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WATER ELECTROLYSIS IN ACID MEDIUM

In acid water electrolysis where solid polymer electrolyte is the electrolyte of choice significantly higher operational current densities are possible. This manuscript discuses progress on material development for acid water electrolysers. The stability considerations of materials in acid electrolysers are discussed. The types of anode, cathode, and membrane materials which may be used in acid electrolysers are indicated. In particular, a new family of anode materials based on noble metal oxide mixtures are shown. The membranes which may have adequate chemical and physical properties for acid water electrolysers are discussed. The properties of the least costly and most recent advanced membranes are discussed. The limitations of the material properties on the electrolyser performance are shown.

Water is a very poor ionic conductor. At a temperature of 25°C and a pressure of 1 bar, the minimum value of its decomposition voltage is 1.23 V. The voltage applied to the water electrolytic cell may exceed this minimum, and therefore a conductive electrolyte must be added to the water and good electrocatalysts must be used as electrodes so that the reaction can proceed at a technically lower cell voltage. Either alkaline or acidic electrolyte can be used for water electrolysis. For industrial electrolysers, the change in the applied potential has an effect in the cost of the hydrogen production [1]. The electrochemical reactions taking place in the case of water electrolysis can be described in an alkaline or in an acidic electrolyte.

In acidic electrolyte, the two basic reactions at the electrodes are:

on the cathode:

$$4H_3O^+ + 4e^- \rightarrow 4H_2O + 2H_2$$
 (1)

on the anode:

$$6H_2O \rightarrow 4H_3O^+ + O_2 + 4e^-$$
 (2)

net reaction:

$$2H_2O + electricity \rightarrow 2H_2 + O_2 + heat$$
 (3)

The reaction scheme is the following:

Volmer reaction:

$$M + H3O+ + e- \rightarrow MHads + H2O$$
 (4)

followed by:

Heyrowsky reaction:

$$MH_{ads} + H_3O^+ + e^- \rightarrow H_2 + H_2O + M$$
 (5)

and/or

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Tafel reaction:
$$MH_{ads} + MH_{ads} \rightarrow 2M + H_2 \tag{6}$$

where M is the electrode material.

In each case, the highest transport number in the system (the majority current consumer) is found at one electrode, while current is produced at the other. In an acidic water electrolyser, water is produced at the cathode whereas in an alkaline electrolyser it is produced at the anode. The Volmer-Tafel mechanism depends on chemical hydrogen desorption (reactions (6)) and the Volmer-Heyrovsky mechanism depends on electrochemical hydrogen desorption (reactions (5)).

The overpotential (η) of the electrolytic process can be related to the reaction current density (i) and the exchange current density (io) by the Tafel equation (Fig. 1).

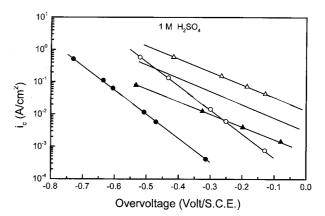


Figure 1.Quasi-steady-state polarization curves for the HER obtained under potentiodynamic conditions at low sweep rate at 2 mV s⁻¹ at 25°C. Φ , Ni in 1 M H₂SO₄; M, Pt in 1 M H₂SO₄; Δ , NiPW₁₂ in 1 M H₂SO₄; -, NiPW₁₂ in 2 M HCl; , NiW₁₂ in 2 M HClO₃. Nickel electrodeposited with phosphotungstic acid was named NiPW₁₂. (From Ref. 1)

$$\eta = V_{app} - V_{eq} = b \ln (i/i_o)$$
 (7)

where $b = RT/\beta nF$ is the Tafel slope which is an intensive parameter, whereas the exchange current density is an

extensive parameter because the former does not depend on the surface area and the latter is influenced by the surface area. Thus, a change in b for the given electrode due to some specific treatment (activation or electroactivation) is usually attributed to electronic factors. However, if the treatment results in a parallel shift of the Tafel slope, it might imply a true change in io. Recent results we have obtained on the HER on different metal and metal alloys electroactivated with several heteropolyacids have shown a true change in io without non-change in the real surface area [1]. The improvement in the electrocatalytic activity through io was attributed to a synergetic effect due probably to the increase of the catalytic active sites on the electrode surface.

The applied potential (V_{app}) to an electrolysis cell and necessary to produce a given current, e.g. a given rate of production of hydrogen (in our case), depends upon the overpotential (η) present. The applied potential is given by:

$$V_{app} = V_{eq} + \eta_a + |\eta_c| + |R$$
 (8)

where V_{eq} is the thermodynamic cell voltage or the minimum value of the decomposition voltage. The applied potential depends on the anodic (η_a) and cathodic (η_c) overpotential; the ohmic drop in the electrode/electrolyte interface and connecting circuits and on the minimum potential. Thus, the voltage applied to the water electrolytic cell may exceed the minimum potential (Veg). The overpotentials represent the cost of electrical energy we pay to drive the process at an industrial rate including the mass transfer resistances. The ohmic drop includes the electrolyte, the membrane, the interelectrode gap, the electrode structure and the connecting circuits. The electrical energy needed to generate hydrogen is directly proportional to Vapp. Thus, as been seen in equation (7). The cost (CE) per mole of producing hydrogen is proportional to the overpotential (η) and at given rate of production, to log i_0 in equation (9).

$$C_E = aq \eta = aqb \ln (i/i_0)$$
 (9)

where a is the cost of a unit of electrical energy (\$ per kilowatt hour) and q is the electrical charge needed.

A typical conventional industrial electrolyser operates with about 2 volts (some are more efficient) per cell voltage and current density of 10³ Am⁻². In industrial plants, one of the best ways to contribute in reducing the applied potential, e.g. the electrolytic costs, is to look for new cathodes and anodes which have high active site density and/or surface effective area. The increase in the active site density will contribute to the improvement in the electrocatalytic effect and is related to the electronic factors of the material surface. The surface area is the geometric factor of the material. The effect of these two parameters on the Tafel slope and the exchange current density must be well studied for

composite materials and electroactivated electrodes. The surface roughness may be a limiting parameter for the electrocatalytic properties if the roughness may increase the active sites density. In other words, a material with high surface roughness and low active site density may be a poor electrocatalyst, but an electrode with low surface roughness and high active site will be a good electrocatalyst. The relative contribution of the surface roughness and the active sites of composite materials in the improvement of their electrocatalytic properties for the HER must be studied. The parameters which are relevant in industrial electrolysers are the electrode activities and stabilities which can be affected by the electrode surface modification of known materials on by the fabrication of new materials.

Acid electrolysers operate in a more aggressive corrosive environment at the cathode than aqueous alkaline electrolysers, as Pourbaix's Atlas [2] shows. More noble materials are required for acidic electrolysers than for alkaline electrolysers. New materials investigation is a key factor for acidic electrolyser development. The following paper will discuss progress on acidic water electrolysers and openings for the future.

MATERIALS IN WATER ELECTROLYSIS IN ACID MEDIUM

Stability considerations

Acidic water electrolysers operate in industrial applications at the upper low-temperature range (70-150°C) under different oxidising and reducing conditions at the cathode, the anode and the diaphragm, respectively. This necessitates different electrodes and the construction of an acid resistant environment. Metal oxide stability depends on the pH and on the metal. For example, a metallic cation soluble in acidic solutions will give stable oxide at the cathode in an alkaline electrolyte. These considerations are purely thermodynamic. The kinetic stabilities are sometimes very different, and thermodynamic stabilities under the working conditions are required. On the anode side, analogous considerations apply. In a practical electrolyser process, the anode is at a range of potentials where only noble metals are supposed to be resistant to degradation. Anode stability depends, of course, on the nature of the metal, the electrolyte composition and polarisation conditions (the current density of the electrolyser process). During the process of anodic polarisation of metals, oxides and hydroxides dissolving in the electrolyte solution can be formed, which results in metal stability loss. For example, when anodic polarisation in an acid solution is even small (less than 100 mV), non-noble metals will be dissolved in hot acid solution. The dissolution products may change the surface structure and chemical composition, leading to a decrease in the service life of the

electrocatalysts. The service life of an electrocatalyst may be increased by different means [3]: a) changing the process of electrocatalyst manufacture, b) changing the composition of a multicomponent electrocatalyst; or c) selecting more stable carriers or creating a layer between a carrier and an electrocatalyst or between the electrolyte and the electrocatalyst. The membrane or diaphragms to be used in water electrolysers must have high corrosion resistance in strongly acidic media; they must be resistant to the atomic oxygen or hydrogen produced and they must be very safe. If the corrosion rate increases with temperature, it will not be possible to increase the electrolyser efficiency by increasing the temperature. However, the mechanical resistance, of course, decreases when the corrosion rate increases. The service life and efficiency of the electrolysers may be increased if the chemical and thermal stability of the electrodes and membranes are excellent. The stability of the membranes may be improved if they exhibit the following properties: a) low wettability; b) high porosity; and c) low electrical resistance in the electrolyte medium. As an example, water electrolysis in molten hydroxides is still limited because no sufficient long-term stable diaphragms have been developed.

Electrode and membrane development for acidic water electrolysers

Electrodes

The development of active cathodes based on conducting oxide materials for the hydrogen evolution reaction has gained considerable interest over the last 30 years. Since the first work was done by Trasatti [4] on hydrogen evolution on oxides, some of them have been proposed for technological applications [5-7]. R uQ and IrO2 were indicated to be the best electrocatalysts in acidic solutions [8-11]. But their behaviour is affected by hysteresis phenomena [12]. It was found that the activity of RuO2 was the worst for oxygen evolution in alkaline solutions, while its electrochemical behaviour for hydrogen evolution is the same for both acidic and basic solutions. In contrast, it was found that the electrochemical behaviour of IrO₂ for hydrogen evolution is significantly influenced by pH [13]. Trasatti et al [14] have shown that the Tafel slope of as prepared electrodes for hydrogen production in acid is close to 40 mV and independent of oxide composition. The Tafel slope changes on electrodes aged by H2 evolution: it varies from about 60 mV for pure RuO2 to about 20 mV for pure IrO2. Thus, these electrodes are more useful for hydrogen production in an acid medium.

It has been shown that ruthenium dioxide (RuO_2) and iridium dioxide (IrO_2) are the most promising candidates for hydrogen cathodes. The electrocatalytic activity for the hydrogen evolution reaction on RuO_2 [15–19], IrO_2 [16, 19–21] and mixed of RuO_2 and IrO_2

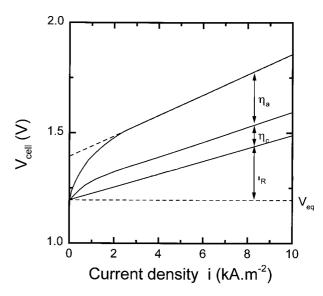


Figure 2.Contribution of the different terms of the cell voltage of a water electrolysis cell. (From Ref. 1)

[19, 22, 23] has been studied in acidic solutions [15, 16, 19, 20–23]. The kinetics of the hydrogen evolution reaction on RuO_2 [24, 25] and IrO_2 [24] were studied by ac impedance spectroscopy, X-ray photoelectron spectroscopy, and Auger analysis [26, 27]. Degradation products were deduced. This phenomenon was associated with an improvement of the electrocatalytic properties of the electrode for the hydrogen evolution reaction. It was shown that ruthenium oxide, iridium oxide and the Ru_x -Ir $_x$ O $_2$ layer can be activated through cathodic polarization, leading to an increase of the electrocatalytic activity for the hydrogen evolution reaction by a factor up to 100 [28]. This was attributed to a significant increase in the amount of hydroxyl groups and water molecules detected by XPS.

Anodic iridium oxide [29] and thermally oxidised iridium oxide films [30] were shown to be remarkably stable in acidic solution under the hydrogen evolution reaction. After thermal treatment of the thermally oxidised iridium oxide films, the electrodes exhibited a roughness factor of several hundreds. Anodic iridium oxide films were found to be stable under hydrogen evolution and a better activation for the hydrogen evolution reaction was achieved with this electrode than with thermal iridium oxide films [31].

The electrochemical properties of conductive transition metal oxides for electrocatalysis have been described [32]. The stability of oxide cathodes is enhanced first by increasing their metallic conductivity. Because their eventual ohmic drop across thin films is negligible, they can be used as electrodes in practical systems [33]. When mixed oxides formed intimate mixtures at an atomic level, hydrogen evolution on these electrodes may be enhanced by synergetic effects. It has been shown that the mixed oxides of $\text{Co}_3\text{O}_4 + \text{RuO}_2$ show an activity for H_2 evolution increasing

exponentially with the RuO₂ content [34]. This was related to the surface enrichment by active RuO₂. The Tafel slope changes from 120 mV on pure Co_3O_4 to 30 mV for intermediate compositions and to 40 mV for pure RuO₂. It has also been shown that electrocatalysts based on ball milled nanocrystalline Ti–Ru–Fe–O catalyst powder exhibited a high activity for the HER in chlorate electrolyte [35]. The multilayer structure of the electrode may be responsible for the high catalytic activity for the HER. Long term stability analysis is necessary for technological applications.

Some mixed metal-metal oxide electrocatalysts have also been investigated as new hydrogen cathodes for water electrolysis in an acid medium [36-43]. It was shown that nickel electrodeposited with various heteropolycompounds had better electrocatalytic parameters for the HER than nickel electrodeposited without heteropolyacids [36-40]. Good stability of the electrodes was observed during 1000 h life-tests in the laboratory on electrodes of 2 cm². It was shown that for the Volmer step of the H.E.R. analogous results were obtained on Pd modified at the surface by heteropolyacids [42]. Because of these interesting results, they studied the electrocatalytic activity for the hydrogen evolution reaction (H.E.R.) in an acid medium on palladium or platinum dispersed in carbon electrodes electroactivated with and without $SiW_{12}O_{40}^{4-}$ (STA) or $PW_{12} O_{40}^{3-} [44-49]$ The best H.E.R. performances and long-term stability were observed on electrodes electroactivated with STA [43]. The aim of these studies was to develop alternative non-noble materials for the HER in solid polymer electrolyte electrolysers. Thus, electrodes of very low noble metal loading with hetero and/or isopolycompounds onto carbon have been fabricated for water electrolysers and fuel cell electrodes [45, 49]. These various experimental results were explained by the concept on synergetic materials [50].

Industrial anodes have been customarily based on a RuO2 + TiO2 mixture, where RuO2 is the active component and TiO2 the stabilising agent. The substitution of IrO2 for RuO2 in "dimensionally stable anodes" (DSA) has been found suitable for gas-evolving anodic reactions in acid media. Another component, such as CeO2 is often added in order to enhance selectivity for the desired reaction or to increase anodic stability. Trasatti et al. [51] have shown that Tafel slopes of the OER on $Ir_{0.3}Ti_{0.7-x}Ce_xO_2$ (O $\leq x \leq 0.7$) were independent of CeO2 content, with a value around 30 mV. The reaction order with respect to H+ was zero at constant overpotential and ionic strength. Some inhibition of the oxygen evolution reaction is observed as Ti is replaced by Cr. Martelli et al. [52] provided a for a deactrivation mechanism for oxygen-evolving DSA. It was claimed that this scheme is very helpful in obtaining modified electrocatalytic coatings and electrode structures, and can operate for a long time with good and stable performances. It has

been shown that iridium oxide is a good electrocatalyst for the oxygen evolution reaction [53–57]. The amount of hydroxyde groups may be responsible of the catalytic activity.

From the various electrocatalysts developed for acid water electrolysis, noble base electrodes and oxide base electrodes are the best electrodes for this technology. But, further development of new materials in this field is needed. As an example, it is known that the development of efficient and less expensive electrodes for the oxygen evolution reaction will make the electrolysis process economical. The field is still open to new developments and improvements because a lot of parameters must be optimized.

System and membrane issue

To decrease the cost of electrocatalytically produced hydrogen to a level comparable to other production levels such as coal gasification and gas reforming, new more efficient electrocatalysts are needed for technological applications in particular for advanced water electrolysers which must operate at current densities above 10 kA.cm⁻².

The production of hydrogen from the electrolysis of water is more efficient in an acid solution, where a solid polymer electrolyte (SPE) is the electrolyte of choice because significantly higher operational current densities are possible [58-60]. This technology is the most promising candidate for low-temperature fuel cells. In water electrolysis, solid polymer electrolysis was first introduced by the General Electric Company in the early 1970s [61-65]. The development of the technology has been delayed by investment costs because the only sufficiently stable material for the anode side (Nafion^(R)) is very expensive. Better and less expensive electrocatalysts and long-term stability are still needed for proton membrane water electrolysers. The first high-efficiency SPE electrolyser was based on Pt and Ru-|r-Ta electrocatalysts for the cathode and the anode respectively, both directly deposited on a Nafion^(R) membrane [60-67]. Roughening the surface of the membrane [68] or using composite structures [69] were methods proposed to improve the performance characteristics of this type of electrolyser. Advanced technology has also been reported [70]. The loading of platinum onto carbon had been also improved to 0.4 mg Pt.cm⁻² under optimum conditions of temperature and pressure [71]. Nafion^(R) impregnation of the electrode to create an improved three-dimensional reaction zone at the electrode-proton exchange membrane interface was the method used by Petrov et al [72] to develop an electrolyser for higher energy efficiencies with a Ru-Ir-Ta oxide anode and a Pt-black cathode. It was indicated that at 85°C and at 1 A.cm⁻², the cell voltage was 1.85 V, a value which was almost constant for a period of over 1,000 h. Durand et al [73-78] showed that metallic electrodes (Pt, Ir, Ru) and IrO2 electrodes on a

laboratory scale give interesting parameters for the SPE electrolyser. The composites prepared had low noble metal loadings (< 1 mg cm⁻²). Based on the electrodes, it was claimed that SPE electrolysers exhibited low cell voltage (1.75 V at 1 A.cm⁻² and 80°C) and long term-stability (over 15,000 h of continuous electrolysis) [73, 74]. But in life-tests performed up to 20,000 h at 0.5 A.cm⁻² using Pt as the anodic and cathodic material, the anodic overvoltage was rather high due to a cathodic overvoltage and membrane resistivity. Consequently, they have shown [79] that purification of water using ion-exchange resins was also useful in preventing a poisoning of the membrane itself, and, for purified water, assemblies using Pt cathodes and IrO2 anodes were found to be a good compromise between performance and stability.

Up to now, for solid polymer electrolyte or acid electrolysers, proton-conducting cation-exchanging perfluorinated sulphonic acid membranes in the form of Nafion^(R) or Dow Chemical menbranes can serve as the separator and the electrolyte simultaneously. They contain sulphonic acid groups (-SO₃H) which in contact with water, give polar hydrated sulphonic groups (H+ ag-SO₃ ag). They allow mass and charge transfer in a PTFE insulator. The Nafion^(R) membrane and the Dow membrane differ in their equivalent weights (EW=grams of polymer per mole of fixed - SO₃ - sites). The Dow Chemical equivalent weights (850 EW-800 EW) are lower than those of Nafion^(R) (\exists 1000 EW). The Dow membranes have also shorter side chains [80-81]. The specific conductance of Nafion 117 (1100 EW, 7 mils thick) is $0.08 - \Omega^{-1}$ cm⁻¹. Those of 850 and 800 EW Dow membranes are 0.12 and 0.20 Ω^{-1} cm⁻¹ respectively [82]. Dow membranes exhibited superior performance to the Nafion 117, the major disadvantage of these membranes being their high cost (\$ 70US/ft² for Nafion and \$ 150US/ft² for Dow) [83]. Recently, Ballard Power Systems have developed low-cost (\$ 5-15US/ft²) nonperfluorinated polymer-based electrolytes [84]. Thus, a series of sulphonated polyaromatic polymers were synthesised, and fabricated into membranes via solution casting. A comparison of the performance of the membranes in single solid polymer fuel cells showed that sulphonated polyaromatic membranes perform equally well or better than the standard Nafion 117 [84]. Some other non-perfluorinated membranes are know being developed more widely for fuel cell applications [85]. Developers are expecting that the development of this new generation of low cost solid polymer membranes may have a beneficial impact on industrial acid electrolysers.

CONCLUSION

Due to the costs necessary for utility-scale power, the predicted advantage of water electrolysis from electrolysers has never materialised for mass production. To decrease the cost of producing hydrogen

from water electrolysis to a level comparable to that of other production methods such as coal gasification and gas reforming, new electrocatalysts, cell design, and membranes are needed for technological applications. This implies the development of advanced water electrolysers which operate at current densities above 10 kA.m⁻² e. g. acidic electrolysers. Because of the recent interest in fuel cell systems, new materials, including new membranes, are becoming available for low-temperature fuel cells. Some of them may spill over to acid electrolysers. There have been few successful works carried out of any significance in developing new low-cost and noble-metal-based electrocatalysts for acid or solid polymer electrolyte electrolysers. New materials are the main requirement in this field. Polymer electrolyte is suitable for more advanced water electrolysers operating at high current densities. Thus, electrodes with very low noble metal loading with metal oxides onto carbon must be developed. Developers are hoping that specific methods of preparation or in-situ activation at working conditions will result in the development of good hydrogen cathodes with sufficient practical lifetimes. There has also been a search for low-cost and corrosion-stable oxide anodes, especially with DSA type electrodes. With thin film components, uniformly adherent, active and cost-effective anodes free from cracks, will enable the technology to produce hydrogen at a level comparable to that of gas reforming. The iridium oxide coated titanium anode works reasonably well, but it is expensive. Reduced titanium oxide, a ceramic material trade-named EBONEX, shows good stability but it requires an iridium oxide electrocatalyst as well. The use of ceramic materials should be addressed completely for industrial electrolysers. Nowadays, it is not the cost which will make producing hydrogen from water electrolysis more attractive. But this technology has attracted many materials science specialists and electrochemists involving many developers. A large number of the improvement problems identified here will be on the way to solution. The future of water electrolysis processing may depend on the development of new materials. The trend of adopting new materials for new and improved electrolysers could continue.

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