

Renewable energy storage via hydrogen production, intermittent voltage OER stability testing

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Abstract

The growing concern about global warming and fossil fuels scarcity lead to an increasing interest in renewable energy sources. However, their penetration challenges the current energy generation and distribution systems due to the intrinsic intermittency and decentralization. The need to rethink the present energy sector is evident and the role that storage technologies will play in this scenario is crucial. A systematic effort to research cost-effective, efficient and reliable energy storage solutions is currently undertaken by the scientists and hydrogen storage is among the most promising solutions. However, several shortcomings still have to be addressed. This work aims to test the stability and performance of three low-cost materials, Ni, Ni-Fe-Mo alloy and Stainless Steel 304, for Oxygen Evolution Reaction. Furthermore, an ad-hoc intermittent potential stability test has been designed in order to assess the suitability of the electrode's material to work as renewable energy storage system. This test was applied with different intermittent time steps to SS 304, because it was identified as best performing among the three materials. The experimental results showed that the overall performances, i.e. degradation rate, gas production parameter and cell resistance, were much better in the intermittent potential stability test than in the constant one. The reasons were identified in the re-formation, during each shutdown, of the electrocatalytic thin oxide layer that was consumed at each electrolytic time step. Ultimately, a scenario for hydrogen energy development is proposed, with a particular focus on China that, from the research carried out, seems to have a detailed plan for hydrogen economy development.

Keywords: Renewable energy storage, low-cost electrolysis, OER, intermittent potential stability test.

1. Introduction

The increasing world population, living standards and urbanization drive to an increasing energy demand, particularly in developing countries such as China, India and African nations. Currently, about 89.6% [1] of the total final world energy consumption is produced by non-renewable sources e.g. coal, oil and natural gas. The emissions related to the energy sector represent approximately two-thirds of all anthropogenic greenhouse gases (GHG) emissions and China has the world highest energy-related CO_2 emissions. Furthermore, the scarcity of inexpensive and easily-available fossil fuels in the future proves the need to rethink the world energy supply system. The renewable energy supply system new pathway is anything but an easy task: massive effort on research and development (R&D) have been devoted to the cause since the oil crisis in 1970. But to date, several challenges remains unsolved. The intrinsic fluctuating and unpredictable nature of renewable energy sources, such as photovoltaic (PV) and wind, lead to mismatch between power generation and load

demand. Furthermore, the decentralized electricity surplus or deficit stresses the grid causing frequency balance problems [2]. The solution to the aforementioned issue would be to store the excess energy when and where it is available and release it later during peaks of demand, avoiding curtailment. The need of efficient, inexpensive and reliable energy storage systems is evident and it will be even more needed in the future to allow higher penetration of renewable power. Comparing various energy storage mechanisms, the ones related to hydrogen seem to be promising technologies. H_2 is a highly energetic carbon-free energy carrier, with the highest energy content per unit of mass of any fuel. Using hydrogen as a secondary source of energy does not produce emissions of dust, sulfur, nitrogen oxides, mercury nor CO_2 . However, the environmental impact of the overall process is also due to the primary source of energy used for the H_2 production: low efficiency and high capital costs have to be mentioned among the drawbacks of generating renewable H_2 with the present technologies. In fact, 96% of the currently produced

hydrogen uses low-cost fossil fuels increasing the overall process emissions [3].

1.1. Topic overview

The renewable hydrogen production processes can be divided in water splitting and biomass process; the biomass process can be further divided into thermochemical and biological. Among the biological technologies can be found: direct and indirect bio-photolysis, dark fermentation and photo-fermentation. Thermochemical technology mainly includes pyrolysis, gasification, combustion and liquefaction. While renewable processes to produce H_2 via water splitting include: electrolysis, thermolysis and photolysis. The conventional processes, using as energy sources fossil fuels, include hydrocarbon reforming and pyrolysis [4].

The currently researched hydrogen-based applications for storing renewable electricity are based on water electrolysis and can be grouped as follow:

- Power-to-power: the electricity is converted into hydrogen via electrolysis, it is stored and converted back to electricity with fuel cells or hydrogen gas turbines. The storage efficiency is about 29% (HHV, alkaline electrolysis) [5].
- Power-to-gas: electricity is transformed into H_2 via electrolysis, it is then injected in the natural gas grid. The storage efficiency is 26% [5].
- Power-to-fuel: electricity is transformed into H_2 and then directly used as a fuel in fuel cell electric vehicles. The storage efficiency is about 24% [5].
- Power-to-feedstock: electricity is converted into hydrogen and then used as a feedstock for the refining or chemical industry.

The available hydrogen storage technologies have interesting potential due to the high energy density, fast response time and suitability for use in large-scale energy storage applications. However, these technologies still have high upfront costs, low efficiency and safety concerns that have to be addressed with further R&D.

1.2. Research objective

The objective of this work was to study the potential of storing energy via hydrogen generation, focusing on materials stability testing in close-to-real condition. The experimental investigation was focused on a crucial step of electrolysis, the oxygen evolution reaction (OER), because of its high overpotentials compared to the other half side of the reaction [6]. Driven by the willingness to use low-cost and available materials, three earth-abundant

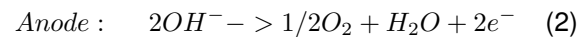
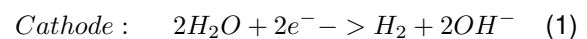
transition metals were chosen for comparing stability and performances. To evaluate the suitability of the electrodes to convert renewable energy, a particular stability test has been designed. The aim was to understand the behaviour of the material when operating in conditions similar to those of intermittent energy sources. The intermittent potential profile designed for the test was applied to several samples changing the pulse width to investigate the material response. Usually electrolyzers are fed with steady or smooth direct current (DC) voltage [7]. The innovative approach of this work is to supply to those systems an intermittent potential. According to Dobi et al. [8], the knowledge about this topic is still incomplete and further research should be performed.

2. Theoretical background

The basic principle of electrolysis is to split water into its fundamental components: hydrogen and oxygen, using electricity as energy input. The simplest electrolysis unit is composed by an anode, a cathode, a power source and an electrolyte. The electrolyte can be basic, neutral or acidic. According to a comparative study by Schalenbach et al. [9], the main difference between PEM and alkaline electrolyzers was a higher cell resistance of the latter. The overvoltage related to the kinetics was reported by the authors to be approximately 30% smaller for acidic water electrolyzer.

2.1. Alkaline water electrolysis

Alkaline water electrolysis is a mature technology that has been developed initially by the petroleum refining industry, and it has a proven lifetime and reliability to date [10]. One of its advantages is that the basic environment allows to employ low-cost and earth-abundant materials. The reactions 1 and 2 show the processes taking place at the cathode and at the anode [11]. The main components of an alkaline water electrolysis cell are diaphragm, electrodes, electrolyte and electrocatalyst.



2.2. Process resistances

Electrolysis is an electrochemical reaction that has some process resistances to be overcome. Figure 1 shows the electrical circuit analogy, in which the losses are represented by resistors. According to Zeng et al. [12], they can be grouped in three main categories: electrical resistances, transport resistances and reaction resistances.

The electrical resistances ($R_{circuit}$ in Figure 1) are due to the energy losses in the cabling and connectors. Transport losses (R_{bubble} , R_{ions} and

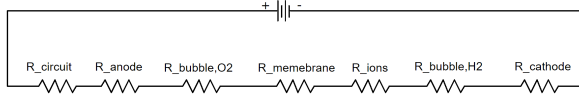


Figure 1: Electrical circuit analogy.

$R_{membrane}$ in Figure 1) are due to the dynamics of the system. They are due to gas bubbles covering the electrode surface and to the reduced electrolyte or membrane ability to transfer ions. Reaction resistances (R_{anode} and $R_{cathode}$ in Figure 1) are related to the activation energy required in OER and HER and are function of the electrode's surface activity.

The **cell potential** is directly related to the energy that has to be provided in order to split water into hydrogen and oxygen. Theoretically, the minimum voltage required is equal to the equilibrium cell voltage: E^o [12]. In particular, it is the potential difference between the equilibrium voltage of anode and cathode (Equation 3).

$$E^o = E_{anode}^o - E_{cathode}^o \quad (3)$$

At $25^\circ C$, the equilibrium cell voltage (E^o) for water electrolysis is $1.229V$ [13] and the Gibbs free energy change is $+237.2kJ\ mol^{-1}$ [14]. As already mentioned, this is the minimum amount of energy required, but still it is not enough to overcome the activation energy needed to start the reaction. Furthermore, at the equilibrium cell voltage, the reaction rate would be too slow due to the resistances previously introduced [12].

Equation 4 provides a schematic way of representing the single components that contribute to the increase of the overall voltage: η_{anode} and $\eta_{cathode}$ are, respectively, the overpotentials at the anode and at the cathode, I is the intensity of the current that flows in the circuit and R_{cell} is the cell resistance, computed as shown in Equation 5.

$$E_{cell} = E^o + \eta_{anode} + \eta_{cathode} + IR_{cell} \quad (4)$$

$$R_{cell} = R_{circuit} + R_{bubbles} + R_{electrolyte} + R_{membrane} \quad (5)$$

Several ways exist to express and compute the **electrolysis efficiency**. The Voltage efficiency (Equation 6) can generally be used because it represents the percentage of voltage actually used to split water compared to the applied voltage [12]. However, there are other commonly used ways to compute electrolysis efficiency e.g. faradaic efficiency, thermal efficiency and others based on the hydrogen production yield.

$$\epsilon_{voltage} = \frac{E_{anode} - E_{catode}}{E_{cell}} \quad (6)$$

2.3. Characterization techniques

Material characterization should be performed before and after the stability test in order to remark the differences. Constant current stability tests are among the most common ways to asses durability, but further supporting analysis, such as electrochemical characterization and mass variation-based tests, should be performed. According to Spori et al. [10], among *ex-situ* analysis, the most important properties to asses are composition and morphology. Material's morphology is studied through electron microscopy, the most common techniques are Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM). Both technologies are based on the response of the sample to a signal generated by a high-energy beam and furthermore, they are non-destructive tests. Material's composition can be investigated with several techniques, among them can be found: Energy-Dispersive X-Ray Spectroscopy (EDS) and X-Ray Photoelectron Spectroscopy (XPS). EDS is used to determine the bulk composition, while XPS is used to evaluate the composition of the sample surface. Finally, X-ray diffraction (XRD) can be used to obtain information about the crystal phase, cristallinity, ordering, and average crystal size.

Among the *In-situ* analysis relevant to evaluate stability, it is worth to mention: electrochemical techniques, i.e. Cyclic Voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS), and mass-variation-based techniques. CV allows to identify specific changes in the oxidation state and if run for thousands of cycles can provide information about stability and oxide formation. EIS is a technique useful to evaluate Ohmic losses. The full impedance spectrum provides information about charge transfer and mass-transport resistances. Mass-variation-based techniques can provide useful information about degradation. Among the available techniques can be found: Electrochemical Quartz-Crystal Microbalance (EQCM) and Scanning Flow Cell coupled with Inductively Coupled Plasma Mass Spectrometry (SFC-ICP-MS).

3. Materials and methods

The materials selected as electrodes for the tests were:

- AISI 304 Stainless Steel (Cr 18.5%; Ni 9.5%; Mn 2%; Si 0.75%; P 0.045%; S 0.03%; C 0.07%; Fe 69%)
- Nickel-Iron-Molybdenum alloy (80% Ni; 5% Mo; Fe 15%)
- Nickel (Pure Ni)

Table 1: PED and GWP of pure Ni, Fe-Ni alloy and AISI 304 Stainless Steel. The data used [15, 16] are based on a geographical region that does not include China, where they have been bought and probably produced, therefore, they provide useful information but are not to be considered exact for the materials used in the experimental section.

Impact category	PED [$\frac{MJ}{Kg}$]	GWP [$\frac{Kg CO_2equiv}{Kg}$]
Ni Class1	147 - 149	7.64 - 7.87
FeNi (80% Ni)	388 - 406	23 - 26
SS 304	32 - 43	2.0 - 5.2

They were chosen according to already existing works, for their electrocatalytic properties and availability. The materials were bought as metal plates from Taobao at the following prices: SS 304 €/m² 17.33, Ni €/m² 107.25 and Ni-Fe-Mo alloy €/m² 153.92. Beside price and performance, environmental impact was taken into account in the decision process, based on Life Cycle Assessment (LCA). From the data collected in Table 1 it is evident that the Primary Energy demand (PED) is higher for Nickel alloys than for Stainless Steel by an order of magnitude. This is mainly due to the high consumption of fuels and electricity in the Nickel primary extraction and refining steps, which account for 60% of the total energy demand [15]. Similarly to PED, the Global Warming Potential (GWP) is higher for Nickel than for Stainless Steel.

3.1. Equipment

Two different types of vessels were used: single chamber cell (Figure 2a) and double chamber cell (Figure 2b). The latter was composed by three different containers: the first hosted the working electrode, the second the counter electrode, while the third, accommodated the reference electrode. The working electrode and counter electrode's chambers were separated by a porous membrane that does not allow gas bubbles to flow from one side to the other, but let ions move freely. The vessels were made out of glass and sealed with Teflon caps.

The reference electrode used for this work was mercury-mercury oxide (Hg/HgO) with *KOH* 1M as inner electrolyte, therefore, in order to express the potential with respect to the Reversible Hydrogen Electrode (RHE) the difference in potential used was 0.926 V [17]. The counter electrode was a platinum plate, connected through a large screw to the support as shown in Figure 2. The electrolyte was an aqueous solution of potassium hydroxide, *KOH* with concentration 1 M and pH 14.

The electrochemical station used for this work was produced by CH Instruments and the software was the version 16.02. Among its functions, the ones used were: (i) cyclic voltammetry, (ii) constant potential chronoamperometry, (iii) intermittent po-



(a) Single chamber cell.

(b) Double chamber cell.

Figure 2: Electrochemical cells used in the experimental work.

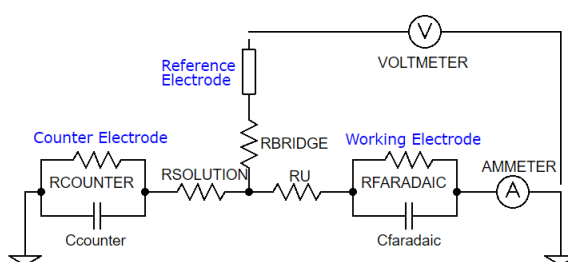


Figure 3: Electrical circuit designed for the tests.

tential chronoamperometry, (iv) open circuit potential and (v) iR compensation.

Figure 3 shows the circuit that was implemented to test the samples. The voltage was applied between the working and the counter electrode, the voltmeter recorded the potential of the working electrode, while the ammeter measures the current that flows between the two electrodes.

3.2. Experimental procedure

The electrolyte was prepared using *KOH* pellets. The procedure was to mix the pellets and the distilled water in a beaker and subsequently, adjust the volume to 0.5 liters in the volumetric flask. The same procedure was followed to prepare the 1 M sulphuric acid *H₂SO₄* solution, needed to rinse the samples before the electrolysis tests.

Prior to the test, the materials needed to be sized, cleaned and marked. Firstly, stripes of 2.5 mm of width were cut to obtain a surface area in contact with the electrolyte of 50 mm². Secondly, the samples were rinsed in ultrasonic water bath with sulphuric acid and water. Finally, they were marked with a small cut on one side to guarantee that it did not vanish during the test.

In order to activate the material, the sample underwent a set of 40 CV at a fast scan rate. If at the end of the first activation cycle the current density was not constant, other CV were imposed to the electrode until the current density reached a con-

stant value.

As last step before the actual stability test, the samples were characterized with CV, EDS, XRD and SEM. CV was set with the following parameters: high voltage 0.8V, low voltage 0.1V, Scan Rate 0.05V/s and iR compensation 90%.

The stability tests were based on amperometric measurements while keeping the potential under certain conditions. Two types of stability tests were used, according to the potential imposed: constant potential and intermittent potential. The constant potential stability tests were performed at 1.8 V vs RHE, with 10h run time and 90% of iR compensation. The intermittent potential stability tests were performed with 1.8 V vs RHE as high potential and 0V as low potential of the working electrode. The pulse width was changed at each experiment, the values used were: 3,000s; 600s; 120s; 24s; 4.8s. The iR compensation was set to 90% and the run time to 20h.

Subsequently to the stability test, characterization analysis i.e. CV, EDS, XRD and SEM were repeated to investigate difference in material activity, composition and morphology.

3.3. Data processing

In order to provide a graphic representation of the stability for each intermittent potential experiment, the average of each time step was calculated and the line passing through the points was plotted. Finally, in order to compare the hydrogen yields, the area underneath the j-t graph was computed and normalized with the experiment run time.

4. Results & discussion

The first set of experiments aimed to compare two different types of vessels. Firstly, the double chamber cell was tested. However, even after several trials it showed poor stability, as can be seen in Figure 4. A crucial experiment was then designed: the electrolyte was to be replaced by a fresh one after 5h of constant potential test. With the new electrolyte the performances were completely recovered, therefore have been concluded that the electrode material was not deteriorated and the problem was caused by other factors. The most likely hypothesis is that the OH^- ions could not properly flow from one electrode to the other, creating a lack of ions in the proximity of the electrodes. The porous membrane was considered to be the limiting factor of the system. However, further experiments should be done to investigate in greater detail the behaviour of the porous membrane.

4.1. Electrode material comparison

The aim of this set of experiments was to compare the electrocatalytic properties of three different materials according to the 10h stability test and the

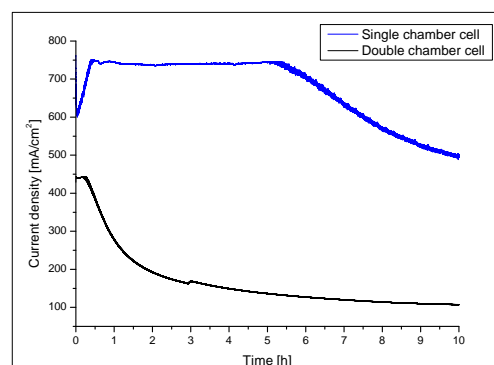


Figure 4: Electrolytic cell comparison, the blue curve is the single chamber cell, the black one is double chamber cell.

characterization techniques aforementioned. An issue remarked during the experimental sessions was the maintenance of a constant electrolyte level with high currents, it was solved by switching to a vessel with a larger free surface and also by changing the shape of the electrode to a thinner stripe.

The differences in stability between the 3 materials are shown in Figure 5 from which is evident that Stainless Steel has a much higher current density compared to the other two materials. The stability, however, is not as good as the other two.

4.1.1 Stainless Steel

After 5.5h the stability of SS dropped drastically. As first hypothesis this drop was due to material degradation caused by the high current density, but comparing the CV before and after the test it was noticed that material performances decreased only by 23% at 1.7 V vs RHE (and recovered in the following hours). Therefore, this drastic decrease in performance cannot be explained by material degradation, but should be imputed to some other environmental factors. Ions concentration and distribution in the electrolyte solution may play a role. Another explanation could be that the passive layer was partly consumed and therefore the electrocatalytic activity was reduced, however, these are speculations and should be proved with further experimental work. During the stability test the cell resistance rose from 2.1Ω to 2.4Ω (14%). The increase was initially explained with the formation of oxides on the electrode surface, they are poor conductors and therefore they would increase the overall cell resistance, but it could be due to formation of other species, or some changes in the electrolyte composition. In order to clearly explain the reasons of this resistance increase further experiments should be performed, giving great attention to the characterization.

4.1.2 Nickel and Ni-Fe-Mo alloy

Analyzing the current density behaviour presented in Figure 5, Ni-based electrodes seem to have a complete different trend compared to Stainless Steel: they did not present an activation period and they were characterized by a lower current density. Knowing that the current density at a particular overpotential is proportional to the amount of active material [18], it can be inferred that a catalytic surface of nickel hydroxides and oxyhydroxides was not formed. The unchanged resistance (for both materials) reinforced this hypothesis, showing that no semi-conductive materials coated the surface during the first moments of the chronoamperometry. Furthermore, the colour of the electrode after the stability test was unchanged, unlike the Stainless Steel electrodes that were turning very dark after the test. As final test, the oxygen content on the electrode surface at the end of the stability test was measured by EDS to be about 6.7%, which confirms that the amount of formed active oxide was quite low. For pure Ni, the reduction in current density recorded with CV before and right after the stability test was computed to be 67%, while for Ni-Fe-Mo alloy, 87%. It is probably due to the passive layer depletion, but further experiments and characterizations should be performed to fully validate this assumption. The performance of Ni-Fe-Mo alloy was slightly better than the one of pure Ni, probably the presence of Iron and Molybdenum helped in the formation of active sites. The reasons of the poor performance of high-Ni-content materials are not clear and only speculative hypotheses could be suggested, further investigations should be performed to fully comprehend the observations. Notwithstanding, some considerations and recommendations about the experimental work can be advanced:

- Pre-treatment of Ni-rich materials can increase the activity. Particularly effective has been found to be a series of cycles that alternate polishing-rinsing-drying and potential cycling [18].
- In order to fully understand the processes, the characterization is crucial. The contact with air or other elements could modify the electrode surface composition. In order to obtain reliable data it would be necessary to test the samples right after the stability test, preserving them against contact with the air and the electrolyte that could promote surface reactions.
- In order to be able to compare the results with already existing experiments in the literature, would be crucial to have a benchmark protocols.

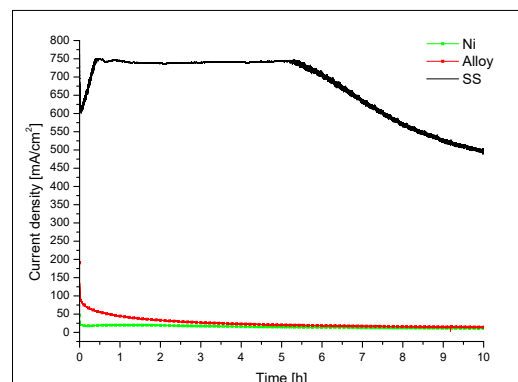


Figure 5: Comparison between Ni (green curve), Ni-Fe-Mo alloy (red curve) and SS (black curve) performance during 10h constant potential stability test.

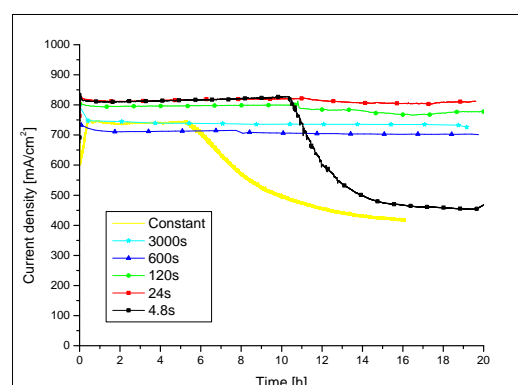


Figure 6: Comparison between different time steps in intermittent stability test and constant potential stability test.

4.1.3 Intermittent potential test

This section reviews several experiments that were performed applying an intermittent potential and recording the current flowing into the system. The intermittent potential pulse-width was changed to study the material response under different conditions. The current density curves of each time step were plotted in one graph to visually compare the results, Figure 6 shows that the stability trends of each time step are comparable, except for 4.8 seconds and constant potential, in which the effect of degradation is evident.

The degradation phenomena remarked in this work were: cell resistance variation and decreased current density. Three parameters were proposed to compare the performances: (i) gas production indicator, (ii) degradation rate and (iii) cell resistance [19]. The gas production indicator, is a parameter directly proportional to the gas production, computed as integral of the j - t curve normalized with the run time. The figures compared are presented in Table 2, from which is evident that the best result was obtained with the 24 seconds time

Table 2: Cell resistance variation based on CV before and after the stability test; degradation rate computed for the entire stability test and hydrogen production indicator based on the integral of the j-t curve normalized with the experiment run time.

Pulse width	3000s	600s	120s	24s	4.8s	Const
Res. variation [%]	-4.1	0	2.2	NA	6.4	13.6
Degr. rate [$\frac{mA}{cm^2h}$]	1.5	1.9	1.1	1.2	37.6	23.8
H ₂ indicator [$\frac{mA}{cm^2}$]	738	708	788	813	674	674

step, followed by the 120 seconds. The worst performance was clearly the 4.8 seconds and constant potential. The degradation rate of each experiment was obtained computing the quotient of the difference between the initial and final values of current density over the working time. The smallest degradation rate was obtained in the 120 seconds test followed by the 24 seconds test. The evident trend from Table 2 is that for an increasing time step, the resistance variation decreases slightly. Furthermore, it was noticed that the resistance varied considerably in the hours following the stability test.

In order to understand the transformations on the electrode's surface, the samples were characterized with EDS. From Table 3 can be seen the difference in composition between a fresh electrode, an electrode that underwent a 16h constant potential test and one that underwent a 20h 4.8s intermittent potential test. The Carbon content on the surface was increased considerably, Iron and Chromium content decreased, while Oxygen, that was not present before, appeared. Also Potassium and Platinum showed up on the electrode surface, coming from, respectively, the electrolyte and the counter electrode.

Information about degradation can be obtained also from the electrode surface color during the stability test. According to experiments performed, the shorter the pulse width, the darker the surface. Leaving the AINSI 304 SS working electrode in the electrolyte after the test promotes a cleaning process that turns its color to bright metal again. Leaving the electrode outside the electrolyte in contact with the air promotes a transition from black to copper-blue color.

Regarding the material activation, from the CV performed before and after each experiment, it was proved that the 120 seconds time step test had the greatest improvement in terms of current density reached. Apart from 4.8 seconds that worsened, all the other tests improved the activity thanks to the intermittent potential supply.

According to Rakousky et al. that tested the influence of current density switching on degradation, the intermittent current profile helps to improve the durability [19, 20]. Similarly to their conclusion, from this experimental work can be stated

Table 3: Composition comparison of Stainless Steel obtained from EDS characterization: before the test (fresh electrode), after constant potential test (constant test) and after 4.8 seconds intermittent test. NA=datum Non Available. K, L, M refer to electron shell.

Element	Amount of substance, mol (%)		
	Fresh electrode	Constant test	4.8s test
CK	09.43	19.01	47.84
FeL	33.79	13.35	11.21
FeK	31.53	25.24	07.54
NiK	02.72	04.00	01.61
NiL	00.00	09.55	08.13
CrL	13.92	00.00	00.00
CrK	07.72	06.10	01.99
SiK	00.50	00.36	00.29
NK	00.00	02.69	NA
PtM	00.00	NA	00.26
KK	00.00	NA	00.15
OK	00.00	19.54	20.82

that the intermittent potential tests proved lower degradation rate, resistance variation and better gas production indicator. Looking at Figure 6 and Table 2, can be seen that 120 and 24 seconds tests show the best results, while the constant potential and 4.8 seconds tests were the worst among all. As conclusion, the pulse width should be tuned to increase the efficiency and reduce the degradation, the short time steps and the constant potential seems to be both the worst, while an optimal time step in the middle can be obtained.

4.2. Recovery effect

The experiment designed to investigate the recovery effect is simple and consists in a repetitive voltammetry at intervals of ten minutes. The cell resistance and current density was recorded at each cycle, until when three CV measurements give the same results and a stable status is reached. Figure 7 displays the data collected for 150 minutes subsequent to the constant potential stability test. The current density at a fixed potential increases at each cycle, up to a certain point in which it stays constant. In the first 30 minutes it increases at a faster rate, while in the second part it slows down.

An issue faced during the experimental work was regarding the measurement of cell resistance, for the data collection was used the iR function of the electrochemical station, but the results were often unstable and several trials were needed to obtain reliable data.

According to Brandon et al. the OER on metallic electrodes always takes place on an oxide surface and never on the pure metal [18]. The formation and influence on OER activity of these electrocatalytic materials is complex and highly sensitive to a large number of parameters, including experimental history of the electrode [21], morphology and oxidation state [22]. The passive oxide layer

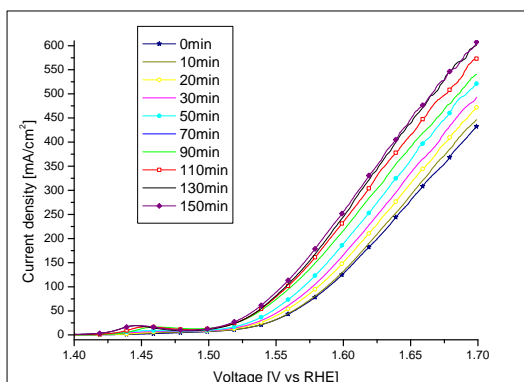


Figure 7: Increasing performance after 16h stability test due to recovery effect, measured with LSV from right after the stability test (0 min) to two and a half hour after (150 min).

is present on metals that are exposed to the air, but anodic polarization was found to be effective in forming an electrocatalytic oxide layer that facilitate OER [23].

In conclusion, the ability of transition metal electrodes to recover the oxide layer during the shut-down periods, seems to be one of the crucial causes of the increasing performance and durability of intermittent potential electrolysis.

5. Scenario

Hydrogen is increasingly seen as a high quality energy carrier [24], it is in fact, particularly suitable for connecting energy supply and energy demand. Furthermore, it can play an important role in the decarbonization of sectors that are notoriously not easy to decarbonize, such as transport and industry [25]. To date, among the hardest obstacles to the development of a world-wide hydrogen economy are included: H_2 transportation, storage and delivery, due to H_2 low volumetric energy density. The delivery infrastructure is considered one of the major challenges and additional research is required to solve current problems of high delivery costs, leakage, low efficiency and gas purity [25]. A solution can be found in the decentralized and small scale production and distribution systems that could guarantee network extensiveness keeping light infrastructures.

The capital cost of hydrogen production technologies represents a major challenge to their competitiveness [25]. Regarding gasification and thermochemical processes, carbon capture and sequestration (CCS) is a research topic to be addressed. It could allow to continue using low cost hydrogen reducing the carbon emission by 80-90%, but is often seen in the literature as a way to "fix the problem" rather than solve it [24].

5.1. Hydrogen energy storage

The cost of renewable electricity is continuously decreasing and in the future it may even become free during some parts of the day, due to high photovoltaic and wind capacity that will be installed. In this scenario of free energy available, the potential of hydrogen production by water splitting is enormous, enabling seasonal storage and improving electricity quality by grid controlling [24]. All this at one condition, the electrolyzers capital expenditure are low enough to make it profitable with the low capacity factors that characterizes renewable energy sources.

From the work published by Saba et al. in early 2018 [2] can be clearly seen a trend indicating a decreasing investment cost in the next years both for PEM and alkaline electrolyzers. The projection of cost for 2030 is similar for the two technologies. Automation and standardization of production process could help to decrease by 50% the costs of both types of electrolyzer [2].

5.2. Hydrogen and energy transition

Implementing a renewable hydrogen economy is complex and the result is uncertain. One of the main barrier to its development is related to the massive infrastructures that should be dismissed and re-build from scratch. However, there is a potential for green hydrogen produced from excess renewable energy in storage applications such as power-to-gas, in fact, after the first system installed in 2016 in the USA, about 30 plants are on the way in Europe. Furthermore, in Germany two systems that use off-peak electricity and feed H_2 into the natural gas grid are about to be installed [24].

The role of policies and incentives is essential to launch and accelerate hydrogen energy transitions. There are several types of energy policies schemes adopted by governments, some of them have the aim to discourage the use of fossil fuels, e.g. the CO_2 tax, and some others to directly incentivize carbon free sources, e.g. the feed in tariff. Among the measures that can be adopted to promote hydrogen economy development can be found: direct subsidies for customers of H_2 based energy systems, support for start-up companies or incentives for H_2 suppliers to develop infrastructures.

5.2.1 China

In the last years, growing concern has been observed among Chinese scientists about air and water pollution in cities and industrial areas. Therefore, enormous effort have been devoted to study green energies and sustainable development.

China is the first hydrogen consumer and producer world wide [26, 27], and the total demand

of hydrogen in 2050 is estimated to be between 25.1 and 70.5 Mtce (ton of carbon equivalent). Currently, it is mostly produced from fossil fuels, but in the future the energy sources used to produce hydrogen can potentially change.

6. Conclusions

A map of the global energy sector trends is provided, with particular focus on the issues that slow down the renewable energy penetration. An overview over the available technologies to produce hydrogen from renewable energy sources with the purpose of energy storage is presented. The theoretical background of water electrolysis is discussed, including process resistances and efficiency. The procedures of the three experiments, the equipment used and the system setup are described: the first experiment had the objective to validate the system design and to define the best vessel, the second to compare the three materials based on their stability and the third, to understand the response of the system in terms of stability and hydrogen yield when exposed to intermittent potential. The considerations for each experiment are presented in the following bullet points.

- The porous membrane separating anode and cathode in the double chamber vessel was identified to probably act as a bottleneck, but further experiments should be performed to confirm the hypothesis.
- The difference in stability and performance between Stainless Steel 304 and Ni-rich materials was found to be remarkable. However, a drastic decrease in SS performance was observed after five hours and a half. To understand the causes further experiments and characterization analysis need to be performed. In order to be able to compare the results the adoption of common standard protocols was found to be crucial.
- The influence of frequent shutdowns on material stability and OER performance was studied in relation to the pulse time step. Among the five different time steps analyzed, the best performance in terms of current density was achieved by the 24 seconds pulse width. The degradation rate was found to be lowest in the 120 and 24 seconds. Overall, the worst resistance variation, degradation rate and gas production was represented by the 4.8 seconds test. In conclusion, the better performance achieved by the intermittent potential test compared to constant potential was explained with the re-formation of the thin oxide layer that was consumed during the electrolysis process. The formation of this passive

film is highly important for water electrolysis, because it is formed by metal oxides and hydroxides that are precious electrocatalysts and increase the overall efficiency of the reaction.

Overall, the results obtained in the present experimental work showed that AINSI 304 Stainless Steel can be a cost-effective material to build electrodes for OER. Furthermore, the power intermittency, typical of renewable energy sources, improves the performances due to the recovery effect. These results were strengthened by recently published works in which was stated that current density switching positively impacts the material degradation.

Ultimately, a scenario for the hydrogen energy transition is proposed with a particular focus on the Chinese energy sector. The potential of hydrogen-based energy storage systems was found to be strictly related to the capital cost of the electrolyzers. Looking at the last 30 years is forecast that capital cost trend will decrease further due to R&D and market penetration. Chinese hydrogen energy sector seems to be effectively enlarging in the last years and the perspective of a Chinese hydrogen economy seems to be plausible.

6.1. Recommendation for future Work

An interesting follow up of this work would be to design a model that is able to predict the efficiency and durability of electrode materials for the purpose of renewable energy conversion and storage.

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