

Review

Review of Anodic Catalysts for SO₂ Depolarized Electrolysis for “Green Hydrogen” Production

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Abstract: In the near future, primary energy from fossil fuels should be gradually replaced with renewable and clean energy sources. To succeed in this goal, hydrogen has proven to be a very suitable energy carrier, because it can be easily produced by water electrolysis using renewable energy sources. After storage, it can be fed to a fuel cell, again producing electricity. There are many ways to improve the efficiency of this process, some of them based on the combination of the electrolytic process with other non-electrochemical processes. One of the most promising is the thermochemical hybrid sulphur cycle (also known as Westinghouse cycle). This cycle combines a thermochemical step (H₂SO₄ decomposition) with an electrochemical one, where the hydrogen is produced from the oxidation of SO₂ and H₂O (SO₂ depolarization electrolysis, carried out at a considerably lower cell voltage compared to conventional electrolysis). This review summarizes the different catalysts that have been tested for the oxidation of SO₂ in the anode of the electrolysis cell. Their advantages and disadvantages, the effect of platinum (Pt) loading, and new tendencies in their use are presented. This is expected to shed light on future development of new catalysts for this interesting process.

Keywords: Green Hydrogen; SO₂ electrolysis; electrocatalysts; Westinghouse cycle

1. Introduction

Nowadays, hydrogen is considered an actor with a significant role in tackling climate change and poor air quality. Hydrogen can, in particular, be produced from a broad range of renewable energy sources, acting as a unique energy core providing low or zero emission energy to all energy consuming sectors. Thus, Europe, through the Fuel Cells and Hydrogen Joint and Undertaking (FCH-JU) assessed different “Green Hydrogen” pathways, which as of today have already become nearly commercial, have already undergone extensive research in past or ongoing programs in Europe, or are internationally providing evidence of their general promise for be ready for commercialization. Figure 1 shows the different processes for producing hydrogen from renewable energy sources, and the ones which were selected as more promising after a deeper evaluation [1].

On the way to a “hydrogen economy” [2] and “Green hydrogen”, the ideal raw material is, obviously, water. However, the single step thermal dissociation of water to hydrogen and oxygen is one of the most challenging processes for producing hydrogen in practice [3], due to its unfavorable thermodynamics.

There are different routes to produce hydrogen with low or zero CO₂ emissions, including promising processes based on water splitting (in which new catalysts are being developed)—photoelectrochemical water splitting [4–6], thermochemical cycles [3,7,8] or hybrid thermochemical cycles [9,10] are some examples. Hybrid thermochemical cycles using a high temperature thermal source have been proposed as one of the most promising technologies for massive hydrogen

production [11]; moreover, they have been included as one of the candidates for “Green hydrogen” production, as it can be seen in Figure 1.

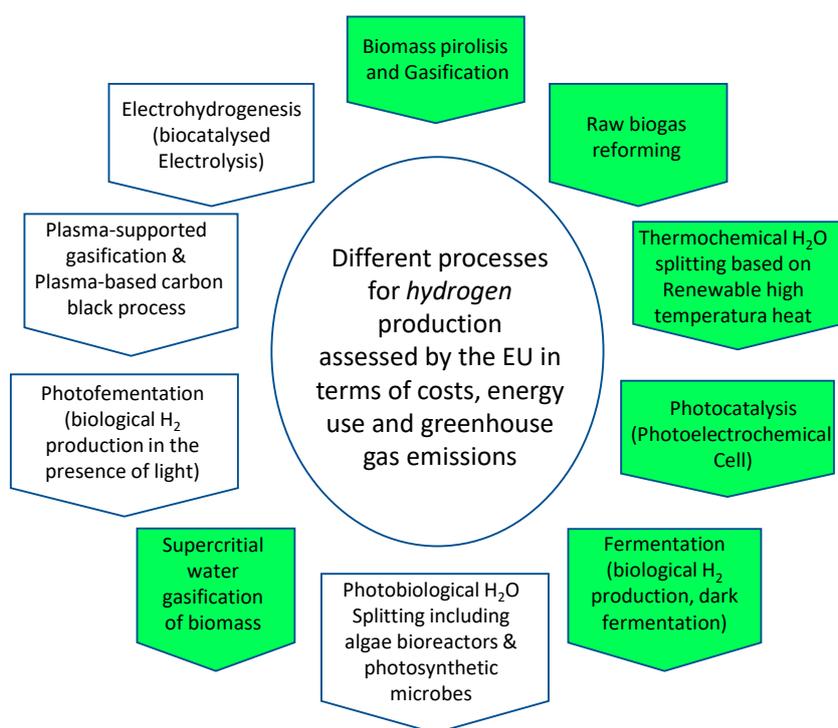


Figure 1. Proposed and selected (highlighted in green) “Green Hydrogen” production pathways in the European Union (EU) (adapted from [1]).

One of the leading thermochemical cycles to produce hydrogen with a high sustainability is the hybrid Sulphur cycle, also known as the Westinghouse cycle. It is a hybrid electrochemical–thermochemical cycle [9]. It was originally proposed in 1975 [12] and developed by Westinghouse electric corporation. The process is labelled “hybrid” because of the substitution of one thermochemical reaction by the electrochemical oxidation of SO_2 with water to yield sulphuric acid and hydrogen [3,13]. What makes this process interesting is its low theoretical cell potential of 0.158 V (versus SHE), which when compared with direct water electrolysis ($E^0 = 1.23$ V versus SHE) makes the Westinghouse process a great alternative in terms of electric energy consumption [3].

Figure 2 shows a possible configuration of the Westinghouse cycle. It consists of two main steps. In the first step, SO_2 is electrochemically oxidized at the anode to form sulphuric acid, protons and electrons ($E^0 = 0.158$ V versus SHE). The protons are conducted across the electrolyte separator to the cathode, where they recombine with the electrons to form hydrogen, according to Equations (1) and (2) [3,13–16].



The second step, common to all sulphur-based thermochemical cycles, is the result of two successive reactions. As sulphuric acid is vaporized (ca. 650 K) and superheated (ca. 900 K), it decomposes into water and sulphur trioxide. The following reaction is the catalytic decomposition, at temperatures higher than 1000 K, of the SO_3 to produce oxygen and sulphur dioxide (Equations (3) and (4)) and downstream are separated [3,13–15].



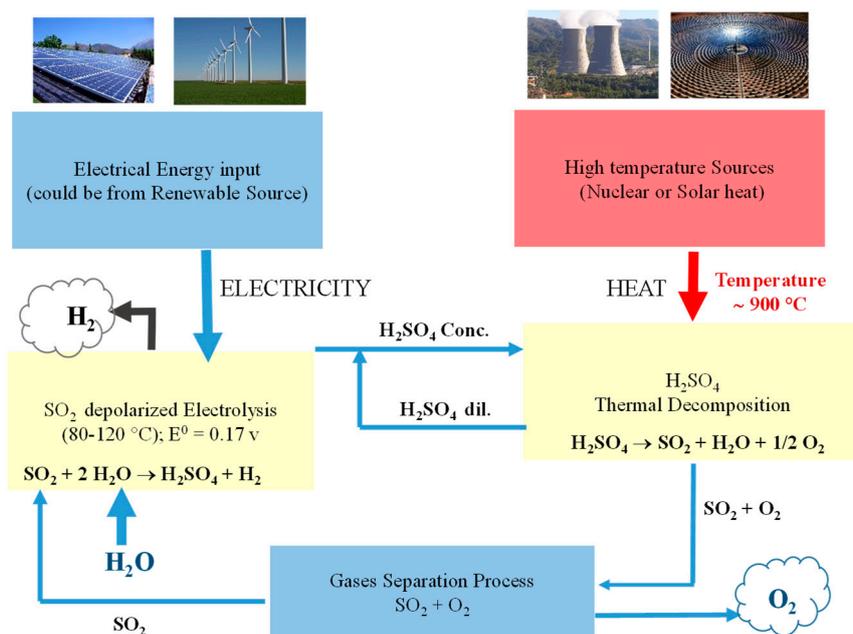


Figure 2. Scheme of the Westinghouse cycle.

The sulphuric acid decomposition has been widely investigated in different studies, such as the one from Sandia National Laboratories [11], and most efforts have been devoted to the optimization of the SO_2 depolarized electrolysis (the electrochemical stage) to increase the global efficiency of the cycle [16]. Challenges for this process are the reduction of the overpotentials in the electrolysis step in order to improve the overall efficiency of the process—the development of high corrosion resistance materials due to the use of acid solutions. Also, as for the thermochemical step in which H_2SO_4 has to be decomposed at very high temperatures, only high-temperature energy sources suitable for this process, such as concentration solar energy or nuclear energy. In terms of efficiency and costs, an optimal efficiency is 47% for a nuclear heat source with a hydrogen cost of 4 \$/kg [3].

The first design of the SO_2 electrolyzer was developed by Westinghouse Corp. in the 1970s, and it consisted of a conventional electrolysis cell with two compartments separated by a membrane [17]. Modern electrolyzers for this process are based on proton exchange membrane fuel cell (PEMFC) technology, where the membrane–electrode–assembly (MEA) is the core of the cell [18]. Figure 3 shows a scheme of a PEM electrolyzer for SO_2 depolarized electrolysis.

As mentioned before, the electrolysis step is one of the parts that has to be optimized. One of the proposed goals for this step is to operate at 0.6 V and 0.5 A/cm² [19]; however, this has not been yet reached.

The anodic electrocatalysts are the key factor to improve SO_2 electrolysis efficiency, as it is necessary to find catalysts with not only high activity but high stability and low costs. At the beginning, anodized electrodes with noble metals like Pt, Pd, Rh, Au, Ru, Re, or Ir were investigated, being the first to achieve better results [20,21]. Now the catalyst technology used in PEMFC systems has been copied, and the electrodes are based on a catalyst supported by carbon-based materials deposited on gas diffusion layers.

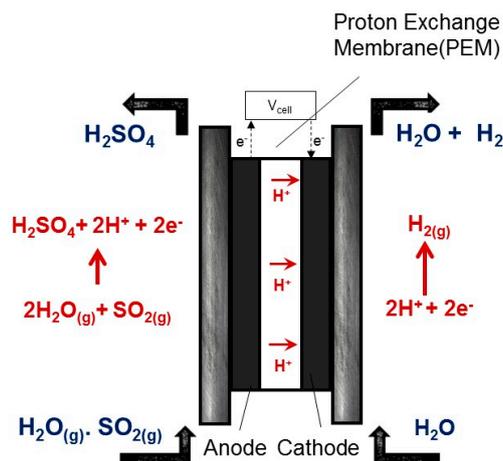


Figure 3. Scheme of a SO_2 depolarized electrolysis cell based on proton exchange membrane (PEM) technology.

This manuscript aims to provide a review on recent developments in electrocatalysts for SO_2 depolarization electrolysis. To the authors' knowledge, there is no review on this topic. In addition, taking into account the great impulse that renewable energies have in the world, and that the hydrogen produced with zero emission technologies can be one of the actors in the future energy scenario, this work can give an overview of the current status and future prospects of the catalysts for improving the electrochemical stage of the hybrid sulphur cycle.

2. Platinum-Based Catalysts

Platinum, as noble metal, is a well-known catalyst that has been widely used in fuel cells. It was one of the first studied catalysts for SO_2 electrolysis to produce hydrogen, showing great catalytic performance for the electro-oxidation of SO_2 ; however, its high price is a disadvantage for this material. For this reason, in recent years different materials have been examined and compared with this noble metal, in order to find a better option to be employed as catalyst.

Seo and Sawyer mention the necessity of pretreating the electrode to activate it, forming an oxide layer at high potentials, which is then stripped when negative potentials are applied to obtain the desired surface characteristics [22]. This paper also shows that the initial preconditioning of the electrode affects its performance. They recommend choosing an initial voltage of -0.15 V (versus Saturated Calomel Electrode, SCE). In a later study [23], the authors investigated the oxidation mechanism of SO_2 on platinum electrodes, demonstrating that the process is mass-diffusion controlled and is an electrochemical–electrontransfer process at potentials lower than those needed for platinum oxide formation (<0.42 V versus SCE). Whereas, a chemical reaction occurs between sulfite and anodically-formed oxide at higher potentials. The same result regarding the oxidation mechanism on platinized platinum supported on porous carbon electrodes was obtained by Wiesener [24]. Appleby and Pinchon compared the catalytic activity of pure black platinum with other noble metals supported on carbon materials, using a rotating-disk paste electrode at 3000 rpm [21]. They obtained 0.3 A/cm² with 10% Pt on Norit BRX at 0.7 V (versus SHE), which they considered a good result. Nevertheless, pure black platinum showed a better catalytic activity, with approximately 0.5 A/cm² at 0.7 V (versus SHE). Platinum supported on 2 μm graphite spheres showed poor activity, probably due to lower surface area, demonstrating that the SO_2 oxidation is highly substrate-dependent. In this work, they suggest using an acid concentration of 50 wt % for optimal results. Lu and Ammon used 50 wt % H_2SO_4 at 25 °C and atmospheric pressure for SO_2 electro-oxidation [20]. Pre-anodized electrodes showed reproducible data when being pre-treated, as mentioned before [22]. The authors obtained a limiting current density of only 1.2 mA/cm² at 0.8 V (versus SHE) for a platinum electrode. In a different study, Lu and Ammon compared the performance of a Pt-catalyzed carbon plate electrode

with a carbon cloth-supported electrode in an SO₂-depolarized electrolyzer [25]. They developed an electrolyzer with a loading of 7 mg/cm² of platinum on the anode and with a potential of 0.77 V (versus SHE) at a current density of 0.2 A/cm² in a new electrolyzer configuration (50 wt % H₂SO₄; 50 °C, atmospheric pressure). In a carried-out endurance test for 80 h at 0.1 A/cm², the stabilized voltage was ca. 675 mV, obtaining a hydrogen purity of 98.7%.

Scott and Taama used a Pt/Ti electrode for the electrolysis of SO₂ for testing its current efficiency [26]. At a current density of 10 mA/cm² and 20 °C, the current efficiency was initially greater than 95% and it decreased with time as the concentration of sulphite fell, indicating that the oxidation of sulphite is almost entirely controlled by mass transfer. Recent works have generally involved high active surface area electrodes, where the catalyst is loaded on dispersed conductive carbon particles. Thus, Weidener et al. [27] prepared a membrane electrode assembly (MEA), spraying an ink containing 40 wt % Pt onto the gas diffusion layer until desired loading was achieved. They obtained a voltage of 0.7 V at 0.3 A/cm² for a catalyst loading of 1 mgPt/cm² and 0.83 V at 0.3 A/cm², using the half Pt loading. Steimke and Steeper compared the performance of two different cells [28]. One of them had porous titanium as the electrode in both the anode and cathode, with platinum black as catalyst on the titanium surface, a loading of 4 mgPt/cm², and a specific area for the catalyst of 25 m²/g. In the second cell, platinum was added to the Nafion membrane. The authors prepared a slurry consisting of 40 wt % platinum on carbon and Nafion solution, which was hot pressed onto the Nafion membrane used in the MEA configuration, the platinum loading for the anode and the cathode was 0.5 mgPt/cm². For the second cell, the authors obtained the lowest cell voltages for the highest tested sulfur dioxide concentration and the highest anolyte flowrate. Later, the same authors [29] tested six different MEA configurations for the electrolysis of SO₂. The best results were obtained for a Pt loading of 0.88 mgPt/cm² onto the anode side with 0.75 mV at 0.3 mA/cm² at 4 bar and 70 °C. For this study, the catalyst containing ink was sprayed on the shiny Teflon-coated side of each gas diffusion layer, until the required Pt loading was achieved. Colón-Mercado and Hobbs compared the catalyst activity of platinum supported on carbon and a pure platinum black electrode [30]. When the Pt was to be supported on carbon, an ink was prepared and placed onto the gas diffusion layer. They also studied the electrocatalytic activity of platinum at different temperatures and acid concentrations. For example, potentials for Pt/C were measured at 0.51 V, 0.56 V and 0.63 V versus SHE in 3.5 M, 6.5 M and 10.4 M H₂SO₄ solutions, respectively, and it exhibited instability in very high H₂SO₄ concentrations (10.4 M) at temperatures of 50 °C and above.

Allen et al. [31] observed that the response of a platinum disk electrode was different depending on the lowest minimum potentials applied in a cyclic voltammetry. Three main oxidative peaks were obtained. The first peak appeared before the formation of platinum oxide which occurs at potentials above 0.90 V (SHE), meaning that peaks II and III were influenced by the formation of these compounds. When the initial voltage was lower than 0.2 V the oxidation scenario was defined to some extent by acid concentration. Furthermore, by increasing acid concentration, the reaction was inhibited.

2.1. Effect of Platinum Loading

At the beginning, the Pt loading in the tests performed by Westinghouse in the 1980s was as high as 10 g Pt/cm². However, new electrode configurations allowed them to reduce the catalyst loading to 1 mgPt/cm², with no penalty on cell performance [17].

Nowadays, as in the case of the PEMFC technology, the aim is to use the minimum Pt loading possible, in order to minimize the costs of the system. As a consequence, the effect of Pt loading has been studied by different research groups. Thus, the effect of Pt loading as a catalyst was studied by Lee et al. [32]. They used a three-electrode electrochemical cell with H₂SO₄ as the electrolyte. Five different Pt loadings were tested (0.40, 0.80, 1.30, 2.34 and 4.02 mg/cm²) by cyclic voltammetry (CV) in a deaerated 4.8 wt % H₂SO₄ solution. The current level of the CVs increased with an increase in the Pt loading amount over the whole potential range. Figure 4 shows the evolution of the current density for a value of voltage depending on the Pt loading.

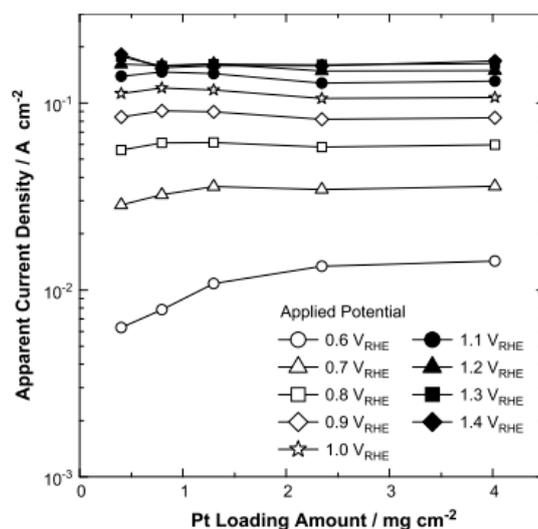


Figure 4. Apparent current density in the potential range of 0.6–1.4 V against platinum (Pt) loading [32]. Reprinted by permission of [24]. Copyright Elsevier Science BV. 2009.

The catalyst electrochemical active surface area (ESA) was calculated with these data, and it was concluded that the ESA did not increase at the same level as the Pt loading increased. This means that utilization of Pt decreased with loading, due to higher inactive sites (interfaces between particles, support and binding material). A study of the effect of Pt loading on SO₂ oxidation was carried out in an SO₂-saturated 50 wt % H₂SO₄ solution. The limiting current density increased as the Pt loading increased. For a cell potential of 0.6 V, the apparent current density increased from 6.3×10^{-3} to 1.4×10^{-2} A/cm² with an increasing Pt loading amount from 0.4 to 4.0 mg/cm². However, the current density remained almost constant at a high potential for the five studied catalyst loadings, indicating that the SO₂ oxidation reaction is controlled by the diffusion of dissolved SO₂ to the electrode in the high anodic over-potential range. Xue et al. [33] also carried out experiments with different Pt loadings in the range of 0.2–2.2 mg/cm². The higher loading amount led to better electrolysis performances, as a result of more electrochemical reaction sites, peaking at 1 mg/cm². Increasing the amount of platinum above that value led to worse performance, due to stacking of catalyst particles on one another. In addition, an excess of platinum increased the diffusion channel length and impeded the accessibility of the electro-active ion to the Pt surface [32,33]. For the authors' set-up, the optimal Pt loading was 1 mg/cm² in terms of platinum utilization, and polarization curves result. These authors also studied the influence of sulphuric acid concentration and temperature on the cell operating voltage, being the best electrolysis performance at 80 and 30 wt % sulphuric acid. Krüger et al. [34] evaluated some MEA manufacturing parameters, one of them being the catalyst loading. Their results are in concordance with studies carried out by previous authors [32,33]. Polarization curves obtained at 80 °C for catalyst loadings of 0.3, 0.5 and 1 mgPt/cm² showed that the best performance was for the catalyst loading of 1 mgPt/cm². However, it should be noted that for the catalyst loadings of 0.3 and 0.5 mgPt/cm², the platinum was supported on carbon, and for the highest catalyst loading platinum black was used.

Staser et al. [35] evaluated the effect of catalyst loading on the anodic overpotential using a model and in the range of 0.001 to 1.5 mg Pt/cm². It was found that the anodic overpotential was mainly dependent on the slow oxidation kinetics, with ohmic losses and concentration losses comprising only a negligible fraction of the total losses. Moreover, at catalysts loadings below 0.1 mg/cm² the anodic overpotentials increased exponentially, and the optimum loading was found to be 0.2 mg/cm². However, no experimental tests have been found to support these results.

2.2. Combination of Platinum with Other Metals

As platinum has a high cost, the catalytic activity of some catalysts based on platinum but mixed with other metals have been investigated. The goal of this approach is to obtain catalysts as good as platinum, or even better materials for the electrochemical reduction of SO_2 with a lower cost, which would make it easier to scale the process.

Xue et al. [18] studied the electrochemical catalytic activity of different bi-metallic materials based on platinum. Vulcan XC-72R was the support for all catalysts. The metals that were employed were palladium, rhodium, ruthenium, iridium, and chromium. The total metal content was 60 wt %, with an atomic ratio of Pt–M 1:1. The catalyst loading was 1 mg metal/cm². Figure 5 shows the performance of each catalyst, and for comparison purposes, platinum supported on a Vulcan XC-72R is also shown. The catalysts were evaluated at room temperature and in 30 wt % sulphuric acid concentration. The results showed that the best catalyst was 60 wt % Pt–Cr/XC72R, which was better than the catalyst containing only platinum.

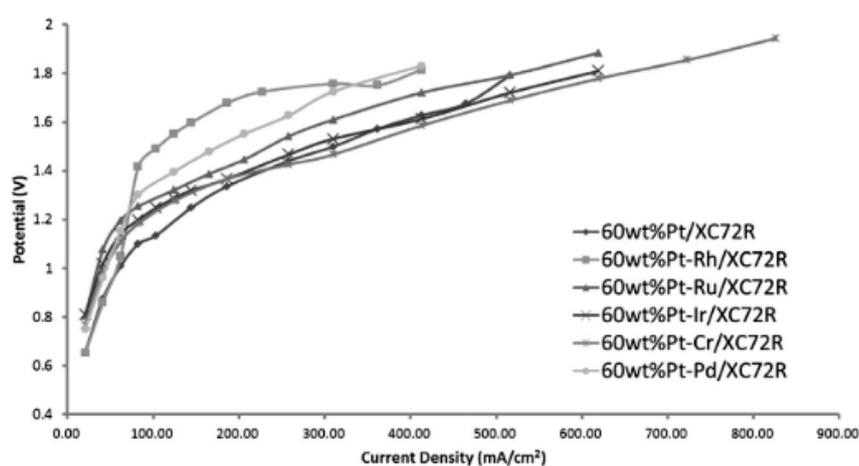


Figure 5. Polarization curves of Pt/C and Pt-based bimetallic catalysts for SO_2 depolarized electrolysis [18]. Reprinted by permission of [24]. Copyright Elsevier Science BV. 2014.

In this work [11], the influence of the atomic ratio was also studied. The ratio 1:2 (Pt:Cr) resulted in equal or even better electrolysis performance than that of 60 wt % Pt/C. Also, the catalyst Pt–Ir/C showed promising results.

Falch et al. [36] studied the possibility of using plasma sputtering to form an electrocatalytic film of platinum and palladium. Both metals were sputtered at the same time to obtain bimetallic materials. Catalysts with different molar ratios of Pt and Pd were prepared. The compositions ranged from a Pt composition of 0 (pure palladium) to 1 (pure platinum). This technique allowed homogeneous distribution of both metals in the surface. The onset potential of the prepared catalysts was measured, as it is an indicator of catalytic activity [37–39]. The combinations with the lowest onset potential were Pt_3Pd_2 (0.587 V), Pt_2Pd_3 (0.590 V) and PtPd_4 (0.587 V), which exhibited an onset potential slightly lower than that of pure platinum (0.598 V). The combination with the most promising results was Pt_3Pd_2 , which was further investigated by the same authors [40]. The effect of thermal annealing on that sputtered catalyst and on pure platinum was investigated. Catalyst films were deposited as mentioned previously. The samples were annealed at temperatures ranging from 600 °C to 900 °C. The surface of the materials after deposition were smooth with no cracks; however, when increasing the temperature up to 900 °C, a discontinuous grain surface was formed. They measured the electrochemical surface area for pure platinum and the mixture Pt_3Pd_2 when it was rapidly annealed, and for a non-annealed sample. The annealing process clearly decreases the electrochemical active area, but for the Pt being smaller than for Pt_3Pd_2 , this difference increased with an increase in the annealing temperature. Regarding onset potential, results showed that annealing does not have a positive influence on the

catalyst, because it is higher than when they are not annealed for both platinum and Pt₃Pd₂. However, this technique does increase the lifetime of the catalysts in an acidic environment for Pt and Pt₃Pd₂ and normalised current density. The next step in their research was to add a non-noble metal, aiming better catalyst activity and a lower price. Falch et al. [41] developed a film composed of platinum, palladium and aluminium, which are co-sputtered on a support. They made improvements on the onset potential and in current density, obtaining 396.73 mA/mgPt with the ternary combination Pt₄₀Pd₅₇Al₃. Results changing Pt content show how the normalised current density increases with decreasing platinum content, from 100 mA/mgPt for pure platinum to 400 mA/mgPt for Pt₄₀Pd₅₇Al₃. They concluded that the addition of other metal enhanced the electrocatalytic performance. Also, when annealed the ternary catalyst Pt₄₀Pd₅₇Al₃ increases the amount of aluminium on the surface. Xu et al. [42] synthesized a Pt/CeO₂/C catalyst for enhancing the SO₂ electro-oxidation. ESA measurements showed that adding CeO₂ increased the active area of the catalysts, i.e., Pt/10CeO₂/C (810.60 cm²/mg Pt) and Pt/20CeO₂/C (765.10 cm²/mg Pt), which almost doubled Pt/C (429.10 cm²/mg Pt). The ESA of Pt/30CeO₂/C was 512.90 cm²/mg Pt and that of Pt/40CeO₂/C was 428.40 cm²/mg Pt. Catalysts with a content of CeO₂ below 50% gave current densities lower than for Pt/C, with the best ratio being Pt/20CeO₂/C. The enhanced SO₂ electrooxidation of Pt/CeO₂/C composite catalysts was attributed to the oxygen provided by CeO₂, but no tests in an electrolysis cell were performed to support their findings of the half cell.

As summary, Figure 6 shows the values of voltage reached at different current densities obtained by different authors from 1980 until 2016, where it can be seen that there has been an improvement. However, in all cases the voltages are higher than the target proposed of 0.5 V at 0.5 A/cm².

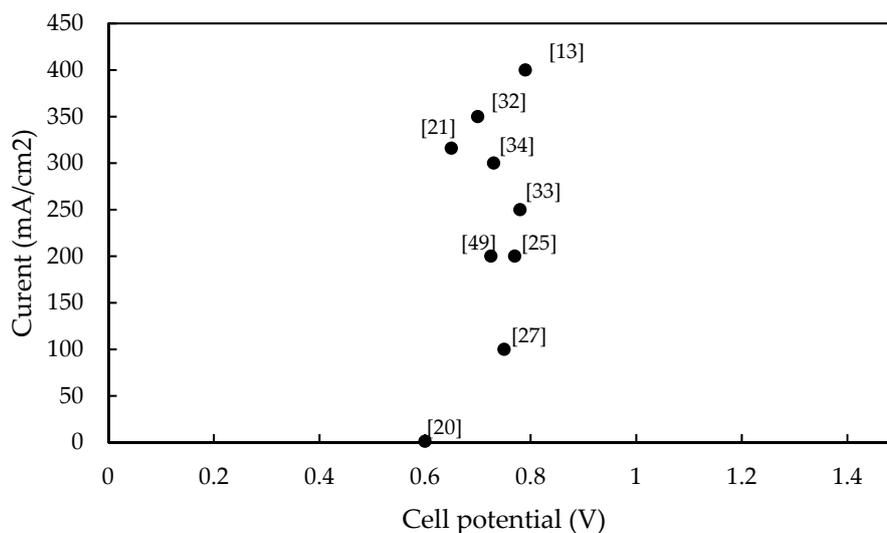


Figure 6. Evolution of cell performance for SO₂ electro-oxidation with platinum-based catalysts. Data taken from bibliography.

3. Gold-Based Catalysts

In the early development of the electrolyzer for the hybrid sulphur cycle, gold was studied together with platinum as a catalyst for SO₂ depolarized electrolysis.

Seo et al. [23] studied the electrochemical oxidation of sulphur dioxide on platinum and gold electrodes. The results on gold electrodes showed that reproducible data is obtained by scanning three or four times between −0.15 and 1.5 V (SCE). Compared with a platinum electrode, gold was easier to activate, due to the ease with which gold surface oxide films dissolve in acid solutions. However, extensive cathodization inhibited the electrode activity. They also distinguished two modes for the electrochemical oxidation of SO₂ on gold, a pure electrochemical process and a chemical oxidation process. Appleby et al. [21] determined that gold is less promising than platinum, because

the oxidation of SO₂ involves participation of chemisorbed H, OH or O species. Rates for these processes are strongly influenced by the chemisorption properties of the substrate, and are several orders of magnitude higher on platinum than on gold. On the contrary, Samec and Weber [43] studied the oxidation of SO₂ dissolved in 0.5 M H₂SO₄ on a rotating disc gold electrode. These authors reported a considerable enhancement of the SO₂ oxidation reaction after a preliminary voltammetry cycle to potentials encompassing SO₂ reduction. They proposed that oxidation of SO₂ on gold electrodes proceeds through an adsorbed intermediate, which is displaced from the electrode at voltages higher than 1.5 V when the oxide is formed; the oxidation current decreases to a fraction of the limiting current density at that potential. The authors also mention that SO₂ oxidation is a mass transfer-controlled process to the electrode. Similar results to Seo et al. [23] were obtained by Lu and Ammon, which showed similar catalytic activity for gold and platinum with similar limiting current densities (1.2×10^{-3} mA/cm² for Pt and 2×10^{-3} mA/cm² for Au) [20]. Quijada et al. studied the electrochemical behaviour of SO₂ with polycrystalline gold electrodes. They observed the reduction [44] and the oxidation [45] of SO₂ on gold electrodes. Regarding the oxidation of SO₂ on gold electrodes, it starts at a potential of 0.6 V, with a peak located between 0.75 and 0.85 V. This peak was higher when the concentration of SO₂ dissolved in H₂SO₄ increased, making evident that this process is mass transfer-controlled, as mentioned before, and similar as on platinum electrodes. These authors also used sulphur-modified gold electrodes from the study of Samec and Weber [43]. SO₂ was reduced on the gold electrode, and then the effect of sulphur coverage on the kinetics of the SO₂ oxidation was examined. In those conditions, the oxidation of the SO₂ peak shifts to lower potentials, for a sulphur coverage of 0.5—from that point the oxidation peak shifts back. They concluded that gold exhibits a far better performance towards SO₂ oxidation when compared to platinum. O'Brien et al. [46] compared sulphur catalysis on gold and platinum. They observed that less sulphur is formed on gold electrodes, and it does not affect the catalytic activity as much as on platinum. Allen et al. [31] observed that a gold substrate is naturally catalytically active and does not require sulphur coverage for high activity; in addition, the oxidation mechanism on gold does not change with E_{low} , whereas on platinum it does. Kriek et al. [19] modelled the electro-oxidation of SO₂ on transition metals. By calculating the maximum oxidation rate, they observed that platinum and gold are the best candidates among metals for SO₂ oxidation. They concluded that there are a limited number of metals that can be employed, due to different criteria such as inhibiting SO₂ reduction, no surface dissolution, and the metal must not be poisoned by atomic sulphur. Santasalo-Aarnio et al. [47] coated stainless steel bipolar plates with a gold layer, in order to catalyse the SO₂ oxidation and to improve the stainless steel corrosion tolerance at operation conditions. Au-coated stainless-steel bipolar plates were tested in a 100 cm² electrolyser for five days, and results showed that no significant loss of performance occurred. SO₂ oxidation occurs at potentials higher than 0.6 V for this electrode. Polarization curves at day one were very similar to the one at day four, indicating that the Au-coated bipolar plates have good durability and that the coating was not damaged. Nevertheless, the achieved current was very low for both days, and almost 0.5 A at 0.9 V was achieved in a 100 cm² single cell, which means that the current density was only around 5 mA/cm².

4. Palladium-Based Catalysts

Palladium, as noble metal, has been studied both pure and supported as a catalyst for SO₂ oxidation. The first studies on palladium were carried out by Lu and Ammon; in this work, the results showed a better catalytic activity for palladium than for platinum, due to a higher limiting current density for the palladium electrode [20]. They also studied the oxidation of SO₂ on palladium electrodes at different temperatures (25, 50, 70 and 90 °C), obtaining the best current density for a potential of 0.6 V (SHE) at 90 °C (1.9×10^{-3} A/cm²). They prepared a catalyst based on palladium oxide supported on carbon, which again, gave higher current densities than a catalyst based on black platinum supported on carbon. What is more, the authors prepared a catalyst consisting of palladium oxide–titanium oxide supported on titanium, which exhibited an electrocatalytic activity quite comparable to the black-Pt/Ti.

Scott and Taama studied the oxidation of SO_2 on palladium electrodes, palladium coated graphite, and palladium-coated Ebonex (a Magneli-phase suboxide of titanium, predominantly Ti_4O_7) [26]. In this work, the palladium electrode gave a higher limiting current density than platinum. Regarding palladium-coated graphite a palladium coated Ebonex, linear sweep voltammetry shows complex curves exhibiting higher current densities than Pd, probably due to its greater exposed surface area. However, the Pd-coated electrodes showed deterioration. Colón-Mercado and Hobbs examined a Pd supported on carbon catalyst, which showed worse catalytic activity when compared with a catalyst based on platinum and supported on carbon. Furthermore, the Pd-based catalyst was less stable [30].

5. Catalysts Based on Other Compounds

Most of the works regarding SO_2 catalysis have been carried out with special interest on platinum, and to a lesser extent, on gold and palladium. However, aiming to develop a material with good catalytic properties and lower price, some other materials have been studied for SO_2 electro-oxidation.

Wiesener [24] carried out SO_2 electro-oxidations with catalysts based on mixtures of V_2O_5 and Al_2O_3 with different ratios. The main problem for this catalyst is its stability in acidic solutions. The optimal V/Al ratios were 1:3 and 1:6, because only a portion of vanadium was dissolved, with an amount ranging from 75 to 80% remaining in the catalyst. In general, this mixture showed worse catalytic activity than platinum. Appleby and Pinchon examined the catalytic activity of active carbons, graphites, carbon blacks, transition metal carbides, and precious metals supported on carbons [21]. Their results showed that graphites and carbides had no catalytic activity for SO_2 electro-oxidation. Active carbons had intermediate activity, but current densities were too low for use in any practical device. Lu and Ammon studied catalysts like $\text{RuO}_x\text{-TiO}_2$ and $\text{IrO}_x\text{-TiO}_2$, supported on titanium, ruthenium, rhenium, iridium and rhodium (Figure 7) [20]. Ru showed similar catalytic activity as platinum; however, Ir, Re and Rh electrodes were relatively inactive for SO_2 oxidation; also, $\text{RuO}_x\text{-TiO}_2/\text{Ti}$ and $\text{IrO}_x\text{-TiO}_x/\text{Ti}$ electrodes are very ineffective for the electrochemical oxidation of SO_2 in acidic media.

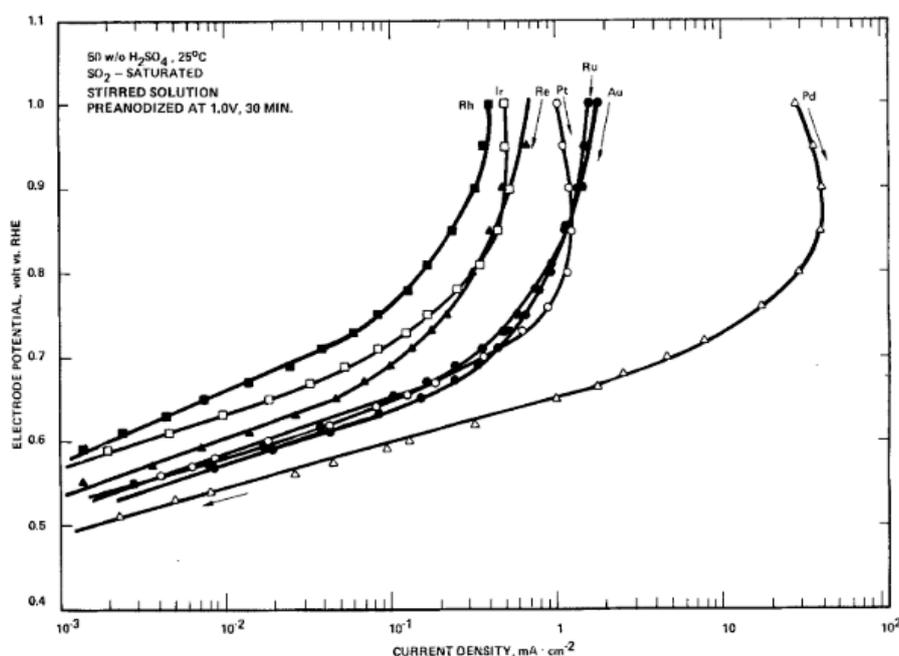


Figure 7. Tafel plots for SO_2 oxidation on smooth electrodes of Pt, Pd, Au, Ru, Re, Ir, and Rh in 50 wt % sulphuric acid at 25 °C [20]. Reproduced with permission of [12]. Copyright Electrochemical Society. 1980.

Scott and Taama also carried out voltammograms for glassy carbon, graphite electrodes, and lead oxides showing instability at high potentials [26]. Mu et al. [48] worked on the electrochemical oxidation of sulfur dioxide on nitrogen-doped graphite (NG) treated at temperatures ranging from 700 to 1000 °C. The catalytic activity of this material was compared with the activity of commercial 50% platinum supported on carbon and only Vulcan carbon XC-72. The results showed that NG treated at temperatures above 900 °C have better catalytic activity than the Vulcan carbon XC-72 without Pt, but worse than 50% Pt/C. The BET surface area was measured for the doped graphite and increased with the temperature of the thermal treatment—for example, the BET area for NG800 (thermal treatment at 800 °C) was 301 m²/g, and for NG1000 (thermal treatment at 1000 °C) it was 425.8 mg/cm². Potgieter et al. [49] evaluated polycrystalline rhodium as a catalyst for SO₂ electro-oxidation. When compared with platinum, Rh showed a lower catalytic activity and was more susceptible to poisoning by adsorbed intermediate sulphur species. Similar to Pt, for Rh a decrease in starting potential resulted in an increase on the onset potential, but the catalytic activity of Rh was very limited compared with Pt, which may indicate that Rh is not suitable for SO₂ electro-oxidation. Tulskiy et al. [50] studied graphite anodes coated with different catalysts, which were Pt, MoO₃, RuO₂ and WO₃. Polarization curves showed that the catalytic activity of those materials could be arranged following the sequence Pt > RuO₂ > MoO₃ > WO₃. Zhao et al. [51] developed an Fe–N-Doped carbon-cladding catalyst with excellent SO₂ electrooxidation performance, close to the performance of Pt/C. It showed better stability when tested in H₂SO₄. Linear sweep voltammetry shows a catalytic activity similar to 20% Pt/C below 0.7 V (NHE). Physical characterization of the Fe–N-Doped carbon cladding showed a high surface area, mesoporous structures, and large pore volumes, which contribute to the formation of active sites and fast transport of reactants, which are beneficial for SO₂ electro-oxidation.

6. New Tendencies

The typical proton exchange membrane used in the electrolysis cell is a Nafion membrane. However, Nafion-based membranes have several limitations, including the inability to operate at elevated temperatures and decreased performance observed when exposed to high acid concentrations [35,52]. Thus, nowadays there is a tendency to work with Polybenzimidazole-based membranes (PBI), which work at high current densities to produce high sulphuric acid concentrations, and hence improve the efficiency of the electrolysis step of the cycle, as their proton conductivity does not rely on water [52]. These type of PBI-based membranes have been proposed for operating at high temperature (100–200 °C) for PEMFC technologies since 1995 [53–56]. In the case of the SO₂ electrolysis, high temperatures will have a positive impact, as the voltage losses (e.g., kinetic and ohmic resistances) would decrease [52] and the acid concentration produced could be higher [57]. Nevertheless, although the use of PBI-based membranes (sulfonated one) dates from 2012 [52], tests at temperatures higher than 90 °C were not performed. Garrick et al. [58] has recently shown results with a sulfonated PBI membrane and commercial electrodes from BASF with 1.0 mgPt/cm² for both anode and cathode in a SO₂ electrolysis cell operating at 110 °C. They concluded that the membrane resistance was not adversely affected by acid concentration, which offers benefits not seen when using Nafion. On the other hand, the large anodic overpotentials that exists in this system suggest a need for improved catalysts, and kinetics would improve with the higher temperatures afforded PBI-based membranes [58]. In this sense, higher temperatures will mean new challenges for new materials for this system, not only in terms of membranes and catalysts, but other parts of the cell. Our group has recently been working on the improvement of the Westinghouse cycle, using PBI-based membranes and novel catalyst supports for the electrochemical stage of that cycle. In the case of the catalyst support, we have proposed SiC–TiC based materials, according the previous results obtained for high temperature PEMFCs [59–62]. Recent results obtained by our group and not published yet have demonstrated that these non-carbonaceous supports can be a good candidate for the SO₂ electrolysis at high temperatures and very highly acidic conditions. Table 1 shows the values of the current at 1.0 V of cyclic voltammetry in sulphuric acid 1 M, reached before and after some electrochemical

characterization tests of different catalysts. One of them is Pt supported on Vulcan carbon, and is commercial available; the other two catalysts were synthesized in our labs using the same method reported elsewhere [63], but with different support materials—in one case, the catalyst support was Vulcan XC 72, and the other was a binary carbide, SiC–TiC.

Table 1. Current values at 1.0 V of cyclic voltammetry, carried out before and after electrochemical tests of Pt-based catalysts supported on different materials.

	Intensity (A)	
	Before	After
Pt/C Commercial	0.31	0.29
Pt/C handmade	0.30	0.27
Pt/SiC–TiC	0.22	0.32

It can be observed that the highest currents were achieved by the catalysts based on carbon supports. After some electrochemical characterization tests (out of the scope of this manuscript) that could be considered as an accelerate degradation test, the activity of the catalysts based on carbon supports, as well as the commercial and the handmade catalysts decreased around 6.4% and 10%, respectively. On the other hand, the activity of the catalysts based on the binary carbide support increased, which means that these novel supports show a high electrochemical stability for the electrochemical oxidation of SO₂ and are very promising for this electrochemical system.

7. Conclusions

This review points out that Pt-based catalysts are the most promising materials to be implemented in the electrolyzers of the Westinghouse process. Nevertheless, their performance is still lower than the target required for full scale applications (at least 0.5 A/cm² at a cell voltage of 0.6 V is recommended), as can be observed in Table 2, where the most relevant catalysts reported in this work are shown. Further work has to be done in the coming years in order to reach a marketable technology.

Table 2. Most relevant results for different catalysts employed on SO₂ electrolysis.

Ref.	Year	Catalyst	Electrode	Current (A/cm ²) (@ V vs. RHE)	Pressure (bar)	Temperature (°C)	[H ₂ SO ₄] (wt %)	Test Array
[24]	1973	V/Al ₂ O ₃ (1:3)	6.9 mgV/Al/cm ²	0.048 (0.69)	1	100	3.8 (M)	half cell
[21]	1980	Platinum	3 mgPt/cm ²	0.316 (0.65)	1	50	55	half cell
[25]	1982	Pt/C	7 mgPt/cm ²	0.200 (0.77)	1	50	50	single cell
[26]	1999	Pd	Palladium electrode	0.033 (0.76)	1	25	0.5 (M)	half cell
[26]	1999	Graphite	Graphite electrode	0.021 (0.76)	1	70	0.5 (M)	half cell
[28]	2005	Pt/C	0.88 mgPt/cm ²	0.300 (0.73)	4	70	30	single cell
[13]	2007	Pt/C	1 mgPt/cm ²	0.400 (0.79)	1	80	(SO ₂ gas)	single cell
[45]	2012	Au	Au electrode	0.080 (0.70)	1	22	1 (M)	half cell
[33]	2013	Pt/C	1 mgPt/cm ²	0.100 (0.75)	1	80	30	single cell
[18]	2014	Pt–Cr(1:2)/C	1 mgPt–Cr/cm ²	0.020 (0.80)	1	25	30	half cell
[48]	2015	NG	2 mg	0.15 A (0.9)	1	25	0.5 (M)	rotating disk
[47]	2016	Au	Au coating on 904L	0.005 (0.90)	1	25	15	single cell
[47]	2016	Au	Au coating on 904L	0.045 (0.75)	1	25	15	half cell
[49]	2016	Pt	Platinum electrode	0.200 (0.73)	1	25	0.5 (M)	rotating disk
[50]	2016	RuO ₂	3 mgRuO ₂ /cm ²	0.1 (0.74)	1	25	0.5 (M)	single cell
[50]	2016	WO ₃	3.8 mgWO ₃ /cm ²	0.1 (0.84)	1	25	0.5 (M)	single cell

As it is a general trend in the development of low-temperature fuel cells and electrolyzers, researchers try to decrease the Pt loading, in order to lower the price and make this technology more competitive. Nowadays, the typical Pt loading in the electrolyzers of the Westinghouse process is around 1 mg Pt/cm². However, this value may be easily decreased if novel deposition techniques and novel supports are translated from already existing PEMFC technology. Another way that is currently being used to the face decrease in the use of Pt is replacing it with other metals. Pt–Cr and Au catalysts are the most promising substitutes of Pt catalysts, although results obtained with them are currently

far away from the desired targets. A final way to improve the SO₂ depolarized electrolysis for the production of hydrogen is the rise in the operation temperature, which will favor the kinetics of the process, and hence, decrease the requirements of Pt in the electrode. However, this increase must face important challenges, such as the lower cell durability because of the higher thermal stress, which affects not only the catalyst but also other cell components, such as the membranes.

Anyhow, it is important to keep in mind that most of the results found in the literature come from studies carried out in half cells or in three-electrode assemblies using rotating electrodes. More essays in complete electrolyzers are required to support the results obtained with those catalysts, as well as clarifying the more relevant aspects of the scale-up of the process. Hence, there is still a very wide slot in this technology for development, which hopefully will be filled in the next years.

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