of electrolyzer technology [1]. The research of electrolysis for hydrogen production using freshwater has yielded good results; however, research of seawater electrolysis for hydrogen production is still at the early stage [5]. To make seawater electrolysis energy-efficient and cost-effective, highly active non-noble-metal-based catalysts for boosting the oxygen evolution reaction (OER) e and the hydrogen evolution reaction (HER) are necessary. In this frame could be a winning choice, for the electrochemical property, using a nanostructured system based on Fe. In this work, we have fabricated and tested NiFe nanostructured electrodes for sea water electrolyzers.

**2. Methods**

All nanostructured electrodes were fabricated with a two-step electrodeposition method. The nanostructures were obtained by nanoporous polycarbonate membrane (Whatman) which acted as template. On a surface of membrane, after gold sputtering, a Ni layer was electrodeposited via potentiostatic deposition using as Watt’s bath. This layer acts as a mechanical support and current collector (CC) for the nanostructures. NWs electrodeposition was carried out by pulsed potential using the Watt’s bath containing different concentrations of FeSO4·7H2O. All electrodepositions were carried out at room temperature using a three-electrode cell with a Pt mesh as a counter-electrode and a SCE as a reference. After NWs deposition, the polycarbonate membrane was dissolved in CH2Cl2 at room temperature. The electrochemical and electrocatalytic tests were carried out at room temperature in 30 wt% KOH aqueous solution using a three electrodes cell. A Ni sheet was employed as counter-electrode, and Hg/HgO (0.165 V vs. SHE) as reference. In the following, all potentials will be referred to the value of reversible hydrogen electrode (RHE, -0.826 V vs. SHE) at pH 14. A FEG-ESEM microscope (QUANTA 200 by FEI) was employed to investigate morphology of nanostructured electrode. Energy Dispersive Spectroscopy (EDS) was used to analyze NWs composition. RIGAKU X-ray diffractometer (D-MAX 25600 HK) was used for x-ray diffraction (XRD).

**3. Results and discussion**

EDS analyses reveals that the NWs composition does not change linearly with the composition of deposition bath but are richer in Fe. This result is coherent with literature data [6], in fact the electrodeposition of iron alloys is known as anomalous co-deposition consisting in the preferentially deposition of the less noble metal with respect the noble one, that complicates the control of alloy composition. The SEM images show that NWs replicate the morphology of the template. The electrochemical and electrocatalytic characterizations of the electrodes were performed by cyclic voltammetry (CV), quasi steady-state polarization (QSSP) and galvanostatic polarization. By CVs at different scan rates, specific capacitance was evaluated, by the double layer capacitance method, that is directly proportional to the real electrode surface. By comparison with a Ni planar sheet, we found that specific capacitance of each nanostructured electrode is at least 5-7 times higher. Thus, the nanostructured electrodes have a very high real surface area compared to planar electrode. To study the stability over time, constant current density mid-term tests were carried out for 6 h at -50 mA cm-2 and 50 mA cm-2 for HER and OER, respectively. The results showed good stability over time. For both HER and OER, the NiFe alloy with 79% of Fe was found to be the most stable and the best performing.

Test was carried out both in 30% w/w KOH solution and in the same solution also containing 0.5 M of NaCl, in order to simulate the possible use of these electrode in sea water. In the presence of NaCl, during the 125 h of electrolysis, the electrode potential remained below 1.6 V vs. RHE, i.e., lower than the hypochlorite formation potential. Consequently, it is possible to conclude that there is no formation of hypochlorite. The electrodes used for the long-term tests were further analyzed by SEM showing a good mechanical and chemical stability of NiFe electrodes also in solution containing NaCl.

**4. Conclusions**

In this work, nickel-iron alloy nanostructured electrodes obtained by template electrosynthesis method are investigated for both hydrogen and oxygen evolution reactions. We found that alloy rich in Fe, about 79% have good performance for both HER and OER.

The key test was carried out in alkaline solution also containing 0.5 M NaCl to simulate seawater condition. We found that the presence of chlorine does not seem to affect the stable functioning of electrode in the short or long term. This is a very promising result because it would allow the application for seawater electrolyzers.

**References**

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