

Implementation of Cobalt Clathrochelates in Polymer Electrolyte Water Electrolysers for Hydrogen Evolution

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The purpose of this communication is to provide a review of main electrocatalysts used in PEM water electrolysis cells for both the hydrogen and oxygen evolution reactions, with a special emphasis on nanoscale structures including unsupported and supported nano-particles as well as substrate-adsorbed molecular compounds. Performances obtained using conventional platinum group metal electrocatalysts (platinum for the hydrogen evolution reaction and iridium dioxide for the oxygen evolution reaction) are compared to those measured on non-conventional membrane-electrode assemblies in which platinum has been replaced by cobalt-containing clathrochelates. Results on both performance and stability issues are reported. Some perspectives for enhanced performances of PEM water electrolysis cells are also discussed.

1. Introduction

From a historical perspective, the concept of solid polymer electrolyte (SPE) cell was introduced in the early 1950s, at the dawn of the US space program, and was considered at that time as an innovative approach for the development of a new generation of H₂/O₂ fuel cells that could operate efficiently in zero-gravity environments (Grubb, 1959). In the 1960s, innovative perfluorosulfonated ionomers became commercially available and this open the way to technological development of Polymer Electrolyte Membrane (PEM) water electrolysers. Electrolyzers (up to several tens of H₂ normal cubic meters per hour or Nm³ H₂/h) were first developed for the production of oxygen of electrolytic grade in anaerobic environments such as submarines. Gradually, concern about climate change offered new market opportunities for the technology. PEM water electrolysis is now considered as a key process of increasing interest for the development of a hydrogen refuelling infrastructure, but also for operation of power grids in a more flexible way and for the large scale storage of renewable energy sources (so-called hydrogen economy in which hydrogen is used as an energy carrier). In conventional PEM water electrolysers (Millet, 2011), platinum is used at the cathode for the hydrogen evolution reaction (HER) and iridium or iridium oxide is used at the anode for the oxygen evolution reaction (OER). Although the relative cost share of platinum group metal (PGM) electrocatalysts is limited (up to a few percent) in industrial systems, there is a need to anticipate future cost reduction requirements and to develop alternative low-cost electrocatalysts that could sustain significantly high operating current densities (in the multi Amp.cm² range) and would remain stable on the long-term (for market implementation, operation in the 10⁴-10⁵ hours range of operation is desirable). The purpose of his paper is to review the situation and discuss some alternative solutions.

2. Experimental section

A schematic diagram, showing the cross-section of a PEM water electrolysis cell, is pictured in figure 1. This is a symmetrical and compact structure: the total thickness usually ranges between 5 and 7 mm. The active electrochemical cell component at the centre of the cell is the membrane – electrode assembly (MEA), which separates the anodic and cathodic compartments. The MEA is usually made a thin (0.15 –

0.2 μm thick) proton-conducting membrane (see 1 in figure 1) of perfluoro-sulfonated ionomer material. Nafion[®] (from DuPont de Nemours Co.) is the most popular material used for such applications (Mauritz and Moore, 2004). The membrane is also called SPE (solid polymer electrolyte). In PEM cells, the SPE is used for the dual purpose of conveying electric charges (hydrated protons) from anode to cathode and separating reaction products (oxygen and hydrogen). The acidity of the SPE is equivalent to that of a 1 M aqueous solution of sulphuric acid ($\text{pH} \approx 0$). Only platinum group metals (PGM) can sustain such corrosive environment. Electrochemical half-cell reactions take place only at the surface of catalyst/electrolyte interfaces and cost considerations require the use of catalyst nanoparticles to reduce PGM loadings. Coming back to figure 1, each surface of the SPE is coated by a catalytic layers. The cathodic catalytic layer (see label 2c in figure 1) is a micrometer thick porous layer of unsupported or carbon-supported platinum nano-particles (figure 2-a), embedded in recast ionomer chains. Platinum is an excellent catalyst for the hydrogen evolution reaction (HER) in acidic environments. It is chemically stable and exhibits an un-surpassed high exchange current density. Due to the scarcity and cost of the element, palladium or platinum-palladium alloy nano-particles can alternatively be used. The anodic catalytic layer (see label 2a in figure 1) is a micrometer thick porous layer of unsupported iridium or iridium dioxide (nano-)particles (figure 2-b), also embedded in ionomer chains. Iridium dioxide is not as active as ruthenium dioxide but significantly more stable, in particular at the potential of operation of PEM anodes (usually $\approx 1.8\text{-}2.0$ V vs. RHE).

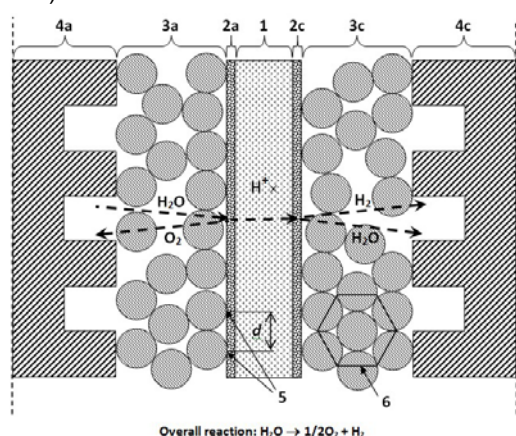


Figure 1: cross-section of a PEM water electrolysis cell (legend : see text).

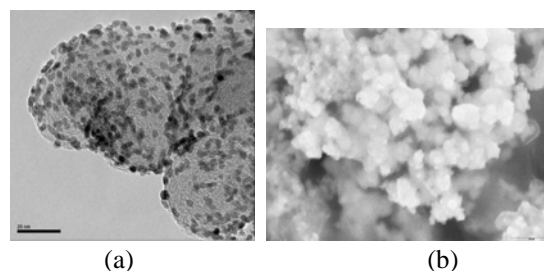


Figure 2: (a) carbon-supported Pt nano-particles for the HER; (b) unsupported IrO₂ nano-particles for the OER.

In order to reduce as much as possible charge transfer overvoltages, the roughness factor of these two catalytic layers must be as high as possible (the roughness factor f_r of a metal/electrolyte interface is defined as the dimensionless ratio of the real surface area to the geometrical surface area of the interface; $f_r = 1$ when smooth interfaces are used). This is usually obtained by designing micrometer-thick 3D layers and typical f_r values are in the 200-800 range. In figure 1, the central MEA (1 + 2a + 2c) is clamped between two millimeter-thick porous current distributors (labels 3a and 3c), which in turn are also clamped between two ending bipolar plates (labels 4a and 4c) equipped with channels of proper shape and dimension to ensure the circulation of liquid water and the collection of liquid-gas biphasic mixtures during electrolysis. Current distributors are usually made of sintered titanium particles. The shape of these particles (they can be spherical or not, of homogeneous size or not) dictates the porosity of the plates. The purpose of these two components is to insure mass transport (through the pores) and transport of electricity (through bulk particles). An optimum porosity is required to insure both functions. During water electrolysis, a flow of liquid water is pumped through the anodic compartment. Liquid water flows from left to right through the anodic current distributor up to the anodic catalytic layer (2a) where it is decomposed into gaseous oxygen and protons. While protons migrate through the MEA down to the cathode, oxygen flows back to the channels of bipolar plate 4a. Liquid water and gaseous oxygen flow in opposite directions. Best results are obtained when pores of different size are available. On the right side of the cell, migrating protons are reduced into gaseous hydrogen at the cathodic catalytic layer and molecular hydrogen flows across the porous cathodic current distributor 3c up to the channels of the cathodic bipolar plates. Migrating protons are usually hydrated and water molecules are released at the cathode. This

continuous flow of water across the SPE is used for thermal management and is usually recycled to the anode.

3. Results and discussion

3.1 Performances with conventional PGM catalysts

Figure 3 shows two typical polarization curves measured with two SPEs of different equivalent weight and different thickness (Nafion 115 and 117 whose thicknesses in the dry state are 175 and 125 μm respectively). The grey rectangle in the middle of the figure delimits state-of-the-art performances. An enthalpic efficiency of 80 % is common good practice at 1 $\text{A}\cdot\text{cm}^{-2}$. Such performances are usually obtained using 0.5 $\text{mg}\cdot\text{cm}^{-2}$ Pt loadings and 1-2 $\text{mg}\cdot\text{cm}^{-2}$ IrO_2 loadings. Similar performances are obtained using palladium in place of platinum (Grigoriev *et al.*, 2008). In spite of this high efficiency, market applications are calling for higher performances. By increasing operating current density at constant cell voltage, more compact electrolyzers can be designed and capital expenses can be reduced. By reducing cell voltage at constant current densities, more efficient cells are obtained and operational expenses are reduced. Recent progresses have been made to reduce PGM contents while maintaining similar levels of performance but usually there is a negative impact on performance durability.

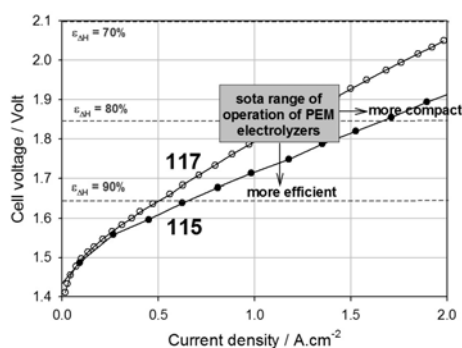


Figure 3: typical polarization curves measured during PEM water electrolysis.

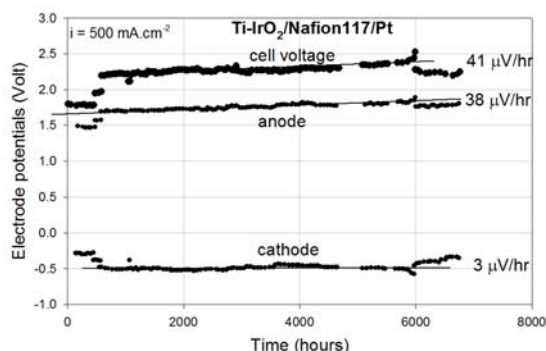


Figure 4: typical results of durability experiments measured during PEM water electrolysis.

Figure 4 shows the result of some durability experiments. Performances of both anode and cathode tend to decrease with time. Same comment for non-MEA titanium cell components. Market applications are calling for long-term performances (in the upper range of 10^4 - 10^5 hours of operation) and the challenge for the electrochemical engineer is to analyze degradation mechanisms and implement appropriate solutions.

3.2 Performances with non-conventional catalysts

For different reasons, there is a need to use alternative non-PGM electrocatalysts for the HER and the OER in acidic PEM media. Cost is of course a key driver for this kind of research but there are other reasons. In particular, platinum is highly sensitive to trace amounts of metallic impurities that may incorporate the SPE during operation. Such impurities are usually released from the stainless steel piping in contact with the highly de-ionised water pumped in the circuit. Metallic cations (iron, chromium, nickel) can incorporate the SPE by simple ion-exchange process, and then, they are reduced to the metallic state at the cathode, at the surface of platinum particles, to form metallic layers. As a result, the HER overvoltage tends to increase and electrochemical performances cannot be maintained on the long-term. The use of less sensitive catalyst would alleviate these risks and also offer the possibility to electrolyze less purified feed water.

In this communication, we report some recent advances obtained with new inorganic materials that can be used to replace platinum. In alkaline water electrolysis technology, nickel or cobalt are used as electrocatalysts for the HER and the OER. But such metals, in spite of some advantages (low cost, high activity for the reactions of interest) cannot sustain the acidic environment of PEM cells. The idea developed in our group is to use molecular compounds that contain cobalt or nickel active centres. Some significant results have been obtained using cobalt complexes (clathrochelates) of figure 5 (Pantani *et al.*, 2007), (Pantani *et al.*, 2008). This is a family of boron-capped tris(glyoximate) complexes. The metal active centre is covalently bounded to a shield of organic ligands that are selected and used for different purposes: (i) to protect the active centre from corrosion (at rest potential, the Co^{II} species is stable but

does not dissolve in the electrolyte); (ii) to tune the redox potential of the active centre to the potential of interest (0 Volt versus RHE for the HER); (iii) to covalently bond the complex at the surface of carbonaceous substrates used as electronic carriers in the catalytic layers. The electrochemistry of these positively charged compounds is very rich. By selection of appropriate radicals (R and X substitutes in figure 5), the redox potential of the reacting metal centre can be significantly shifted along the potential axis. Cyclic voltamograms (CVs) of three different cobalt clathrochelates measured in the same media using the same experimental conditions are plotted in figure 6. Curve (a) is the CV of the $[\text{Co}(\text{dmg})_3(\text{BC}_6\text{H}_2\text{F}_3)_2]^+ \text{BF}_4^-$ species (dmg stands for dimethyl glyoximate). Redox potentials of the $\text{Co}^{\text{I}}/\text{Co}^{\text{II}}$ and $\text{Co}^{\text{II}}/\text{Co}^{\text{III}}$ redox couples are -0.73 and $+0.28$ V vs. SCE respectively. By substitution of boron with fluorine, the CVs are shifted toward more positive potential values. Curve (b) is the CV of the $[\text{Co}(\text{dmg})_3(\text{BF})_2]^+ \text{BF}_4^-$ species. Redox potentials of the $\text{Co}^{\text{I}}/\text{Co}^{\text{II}}$ and $\text{Co}^{\text{II}}/\text{Co}^{\text{III}}$ redox couples are now -0.66 and $+0.38$ V vs. SCE respectively, corresponding to a translation of approximately 100 mV. When methyl groups are replaced by phenyl groups, the CV is further shifted. Curve (c) is the CV of $[\text{Co}(\text{dpg})_3(\text{BF})_2]^+ \text{BF}_4^-$ species (dpg stands for diphenyl glyoximate). Redox potentials of the $\text{Co}^{\text{I}}/\text{Co}^{\text{II}}$ and $\text{Co}^{\text{II}}/\text{Co}^{\text{III}}$ redox couples are this time -0.38 and $+0.46$ V vs. SCE respectively, corresponding to an additional mean translation of approximately 200 mV.

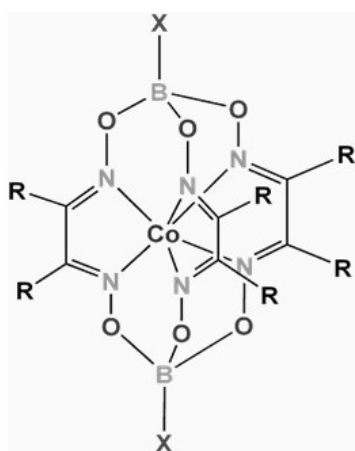


Figure 5: general structure of cobalt clathrochelates.

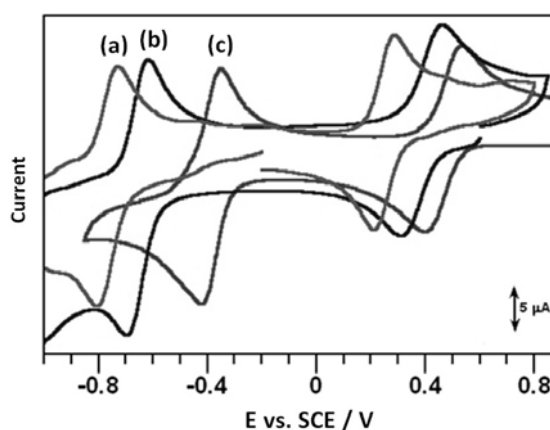


Figure 6: cyclic voltamograms measured in 0.9 mM solutions of complexes in acetonitrile (at 20°C, 100 mV/s).

The electrochemical activity of these molecular compounds is illustrated in figure 7. Again, CVs have been recorded in acetonitrile. At rest potential, the stable cobalt species is Co^{I} . It can either be reversibly oxidized to form Co^{III} species during anodic potential scans or reversibly reduced down to Co^{I} during cathodic potential scans (curve a). When increasing amounts of aqueous solutions of protons (HClO_4) are added, a reduction wave of increasing magnitude (curves b, c) develops. The faradaic current leads to the formation of molecular hydrogen.

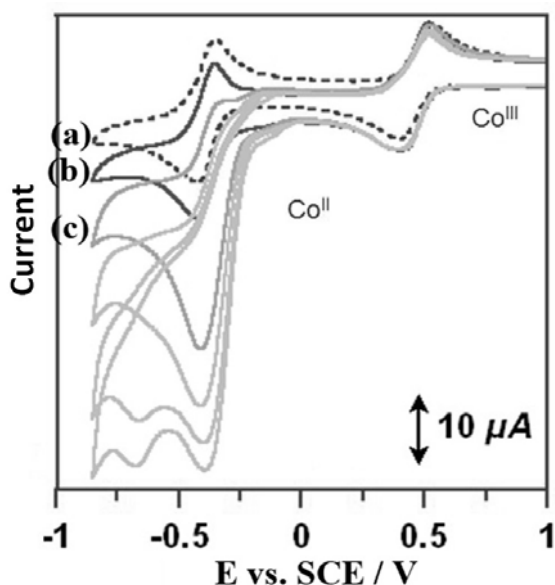


Figure 7: cyclic voltammograms measured in a 0.9 mM solution of $[\text{Co}(\text{dpg})_3(\text{BF})_2]^+ \text{BF}_4^-$ in acetonitrile (at 20°C, 100 mV/s).

The reduction current leading to the formation of hydrogen is triggered by the formation of Co^{I} species. It is not totally clear whether the transferred electron remains on the cobalt centre or is delocalised on the ligand. Nevertheless, the formation of this reduced species is a prerequisite for the onset of the proton reduction wave. The higher the potential of formation of this reduced species, the sooner the reduction wave appears (the thermodynamic voltage of proton reduction is -0.25 V vs. SCE at pH = 0).

Such compounds can be implemented in PEM water electrolysis cells after surface adsorption on electronic carrier of large surface area. Most appropriate substrates are carbonaceous powders such as those used in PEM fuel cell technology. A mixture of carbon powder and complex is dispersed in an alcoholic solution of ionomer and sprayed over the surface of the SPE using an automated ink printer. The anodic catalytic layer is deposited using a similar procedure. After drying, the MEA is mounted in the electrolysis cell for characterization. An activation procedure is required before best cell performances can be obtained. Some polarization curves measured during the activation of a membrane – electrode assembly that contains a IrO_2 anode and a cathode with the complex of figure 5, adsorbed onto Vulcan XC-72 (Cabot Co.), are plotted in figure 8.

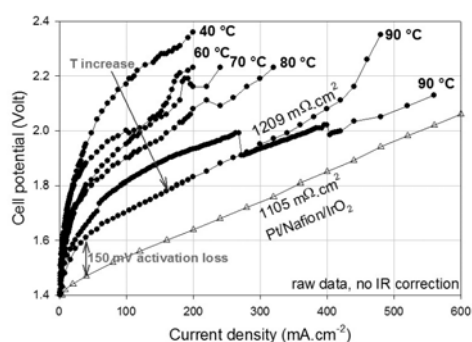


Figure 8: Polarisation curves measured at different temperatures on a 250 cm² PEM water electrolysis cells containing a IrO_2 anode and a carbon-boron-capped tris(glyoximate) cobalt complexes cathode. (Δ) reference curve with Pt at cathode.

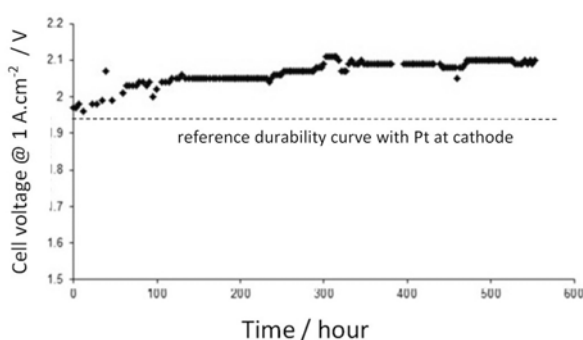


Figure 9: Durability test performed at 1 A/cm² and 80°C on a PEM water electrolysis cells containing a IrO_2 anode and a carbon-boron-capped tris(glyoximate) cobalt complexes cathode.

During activation, the operating temperature and current density are gradually increased. The activation can take several hours. During that period, the large charge transfer overvoltage observed at low current densities gradually decreases. At the end, the polarization curve of the activated MEA is close to the reference curve measured in the same cell on a conventional platinum MEA. In the case reported in figure 8, the cobalt clathrochelate cathode remains less efficient than the Pt one. Nevertheless, good

electrochemical performances are: a cell efficiency $\epsilon_{\Delta H} \approx 80\%$ is measured at a current density of $500 \text{ mA}\cdot\text{cm}^{-2}$ and 90°C . The situation can be further improved using different complexes of the same family with more electro-negative radicals. Some ageing tests have been performed to evaluate durability performances. During the test, step-like transient current loads ranging from 0 to $2 \text{ A}\cdot\text{cm}^{-2}$ were applied and the stationary cell voltage at $1 \text{ A}\cdot\text{cm}^{-2}$ was recorded every 8 hours. Results are plotted in Figure 9. A reference durability curve measured with a conventional Pt/IrO₂ MEA using the same Nafion 117 SPE is also plotted for comparison. In spite of the aggressive conditions of the test, figure 9 shows that the performances remain reasonably stable over the period. This is a good illustration of the performances of such catalysts and the demonstration that there are some credible alternative for the replacement of platinum in PEM water electrolysis cells. The situation is of course more challenging for the replacement of iridium dioxide at anodes.

4. Conclusions

PEM water electrolysis is a somewhat young technology that appeared in the 1970s when appropriate polymer electrolyte materials became commercially available. The technology has been used mostly for some niche applications, in particular for oxygen generation in anaerobic environments. New markets opportunities are appearing for hydrogen of electrolytic grade because water splitting appears to be the best option to convert transient electricity load profiles into easy-to-store and distribute chemical energy carriers. On the short term, hydrogen refuelling stations are expected to be deployed in industrial countries for clean transportation usages. On the longer term, the possibility of deploying large water electrolyzers for seasonal energy storage is also under consideration. Main advantages of this technology are: (i) no need for corrosive electrolyte; (ii) possibility to operate at elevated current densities (the multi $\text{A}\cdot\text{cm}^{-2}$ range is accessible); (iii) possibility to operate safely at elevated pressure (prototypes operating above 100 bars have been successfully tested); (iv) possibility to operate under pressure differences, to release oxygen at atmospheric pressure; (v) well-adapted to operation with transient power loads. Cost considerations are calling for the development of novel electrocatalysts that will contain few if any platinum group metals. Molecular chemistry offers some interesting alternative solutions to this problem. Results reported in this communication demonstrate that some cobalt clathrochelates, a family of oxime complexes, are active with regard to the hydrogen evolution reaction in acidic media. They have been successfully implemented at the cathode of PEM water electrolysis cells, demonstrating good performances and durability in view of commercial applications.

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