Recent Progress in Catalysts for Hydrogen-Chlorine Regenerative Fuel Cells

Mireya Carvela, Alexandra Raschitor, Manuel A. Rodrigo and **Justo Lobato** *

Chemical Engineering Department, Enrique Costa Novella Building, Av. Camilo Jose Cela n 12, University of Castilla-La Mancha, 13004 Ciudad Real, Spain; mireya.carvela@uclm.es (M.C.); alexandra.raschitor@uclm.es (A.R.); Manuel.Rodrigo@uclm.es (M.A.R.)
* Correspondence: justo.lobato@uclm.es; Tel.: +34-926-295-300

Abstract: The increasing energy demand and the subsequent climate change consequences are supporting the search for sustainable alternatives to fossil fuels. In this scenario, the link between hydrogen and renewable energy is playing a key role and unitized hydrogen-chlorine (H_2-Cl_2) regenerative cells (RFCs) have become promising candidates for renewable energy storage. Described herein are the recent advances in cell configurations and catalysts for the different reactions that may take place in these systems, that work in both modes: electrolysis and fuel cell. It has been found that platinum (Pt)-based catalysts are the best choice for the electrode where hydrogen is involved, whereas for the case of chlorine, ruthenium (Ru)-based catalysts are the best candidates. Only a few studies were found where the catalysts had been tested in both modes and recent advances are focused on decreasing the amount of precious metals contained in the catalysts. Moreover, the durability of the catalysts tested under realistic conditions has not been thoroughly assessed, becoming a key and mandatory step to evaluate the commercial viability of the H_2-Cl_2 RFC technology.

Keywords: chlorine; electrocatalysts; hydrogen; regenerative fuel cell

1. Introduction

Despite the hard times that we are living now, with the human tragedy caused by the COVID-19 pandemic and its strong influence on the industrial production, energy remains as an important issue and is still a key element for society development. In this context, global energy demand was found to decrease during the first quarter of 2020 due to the pandemic effect [1] and, as seen in Figure 1, the statistics revealed that the global demands of coal and oil were most affected by this situation, decreasing by nearly 8 and 5%, respectively, as compared with the same period of 2019. Meanwhile, the gas demand decreased only by 2% and, in contrast, renewable energy increased by almost 1.5% [1]. The higher decrease in the use of non-renewable sources may help to explain the significant improvement of the global environmental quality noticed in the first quarter of 2020, which was especially outstanding if the attention is focused on the closing of the ozone gap [2–4].

This is a relevant example that supports that large-scale stationary applications of renewable energy sources are required to sustain human development [5]. Moreover, renewable energy reduces air pollution, making people less vulnerable to respiratory diseases, as evidenced in a recent analysis that correlated a higher morbidity of COVID-19 deaths with the higher air pollution levels in cities [6].
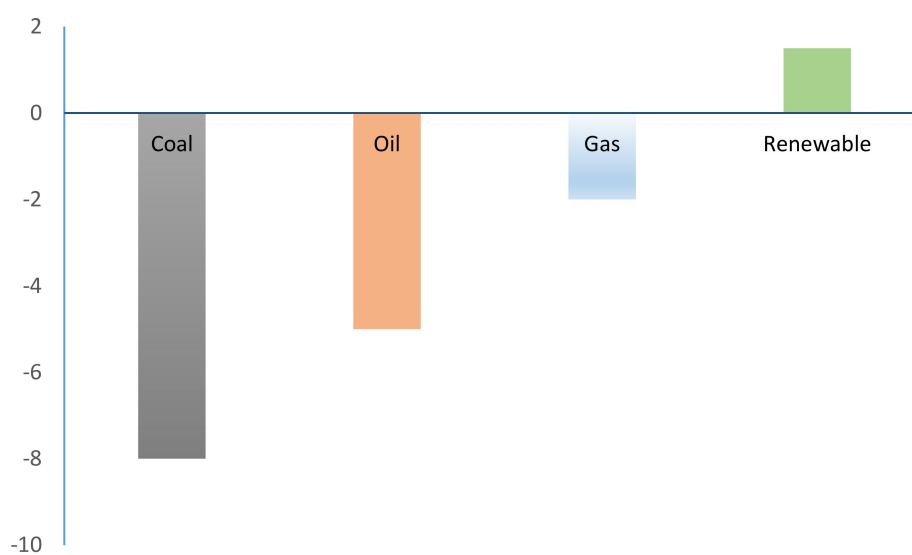
Figure 1. Variation (in %) of demand of different energy sources during the first quarter of 2020 compared with the same period of 2019, according to the International Energy Agency (https://www. iea.org/reports/global-energy-review-2020).

Nevertheless, not everything is an advantage in the use of renewable sources of energy, and there are various well-known drawbacks such as cost, intermittency, grid connection, and storage, which become real challenges that must be overcome in order to facilitate their penetration in the energy market [7–9]. It is worth to highlight the energy storage devices for stationary applications, which are becoming one of the most critical bottlenecks to reach a more sustainable society. There are numerous candidates for facing this challenge and they can be classified into two groups [10]. The first incorporates capacitors or supercapacitors that are able to store renewable energy directly and have very high efficiencies, but low energy density and difficult regulation because they discharge in a very short period. The second group incorporates devices that convert renewable energy into another form of energy, such as kinetic (flywheels), potential (hydro pumping), or chemical. Within this last group, the most appealing technologies are the electrochemical energy storage (EES) systems that can efficiently store surplus electricity as chemicals, which can again regenerate electricity when demanded [10]. The lack of geographical requirements, easy modular design, and smaller water and carbon footprints are some of the advantages of EES, as compared with other storage technologies [11]. The combination of water electrolyzers and hydrogen-based fuel cells is a good example of this kind of system where hydrogen is used as an energy carrier [11]. Hydrogen may also be sustainably produced from other renewable energy sources, such as thermochemical cycles [12]. Their off-the-grid applications include transportation, propulsion, and residential utilization.

The unitized regenerative fuel cell (URFC) is a compact version of a regenerative electrochemical cell, a system which can operate as an electrolyzer or fuel cell, and becoming one of the most promising technologies for renewable energy storage. In the electrolytic mode, the URFC produces a chemical product (like hydrogen) from surplus electricity which becomes fuel to store the excess energy. Then, when demanded, in the fuel cell mode it transforms this fuel into electricity, trying to meet different consumption requirements. Among the advantages of this system, it is worth mentioning its high specific energy, sustainability (pollution-free), and most importantly, the decoupled energy storage capacity with rated power [13]. One of its limitations is the high overvoltage during the oxygen evolution reaction (OER) or oxygen reduction reaction (ORR), which restricts the energy storage efficiency. In addition, most of these energy storage systems are based on the use of oxygen as a comburent, which leads to the necessity of high amounts of platinum on the electrode in charge of its transformation and also to harsh operation conditions which have associated severe corrosion of catalysts and supporting materials, reducing the service lifetime of the cathode [14]. For this reason,

in the recent years, attention has been focused on other comburents, among which halogens have demonstrated to be very promising [11]. In Figure 2, the three types of halogens that have been proposed and the wide variety of reactions that explain the performance of each system can be seen.
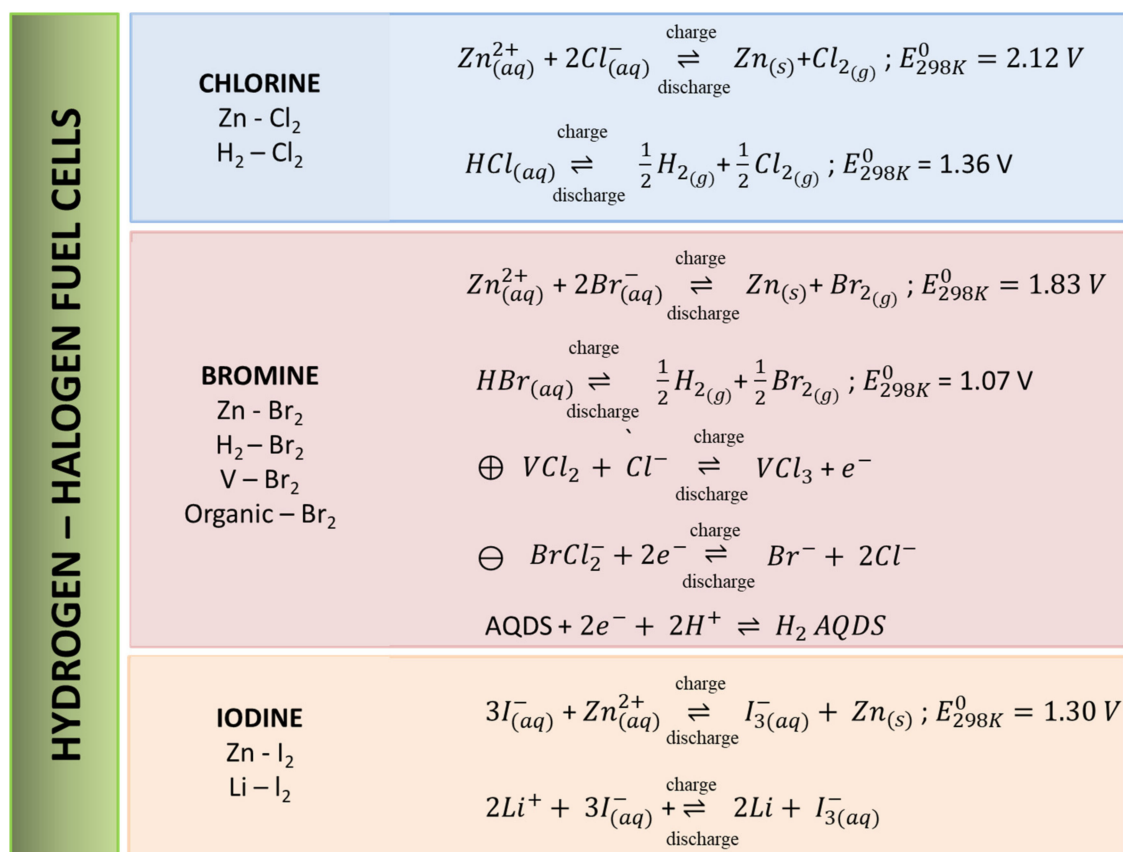

HYDROGEN – HALOGEN FUEL CELLS

CHLORINE
Zn - Cl_2
$H_2 - Cl_2$

$$Zn^{2+}_{(aq)} + 2Cl^-_{(aq)} \underset{discharge}{\overset{charge}{\rightleftharpoons}} Zn_{(s)} + Cl_{2(g)} \; ; E^0_{298K} = 2.12 \; V$$

$$HCl_{(aq)} \underset{discharge}{\overset{charge}{\rightleftharpoons}} \frac{1}{2}H_{2(g)} + \frac{1}{2}Cl_{2(g)} \; ; E^0_{298K} = 1.36 \; V$$

BROMINE
Zn - Br_2
$H_2 - Br_2$
V - Br_2
Organic - Br_2

$$Zn^{2+}_{(aq)} + 2Br^-_{(aq)} \underset{discharge}{\overset{charge}{\rightleftharpoons}} Zn_{(s)} + Br_{2(g)} \; ; E^0_{298K} = 1.83 \; V$$

$$HBr_{(aq)} \underset{discharge}{\overset{charge}{\rightleftharpoons}} \frac{1}{2}H_{2(g)} + \frac{1}{2}Br_{2(g)} \; ; E^0_{298K} = 1.07 \; V$$

$$\oplus \; VCl_2 + Cl^- \underset{discharge}{\overset{charge}{\rightleftharpoons}} VCl_3 + e^-$$

$$\ominus \; BrCl^-_2 + 2e^- \underset{discharge}{\overset{charge}{\rightleftharpoons}} Br^- + 2Cl^-$$

$$AQDS + 2e^- + 2H^+ \rightleftharpoons H_2 \, AQDS$$

IODINE
Zn - I_2
Li - I_2

$$3I^-_{(aq)} + Zn^{2+}_{(aq)} \underset{discharge}{\overset{charge}{\rightleftharpoons}} I^-_{3(aq)} + Zn_{(s)} \; ; E^0_{298K} = 1.30 \; V$$

$$2Li^+ + 3I^-_{(aq)} + \underset{discharge}{\overset{charge}{\rightleftharpoons}} 2Li + I^-_{3(aq)}$$

Figure 2. Main reactions that take place in different types of hydrogen-halogen fuel cells.

Chlorine URFCs have appealing properties such as fast kinetics and high reduction potential [15] and, because of that, one of more promising alternatives for energy storage, is the hydrogen-chlorine (H_2-Cl_2) regenerative electrochemical cell, which operates according to Equation (1).

$$HCl_{(aq)} \dots \underset{discharge}{\overset{charge}{\leftrightarrows}} H_{2(g)} + \frac{1}{2}Cl_{2(g)} \dots E^0 = 1.36 \; V \tag{1}$$
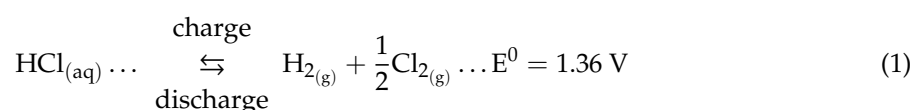
The lower activation overpotentials for the Cl_2 electrode, as compared with oxygen [16], and much higher exchange current density [17] are two of the most relevant advantages associated with this system. To operate successfully, the used catalysts must be tailored to promote the electrochemistry of chlorine. The most used materials are formulations of mixed metal oxides (MMOs) rich in ruthenium (Ru) oxides because they exhibit excellent electrocatalytic properties for chloride oxidation. However, at the same time, their main weakness is that the required Ru metal loading is typically very high and MMOs may turn into an expensive electrode choice for a halogen-based electricity storage technology. For this reason, the reduction in Ru loading without affecting the electrocatalytic properties is an important challenge. With less success, other materials have been tested for this process, including stainless steel in the photoelectrochemical production of hydrogen and chlorine from acid wastes [18], carbon-based materials (such as carbon cloth or carbon paper) [19], titanium, nickel, or copper [20]. More recently, the use of nanomaterials has attracted the attention of researchers because of their outstanding proprieties and operation results [21,22]. Their nature, size of the layer,

and even the deposition methods have shown to be important aspects to reach high efficiencies in the operation of regenerative fuel cells (RFCs).

Thus, in this work, authors discuss recent progresses in the H_2-Cl_2 regenerative electrochemical cell process, highlighting catalysts that are used in this system and gather valuable information about the cell configurations that are used currently in the development of this promising technology.

2. Hydrogen-Chlorine Fuel Cells Configuration

The regenerative fuel cell operates in two steps: charge (electrolyzer mode) and discharge (fuel cell mode), as shown in Figure 3. The chemical species that are involved in the process are hydrogen, chlorine, and hydrochloric acid. In the fuel cell operation mode, the anode reaction is the same as for the hydrogen–oxygen fuel cells (Equation 2), reducing hydrogen gas and producing protons that are transferred to the cathode compartment throughout the proton-exchange membrane (PEM). On the cathode, the reduction of gaseous chlorine produces chloride, which together with the protons transferred from the anode forms hydrochloric acid (Equation 3). The HCl formed can be further dissolved in water or kept as an anhydrous gas. In the latter case, it can be stored as a pressurized gas.
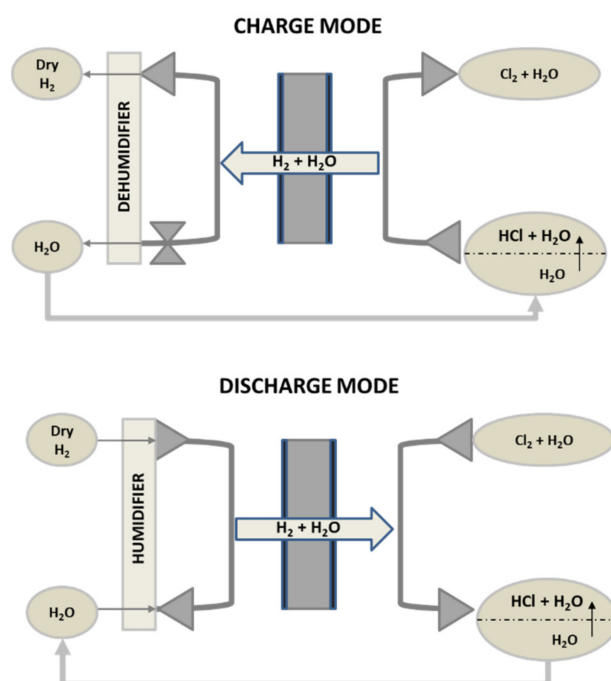
$$H_2 \leftrightarrow 2H^+ + 2e^- \ (E_0 = 0 \ V) \tag{2}$$

$$Cl_2 + 2e^- \rightarrow 2Cl^- \ (E_0 = 1.36 \ V) \tag{3}$$

Figure 3. Schematic operating mode of a regenerative chlorine fuel cell.

In the operation in electrolyzer mode, the oxidation of chloride into chlorine takes place on the anode (Equation (4)), together with the oxidation of water to oxygen (Equation (5)). The first is the primary reaction expected in this regenerative cell, while the second is a non-desired side reaction, whose extension needs to be minimized. On the other electrode, formation of hydrogen according to Equation (2) is the expected main reaction.

$$2Cl^- \rightarrow Cl_2 + 2e^- \ (E_0 = -1.36 \ V) \tag{4}$$

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \ (E_0 = -1.23 \ V) \tag{5}$$

Although the use of chlor-alkaline technologies in fuel cell or electrolyzer mode dates back more than one century, the first regenerative cell using hydrogen and chlorine as the reactive gases [23,24] was first proposed in the late 1970s. In these first devices, the regenerative cell included a porous matrix where the electrolyte was embedded. A water-free electrolyte (typically phosphoric acid, sulfuric acid, or solid NaCl) was proposed to dissolve the gaseous HCl, H_2, and Cl_2, and to carry out the electrochemical reactions within the cell. On the opposite side of the matrix, gas diffusion electrodes were placed and the corresponding catalysts were deposited on the electrodes according to the reactions that were aimed to take place on each side. The reactants were supplied under pressure through the hydrogen and chlorine chambers. At the same period, a group at Brookhaven National Laboratory was one of the first to test regenerative H_2-Cl_2 cells using proton-exchange membranes (such as the well-known Nafion membrane manufactured by Dupont, with a much lower thickness of only 250 μm), the same used for H_2-O_2 fuel cells [25]. In this case, the chlorine gas was fed as an aqueous HCl solution to be sure that the Nafion membrane was humidified in order to assure proton conductivity. Nevertheless, the maximum HCl concentration allowed was 10 wt. %. because higher concentrations led to lower conductivity of the membrane and, in addition, corrosion of carbon electrodes appeared. This approach was much better than the first and, nowadays, thinner Nafion membranes (50 μm thick) are used in order to decrease ohmic resistance [17]. These first prototypes had potentially superior power and higher energy densities than H_2-O_2 systems, and the chlorine-based regenerative fuel cell system was initially considered for space application because of the good results obtained [16].

After this initial period, capital cost consideration became a matter of paramount importance and many other prototypes were proposed. Among them, a membrane-less H_2-Br_2 fuel cell has been proposed recently [26], whose design can be extrapolated to a H_2-Cl_2 fuel cell, feeding Cl_2 instead of Br_2 in the fuel cell mode and HCl instead of HBr in the electrolyzer mode. It was claimed that a higher power density storage may be achieved because, as there is no separator (membrane), higher concentration of both reactants may be used. Moreover, bubble formation was avoided with this membrane-less cell, in turn avoiding operative problems. In this cell, it must be pointed out that a laminar flow is reached as it relies on diffusion to separate reactants. The design is similar to air-breathing H_2-O_2 fuel cells [27]. More recently, our group proposed a novel configuration of H_2-Cl_2 fuel cell systems, denoted by the word "electro-absorbers" [28]. Figure 4 shows the configuration of these prototypes and their characteristics.
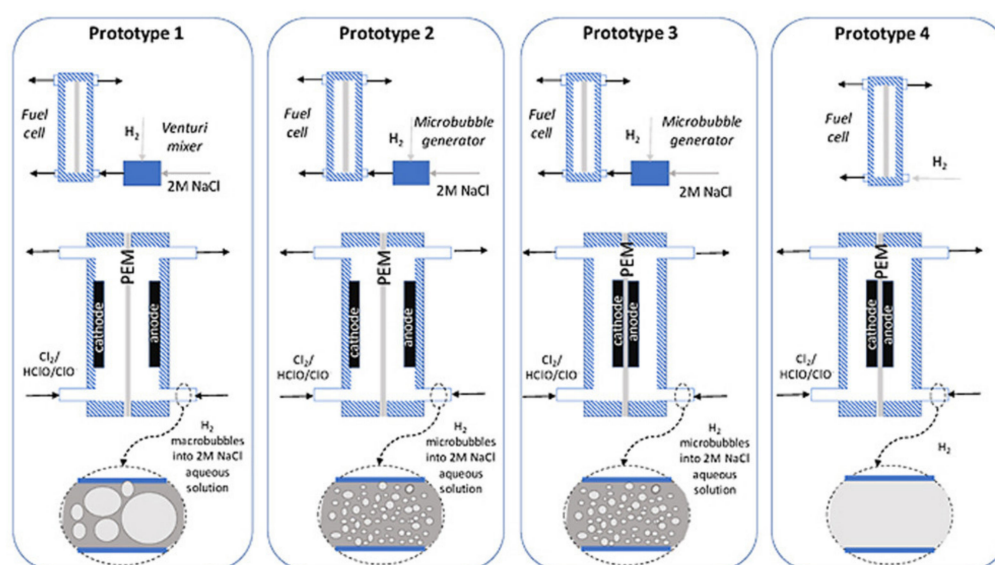

Figure 4. Prototypes of a gas-liquid hydrogen-chlorine (H_2-Cl_2) fuel cell for energy storage proposed by Carvela et al., 2020. Reprinted with permission from [28].

The same membrane (Nafion 117) and electrodes were used in all prototypes, changing only the function of the membrane as further detailed. Thus, in the case of prototypes 1 and 2, the membrane was used to separate the anolyte from the catholyte (with a total electrode gap of 1 cm), whereas in prototypes 3 and 4, the membrane acted as the electrolyte and it was sandwiched between the electrodes forming the conventional membrane electrode assembly (MEA) and obtaining an electrode gap lower than 180 μm (which is the thickness of Nafion 117). Another important difference between the four cells was the feeding mode of hydrogen to the anode. Hydrogen was fed after absorption in an NaCl solution by means of a jet mixer (cell 1) or a mechanical device to produce H_2 microbubbles (cells 2 and 3). Cell 4 was fed with hydrogen gas. Interesting findings were achieved during the essays with these four cells. Considering energy efficiency based on the use of hydrogen, the cell prototype equipped with the MEA and fed with tiny bubbles was found to attain higher efficiency (approximately 100 mWh/mol H_2), followed by cell 1, which was able to produce approximately 70 mWh/mol H_2. These results allow to highlight that the gas-liquid cells can outperform conventional fuel cells using hydrogen gas. The option of using microbubbles of H_2 absorbed in a liquid solution was also found to be very promising.

3. Catalyst

3.1. Catalyst for Hydrogen Reaction

Platinum is considered as the best catalyst for hydrogen evolution reaction (HER) with almost zero overpotential and very good durability [29,30]. However, it has important weaknesses. Thus, its high demand, scarcity, and subsequent expensive price have led to the necessity of searching for other robust, efficient, and more economic substitutes [31].

In 1839, William Grove was the first scientist to achieve, from electrolyzed water, electrical current. Therefore, he proposed the first fuel cell prototype using platinum wires as electrodes. Since then, many researchers have worked to improve the applicability of platinum (Pt) catalysts in fuel cells [32]. In the beginning, the first fuel cells only used black Pt nanoparticles (NPs) as catalysts for both electrodes. However, it was discovered that using carbon support materials increased the catalytic performance of these nanoparticles which, on the contrary, without support, agglomerate reducing the active area [33]. For this reason, Pt NPs deposited on carbon support are the most popular catalysts in promoting Pt activity toward the HER [34].

In 1923, Foerster et al. [35] constructed a hydrogen-chlorine cell stack consisting of three cells. They discovered that using Pt as an electrocatalyst to carry out the hydrogen reaction is necessary. Thus, a maximum voltage of 2.93 V at 0.2 A was obtained at room temperature with 2 M HCl as the electrolyte. By the early 1960s, Yoshizawa et al. [36] evaluated the performance of hydrogen-chlorine fuel cells. They found that using a carbon gas diffusion electrode with a loading of platinum on the hydrogen side improved the fuel cell performance (maximum energy efficiency of 51%).

These studies pointed out the very important role of the composition of this electrode, which from that moment has been a very important topic of research not only for hydrogen-chlorine, but also for conventional hydrogen-oxygen cells. Thus, in 1965, Bianchi used a Pt support on graphite as hydrogen electrode, getting a maximum power efficiency of 80% at 1.0 V [37]. More recently, Nguyen et al., in 2015, found that for the fabrication of Pt/carbon (Pt/C) catalysts, the Pt NPs need to be distributed in a small and homogeneous size over the entire surface of the carbon carrier, because the Pt content significantly affects its final properties [38]. At this point, the impregnation–reduction method has been considered as the best method to prepare Pt nanoparticles on carbon supports. Therefore, the aim of this study was to evaluate and improve this technique using two reducing steps. In a first step, the synthesis of the Pt electrocatalyst was carried out by the impregnation–reduction method with sodium borohydride reductant, as described by Sung et al. [39] and, in the second step, the synthesis method was done with ethylene glycol reductant, as described by Kumar et al. [40]. With that, the cyclic voltammetry curves were found to be like that of the Pt black powder catalyst.

PEM water electrolysis was carried out and the typical current–voltage curves recorded at 25 °C were at the current density of 1.0 A cm^{-2}, applying voltages of about 2.0 V [38]. These results led to the conclusion that the impregnation–reduction method consisting of two steps with Pt loading about 20% of carbon weight per step is a promising approach for the preparation of cathodic catalysts possessing Pt nanoparticles on a Vulcan XC-72R carrier.

Ehsan et al. have developed new electrocatalysts of platinum thin films for HER. Platinum NPs are normally deposited on a carbon support, which suffers corrosion due to electro-oxidation on the electrode surface. Consequently, these researchers have studied the influence of support on HER, comparing different materials: carbon (C), titanium (Ti), and nickel foil (NF). Using these thin-film catalysts, due to their morphology, the active area was increased and their electrocatalytic activity was significantly improved. As can be seen in Figure 5, the Pt/Ti electrode showed better activity, suggesting better mass diffusion. It was shown that using Pt/Ti and Pt/NF as electrodes produced 10 mA cm^{-2} at overpotentials of 28 mV and 26 mV, respectively, with better performance than the commercial Pt/C electrode (approximately 39 mV) [41].
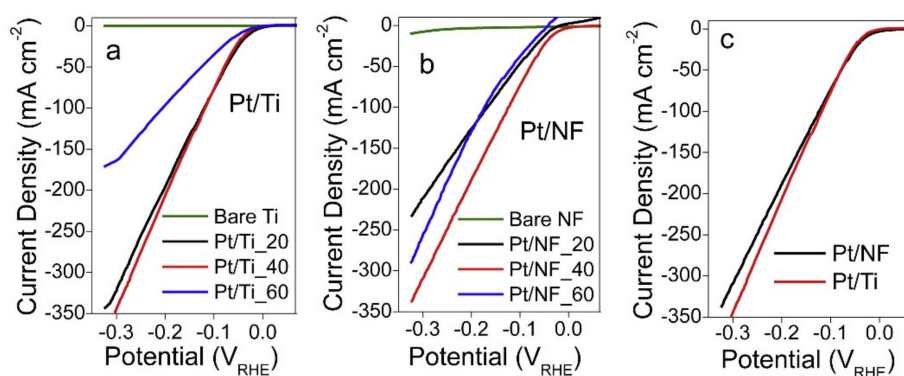

Figure 5. Linear sweep voltammetry of Pt/Ti (**a**) and Pt/NF (**b**) as a function of film deposition time (20–60 min). Comparative LSVs (**c**). Reprinted with permission from [41].

Pt-based catalysts are also the most effective catalysts for both electrolyzers and fuel cells. However, their high cost made necessary the development of new and cheaper catalysts that combine platinum with other metals maintaining and even improving catalytic efficiency [42].

Many studies have shown that the Pt catalytic performance not only improves when combined with other metals, but it has also been found that the combination with metal oxides allows the use of Pt in oxidative environments. Specifically, titanium oxide (TiO_2) is the most widely used because it has good mechanical properties and is very stable in both acidic and oxidizing environments [43].

Recently, our group performed a study using the same composition for the electrode that carries out the chlorine reaction ($Ru_{0.3}Ti_{0.6}Pt_{0.1}$/Ti) and working under the same operating conditions to compare a single catalyst (Pt) and a binary catalyst ($Pt_{0.2}Ti_{0.8}$) with a Pt loading of 0.65 mg$_{Pt}$ cm^{-2} deposited on Ti ($Pt_{0.2}Ti_{0.8}$/Ti) and on Vulcan carbon (Pt/XC Vulcan) [28,44], in order to evaluate the influence of the catalyst support and catalyst composition. Significant differences in hydrogen production were observed, obtaining an efficiency of 98% for $Pt_{0.2}Ti_{0.8}$/Ti and 84% for the Pt/C electrode. Therefore, these results confirmed that the change of catalyst improves the performance of the reversible hydrogen-chlorine PEM fuel cell, in electrolysis mode.

Nowadays, it has been sought to optimize the supporting materials, as investigated by Wu et al. in their work in 2017 [45]. They designed a new composite based on carbon and mesoporous TiO_2 as a Pt support. The results showed that by using this support it is possible to improve the stability of the commercial Pt/C catalyst up to 6 times.

In order to reduce the cost of Pt electrocatalysts, new catalysts have been developed based on ruthenium oxide (RuO_2) and iridium oxide (IrO_2) electrodes as active electrocatalysts for hydrogen evolution. In the work of Cheng et al. in 2010, carbon-supported IrO_2 and RuO_2 were prepared using

a wetness method followed by calcination at various temperatures [46]. After studying these new catalysts, they demonstrated that the performance of IrO_2/C (25 wt. %; 0.5 mg_{IrO2} cm^{-2}) for HER was similar to that of the conventional Pt/C electrocatalyst (28.4 wt. %; 0.5 mg_{Pt} cm^{-2}), with Tafel slopes of 15.5, 26, and 13.6 mV dec^{-1}, respectively, for Pt/C, RuO_2/C, and IrO_2/C in the low current density range (10^{-6}–10^{-3} A cm^{-2}). In addition, they evaluated the efficiency of a water electrolyzer with RuO_2/C, IrO_2/C, and Pt/C used as electrocatalysts at 1 A cm^{-2} and 80 °C, obtaining efficiencies of 80.3%, 85.9%, and 86.4%, respectively.

Interesting results were also obtained in the work of Su et al., 2016, in which a Ru-based electrocatalyst was used to promote HER. RuCo nanoalloys encapsulated in nitrogen-doped graphene layers (RuCo@NC) were developed following an in-situ method consisting of one-step annealing of Ru-doped Prussian blue analogs. The RuCo@NC hybrid material with 3.58 wt. % Ru showed a high electrocatalytic performance toward HER in basic conditions, even superior to the commercial 20 wt. % Pt/C catalysts [31].

3.2. Catalyst for Chlorine Species Reactions

Chlorine evolution reaction (CER) has been an essential reaction in electrochemistry because of its importance in the chlor-alkali process, among others. Precious metal catalysts are commonly used to increase the kinetics of the chlorine reaction in regenerative fuel cells. It is also not necessary to use large amounts of precious metals to act as good electrocatalysts for hydrogen-chlorine regenerative cells. Two of the most widely used electrocatalysts for the chlorine electrode are platinum and ruthenium oxide (RuO_2) [11].

3.2.1. Platinum-Based Catalysts

The Pt electrocatalyst, specifically as nanoparticles loaded on a carbon support (Pt/C), shows remarkable electrochemical performance for chlorine reduction reaction (CRR); however, it shows lower electrocatalytic performance for chlorine evolution reaction (CER) [47]. Platinum is one of the most used metals as a catalyst in fuel cells, benefiting mainly from its higher catalytic activity and better stability than other noble metals.

Chang and Wick (1935) were among the first to study the influence of a Pt electrode for both chlorine evolution and its reduction. They showed that this electrode mainly performs better for chlorine evolution, in accordance with the theory of Erdey-Gruz and Volmer, than for chlorine reduction [48]. Over the next few years, Yeo et al. [49] studied the performance of a hydrogen-chlorine regenerative cell using different electrodes on the chlorine side. One of the catalysts used was Pt, but they verified that, as the potential of chlorine (0.27 V) was more positive than that of $Pt/PtCl_4^-$ the electrode suffered corrosion. As a result, the cell was mass transfer limited on discharge. At the beginning of the 21st century, Thomassen et al. evaluated the performance of a hydrogen-chlorine fuel cell system using gas diffusion electrodes. In addition, they studied the stability of Pt as an electrocatalyst for chlorine reduction. They concluded that a formulation consisting of 20 wt. % Pt on carbon (Pt/C, 0.5 mg_{Pt} cm^{-2}) was not stable as cathode material, since Pt dissolved in the presence of chlorine, forming chloroplatinic acid (H_2PtCl_6). Cell performance decreased by 45% using only platinum as a catalyst [50].

Recenlty, it has been found that atomically dispersed catalysts improve the catalytic efficiency of precious metals. Mainly, it has been demonstrated that an electrocatalyst of atomically dispersed $Pt–N_4$ sites doped on carbon nanotubes (Pt_1/CNT) is capable of catalyzing CER with excellent activity and selectivity. Tafel analyses showed that the CER kinetics was faster in Pt_1/CNT (38 mV dec^{-1}) than in more conventional catalysts such as PtNP/CNT and Ru/Ir based on MMO (52 mV dec^{-1} and 60 mV dec^{-1}, respectively) [51].

Therefore, it can be concluded that using only Pt as an electrocatalyst for the electrode, where the oxidation–reduction (redox) reaction of chlorine takes place, is not as feasible as it seemed in the first research. Platinum is too expensive, especially considering the low electrocatalytic activity and stability it has for CER [52]. Furthermore, taking into account that the main support material is carbon,

which suffers corrosion, the most viable option is to improve the structure of Pt as an electrocatalyst with the addition of other metals and thus, optimizing support materials. Electrocatalytic oxidation can cause a decrease in the efficiency of Pt as a catalyst due to the formation of intermediates, which occupy the active sites. For this reason, other metals are added to improve the catalytic activity of Pt [52].

In 1992, Shibli and Noel [53] were among the first to evaluate the performance of hydrogen-chlorine fuel cells with different bimetallic catalysts, both for hydrogen oxidation and chlorine reduction. Therefore, they studied the efficiency of CRR in this system, using Pt- (5 wt. %), Pt-Ru- (2.5 wt. % Pt and 5 wt. % Ru) and Pt-Ir-loaded (2.5 wt. % Pt and 5 wt. % Ir) catalysts on carbon gas diffusion electrodes. The main conclusion drawn from this study was that using bimetallic catalysts improved the CRR, specifically using Pt-Ir. In addition, the stability of this hydrogen-chlorine fuel cell system was studied for 300 h, working at a constant density of 100 mA cm^{-2} and producing a cell voltage of 1.0 V. The cell functioned efficiently for that time; however, the stability of the electrode decreased after 300 h, due to either deactivation or mechanical damage suffered during the H_2-Cl_2 fuel cell performance.

3.2.2. Ruthenium-Based Catalysts

Ruthenium oxide (RuO_2), is considered as one of the most active electrocatalysts for CER. Pure metals are less stable than oxides because they can be further oxidized [54]. Beyond its excellent catalytic properties, using RuO_2 as an electrode material ensures cost reduction, since, despite not being cheap, this precious metal is much cheaper than the rest of Pt-group materials (Ru approximately $42 per oz vs. Pt approximately $992 per oz), and also increases both chlorine evolution efficiency and its stability [55].

RuO_2 is used mainly for the production of chlorine as a part of mixed metal oxides (MMOs). The bare oxide electrodes have been demonstrated to reach long service lifetimes [56]. However, they suffer corrosion due to the harsh reaction conditions of chlorine and oxygen evolution to which the electrode is exposed in industrial chlor-alkali processes, among others. Therefore, to improve corrosion resistance and increase coating stability for chlorine evolution, RuO_2 is used in a mixture with other oxides such as IrO_2, TiO_2, ZrO_2, and Ta_2O_5 [57].

Even if RuO_2 is cheaper than other materials such as platinum, the decreasing reserves of Ru present a problem [58] and, therefore, new electrocatalysts need to be developed in order to reduce the amount used and by enhancing its electrocatalytic properties [59].

In 1979, the electrochemical oxidation and reduction of hydrogen and chlorine were evaluated using different electrode materials, including RuO_2/TiO_2. This work showed that CER was faster and reversible than oxygen evolution reaction (OER), leading to low activation losses at the chlorine-side electrode. Furthermore, once they studied the influence of the catalyst, they started a regenerative hydrogen-chlorine system with these electrodes, producing a maximum electric-to-electric efficiency of 95% [49].

In recent studies, the hydrogen-chlorine system has been improved in order to produce energy more efficiently. In 2006, Thomassen et al. evaluated the concepts of the novel hydrogen-chlorine fuel cells concluding that chlorine reduction kinetics are much faster than oxygen reduction reaction (ORR) when RuO_2 is used as a catalyst in the chlorine reaction. However, no relevant data were obtained from this study due to the corrosion in the electrode [60].

Recently, many new techniques have been developed to optimize and decrease the use of Ru as a catalyst. In this regard, a very interesting technique is nanocasting [61], which was used by Han et al. to synthesize a structurally controlled, ordered, mesoporous RuO_2 replica with mesoporous KIT-6 silica material as a template. This study revealed that the use of this new catalyst enhanced the electrocatalytic activity of commercial RuO_2 nanoparticles, whose peak current density for CER of structure-controlled (SC) RuO_2 was 1.75 times higher than that of RuO_2 nanoparticles (approximately 600 mA cm^{-2} and 350 mA cm^{-2}, respectively) [58].

RuO_2 presents low stability in acidic environments, so improvements have been studied to use this electrocatalyst for chlorine reaction. Goryachev et al., in 2020, proposed RuO_2(110)/Ru(0001) single crystal model electrodes to evaluate the stability of RuO_2(110) under acidic chlorine and oxygen evolution reaction conditions in 0.5 M HCl and 0.5 M H_2SO_4 electrolytes [57].

Heo et al. (2020) prepared black TiO_2 nanotube arrays deposited with RuO_2 by pulsed electrodeposition and investigated them as three-dimensional supporting electrodes for chlorine and hydrogen evolution [62]. RuO_2-loaded black titania achieved high chlorine evolution activity (10 and 100 mA cm^{-2} at 1.090 and 1.125 V, respectively) with a faradaic efficiency of 95.25%. On the contrary RuO_2-loaded titania did not present activity, even if hydrogen evolution reaction performance was similar. This fact revealed the importance of the type of titania support in the conducting property at anodic potentials and chlorine evolution activity. In addition, it was demonstrated that black titania materials can increase the electrocatalytic activity of anodic reactions.

Ru-Based Bimetallic Catalysts

From the results discussed in the previous section, it may be highlighted that RuO_2 is the most active catalyst for chlorine evolution reaction due to its low overpotential and low cost. However, its catalytic activity is reduced because the oxidation state of ruthenium increases during long-term operation [63]. For this reason, mixing two or more metals and metal oxides can help to improve electrocatalytic properties by changing microstructure, surface composition, or morphology of electrocatalyst components, leading to the use of good electrocatalysts in reversible hydrogen-chlorine PEM fuel cells [64].

Different kinds of metal oxides are used as electrocatalyst materials to improve CER performance in chlor-alkali industry. RuO_2-based coatings, like pure RuO_2 and RuO_2-TiO_2, have good electrocatalytic properties, but other metal oxides are also used to increase coating stability during long-term operation at high anodic potentials.

RuO_2 mixed with TiO_2 (titanium oxide) is one of the most widely used catalysts (known as DSA, trademark) to perform chlorine evolution due to its stability and catalytic activity. The chlorine evolution efficiency of RuO_2-TiO_2 electrodes depends on several parameters such as their surface area or composition. In 2017, Luu et al. proposed a new model of an electrocatalyst that improves the performance of CER based on RuO_2 and TiO_2 mixed using polystyrene templates [65]. Their research showed a promising electrode material with high chlorine evolution efficiency and, in addition, its use lowers energy consumption costs.

Iridium oxides (IrO_2) present the best mechanical properties. For example, the electrical conductivity is higher than that of commercial catalysts, allowing to increase CER performance [66]. However, IrO_2 is more stable for oxygen than for chlorine evolution reaction. Thus, a mixture of IrO_2 and RuO_2 can be an appropriate electrocatalyst to enhance CER performance in a reversible hydrogen-chlorine system due to the advantageous properties of both oxides [47,63]. Finke et al. (2019) proposed to enhance the catalytic activity of CER and OER electrocatalysts by atomic layer deposition of TiO_2 [67]. In this work, they showed that OER performance, represented in Ezc (potentials of zero charge), improved 9 times as compared with the conventional iridium catalyst (Figure 6).
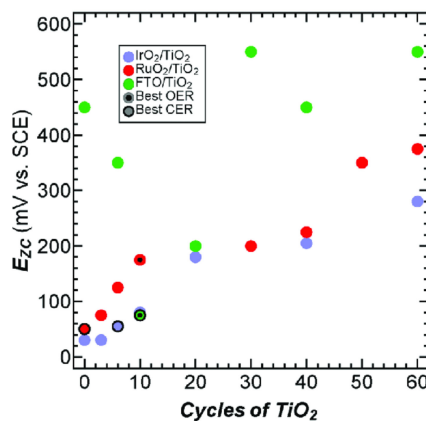

Figure 6. E_{ZC} of iridium oxide (IrO_2), ruthenium oxide (RuO_2), and FTO electrodes coated with various cycles of titanium oxide (TiO_2). Reproduced with permission from [67].

In recent years, other non-noble metal catalysts such as Mo, Co, and Ni, have shown a catalytic performance comparable to that of Pt in acid media [68]. For example, Ru-Co and Ru-Mn exhibit higher catalytic capacity and better electrical conductivity and stability, with a significantly reduced precious metal composition, as compared with commercial RuO_2 electrodes. Mondal et al. synthetized and tested two novel electrode materials based on Ru, Co, and Mn oxides [69]. This study demonstrated that the durability of these electrodes, as compared with pure RuO_2, was greater and therefore, new advances are expected in these electrocatalysts for use in the hydrogen-halogen regenerative fuel cell.

The Ru-Co and Ru-Mn alloys, fabricated by wet chemical synthesis methods as coatings on titanium metal substrates, are also interesting options. They exhibit high catalytic capacity and good electrical conductivity good stability, with a significantly reduced precious metal composition compared with commercial chloride oxidation electrodes (MMO) [70]. As discussed before, Ru is quite expensive, so its content was as low as 1% and it was alloyed with inexpensive metals, such as cobalt and manganese, when tested. It was found that the electrochemical activity was well-maintained, and stability tests showed a negligible mass loss. Moreover, the halogen redox performance was not diminished as compared to pure RuO_2 or commercially available MMOs.

Huskinson et al. (2012) developed a high-performance hydrogen-chlorine regenerative fuel cell that incorporated a $(Ru_{0.09}Co_{0.91})_3O_4$ alloy deposited on carbon as the chlorine electrode. No significant activation losses were observed, even with chlorine electrode precious metal loadings of 0.15 mg_{Ru} cm^{-2}. It is worth to mention that, in this study, a cost analysis of electrocatalyst loading was performed. It was found to be about \$1.11 kW^{-1} for precious metals on the chlorine electrode at a power density of 0.5 W cm^{-2} and a Ru price of \$3700 kg^{-1}, the cost being negligible when compared to a grid-scale storage system [17].

Based on the study of the effect of the chlorine electrode composition on the performance of reversible chlor-alkali electro-absorption cells carried out by Carvela et al. in 2020 [44], two new chlorine redox catalysts were developed to be used in this novel system: $Ti/Ru_{0.3}Ti_{0.7}O_2$ and $Ti/Ru_{0.5}Ir_{0.5}O_2$; these electrodes were manufactured using the Pechini method and novel laser and microwave technologies, respectively. In conclusion, $Ti/Ru_{0.5}Ir_{0.5}O_2$ electrode showed good electrocatalytic activity for both CER and HER, while the $Ti/Ru_{0.3}Ti_{0.7}O_2$ presented worse results in this regard. However, using Ir as a catalyst also favors the formation of oxygen, so CER competes with OER, thus reducing the conversion into chlorine. Therefore, the mixed states of metal–metal oxide are effectively considered as prominent electrocatalysts for regenerative PEM fuel cells (RFCs).

Ru-Based Trimetallic Catalysts

The use of electrocatalysts based on the combination of various metal oxides has been revealed as an effective method to improve the stability, activity, or selectivity, and catalytic properties of these electrodes during CER, as described in the previous sections. Based on the positive effects obtained by combining two metal oxides, an alternative based on the addition of a new metal oxide has been developed in different research studies, opening the path to the evaluation of ternary oxide systems [71].

On the basis of the results obtained in research developed through the combined use of three metal oxides as electrocatalysts, it can be stated that this method represents a viable option to consider, since the mixture of metal and metal oxides may result in an efficient catalyst to enhance the CRR and CER processes [47].

Nowadays, the most used electrodes are based on a mixture of TiO_2-RuO_2-IrO_2 applied on a Ti support. In 2007, the effect of IrO_2 loading on RuO_2-IrO_2-TiO_2 electrodes was studied by Yi et al. [72]. In this work, they prepared three electrodes with different compositions, modifying the amount of IrO_2: 0.9, 1.0, 0.3, 0.4, and 0.5 mg_{TiO2} cm^{-2}. They verified that the electrode with the highest IrO_2 content increased by almost double the lifetime of the electrode with the lowest amount. In 2009, Panic et al., studied the effect of the addition of colloidal iridium oxide into sol–gel-processed RuO_2-TiO_2 coatings, achieving higher activity for CER and OER and reducing the corrosion rate of $Ti_{0.6}Ru_{0.4}O_2$ coatings on

titanium in comparison to coatings prepared by the conventional thermal decomposition procedure. IrO_2 improved the electrocatalytic activity and capacitive and stability properties of titanium electrodes activated by RuO_2-TiO_2 coatings. However, the addition of IrO_2 decreased its CER activity [59]. Zeradjanin et al. found that the use of ternary Ti-Ru-Ir oxide based on DSA was more selective for chlorine evolution reaction than for oxygen evolution reaction, giving rise to high gas current efficiencies (60–90%) [71].

Our research group has proposed an alternative to improve the electrocatalytic activity of RuO_2 by combining it with TiO_2 and Pt [44]. On one hand, the presence of TiO_2 enhances the stability of the electrode material and CER by rapid charge transport, and on the other hand, the amount of Pt improves the catalytic activity and durability of the electrode [73]. Four new catalysts based on RuO_2 deposited on Ti were developed by our group, with different ratio molar compositions: $Ru_{0.2}Ti_{0.6}O_2Pt_{0.2}$, $Ru_{0.3}Ti_{0.6}O_2Pt_{0.1}$, $Ru_{0.4}Ti_{0.5}O_2Pt_{0.1}$, and $Ru_{0.45}Ti_{0.5}O_2Pt_{0.05}$. These electrodes were used in a regenerative hydrogen-chlorine cell in order to study the influence of the catalyst used in the chlorine electrode on the reversibility of the system, as can be seen in Figure 7. In view of the results obtained, it was stated that the molar ratio of Ru:Pt influenced the chlorine production efficiency, being practically double for a ratio of 4 compared to 1 (8.0 mmol Cl_2/Wh). Therefore, increasing the amount of Pt in the catalyst does not improve the chlorine reaction but, on the other hand, Ru does influence CER performance. In addition, the maximum power obtained was 6.1 mW cm^{-2} with a specific power generated of around 50 mWh g^{-1} hydrogen [44]. Moreover, comparing these results with the electrocatalysts described in the previous section, which were developed by our researchers, it was concluded that using a ternary Ru-Ti-Pt system improved Cl_2 production efficiencies (98% for $Ru_{0.3}Ti_{0.6}O_2Pt_{0.1}$/Ti, 80% for $Ru_{0.5}Ir_{0.5}O_2$/Ti, and 72% for $Ru_{0.3}Ti_{0.7}O_2$/Ti) [28]. Clearly platinum plays a significant role in the composition of these catalysts.
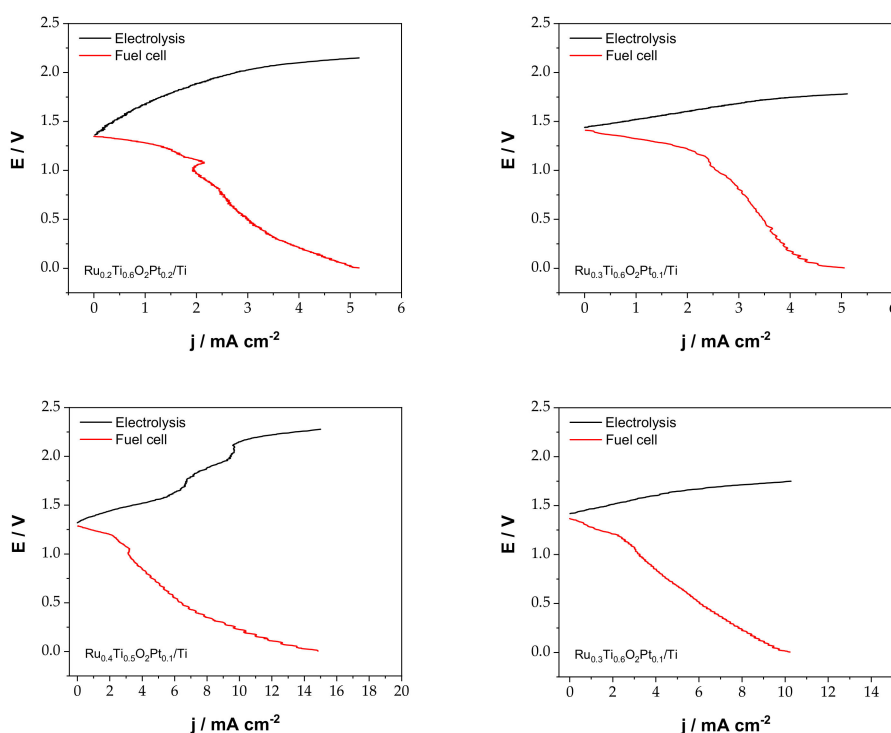

Figure 7. Potential vs. current density for the cell operated in both electrolysis and fuel cell mode at 25 °C and atmospheric pressure with different chlorine electrodes: $Ru_{0.2}Ti_{0.6}O_2Pt_{0.2}$, $Ru_{0.3}Ti_{0.6}O_2Pt_{0.1}$, $Ru_{0.4}Ti_{0.5}O_2Pt_{0.1}$, and $Ru_{0.45}Ti_{0.5}O_2Pt_{0.05}$ [28].

3.2.3. Catalysts Based on Other Compounds

In order to further improve the stability of these active oxides, the addition of other materials like TiO_2, Ta_2O_5, and ZrO_2 has been investigated [74]. Thus, Deng et al. (2019) studied the surface morphologies of IrO_2-Ta_2O_5-TiO_2 electrodes with different TiO_2 mole fractions and observed that many fine grains appeared on the surfaces of IrO_2-Ta_2O_5-TiO_2 electrodes, which could improve electrochemical active surface area and electrocatalytic activity. The IrO_2-Ta_2O_5-TiO_2 electrode, whose loading was 0.7 mg cm^{-2}, presents a high electrochemically active surface and a low Tafel slope (50.1–51.5 mV dec^{-1}), which makes it the electrode with the highest CER performance. At the same time, the IrO_2-Ta_2O_5-TiO_2 electrode has very excellent chloride evolution selectivity, which has greatly inhibited the occurrence of oxygen evolution [75].

4. Performance of the Regenerative H_2-Cl_2 Fuel Cells

In order to allow readers to have detailed information about the topics discussed in the previous sections, Table 1 summarizes the most important data, ranked according to the year of completion. In this way, the enhancements and advances in this technology over the last years can be checked, and the efficiency of the different materials (both individually and in combination) used as electrocatalysts in a hydrogen-chlorine regenerative cell can be compared.

From this chronological perspective, the following statements can be drawn:

- Over the years, new techniques have been used for the development of new catalysts and it has generally meant a substantial enhancement in the efficiency of hydrogen-chlorine regenerative cells.
- The use of Ru instead of Pt implied an increase in the catalytic activity of the electrode in chlorine evolution reaction.
- The combination of two metal oxides generally improves the results obtained by using a pure metal (up to 84% for $(Ru_{0.09}Co_{0.91})_3O_4$/C as the chlorine electrode).
- Adding a new metal (Pt) to Ru-based bimetallic catalysts does not, generally, improve the performance of H_2-Cl_2 fuel cells.
- The best electric-to-electric efficiency (EFE) results have been obtained in research carried out by our group, at present, in which only ruthenium oxide was used as a catalyst on the chlorine side. These results were obtained by using carbon as a support and introducing dry chlorine into the cell, which changed the operating conditions when compared to the rest of the cells.

Table 1. Comparison of recent research on the regenerative H_2-Cl_2 system. Performance described in terms of energy efficiency (EE), electric-to-electric efficiency (EFE), power efficiency (PE), and maximum cell voltage (MCV), where applicable.

Electrode Hydrogen Side	Electrode Chlorine Side	Manufacturing Procedure	Exp. Setup Electrolysis	Exp. Setup Fuel Cell	Performance Electrolysis	Reference / Fuel Cell	Conclusions Pros (+)	Conclusions Cons (−)
Graphite Non-electrocatalyst	Graphite Non-electrocatalyst	Three cells; Surface area electrode (SAE): 60 cm^2; Separators: 2 mm thick earthenware	X	I = 0.2A; T = 25 °C; Cl_2 = 1.5 L h^{-1}; H_2 = 12 L h^{-1}	H_2 = 2% Cl_2 = 91%	[35]	-Low H_2 consumption	-Necessary to platinize the electrode; high flow rate of hydrogen
Pt/C	Pt/C	-	X	j = 40 mA cm^{-2}; T = 50 °C; 5.0–8.0 M HCl	EE = 41% and 51%	[36]	-Carbon gas diffusion electrodes	-High conductivity is required (5.0 M HCl, as minimum)
Platinized graphite	Percolating porous graphite	-	X	E = 1.0 V	j = 50 mA cm^{-2} PE = 80%	[37]	-The cell performance remained constant	-Low activity for CRR due to the lack of a catalyst
Platinized graphite	Ruthenized titanium (RuO_2/TiO_2)	Cell flow-by and flow-through; Membrane: Nafion (0.025 cm); SAE: 46 cm^2	H_2 gas; Cl_2 dissolved in HCl; j = 100 mA cm^{-2}; T = 40 and 80 °C; Electrolyte = 10% HCl; 8 cm^3 s^{-1}	H_2: non-electrolyte; Cl_2: HCl; j = 100 mA cm^{-2}; Cl_2 P = 5 atm; Electrolyte = 10 % HCl	EFE = 85 and 90% (40–80 °C)	[49]	-Fast electrode kinetics of the system -Electrolysis and fuel cell reaction in the same cell	-Mass transfer limitations during discharge -Parasitic reactions
Pt-Ir/C 2.5 wt. % Pt; 5 wt. % Ir	Pt-Ir/C 2.5 wt. % Pt; 5 wt. % Ir	Non-membrane; SAE: 15 cm^2; Separators: neoprene rubber; Electrode distance: 6 mm	X	j = 100 mA cm^{-2}; T = 60 °C; Cl_2 P = 60 mm Hg; Electrolyte = 5 M HCl; 7 mL min^{-1}	MCV = 1.0 V Stable for 300 h	[53]	-A long-term stability in performance of the cell -Low Pt content	-Electrode corrosion -Passivation -Mechanical damage
Pt/C 20 wt. % Pt 1 mg_{Pt} cm^{-2}	RuO_2/C 0.8 mg_{Pt} cm^{-2}	Surface area electrode: 6.25 cm^2	X	j = 3 00 mA cm^{-2}; T = 25 °C; Electrolyte = 1 M HCl	MCV = 1.05 V Stable for 120 h	[50]	-Non-platinum for chlorine electrode	-Long-term stability decreases in the performance of the cell by 45%
Pt/C 20 wt. % Pt 0.5 mg_{Pt} cm^{-2}	$(Ru_{0.09}Co_{0.91})_3O_4$/C 0.15 mg_{Ru} cm^{-2}	Circular endplates; Separators: PTFE; SAE: 2 cm^2; Membrane: Nafion; Assembly: Membrane electrode assembly (MEA) (10.2 nm)	T = 50 °C	Anolyte: non-humidified H_2 or humidified H_2 (50–100 mL min^{-1}); Catolyte: HCl + bubbles of Cl_2 (0 M, 1 M, and 2 M); T = 50 °C; Cl_2 P = 12–70 psig	Maximum power density = 0.4 W cm^{-2} EFE = 84%	[17]	-Maximum power density is twice that of previous literature values -Low Ru content -Oxygen evolution is slow -No significant activation loss	-The hydrogen electrode requires humidification
$Ti_{0.8}O_2Pt_{0.2}/Ti$ 40 wt. % Pt 0.65 mg_{Pt} cm^{-2}	$Ru_{0.2}Ti_{0.6}O_2Pt_{0.2}/Ti$ 38 wt. % Ru; 40 wt. % Pt 0.65 mg_{Pt} cm^{-2}	Cell flow-by housing (7.5 cm × 7.5 cm); Surface area electrode: 2 cm^2; Membrane: Nafion; Assembly: non-MEA	j = 100 mA cm^{-2}; T = 25 °C; P = 1 atm; Anolyte = 2.0 M NaCl; Catholyte = 2.0 M NaCl	E = 0.5 V; T = 25 °C; P = 1 atm; Anolyte = macrobubbles H_2; Catholyte = HClO (1 M HCl + 1 M ClO$^-$)	H_2 production = 88% EFE = 46%	[44]	-Electrodes have higher efficiency for long periods of time -Reversibility -Electrolysis and fuel in the same cell -Low oxygen production -High hydrogen production	Electrodes with a certain amount of Pt -High electrode gap
$Ti_{0.8}O_2Pt_{0.2}/Ti$ 40 wt. % Pt 0.65 mg_{Pt} cm^{-2}	$Ru_{0.3}Ti_{0.6}O_2Pt_{0.1}/Ti$ 38 wt. % Ru; 40 wt. % Pt 0.65 mg_{Pt} cm^{-2}				H_2 production = 98% EFE = 74%	[44]		
$Ti_{0.8}O_2Pt_{0.2}/Ti$ 40 wt. % Pt 0.65 mg Pt cm^{-2}	$Ru_{0.4}Ti_{0.5}O_2Pt_{0.1}/Ti$ 38 wt. % Ru; 40 wt. % Pt 0.65 mg Pt cm^{-2}				H_2 production = 97% EFE = 60%	[44]		
$Ti_{0.8}O_2Pt_{0.2}/Ti$ 40 wt. % Pt 0.65 mg_{Pt} cm^{-2}	$Ru_{0.45}Ti_{0.5}O_2Pt_{0.05}/Ti$ 38 wt. % Ru; 40 wt. % Pt 0.65 mg Pt cm^{-2}				H_2 production = 84% EFE = 13%	[44]		

Table 1. *Cont.*

Electrode		Manufacturing Procedure	Experimental Setup/Operation Conditions		Performance	Reference	Conclusions	
Hydrogen Side	Chlorine Side		Electrolysis	Fuel Cell	Electrolysis	Fuel Cell	Pros (+)	Cons (−)
Pt/C 40 wt. % Pt 0.65 mg$_{Pt}$ cm^{-2}	Ru$_{0.3}$Ti$_{0.6}$O$_2$Pt$_{0.1}$/Ti 38 wt. % Ru; 40 wt. % Pt 0.65 mg$_{Pt}$ cm^{-2}	Cell flow-by housing (7.5 cm × 7.5 cm) SAE: 2 cm^2 Membrane: Nafion Assembly: MEA	j = 100 mA cm^{-2} T = 25 °C P = 1 atm Anolyte = 2.0 M NaCl Catholyte = 2.0 M NaCl	E = 0.5 V T = 25 °C P = 1 atm Anolyte = H$_2$ microbubbles Catholyte = HClO (1 M HCl + 1 M ClO$^-$)	H$_2$ production = 84% EFE = 48%	[28]	-Minimum distance between electrodes -Low mass transfer losses at the hydrogen electrode -Reversibility of the system -Non-platinum content for the chlorine electrode -Low metal precious content -Higher mechanical stability -Electrodes do not require thermal treatment -Novel reactor of non-porous graphite material -Non-platinum on chlorine electrode	-Electrodes with a certain amount of Pt -Electrodes require thermal treatment
Pt/C 40 wt. % Pt 0.65 mg$_{Pt}$ cm^{-2} Pt/C 40 wt. % Pt 0.65 mg$_{Pt}$ cm^{-2}	Ru$_{0.3}$Ti$_{0.7}$O$_2$/Ti 38 wt. % Ru 0.65 mg$_{Pt}$ cm^{-2} Ru$_{0.5}$Iri$_{0.5}$O$_2$/Ti 38 wt. % Ru 0.65 mg$_{Pt}$ cm^{-2}				H$_2$ production = 72% EFE = 33% H$_2$ production = 80% EFE = 45%	Carried out by our research group, not published yet		-Parasitic reactions -Formation of oxygen -Low stability of the cell performance
Pt/C 40 wt. % Pt 0.65 mg$_{Pt}$ cm^{-2}	RuO$_2$/C 38 wt. % Ru 0.65 mg$_{Pt}$ cm^{-2}	Cell (graphite): 15 cm × 15 cm SAE: 25 cm^2 Membrane: Nafion		E = 0.5 V Anolyte = humidified H$_2$ Catholyte = dry Cl$_2$	H$_2$ production = 99.7% E = 530 Wh/mol Cl$_2$ EFE = 78%			-High ohmic resistance -The hydrogen electrode at least requires humidification

5. Conclusions

Hydrogen-chlorine regenerative fuel cells can be used for energy storage. Although it is known that there are other more developed alternatives, such as batteries or H_2-O_2 fuel cells, this technology may still have its niche market. Most of the research efforts on these systems have been focused on catalysts and, although chlorine-based cells have been largely studied over the past couple of decades, it is still receiving great attention because of the recent boost of renewable energy.

Regarding the different cell configurations that have been reviewed, it is clear that the MEA-based one is mostly used by researchers. Nevertheless, the idea of feeding hydrogen as microbubbles in a liquid phase has been found to be very attractive as the compression power and cost could be decreased. The catalysts that are used in these systems have been evaluated from two different point of views.

(i)   Those that are used in the electrode where hydrogen reactions take place. In this case, it can be concluded that Pt-based catalysts are the best, and recent trends are looking for novel-non-carbonaceous supports to avoid the corrosion of carbon-based catalyst supports.

(ii)   Those that are used in the electrode where redox chlorine reactions take place. In this case, RuO_2-based catalysts are the best option. Nevertheless, this electrode has received more attention than numerous other "catalyst configurations" and bimetallic or trimetallic catalysts, which have been assessed with the aim of improving the properties of the catalysts for these reactions and reducing the costs of the catalyst.

The authors did not find many experiments using actual regenerative H_2-Cl_2 fuel cells, i.e., tests where the catalysts were working in electrolysis and fuel cell modes. Most of the catalysts were evaluated only in one mode. These essays are mandatory to evaluate the efficiency of the system. Moreover, durability issues of the catalysts used in these systems are unknown. From the authors' point of view, this item should be the next step to evaluate the feasibility of this technology and improve the level of technology readiness

Author Contributions: J.L. and M.A.R. contributed to the design, implementation of the research meanwhile M.C. and A.R. carried out the information search and proposed comparative discussions. Frequent group meetings between the authors helped to analyze and organize the findings until obtaining the final manuscript. All authors have read and agreed to the published version of the manuscript.

Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

CER	chlorine evolution reaction
CRR	chlorine reduction reaction
EE	energy efficiency
EES	electrochemical energy storage
EFE	electric-to-electric efficiency
FTO	fluorine-doped tin oxide
HER	hydrogen evolution reaction
LSV	Linear sweet voltammetry
MCV	maximum cell voltage
MEA	membrane electrode assembly
MMO	mixed metal oxide
NPs	nanoparticles
NF	nickel foil
PE	power efficiency

PEM   proton-exchange membrane
OER   oxygen evolution reaction
ORR   oxygen reduction reaction
URFC   unitized regenerative fuel cell

References

1. Madsen, H.T.; Søgaard, E.G.; Muff, J. Study of degradation intermediates formed during electrochemical oxidation of pesticide residue 2,6-dichlorobenzamide (BAM) in chloride medium at boron doped diamond (BDD) and platinum anodes. *Chemosphere* **2015**, *120*, 756–763. [CrossRef] [PubMed]

2. Arora, S.; Bhaukhandi, K.D.; Mishra, P.K. Coronavirus lockdown helped the environment to bounce back. *Sci. Total Environ.* **2020**, *742*, 140573. [CrossRef] [PubMed]

3. Naderipour, A.; Abdul-Malek, Z.; Ahmad, N.A.; Kamyab, H.; AshokKumar, V.; Ngamcharussrivichai, C.; Chelliapan, S. Effect of COVID-19 virus on reducing GHG emission and increasing energy generated by renewable energy sources: A brief study in Malaysian context. *Environ. Technol. Innov.* **2020**, *20*, 101151. [CrossRef] [PubMed]

4. SanJuan-Reyes, S.; Gómez-Oliván, L.M.; Islas-Flores, H. COVID-19 in the environment. *Chemosphere* **2021**, *263*, 127973. [CrossRef] [PubMed]

5. Zhang, H.; Li, X.; Zhang, J. *Redox Flow Batteries: Fundamentals and Applications*; CRC Press: Boca Raton, FL, USA, 2017.

6. Layke, J.H. 3 Reasons to Invest in Renewable Energy Now. *World Resources Institute*. 26 June 2020. Available online: https://www.wri.org/blog/2020/05/coronavirus-renewable-energy-stimulus-packages (accessed on 15 July 2020).

7. Ahmad, S.; Tahar, R.M. Selection of renewable energy sources for sustainable development of electricity generation system using analytic hierarchy process: A case of Malaysia. *Renew. Energy* **2014**, *63*, 458–466. [CrossRef]

8. Ehteshami, S.M.M.; Chan, S.H. The role of hydrogen and fuel cells to store renewable energy in the future energy network—Potentials and challenges. *Energy Policy* **2014**, *73*, 103–109. [CrossRef]

9. Gahleitner, G. Hydrogen from renewable electricity: An international review of power-to-gas pilot plants for stationary applications. *Int. J. Hydrogen Energy* **2013**, *38*, 2039–2061. [CrossRef]

10. Yang, Z.; Zhang, J.; Kintner-Meyer, M.C.W.; Lu, X.; Choi, D.; Lemmon, J.P.; Liu, J. Electrochemical Energy Storage for Green Grid. *Chem. Rev.* **2011**, *111*, 3577–3613. [CrossRef]

11. Jameson, A.; Gyenge, E. Halogens as Positive Electrode Active Species for Flow Batteries and Regenerative Fuel Cells. *Electrochem. Energy Rev.* **2020**, 1–35. [CrossRef]

12. Díaz-Abad, S.; Millán, M.; Rodrigo, M.; Lobato, J. Review of Anodic Catalysts for SO2 Depolarized Electrolysis for "Green Hydrogen" Production. *Catalysts* **2019**, *9*, 63. [CrossRef]

13. Wang, Y.; Leung, D.Y.; Xuan, J.; Wang, H. A review on unitized regenerative fuel cell technologies, part-A: Unitized regenerative proton exchange membrane fuel cells. *Renew. Sustain. Energy Rev.* **2016**, *65*, 961–977. [CrossRef]

14. Mitlitsky, F.; Myers, B.; Weisberg, A.H. Regenerative Fuel Cell Systems. *Energy Fuels* **1998**, *12*, 56–71. [CrossRef]

15. Cho, K.T.; Tucker, M.C.; Weber, A.Z. A Review of Hydrogen/Halogen Flow Cells. *Energy Technol.* **2016**, *4*, 655–678. [CrossRef]

16. Anderson, E.B.; Taylor, J.E.; Wilemski, G.; Gelb, A. A high performance hydrogen/chlorine fuel cell for space power applications. *J. Power Sources* **1994**, *47*, 321–328. [CrossRef]

17. Huskinson, B.; Rugolo, J.; Mondal, S.K.; Aziz, M.J. A high power density, high efficiency hydrogen-chlorine regenerative fuel cell with a low precious metal content catalyst. *Energy Environ. Sci.* **2012**, *5*, 8690. [CrossRef]

18. Chehade, G.; Alrawahi, N.; Yuzer, B.; Dincer, I. A photoelectrochemical system for hydrogen and chlorine production from industrial waste acids. *Sci. Total Environ.* **2020**, *712*, 136358. [CrossRef]

19. Thomassen, M.; Børresen, B.; Scott, K.; Tunold, R. A computational simulation of a hydrogen/chlorine single fuel cell. *J. Power Sources* **2006**, *157*, 271–283. [CrossRef]

20. Yang, W.; Chen, S. Recent progress in electrode fabrication for electrocatalytic hydrogen evolution reaction: A mini review. *Chem. Eng. J.* **2020**, *393*, 124726. [CrossRef]

21. Pandiyan, G.K.; Prabaharan, T. Implementation of nanotechnology in fuel cells. *Mater. Today Proc.* **2020**. [CrossRef]

22. Tri, P.N.; Nguyen, T.A.; Rtimi, S.; Plamondon, C.M.O. Chapter 1—Nanomaterials-based coatings: An introduction. In *Nanomaterials-Based Coatings*; Tri, P.N., Nguyen, T.A., Rtimi, S., Plamondon, C.M.O., Eds.; Elsevier: Amsterdam, The Netherlands, 2019; pp. 1–7.

23. Maricle, D.L. Hydrogen/Chlorine Regenerative Fuel Cell. U.S. Patent No 4,128,701, 5 December 1978.

24. Maricle, D.L. Anhydrous H_2-Cl_2 Regenerative Fuel Cell. U.S. Patent No 4,129,683, 5 December 1978.

25. Tolmachev, Y.V. Hydrogen-halogen electrochemical cells: A review of applications and technologies. *Russ. J. Electrochem.* **2013**, *50*, 301–316. [CrossRef]

26. Braff, W.A.; Bazant, M.Z.; Buie, C.R. Membrane-less hydrogen bromine flow battery. *Nat. Commun.* **2013**, *4*, 2346. [CrossRef] [PubMed]

27. Brushett, F.R.; Zhou, W.-P.; Jayashree, R.S.; Kenis, P.J.A. Alkaline Microfluidic Hydrogen-Oxygen Fuel Cell as a Cathode Characterization Platform. *J. Electrochem. Soc.* **2009**, *156*, B565–B571. [CrossRef]

28. Carvela, M.; Lobato, J.; Rodrigo, M.A. Storage of energy using a gas-liquid H2/Cl2 fuel cell: A first approach to electrochemically-assisted absorbers. *Chemosphere* **2020**, *254*, 126795. [CrossRef] [PubMed]

29. Du, N.; Wang, C.; Wang, X.; Lin, Y.; Jiang, J.; Xiong, Y. Trimetallic TriStar Nanostructures: Tuning Electronic and Surface Structures for Enhanced Electrocatalytic Hydrogen Evolution. *Adv. Mater.* **2016**, *28*, 2077–2084. [CrossRef]

30. Zhu, L.; Lin, H.; Li, Y.; Liao, F.; Lifshitz, Y.; Sheng, M.; Lee, S.-T.; Shao, M. A rhodium/silicon co-electrocatalyst design concept to surpass platinum hydrogen evolution activity at high overpotentials. *Nat. Commun.* **2016**, *7*, 12272. [CrossRef] [PubMed]

31. Su, J.; Yang, Y.; Xia, G.; Chen, J.; Jiang, P.; Chen, Q. Ruthenium-cobalt nanoalloys encapsulated in nitrogen-doped graphene as active electrocatalysts for producing hydrogen in alkaline media. *Nat. Commun.* **2017**, *8*, 14969. [CrossRef] [PubMed]

32. Appleby, A. From Sir William Grove to today: Fuel cells and the future. *J. Power Sources* **1990**, *29*, 3–11. [CrossRef]

33. Yu, X.; Ye, S. Recent advances in activity and durability enhancement of Pt/C catalytic cathode in PEMFC. *J. Power Sources* **2007**, *172*, 133–144. [CrossRef]

34. Chen, Y.; Yang, X.; Kitta, M.; Xu, Q. Monodispersed Pt nanoparticles on reduced graphene oxide by a non-noble metal sacrificial approach for hydrolytic dehydrogenation of ammonia borane. *Nano Res.* **2017**, *10*, 3811–3816. [CrossRef]

35. Foerster, F.; Nobis, A.; Stötzer, H. Über die Wasserstoff-Chlor-Kette. Zeitschrift für Elektrochemie und angewandte physikalische. *Chemie* **1923**, *29*, 64–79. [CrossRef]

36. Yoshizawa, F.H.S.; Takehara, Z.; Kanaya, J.Y. Studies of Hydrogen-Chlorine Fuel Cell. I. Basic Studies of the Hydrogen-Chlorine Fuel Cell at Low Temperature. *J. Electrochem. Soc. Jpn.* **1962**, *30*, E10–E16. [CrossRef]

37. Bianchi, G. Improved Porous Electrode for Studying Electrocatalytic Reactions of Gases and Vapors. *J. Electrochem. Soc.* **1965**, *112*, 233–238. [CrossRef]

38. Du Nguyen, H.; Nguyen, T.T.L.; Nguyen, K.M.; Ha, T.H.; Nguyen, Q.H. Preparation of the vulcan XC-72R-supported Pt nanoparticles for the hydrogen evolution reaction in PEM water electrolysers. *Adv. Nat. Sci. Nanosci. Nanotechnol.* **2015**, *6*, 25012. [CrossRef]

39. Choi, B.; Yoon, H.; Park, I.-S.; Jang, J.; Sung, Y.-E. Highly dispersed Pt nanoparticles on nitrogen-doped magnetic carbon nanoparticles and their enhanced activity for methanol oxidation. *Carbon* **2007**, *45*, 2496–2501. [CrossRef]

40. Kumar, S.S.; Hidyatai, N.; Herrero, J.S.; Irusta, S.; Scott, K. Efficient tuning of the Pt nano-particle mono-dispersion on Vulcan XC-72R by selective pre-treatment and electrochemical evaluation of hydrogen oxidation and oxygen reduction reactions. *Int. J. Hydrogen Energy* **2011**, *36*, 5453–5465. [CrossRef]

41. Ehsan, M.A.; Suliman, M.H.; Rehman, A.; Hakeem, A.S.; Al Ghanim, A.; Qamar, M. Fabrication of platinum thin films for ultra-high electrocatalytic hydrogen evolution reaction. *Int. J. Hydrogen Energy* **2020**, *45*, 15076–15085. [CrossRef]

42. Lin, R.; Cai, X.; Zeng, H.; Yu, Z. Stability of High-Performance Pt-Based Catalysts for Oxygen Reduction Reactions. *Adv. Mater.* **2018**, *30*, e1705332. [CrossRef]

43. Anwar, M.T.; Yan, X.; Shen, S.; Husnain, N.; Zhu, F.; Luo, L.; Zhang, J. Enhanced durability of Pt electrocatalyst with tantalum doped titania as catalyst support. *Int. J. Hydrogen Energy* **2017**, *42*, 30750–30759. [CrossRef]

44. Carvela, M.; Conti, J.; Lobato, J.; Scialdone, O.; Rodrigo, M. Effect of the anode composition on the performance of reversible chlor-alkali electro-absorption cells. *Sep. Purif. Technol.* **2020**, *248*, 117017. [CrossRef]

45. Wu, X.; Zhuang, W.; Lu, L.; Li, L.; Zhu, J.; Mu, L.; Li, W.; Zhu, Y.; Lu, X. Excellent performance of Pt-C/TiO2 for methanol oxidation: Contribution of mesopores and partially coated carbon. *Appl. Surf. Sci.* **2017**, *426*, 890–896. [CrossRef]

46. Cheng, J.; Zhang, H.; Ma, H.; Zhong, H.; Zou, Y. Study of carbon-supported IrO2 and RuO2 for use in the hydrogen evolution reaction in a solid polymer electrolyte electrolyzer. *Electrochim. Acta* **2010**, *55*, 1855–1861. [CrossRef]

47. Sadhasivam, T.; Dhanabalan, K.; Roh, S.-H.; Kim, T.-H.; Park, K.-W.; Jung, S.; Kurkuri, M.D.; Jung, H.-Y. A Comprehensive review on unitized regenerative fuel cells: Crucial challenges and developments. *Int. J. Hydrogen Energy* **2017**, *42*, 4415–4433. [CrossRef]

48. Chang, F.T.; Wick, H. Halogen Overvoltage. *Z. Phys. Chem. A* **1935**, *172*, 448.

49. Yeo, R.S.; McBreen, J.; Tseung, A.C.C.; Srinivasan, S.; McElroy, J. An electrochemically regenerative hydrogen-chlorine energy storage system: Electrode kinetics and cell performance. *J. Appl. Electrochem.* **1980**, *10*, 393–404. [CrossRef]

50. Thomassen, M.; Børresen, B.; Hagen, G.; Tunold, R. H2/Cl2 fuel cell for co-generation of electricity and HCl. *J. Appl. Electrochem.* **2003**, *33*, 9–13. [CrossRef]

51. Lim, T.; Jung, G.Y.; Kim, J.H.; Park, S.O.; Park, J.; Kim, Y.-T.; Kang, S.J.; Jeong, H.Y.; Kwak, S.K.; Joo, S.H. Atomically dispersed Pt–N4 sites as efficient and selective electrocatalysts for the chlorine evolution reaction. *Nat. Commun.* **2020**, *11*, 1–11. [CrossRef] [PubMed]

52. Wei, S.; Shi, L.; Ren, Z.; Zhang, A.; Ming, R.; Chai, B.; Zhu, Y. Preparation of electrolyzed oxidizing water with a platinum electrode prepared by magnetron sputtering technique. *RSC Adv.* **2017**, *7*, 45377–45384. [CrossRef]

53. Shibli, S.; Noel, M. Platinum-iridium bimetal catalyst-based porous carbon electrodes for H$_2$-Cl$_2$ fuel cells. *Int. J. Hydrogen Energy* **1993**, *18*, 141–147. [CrossRef]

54. Iwakura, C.; Hirao, K.; Tamura, H. Anodic evolution of oxygen on ruthenium in acidic solutions. *Electrochim. Acta* **1977**, *22*, 329–334. [CrossRef]

55. Le Luu, T.; Kim, C.; Yoon, J. Sonoelectrodeposition of RuO2 electrodes for high chlorine evolution efficiencies. *J. Korean Soc. Water Wastewater* **2017**, *31*, 397–407. [CrossRef]

56. Zafar, M.S.; Tausif, M.; Ul-Haq, Z.; Ashraf, M.; Hussain, S. New Development of Anodic Electro-catalyst for Chlor-alkali Industry. *Port. Electrochim. Acta* **2016**, *34*, 257–266. [CrossRef]

57. Goryachev, A.; Pascuzzia, M.E.C.; Carlàb, F.; Weber, T.; Over, H.; Hensena, E.J.M.; Hofmanna, J.P. Electrochemical stability of RuO2(110)/Ru(0001) model electrodes in the oxygen and chlorine evolution reactions. *Electrochim. Acta* **2020**, *336*, 135713. [CrossRef]

58. Han, J.; An, H.J.; Kim, T.-W.; Lee, K.-Y.; Kim, H.J.; Kim, Y.; Chae, H.-J. Effect of Structure-Controlled Ruthenium Oxide by Nanocasting in Electrocatalytic Oxygen and Chlorine Evolution Reactions in Acidic Conditions. *Catalysts* **2019**, *9*, 549. [CrossRef]

59. Panić, V.V.; Dekanski, A.; Mitrić, M.; Milonjić, S.K.; Miskovic-Stankovic, V.; Nikolić, B.Ž. The effect of the addition of colloidal iridium oxide into sol–gel obtained titanium and ruthenium oxide coatings on titanium on their electrochemical properties. *Phys. Chem. Chem. Phys.* **2010**, *12*, 7521–7528. [CrossRef] [PubMed]

60. Thomassen, M.; Sandnes, E.; Børresen, B.; Tunold, R. Evaluation of concepts for hydrogen—Chlorine fuel cells. *J. Appl. Electrochem.* **2006**, *36*, 813–819. [CrossRef]

61. Ren, Y.; Ma, Z.; Bruce, P.G. Ordered mesoporous metal oxides: Synthesis and applications. *Chem. Soc. Rev.* **2012**, *41*, 4909–4927. [CrossRef]

62. Heo, S.E.; Lim, H.W.; Cho, D.K.; Park, I.J.; Kim, H.; Lee, C.W.; Ahn, S.H.; Kim, J.Y. Anomalous potential dependence of conducting property in black titania nanotube arrays for electrocatalytic chlorine evolution. *J. Catal.* **2020**, *381*, 462–467. [CrossRef]

63. Audichon, T.; Mayousse, E.; Morisset, S.; Morais, C.; Comminges, C.; Napporn, T.W.; Kokoh, K.B. Electroactivity of RuO2–IrO2 mixed nanocatalysts toward the oxygen evolution reaction in a water electrolyzer supplied by a solar profile. *Int. J. Hydrogen Energy* **2014**, *39*, 16785–16796. [CrossRef]

64. Moradi, F.; Dehghanian, C. Addition of IrO2 to RuO2+TiO2 coated anodes and its effect on electrochemical performance of anodes in acid media. *Prog. Nat. Sci.* **2014**, *24*, 134–141. [CrossRef]

65. Le Luu, T.; Kim, C.; Kim, S.; Kim, J.; Yoon, J. Fabricating macroporous RuO2-TiO2 electrodes using polystyrene templates for high chlorine evolution efficiencies. *Desalination Water Treat.* **2017**, *77*, 94–104. [CrossRef]

66. Kong, F.-D.; Zhang, S.; Yin, G.-P.; Zhang, N.; Wang, Z.-B.; Du, C.-Y. Pt/porous-IrO2 nanocomposite as promising electrocatalyst for unitized regenerative fuel cell. *Electrochem. Commun.* **2012**, *14*, 63–66. [CrossRef]

67. Finke, C.E.; Omelchenko, S.T.; Jasper, J.T.; Lichterman, M.F.; Read, C.G.; Lewis, N.S.; Hoffmann, M.R. Enhancing the activity of oxygen-evolution and chlorine-evolution electrocatalysts by atomic layer deposition of TiO2. *Energy Environ. Sci.* **2019**, *12*, 358–365. [CrossRef]

68. Liab, J.; Zhoud, Q.; Shenc, Z.; Lic, S.; Pue, J.; Zhongc, C.; CaoC, M.; Jinc, X.; Zhangc, H.; Wangb, Y.; et al. Synergistic effect of ultrafine nano-Ru decorated cobalt carbonate hydroxides nanowires for accelerated alkaline hydrogen evolution reaction. *Electrochim. Acta* **2020**, *331*, 135367. [CrossRef]

69. Mondal, S.K.; Aziz, M.J.; Rugolo, J. Alloy Oxide Electrocatalysts for Regenerative Hydrogen-Halogen Fuel Cell. *MRS Proc.* **2011**, *1311*. [CrossRef]

70. Ghosh, S.K.; Rahaman, H. Chapter 16—Noble metal–Manganese oxide hybrid nanocatalysts. In *Noble Metal-Metal Oxide Hybrid Nanoparticles*; Mohapatra, S., Nguyen, T.A., Nguyen-Tri, P., Eds.; Woodhead Publishing: Sawston, UK, 2019; pp. 313–340.

71. Zeradjanin, A.R.; Menzel, N.; Schuhmann, W.; Strasser, P. On the faradaic selectivity and the role of surface inhomogeneity during the chlorine evolution reaction on ternary Ti–Ru–Ir mixed metal oxide electrocatalysts. *Phys. Chem. Chem. Phys.* **2014**, *16*, 13741–13747. [CrossRef] [PubMed]

72. Yi, Z.; Kangning, C.; Wei, W.; Wang, J.; Lee, S. Effect of IrO2 loading on RuO2–IrO2–TiO2 anodes: A study of microstructure and working life for the chlorine evolution reaction. *Ceram. Int.* **2007**, *33*, 1087–1091. [CrossRef]

73. Weibel, A.; Bouchet, R.; Knauth, P. Electrical properties and defect chemistry of anatase (TiO2). *Solid State Ion.* **2006**, *177*, 229–236. [CrossRef]

74. Oakton, E.; Lebedev, D.; Povia, M.; Abbott, D.F.; Fabbri, E.; Fedorov, A.; Nachtegaal, M.; Copéret, C.; Schmidt, T.J. IrO2-TiO2: A High-Surface-Area, Active, and Stable Electrocatalyst for the Oxygen Evolution Reaction. *ACS Catal.* **2017**, *7*, 2346–2352. [CrossRef]

75. Deng, L.; Liu, Y.; Zhao, G.; Chen, J.; He, S.; Zhu, Y.; Chai, B.; Ren, Z. Preparation of electrolyzed oxidizing water by TiO2 doped IrO2-Ta2O5 electrode with high selectivity and stability for chlorine evolution. *J. Electroanal. Chem.* **2019**, *832*, 459–466. [CrossRef]

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.