



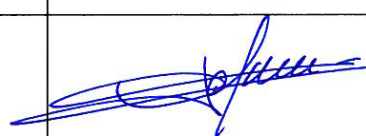
Rapport technique DEHT-DR-10/051

**« NEXPEL Project »
Next-generation PEM electrolyzer for sustainable hydrogen
production**

**WP5 "Porous current collectors and materials for bipolar plate"
Bibliographic review**

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Référence PRODEM 09.02727
Nature du rapport Final

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Bureau financier (Ventes) : M.POIRÉ



Résumé

This document was produced as part of WP5 of the NEXPEL project (Next generation PEM electrolyser for sustainable hydrogen production), funded by European community (SP1-JTI-FCH). WP5 "Porous current collectors and materials for bipolar plate", coordinated by CEA is dedicated to the development of new solutions to replace titanium in porous current collectors and bipolar plates. The main purposes of the bipolar plates are to distribute water in the electrolyser stack for both cooling the device, supply reactive to the anodic sides and evacuate gases produced by the electrochemical reactions: hydrogen and oxygen. In this work, the literature on metal based bipolar plates are reviewed, different ways are presented and discussed.

Mots clés

ÉLECTROLYSE DE L'EAU, ELECTROLYSE PEM, NEXPEL, PLAQUE BIPOLAIRE, POREUX, CORROSION, TITANE



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I. Introduction

This document was produced as part of WP5 of the NEXPEL project (Next generation PEM electrolyser for sustainable hydrogen production), funded by European community (SP1-JTI-FCH). WP5 "Porous current collectors and materials for bipolar plate", coordinated by CEA is dedicated to the development of new solutions to replace titanium in porous current collectors and bipolar plates. The main purposes of the bipolar plates are to distribute water in the electrolyser stack for both cooling the device, supply reactive to the anodic sides and evacuate gases produced by the electrochemical reactions: hydrogen and oxygen. For PEM fuel cells, bipolar plates made of carbon or carbon composites have traditionally been used because of their chemical resistance. However, carbon based bipolar plates have a low mechanical resistance and a rather high electrical resistance and high machining cost. Metals, on the other hand, are to be desired because of very high electric conductivity and very good mechanical properties, but the chemical resistance is rather poor in the humid, acidic and anodic environment.

For PEM water electrolyzers, anodic potentials are so high (typically 1.6 – 2V) that carbon-based and most of metal-based bipolar plates can't be used, due to their rapid oxidation. Titanium that covers with a stable thin native oxide and protective layer is usually used for bipolar plates and current collectors. High costs of machined titanium plates and porous sintered powder lead us to evaluate other solutions to replace titanium in such type of applications.

In this work, a bibliographic review of solutions that could be tested is presented.

1.1 Main Issue

Due to high potential (>2 V vs. RHE at the anodic side) and low pH, materials used as current collectors and bipolar plate in PEM water electrolyzers corrode quickly. Practically, only titanium can be used as stable and conductive material for current collectors and bipolar plates at the anode side.

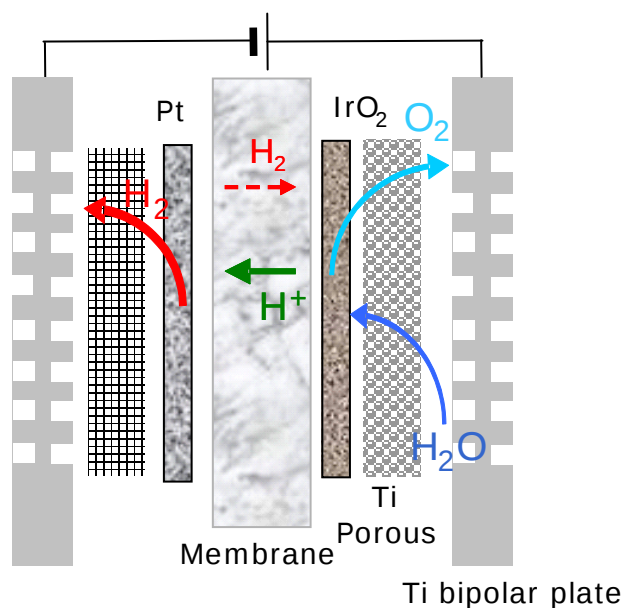


Figure 1 : PEM water electrolyser, description of a cell

Indeed, the main properties required for these elements of the cell are:

- Corrosion resistance (low pH, voltage up to 2.5 V vs. RHE)
- High electrical conductivity (1 to 4 A cm^{-2}) ($>100 \text{ S/cm}$)
- Two phase – flows: liquid feeding and gas evacuation

The key characteristics of materials used as bipolar plate and porous current collector should be roughly the same as for fuel cells:

- high corrosion resistance in water with corrosion current at 0 V vs. RHE and H_2 bubbling $< 1 \mu\text{A/cm}^2$
- high corrosion resistance in water with corrosion current at 2 V vs. RHE and O_2 bubbling $< 20 \mu\text{A/cm}^2$
- interfacial contact resistance at 1 MPa $< 10 \text{ m}\Omega \text{ cm}^2$
- electrical conductivity $>100 \text{ S cm}^{-1}$
- does not dissolve and produce metal ions
- high mechanical strength
- high volume cost-effective manufacturability



1.2 Materials for bipolar plate?

There is little literature available on bipolar plate materials for PEM electrolyzers. However, numerous reviews on PEM fuel cell bipolar plates have been published in the last few years ^[1,2,3,4]. US Department of Energy has made requirements for bipolar plates for fuel cells, these are summarized in Table 1^[5].

Characteristic	Units	2005 Status	2010	2015
Cost	\$ / kW	10	5	3
Weight	kg / kW	0.36	<0.4	<0.4
H ₂ permeation flux	cm ³ sec ⁻¹ cm ⁻² @ 80°C, 3 atm (equivalent to <0.1 mA / cm ²)	<2 x 10 ⁻⁶	<2 x 10 ⁻⁶	<2 x 10 ⁻⁶
Corrosion*	μA / cm ²	<1	<1	<1
Electrical conductivity	S / cm	>600	>100	>100
Resistivity	Ohm.cm ²	<0.02	0.01	0.01
Flexural Strength	MPa	>34	>25	>25
Flexibility	% deflection at mid-span	1.5 to 3.5	3 to 5	3 to 5

Table 1: Performance requirements for PEM fuel cell bipolar plates from US Department of Energy (DoE http://www1.eere.energy.gov/hydrogenandfuelcells/mypp/pdfs/fuel_cells.pdf p.26).

* 1 μA / cm² is equivalent to 11.5 μm y⁻¹ for iron.

Hermann et al.^[4] proposed an interesting review of solutions proposed for PEM fuel cell bipolar plates.

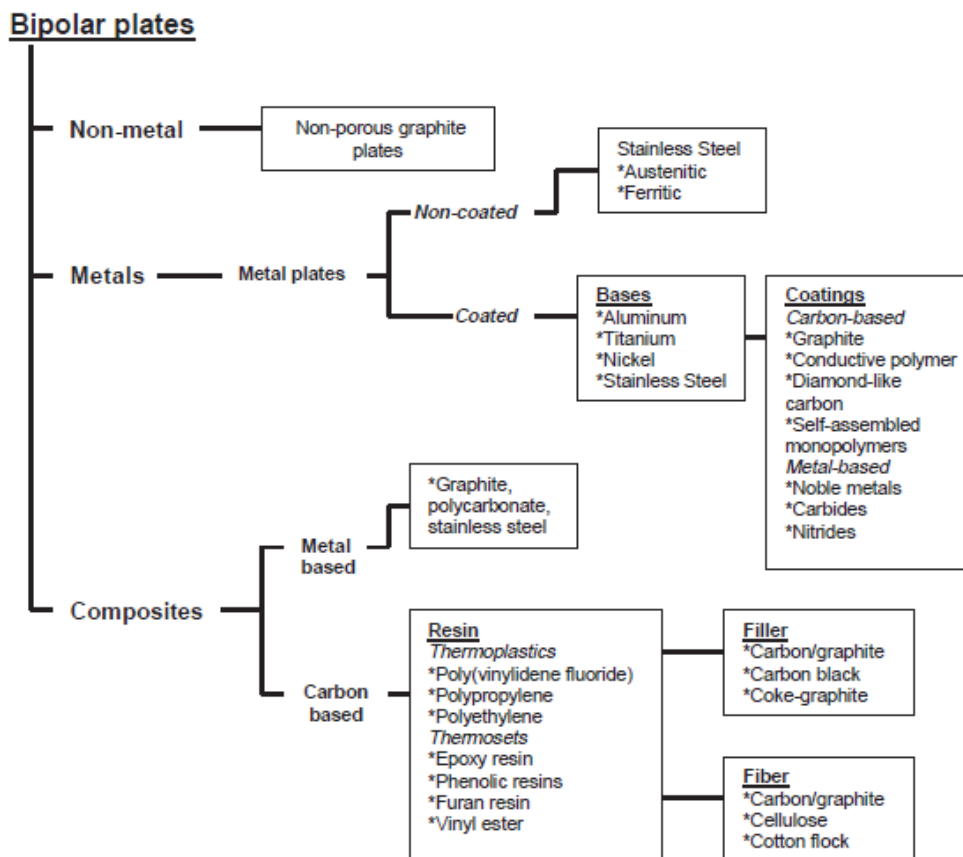


Figure 2 : Classification of materials for BPs used in PEM fuel cells ^[4]

Most of these solutions can't be considered in PEM water electrolysis because of the very high potential of the anodic electrode ($1.5 - 2 V_{SHE}$) compared to cathodic electrode of a PEM fuel cell ($0.5 - 1.1 V_{SHE}$).

Pourbaix diagrams indicate the stability of metals and alloys in different conditions of pH and potential at 298K. At 2V vs RHE and acidic conditions, no metal is chemically stable. It is the same with alloys such as stainless steel or carbon, which oxidize producing carbon dioxide. Moreover, metal compounds that oxidize produce metallic cations often dissolve in acidic conditions and contaminate the proton exchange membrane (decreasing the proton conductivity) and poisoning the catalyst layer.

On several metals, such as titanium, a native oxide layer forms on the surface of the metal and protects against corrosion. This oxide film can also be induced by anodic polarization ^[6]. However, this layer is often less electrically conductive than metal (titanium oxide is considered as a large band gap semiconductor: $E_g \sim 3.2$ eV) and oxidation reduces the



electrical contact at the interfaces between catalyst layer – porous current collector and porous current collector – bipolar plate.

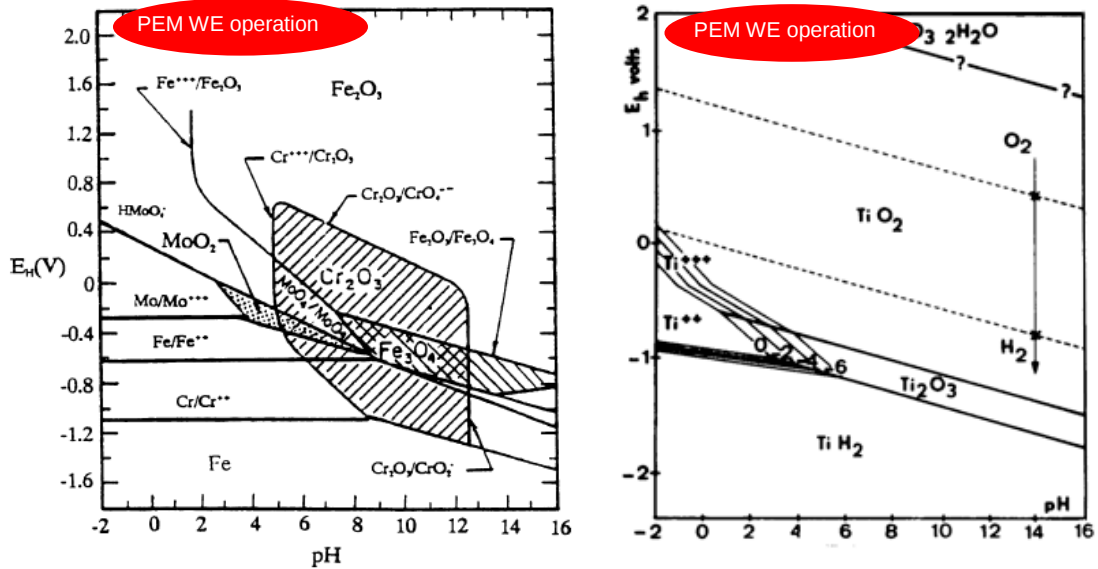


Figure 3: Pourbaix diagrams for stainless steel (left) and titanium (right)

Materials selection of bipolar plates for PEM electrolyzers has only been studied to a small extent in the literature. A few studies have used titanium without evaluating the material itself^[7] or referred to bipolar plates for regenerative fuel cells^[8,9,39].



1.3 Titanium

Titanium is a transition metal, atomic number 22 with a low density (4.506 g cm^{-3}). It is the ninth-most abundant element in the Earth's crust (0.63% by mass) and is mainly produced by Australia, South Africa, Canada and Norway. Titanium price is relatively low ($22 \text{ \$ kg}^{-1}$ [10]) but the titanium plates need an expensive machining to produce bipolar plates.



Figure 4 : Titanium Ingot 6AL4V price evolution during the last 3 years [10]

1.3.1 Safety: titanium ignition risks at high oxygen pressure

A possible risk of the use of titanium reported in literature is its self-ignition under high oxygen pressure [11]. A pilot hydrogen station using a PEM water electrolyser of 40 MPa operation pressure was constructed in Ito Campus of Kyushu University. The initial tests started from November 2005 and an explosion destroyed the station on December 2005. Three pilot hydrogen station of this type were built in Japan, two of three stations were lost by explosion and fires, the last one was decommissioned on March 2007.

Under some conditions, titanium placed in high-oxygen atmospheres may ignite and burn. At room temperature the rate of interaction of titanium and its alloys with oxygen is low; it increases only at temperatures above 623 K. It is believed that the damage of the oxide film and free access of oxygen to the metal surface can lead to the accumulation of heat due to the exothermic reaction of titanium surface oxidation and thus the metal ignites.

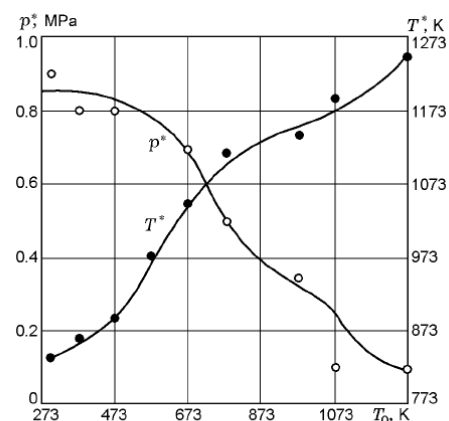


Fig. 2. Critical ignition pressure and maximum temperature of possible heating of juvenile surfaces of VT5-1 alloy specimens in oxygen versus test temperature: points $\circ$ and $\bullet$ refer to the experimental data of [3] and our calculations, respectively.

Figure 5: Critical ignition pressure vs temperature [12]



Self-ignition, at least at room temperature, is possible only if the metal is fractured; if the oxide film is damaged, titanium does not ignite. However, during high-rate fracturing, the temperature of metal can increase rapidly ^[12]. When a fresh titanium surface is exposed to an oxygen atmosphere, it oxidizes rapidly and exothermically. Rate of oxidation depends on O₂ pressure and concentration. When the rate is high enough, heat is given off faster than it can be conducted away and the surface may begin to melt. The reaction becomes self-sustaining because, above the melting point, the oxides diffuse rapidly into the titanium interior, allowing highly reactive fresh molten titanium to react at the surface.

The rate of titanium oxidation depends on oxygen pressure and the temperature in the system. Ignition cannot be induced even at very high pressure when the oxygen content of the environment is less than 35% ^[13]. However, steam as a diluent allows the reaction to proceed at even lower O₂ levels. Even at room temperature, the critical ignition pressure is relatively low (see fig.5).

1.3.2 Titanium embrittlement: hydride formation on titanium surfaces

In presence of hydrogen, hydrides (TiH₂) can form on the titanium surface. When the solubility limit of hydrogen in titanium is exceeded (few hundreds of ppm), absorption of hydrogen results in embrittlement and the risk of cracking under conditions of stress.

The surface oxide film on titanium acts as an effective barrier to penetration by hydrogen and below 80°C hydrogen pickup occurs very slowly, except in cases where severe tensile stresses are present. Moreover, laboratory tests have shown that the presence of as little as 2% moisture in hydrogen gas passivates titanium so that hydrogen absorption does not occur ^[13].

However, hydriding and, as consequence, embrittlement, can occur when hydrogen is directly formed on the surface of titanium at low potential. The presence of moisture does not inhibit hydrogen absorption of this type but several conditions are required: low pH and potentials more negative than -0.70 V vs. SHE ^[14].



II. Replacement of titanium: Metals and alloys

Amongst the materials that exhibit a good chemical inertness, very few resist to an anodic polarization. However, several groups of metals and alloys are proposed candidates and should be discussed.

II.1 Iron based alloys

- **Cast iron** with ferrosilicium (with Si 12-18 wt% - Duriron®^[15], Durichlor®^[16]) show a good resistance against corrosion in oxidative medium. However, high anodic polarization should lead to the dissolution of iron cations.
- **Stainless steel:** many researchers have investigated the possibility of using stainless steel as bipolar plates in fuel cells. The general trend is that higher chromium content prevents corrosion, but the high chromium content also results in high contact resistance. Stainless steel such as high alloy austenitic steels (AISI 316L, 304L or 904L) are highly resistant to corrosion^[17,18].

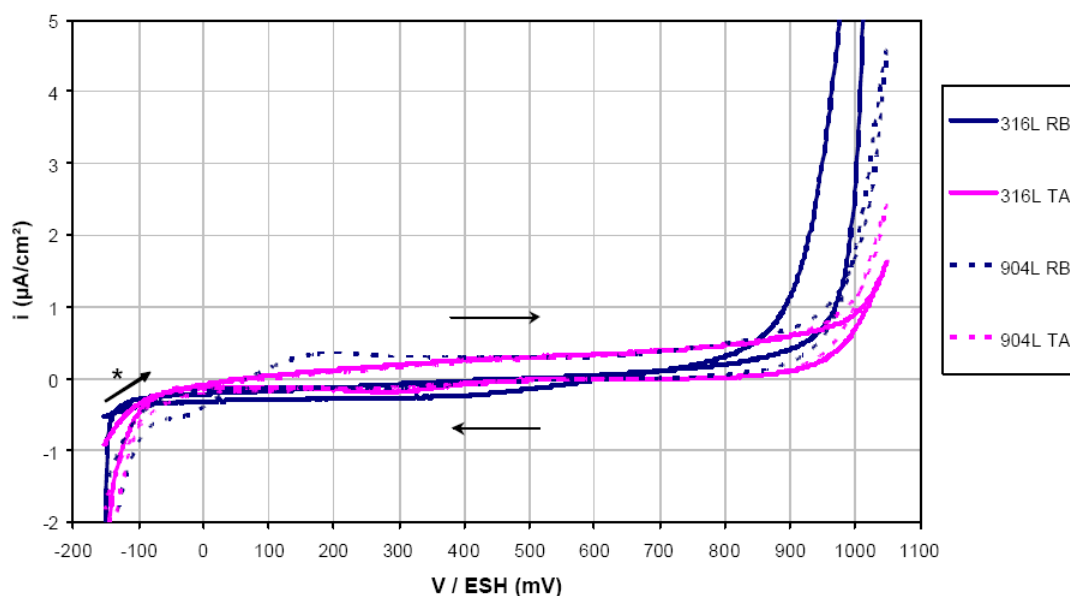


Figure 6 : Corrosion curve of AISI 316L and 904L into water at room temperature

Wang et al^[19,20] have investigated the possibility of using bare steel as bipolar plate material. The corrosion tests were performed in 1 M sulphuric acid added 2 ppm F⁻ at 70 °C. A summary of the results is given in Table 2.



Alloy	Chromium content/ wt. %	Corrosion current at $-0.1 V_{SCE} / \mu A cm^{-2}$	Corrosion current at $0.6 V_{SCE} / \mu A cm^{-2}$	Contact resistance at $140 N cm^{-2} / m\Omega cm^2$	Ref.
316 L	16	400	20	150	[19]
317 L	18	150	10	145	[19]
904 L	20	50	10	140	[19]
349	23	9.5	10	120	[19]
AISI 434	18	200	100	150	[20]
AISI 436	18	80	20	125	[20]
AISI 441	18	600	80	145	[20]
AISI 444	18	80	20	120	[20]
AISI 446	28	6	20	200	[20]

Table 2 : Corrosion current densities and contact resistance for commercially available alloys.

By comparing the corrosion data and the contact resistance in Table 1 and 2, it can be seen that none of the investigated metals fulfill the requirement from DOE. When some of the samples in Table 2 were polarized for some time, the contact resistance increased, probably caused by thickening of the oxide layer.

Park et al. ^[21] made single cells out of titanium, 316 L and 430 stainless steel. In all cases a significant fuel cell performance loss was observed in a 1000 hour test. This was attributed to increased contact resistance, contamination of the membrane and growth of the platinum particles on carbon.

Kumagai et al. ^[22-23] tested nickel free high nitrogen and chromium stainless steel (67 wt. % Fe, 23 wt. % Cr and 1 % N wt. %). Before corrosion testing, the contact resistance was about $40 m\Omega.cm^{-2}$ at $140 N.cm^{-2}$, but after polarization to 0.6 V vs. SCE this value increased about $800 m\Omega.cm^{-2}$. In 0.05 M H_2SO_4 + 2 ppm HF at 0.6 V vs. SCE and 80 °C with bubbling of air, the corrosion current density after 8 hours was $0.04 \mu A cm^{-2}$.

- **Chromium and nickel surface enrichment:** Feng et al ^[24,25] implanted nickel and chromium at the surface of 316 stainless steel. The electrochemistry results reveal that a proper Ni–Cr implant can greatly improve the corrosion resistance of SS316L in the simulated PEMFC environment. However, both the corrosion rate and the contact resistance is about one order of magnitude higher than the DOE target.



- **Adding refractory metals to stainless steel:** Kim et al. ^[26] investigated the possibility of adding tungsten, tantalum and lanthanum to an austenitic stainless steel. Improvements in both the corrosion resistance and contact resistance were observed.
Lee et al. ^[27] added niobium and titanium to 316 stainless steel. After casting, some of the samples were aged at around 1000 °C to precipitate carbides. After aging the contact resistance was about 12 mΩ.cm² at 140 N.cm⁻² for both the alloy containing 3 wt.% niobium and for the alloy containing 0.5 wt.% titanium. The performance for a single cell improved when titanium or niobium was added compared to regular 316 stainless steel.

Both the contact resistance and corrosion rate are too high to meet the DoE target. The surface oxide layer protecting the stainless steel from corrosion has a very low conductivity resulting in a high contact resistance. A few authors have added other alloying elements in order to overcome this problem, but only with limited success.

It seems difficult to use pure iron – based alloys as current collector or bipolar plate in PEM water electrolyzers. However, it is possible to use it as a substrate coated with another material.



II.2 Nickel based alloys

Most of the nickel based alloys are not chemically stable in these conditions of pH and potential.

- **Illium®** (chromium, molybdenum, copper alloys) G, B and 98 seem to be the best corrosion resistant alloys in acidic medium ^[28].
- **Inconel alloys:** Rivas et al. ^[29] corrosion tested both stainless steel (SS304 and SS316) and nickel based alloys (Inconel 600, Inconel 601, Inconel 625, Incoloy 800H). The corrosion tests were performed in 0.5 M sulphuric acid with and without addition of hydrofluoric acid. When only 2 ppm HF was added, hardly any influence of the corrosion current was observed. It was concluded that none of the tested materials can be used on the anodic side because the operating potential of the anode of a PEM fuel cell falls very close to their active-passive transition zones.



II.3 Precious metals

- **Noble metals** such as gold or silver could be considered as chemically stable in acidic conditions and high potentials. However, even on gold, an oxide layer forms on the surface of the metal and can lead to a high contact resistance. Concerning silver, a Ag^+ ion is formed at intermediate potentials.

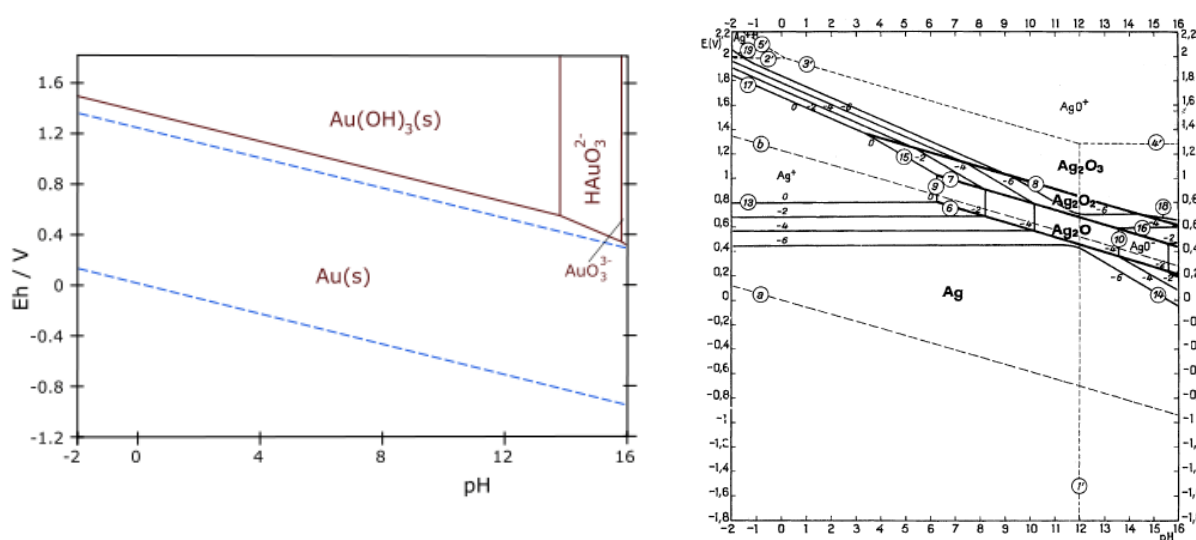


Figure 7 : Pourbaix diagrams of gold and silver

- **Platinum group** Ru, Rh, Pd, Os, Ir, Pt form oxides that are chemically stable in these conditions (excepted Ru).

The high cost of precious metals is the main limitation for their use. However, it is possible to plate/coat another material with such a noble metal ^[30,31].



II.4 Refractory metals

Refractory metals are a class of metals that present a very high melting point (above 2204°C). They also possess an important chemical stability.

hydrogen 1 H 1.0079																	helium 2 He 4.0026						
lithium 3 Li 6.941	beryllium 4 Be 9.0122																	boron 5 B 10.811	carbon 6 C 12.011	nitrogen 7 N 14.007	oxygen 8 O 15.999	fluorine 9 F 18.998	neon 10 Ne 20.180
sodium 11 Na 22.990	magnesium 12 Mg 24.305																	aluminum 13 Al 26.982	silicon 14 Si 28.086	phosphorus 15 P 30.974	sulfur 16 S 32.065	chlorine 17 Cl 35.453	argon 18 Ar 39.948
potassium 19 K 39.098	calcium 20 Ca 40.078	scandium 21 Sc 44.956	titanium 22 Ti 47.867	vanadium 23 V 50.942	chromium 24 Cr 51.996	manganese 25 Mn 54.938	iron 26 Fe 55.845	cobalt 27 Co 58.933	nickel 28 Ni 58.693	copper 29 Cu 63.546	zinc 30 Zn 65.38	gallium 31 Ga 69.723	germanium 32 Ge 72.61	arsenic 33 As 74.922	selenium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.80						
rubidium 37 Rb 85.468	strontium 38 Sr 87.62	ytrium 39 Y 88.906	zirconium 40 Zr 91.224	niobium 41 Nb 92.906	molybdenum 42 Mo 95.94	technetium 43 Tc [98]	ruthenium 44 Ru 101.07	rhodium 45 Rh 102.91	palladium 46 Pd 106.42	silver 47 Ag 107.87	cadmium 48 Cd 112.41	indium 49 In 114.82	tin 50 Sn 118.71	antimony 51 Sb 121.76	tellurium 52 Te 127.60	iodine 53 I 126.90	xenon 54 Xe 131.29						
cesium 55 Cs 132.91	barium 56 Ba 137.33	57-70 *		lanthanum 57 La 138.91	cerium 58 Ce 140.12	praseodymium 59 Pr 140.91	neodymium 60 Nd 144.24	promethium 61 Pm [145]	samarium 62 Sm 150.36	europium 63 Eu 151.96	gadolinium 64 Gd 157.25	terbium 65 Tb 158.93	dysprosium 66 Dy 162.50	holmium 67 Ho 164.93	erbium 68 Er 167.26	thulium 69 Tm 168.93	ytterbium 70 Yb 173.04						
francium 87 Fr [223]	radium 88 Ra [226]	89-102 * *		actinium 89 Ac [227]	thorium 90 Th 232.04	protactinium 91 Pa 231.04	uranium 92 U 238.03	neptunium 93 Np [237]	plutonium 94 Pu [244]	americium 95 Am [243]	curium 96 Cm [247]	berkelium 97 Bk [247]	californium 98 Cf [251]	einsteinium 99 Es [252]	fermium 100 Fm [257]	mendelevium 101 Md [258]	nobelium 102 No [259]						
				* Lanthanide series																			
				** Actinide series																			

Figure 8 : Refractory metals

- **Zirconium and alloys**

Resistance to corrosion of zirconium and alloys such as zircalloy are better than for titanium. However, the price (23 US\$ kg⁻¹ zirconium sponge – earth's crust abundance: 165 mg kg⁻¹) and density (6.52 g cm⁻³) limits the possibility of using these materials to replace titanium.

- **Niobium and alloys**

Very high resistance to corrosion but price is again the limiting factor (49 US\$ kg⁻¹ - earth's crust abundance: 20mg kg⁻¹) and density elevated (8.57 g cm⁻³).

- **Hafnium and alloys**

Corrosion resistance increases, but price and density too (805 US\$ kg⁻¹ - earth's crust abundance: 3 mg kg⁻¹; 13.31 g cm⁻³)

- **Tantalum and alloys**

Chemical resistance of tantalum is the best of all the refractory metals ^[32]. However, as before, its price (180 US\$ kg⁻¹ - earth's crust abundance: 2 mg kg⁻¹) and its density (16.69 g cm⁻³) are too high.



II.5 Conclusions

Titanium and alloys used as bipolar plates and porous current collectors can't be replaced easily by another metal or alloy. High corrosion resistance, low surface contact resistivity and attractive prices are difficult to obtain with a single material.

A possible solution is certainly to use a material with suitable mechanical structural properties, coated with a thin corrosion resistant layer.



III. Replacement of titanium: coating / plating

Aluminium, stainless steel and nickel can be considered as possible alternative materials for bipolar plates. To avoid corrosion, metallic bipolar plates have to be coated with a protective layer. Coatings should be conductive and adhere to the base metal without exposing it. It is essential to avoid the formation of micro-pores and micro-cracks in coatings ^[61].

In the literature, many ways to improve both the contact resistance and the corrosion resistance of stainless steel has been suggested. A summary of some results is given in Table 3.

Base material	Coating material	Corrosion current at $-0.1 V_{SCE} / \mu A cm^{-2}$	Corrosion current at $0.6 V_{SCE} / \mu A cm^{-2}$	Contact resistance at $140 N cm^{-2} / \Omega cm^2$	Ref.
SUS 304	Carbon	<1	~2	0.01-0.02	[33]
316	TiN	0.2	~1	NA	[60]
316	Zr	0.15	0.33	1	[34]
316	ZrN	0.2	4	0.160	[34]
316	ZrNb	0.33	5	NA	[34]
316	ZrNbAu	2.8	1.7	0.006	[34]
316	Ti	3.2	10	NA	[34]
316	2 nm Au	7	6	0.005	[34]
316	10 nm Au	4	4	0.004	[34]
316	1 μm Au	0.8	1	0.004	[34]
316	Carbon	NA	NA	0.013	[34]
304	TiC	0.034	3.7	NA	[35]
304	TiN	0.03*	0.18*	0.019	[36]
304	Ti ₂ N	0.015*	0.18*	0.018	[36]
316	TiN	11	112	0.06	[61]
316	TiAlN	28×10^{-3}	18×10^{-3}	0.01	[61]
316	CrN	23	55	0.03	[61]
316	316	263	7	NA	[61]

Table 3 : Corrosion current densities and contact resistance for commercially available alloys

Amongst the most promising methods are nitridation and carburization. Then, noble metals, metal nitrides and metal carbides are some of the metal-based coating that should be evaluated.



III.1 Precious metals and alloys

- **Gold plating**

Gold plating is certainly the easiest and most common solution to protect an alloy such as stainless steel from corrosion, while maintaining a low electrical contact resistance and limiting the contamination of the MEA due to metal ions coming out of the stainless steel. In Table 3 only gold fulfils the physical property targets of DOE, but the economical target is probably not fulfilled.

Yoon et al.^[34] electroplated gold layers with various thicknesses (2 nm, 10 nm, and 1 μm), it was found that the gold thickness had to be minimum 1 μm to fully cover the surface.

Al. Hentall et al.^[37] machined current collectors for fuel cell from aluminium, then coated with gold by a solution process. Initial performance was very similar to graphite. However, the performance degraded very quickly. The post mortem analysis revealed that some of the Au layer lifted from the plate and became embedded in the membrane.

On the other hand, Wind et al.^[38] used Au-coated bipolar plate (316SS) and clearly demonstrated no difference between the metal-based and graphite plates. Results obtained on fuel cells showed that gold coating was a good diffusion barrier for nickel under the operation conditions of a PEM fuel.

Jung et al.^[39] studied both carbon and 1 μm gold on titanium for a regenerative fuel cell. At high anodic potential the carbon corroded at a high rate. Promising results were presented for gold on titanium, unfortunately no contact resistance or corrosion rate were measured in this article.

Due to high price of gold-coated bipolar plates, this technology stands to face extreme competition from other less expensive corrosion-resistant coatings. Also, coating techniques and surface preparation must be optimized to improve the bonding strength between gold coating and the substrate base plate to eliminate the possibility of separation.



- **Gold - alloy plating**

Y. Yun recently plated 316L stainless steel with gold-titanium and gold-nickel (0,1 μm thick layer of titanium or nickel, then 1-2 μm of gold by e-beam evaporator)^[40]. The coated metallic plates coated with gold and either titanium or nickel showed very uniform and smooth surface morphologies without any lumps or crevices. Treatment of the metallic plates by electropolishing (carried out in corrosive solution of H_2SO_4 and H_3PO_4 at 70–110°C for 20 min) prior to deposition of a surface metal coating was found to give markedly lower electrical resistance than the mechanically polished plates and to be very effective at inhibiting corrosion. Almost no chemical dissolution was detected after 10 hours of immersion in acidic solution (H_2SO_4 pH3, 80°C).

- **Platinum and iridium plating**

Jung et al. ^[9] electrodeposited platinum on titanium. After one hour at 2 V and 75°C, the cell resistance was significantly lower where platinum was electroplated compared to bare titanium or a carbon electrolysis cell.



III.2 Refractory metals and alloys

III.2.1 Titanium and alloys

Titania and titania-based composite coatings on metal surface can be used as protective layers to improve the wear and corrosion resistance. There are many methods to prepare titania coatings on metals such as sputtering, spray pyrolysis^[41], chemical or physical vapor deposition^[34,42], sol-gel and plasma electrolytic oxidation^[43].

Yoon et al^[34] revealed that 0.5 μm titanium layer on stainless steel is not sufficient to protect the metal against corrosion.

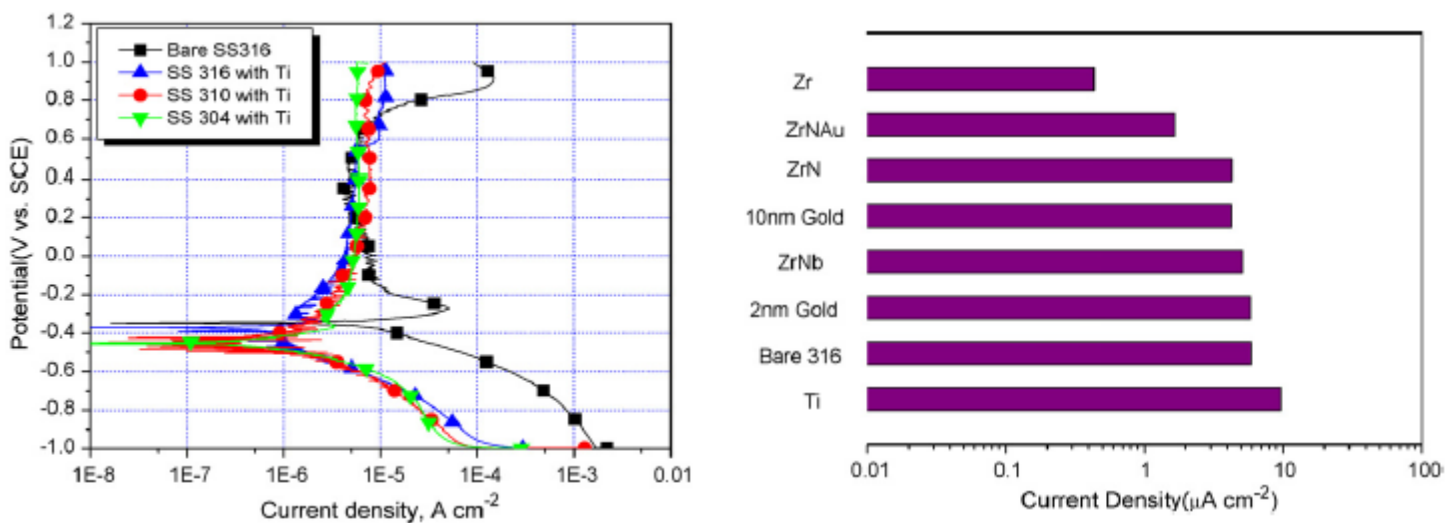


Figure 9 : Polarization curve of the bare SS 304, 310, and 316 with 0.5 μm Ti coating and dissolution rate for metal samples at cathode potential (0.6V vs. SCE)^[34].

Experiments were performed at CEA^[44] in the framework of the DEPEM-HP project (French national program ANR Pan'H program), depositing 5 μm of titanium on the surface of 316L SS. Corrosion experiments shown that such a protective layer was sufficient for corrosion protection when immersed in water at 100°C and 670kPa under air.

III.2.2 Tantalum and alloys

In the home page of The WELTEMP [108] project funded by the European Union, the possibility of using a high temperature (125-175 °C) phosphoric acid doped PBI membrane for water electrolysis is presented. A variety of materials, like advanced steel alloys, refractory metals and ceramics were tested for stability against acidic conditions (H_3PO_4) combined with a strongly anodic potential to simulate the conditions at the anode in an electrolyzer cell. It was found that the only electron conducting materials capable of fully resisting this were tantalum and tantalum coated base metal materials (Tantaline company [45] is a partner in the project !!).

The (<http://www.tantaline.com/>), based in Waltham (Massachusetts, USA), proposes a CVD deposition of tantalum technique as an economical solution to protect metals against corrosion [46,47,48,49].

Treatment is performed at 700-900°C. The gaseous tantalum diffuses into the substrate, typically stainless steel, creating a surface alloy approximately 50 μm thick, then a dense layer of pure tantalum grows to form a pure tantalum surface layer of about 50 μm thickness.

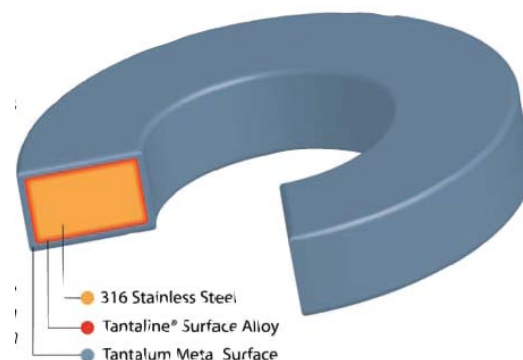


Figure 10: Schematic cross section of a treated 316L ss washer showing the surface alloy diffusion and pure tantalum metal [48]

S. Zein El Abedin et al. [50] and C. Arnoud et al. [51] showed that adherent, dense and uniform Ta-layers of about 500 nm thickness can be electrodeposited on NiTi alloy in ionic liquid containing 0.25 M TaF_5 and 0.25 M LiF at 200°C. The corrosion behaviour of NiTi alloy without and with coating by a thin layer of tantalum was examined in 3.5% NaCl solutions at room temperature. It was found that the coated sample shows high corrosion resistance ($<1 \mu\text{A cm}^{-2}$ at 0.94V vs. NHE).

Electrodeposition at 373K in liquid ionic was performed by Matsunaga et al. [52,53] and S. Legeai et al. [54] and several conditions were evaluated by Ispas et al. [55].



III.2.3 Zirconium and alloys

Yoon et al ^[34] showed great interest in a 0.5 μm zirconium layer on stainless steel for protection of the metal against corrosion. Kamada et al proposed ^[56] to perform plating by electrodeposition.

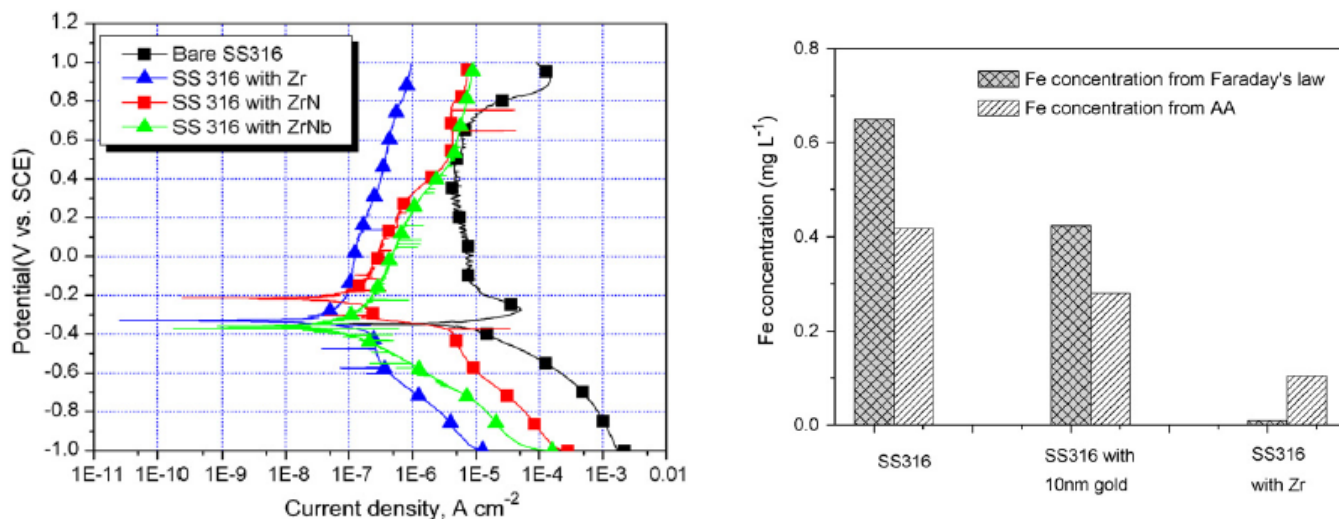


Figure 11 : Polarization test of Zr, ZrN and ZrNb coating on the SS 316 sample with 0.5 μm coatings and comparison of iron concentrations in solution of SS 316, SS 316 with 10nm gold, and SS 316 with Zr samples after the polarization test. ^[34]

III.3 Nitride and carbide - based layer

III.3.1 Nitride based -layer

Brady et al. ^[59] wrote a comprehensive research summary about nitridation of metals. Transition metal nitrides offer an attractive combination of high electrical conductivity and good corrosion resistance, which makes them of interest for protective coatings for metallic bipolar plates. According to the authors, levels of chromium in excess of 30–35 wt. % was needed to form an external, continuous nitride. Corrosion testing in sulphuric acid (pH 3) at 80 °C revealed that a nitrided alloy with composition 50 wt. % nickel and 50 wt. %

chromium and an alloy consisting of 67 wt. % iron, 27 % chromium and 6 wt. % vanadium both passed DOE's target. Before corrosion measurements, the contact resistance at 140 N.cm⁻² for the mentioned alloys were approximately 10 mΩ cm². After the corrosion measurements, the contact resistances were approximately doubled.

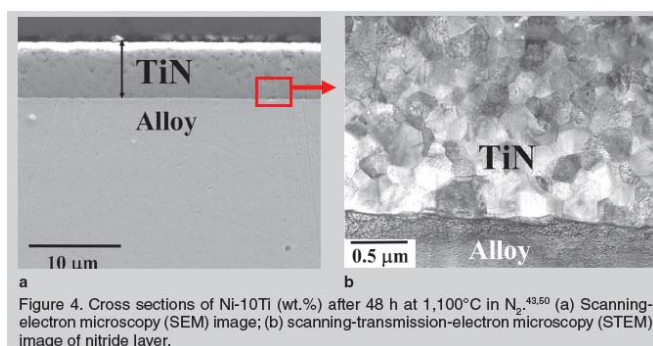


Figure 12 : TiN coating by thermal nitridation ^[58,59]

K. Feng et al. ^[57] performed a surface treatment of titanium sheet with low-temperature and high temperature nitrogen plasma immersion ion implantation (LT-PIII and HT-PIII). Results suggest that high-temperature nitrogen plasma immersion ion implantation can significantly improve the corrosion resistance and conductivity of titanium.

A dense, continuous CrN/Cr₂N surface layer can be formed at a metal surface ^[58]. Then, this material exhibited excellent behaviour during a 4000 h corrosion exposure under simulated anodic and cathodic PEMFC conditions and 1000 h of single-cell fuel cell testing. No evidence of significant pin-hole defects, no increase in surface contact resistance, and virtually no metal ion dissolution were observed. These results show that nitridation can be used to form dense, pinhole free nitride layers to provide protection under aqueous corrosion conditions. TiN layers are also presented ^[59]. A wide range of nitride microstructures, from fine, equiaxed TiN grains to coarse, columnar Ni-Nb-V nitride base phase grains are possible. The advantage of the thermal nitridation (high temperature in N² atmosphere) is the growth of pinhole free layers on components with complex surface geometries to provide corrosion protection in aqueous environments.



Li et al. ^[60] investigated the corrosion behavior of TiN-coated type 316 stainless steel in a simulated PEMFC environment. The authors reported a loss of small part of coatings that had occurred during the immersion tests of TiN coatings (0.01 M HCl +0.01 M Na₂SO₄, 80°C) in O₂ environment for 1000 hours and in H₂ environment for 240 h, respectively. The results revealed that TiN coating can offer 316SS higher corrosion resistance and electric conductivity than bare 316SS material. Further effort to improve the coating quality and evaluation of the long-term stability of 316SS/TiN coating system under simulated conditions are required.

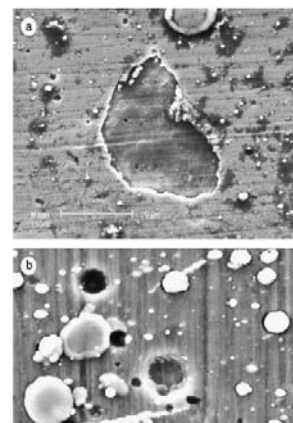


Figure 13: Microscopy images of TiN layer surface after immersion in (0.01 M HCl +0.01 M Na₂SO₄, 80°C)

Kumagai et al. ^[22,23] tested nickel free high nitrogen and chromium stainless steel (67 wt.% Fe, 23 wt.% Cr and 1 wt.% N). In order to improve the high contact resistance TiN nanoparticles was electrophoretically deposited onto the alloy. The TiN coating reduced the contact resistance to about 10 mΩ.cm² at 140 N.cm⁻².

L. Wang et al. deposited TiN, CrN and TiAlN on SS316L by electron beam PVD ^[61]. It was shown that in H₂SO₄ 1 M at 70°C under O₂ bubbling, lowest corrosion rate at 1V vs. Ag/AgCl, 3M KCl were obtained on TiN coating.

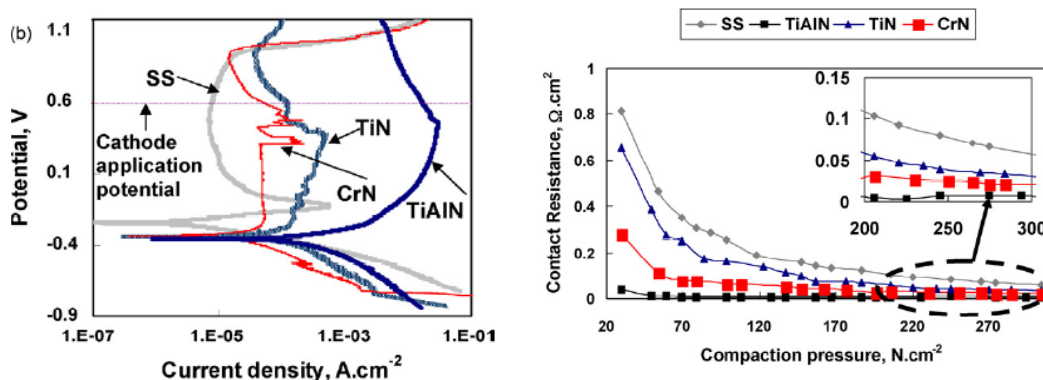


Figure 14: Potentiodynamic curves for TiN, CrN TiAlN – coated SS 316L in 1M H₂SO₄ at 70°C with O₂ purging (potential given vs. Ag/AgCl, 3M KCl ; Contact resistance of samples ^[61]



N.D. Nam et al. [62] deposited TiN/CrN on 316LSS substrates by reactive rf magnetron sputtering. Three hundred millimetre diameter high purity Ti (99.99%) and Cr (99.99%) targets were sputtered for different durations in high purity argon (99.99%) and nitrogen (99.99%) plasma.

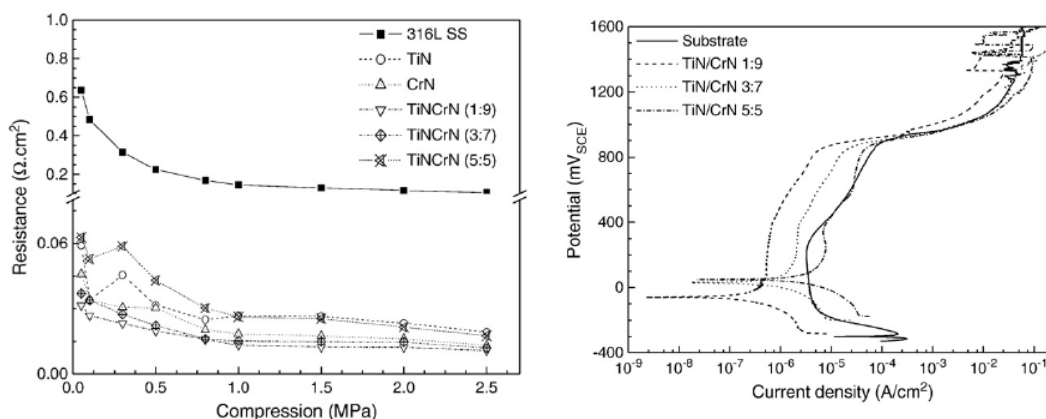


Figure 15 : Contact resistance and polarization curves of TiN/CrN – coated SS316L [62]

Chromium rich surface layers and the presence of nitrides on the outer surface are usually considered as increasing the corrosion resistance of materials. One solution proposed in the literature is to increase the concentration of chromium and nitride at the material surface.

Defects of the surface seem to be the main weakness of the corrosion resistance, Y. Wang and Northwood [63] vapor deposited 15 μm thick TiN on 316 steel, and observed pitting corrosion in defects of the coating layer surface.

- **Fe metallic glass** Fe-C-B-Si-P-Cr-Al-(Mo,Co)-N [64,65]

Fe-based metallic glasses are very attractive as they show a high corrosion resistance. Practical applications are limited in the form of rapidly quenched ribbons and sputtered thin films. Corrosion tests on alloys $\text{Fe}_{69.9-x}\text{C}_{7.1}\text{Si}_{3.3}\text{B}_{5.5}\text{P}_{8.7}\text{Cr}_x\text{Mo}_{2.5}\text{Al}_{2.0}\text{Co}_{1.0}$ ($x = 0.0, 2.3 - 12.3$) show a significant effect of Cr content. However, corrosion resistance is quite similar to 304 grade stainless steel (Fe, <0.08% C, 17.5-20% Cr, 8-11% Ni, <2% Mn, <1% Si, <0.045% P, <0.03% S). The enrichment of Cr oxide in the passive layer and the presence of nitrides on the outer surface are believed to be the origin of the high corrosion resistance of the N-containing Fe-base amorphous alloy.

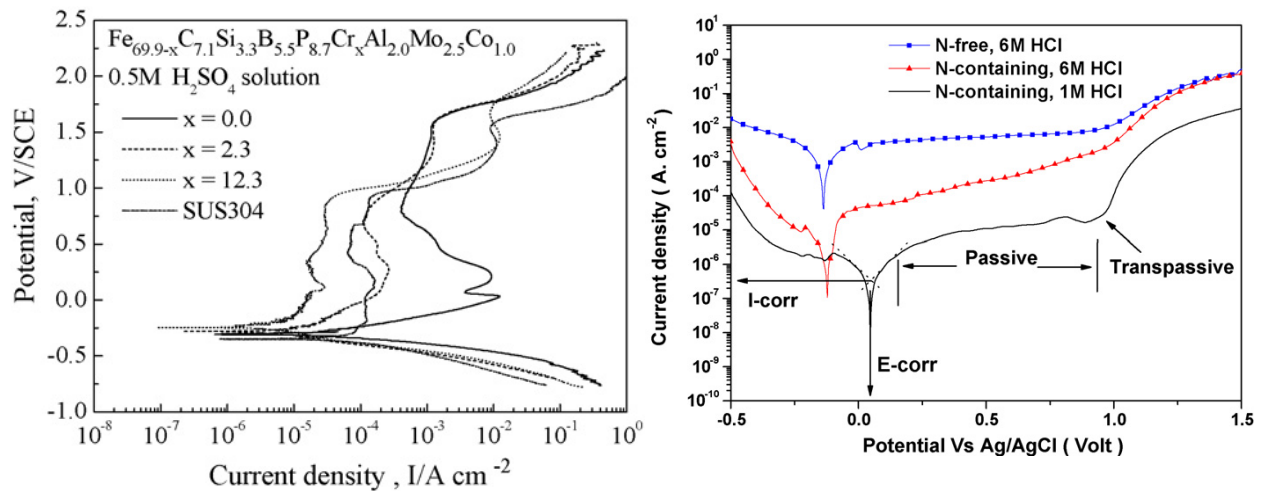


Figure 16 : corrosion curve of Fe-based bulk metallic glasses. Influence of Cr ^[65] content and N content ^[64]

% Cr	0	2.3	12.3	SUS304
Fe	703.6	501.6	8	10
Cr	0	14.3	0.87	1.1
Al	11.9	9.7	2.5	–
Mo	23	18.6	0.19	–
Co	8.7	6.7	0.06	–
Mn	–	–	–	0.5
Si	–	–	–	1
Total	747.2	550.9	11.6	12.6

Table 4 : Concentration of ions after ageing for 336h at 298K in a H₂SO₄ 0.5 M solution, determined by ICP (ppm) ^[65]

If the corrosion rate of such high chromium content iron based metallic glasses is as low as reported, electrical contact resistivity and mechanical resistance still remain open issues. Under identical condition, the Ni₆₀Nb₂₀Ti₁₀Zr₅Ta₅ alloy exhibited a current density of about 0.052 mA cm⁻². Under cathodic environment, corresponding to an operating potential of 0.6V vs. SCE under air bubbling, the passivation current for was approximately equal to 0.06 mA cm⁻², one order of magnitude lower than for the other alloys investigated.

Fleury et al. ^[66] made two iron based amorphous alloys (Fe₅₀Cr₁₈Mo₈Al₂Y₂C₁₄B₆ and Fe₄₄Cr₁₅Mo₁₄Y₂C₁₅B₆N₄) for use as bipolar plates. Both for the contact resistance and the corrosion current the published data was significantly higher compared to DOEs target. A glassy metal alloy was made by Yokoyama et al. ^[67]. From a production point of view the optimal alloy was found to be Ni₆₀Nb₂Cr₁₆-Mo₂P₁₆B₄. The contact resistance for this glassy



metal is reported to be as low as $10 \text{ m}\Omega \text{ cm}^2$ at 8 N cm^{-2} . The I–V performance of a single fuel cell with glassy bipolar plates was superior to that of one with 316 plates, but the performance was a lot worse compared to graphite plates. The corrosion rate, probably measured at open circuit, was measured to be $1.26 \times 10^{-2} \text{ mm y}^{-1}$ corresponding to a current density of approximately $1 \mu\text{A cm}^{-2}$.

Amorphous or glassy metal alloys seem to encounter the same problems as stainless steel. To use another base material than stainless steel seems to be achievable, but by using a more corrosive substrate increase the hazard if surface defects in the coating are present.

III.3.2 Carbide based layer

Tawfik et al ^[2] developed a high corrosion resistant coating which was fabricated of a full densification carbide-based amorphous alloy and applied to both aluminium and stainless steel bipolar plates. The high bonding strength between the coating and the substrate combined with comparable coefficient of thermal expansion for both metals have precluded the possibility of coating delamination.

The full coating densification nature produced by the high velocity oxygen fuel thermal spray system minimized the existence of nano/micro cracks or pinholes in the coating layer that could jeopardize its full proof corrosion protection and complete prevention of corrosive mediums from reaching the substrate.

The carbide-based coating applied on the aluminum bipolar plates for corrosion protection showed excellent durability for harsh corrosive environment inside the fuel cell.

Delblanc Bauer and J-O Carlsson (Univ. Uppsala, Sweden) deposited TiC films on Al_2O_3 substrates by CVD (9% CH_4 , 6% TiCl_4 and 85% H_2 , $1020 - 1080^\circ\text{C}$) ^[68]. Two active peaks at 800mV and 1800mV vs. SCE were recorded. The first one was attributed to the oxidation of Ti^{2+} to Ti^{3+} that immediately reacts with water to form $\text{TiO}_2 \cdot \text{H}_2\text{O}$:

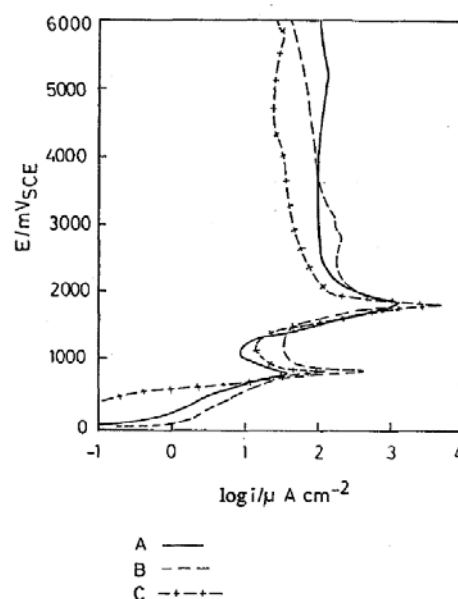
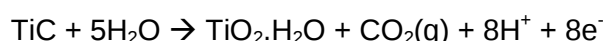
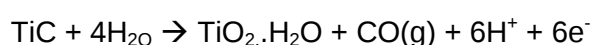


Figure 17: Polarization curves of TiC deposited on Al_2O_3 in 1M HCl at room temperature ^[68]



The second peak was attributed to the oxidation of $\text{TiO}_2 \cdot \text{H}_2\text{O}$ to $\text{TiO}_3 \cdot 2\text{H}_2\text{O}$:



TiC showed no tendency to transpassive corrosion ($< 6 \text{ V vs. SCE}$) and had a high oxygen overpotential ($> 5 \text{ V vs. SCE}$).

Y.J. Ren et al. ^[35] coated TiC on 304SS by high-energy micro-arc alloying technique (HEMAA), with a metallurgical bonding between the coating and the substrate. TiC coating increased the open circuit potential of 304SS by more than 200 mV, and decreased the corrosion current density from 8.3 A cm^{-2} for the bare steel to 0.034 A cm^{-2} for the coated steel. TiC coating did not go through degradation under the condition of potentiostatic polarization at 0.6 V vs. SCE, close to the cathode operation potential of PEMFC, and exhibited high stability during 30-day immersion. It was claimed that TiC coatings prepared by HEMAA became more compact than by PVD, and thus act as more effective barriers to the inward penetration of corrosive species.

In a patent by Laconti et al. ^[69] it was suggested to use titanium carbide casted in a polymer as bipolar plate material both for fuel cells and electrolysis cells. As shown on the following figure, the corrosion current of molded TiC-PVDF plates was below 1 mA cm^{-2} even for potential as high as 2 V. The appearance and thickness did not visibly change and a weight loss of approximatively 1%.

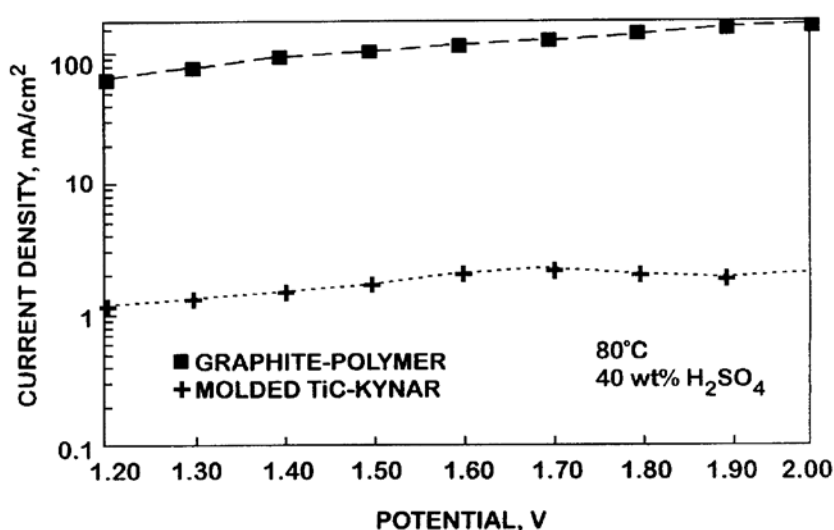


Figure 18 : Current corrosion of a graphite polymer and molded TiC+PVDF versus applied potential ^[69].

III.3.3 Nitro-carbide based layer

Lunarska et al.^[70] (Polish Academy of Sciences, Warsaw) deposited TiN and TiC layers on tool carbon steel by CVD technics (TiCl_4 , H_2 , 1000°C). Tests performed in H_3PO_4 20 wt% (pH=1) shown that TiC and TiN layers protect steel by the decrease in steel area exposed to the aggressive solution, as well as by the promotion of metal passivation.

Formation of TiN on existing TiC layers by PACVD or by TiC sputtering by nitrogen under glow discharge conditions, dramatically improves the protective ability of the coating.

Composite TiN/TiC or TiC/N layers improve the protective ability of the coating in comparison with the TiN or TiC single layers.

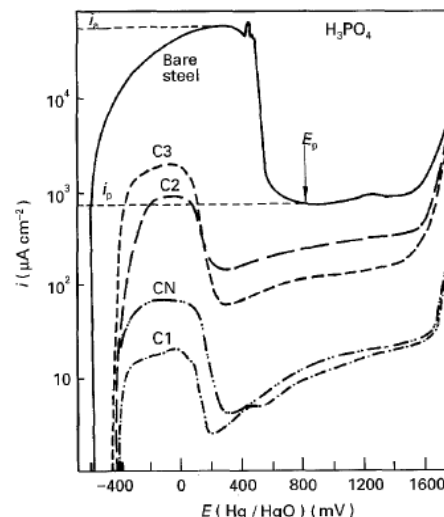


Figure 5 Polarization curves recorded in 20 % H_3PO_4 (pH 1) for bare steel and for specimens covered with LPCVD TiC under different conditions. Parameters marked: i_a , anodic dissolution current density; i_p , passive current density; E_p , passive potential.

Figure 19: Polarization curve on various samples TiC (C1, C2, C3) and TiC-TiN (CN)^[70]

- **TiCN/TiNbCN**^[71]

TiCN and ZrCN have been used as protective coating material due to their excellent properties such as extreme hardness, high thermal conductivity and resistance in severe environments. Deposited on AISI 4140 steel substrate (C :0.4% ; Silicon 0.1% ; Manganese 1% ; Chromium 1% ; Molybdenum 0.2%), by multitarget magnetron reactive rf sputtering, very thin layers and multi layers can be obtained (15 nm – 1,5 μm)



III.4 Coatings Suppliers

The (<http://www.tantaline.com/>), based in Waltham (Massachusetts, USA), proposes a CVD deposition of tantalum technique as an economical solution to protect metals against corrosion.

Impact Coatings (<http://www.impactcoatings.se/>) started as a spin-off from Linköping University in 1997. At present it functions as an interface between industrial assigners and the scientific research field when it comes to thin film coatings. Impact's vision is to be the market leading supplier of PVD technology for electrical contacts. Impact Coatings also produce PVD equipment and industrialize coatings suitable for use in e.g. fuel cell components.

Oy Kromatek Ab (<http://www.kromatek.fi/index.htm>) was established in 1990 and is a subcontractor for the Finnish metal industry which supplies electropolishing and/or hard chromium coatings. The company has around 10 employees working in production and has an extensive experience in hard chromium plating.



IV. Characterization techniques

IV.1 Corrosion test

A standard test for bipolar plate material has not been found. The most common way to test the bipolar plate material is to measure polarization curves, and measure the bulk conductivity and the contact resistance. However, for the most part the tests is not performed at potentials as high as expected at open circuit for fuel cell. Especially for metal based material, the most corrosive potential at the cathode side is at the open circuit potential. The tests were mainly performed at nominal fuel cell conditions (typically 0.8 V vs. RHE), far away from nominal electrolyzer condition (i.e. 2V vs. RHE).

For screening materials a simple electrochemical tests is a good approach but then it is difficult to separate corrosion from other types of degradation and oxygen evolution.

IV.1.1 Experimental setup

- Operating conditions

Electrochemical tests are usually performed in a three electrodes cell using a Hg/Hg₂SO₄/K₂SO₄,sat reference electrode (0.650 V vs. SHE) in order to prevent chloride contamination.

Experiment performed by J. André et al ^[17,18,75] were conducted at 60°C under gas bubbling.

- Choice of the electrolyte

Often the tests are performed at a very high concentration of sulphuric acid, some times as high as 1 M H₂SO₄ in order to accelerate the tests. When a much higher acid concentration than expected in the fuel cell environment is used there is a risk that materials that can withstand fuel cell conditions is rejected.

Kumagai et al. ^[72] investigated corrosion behavior of austenitic stainless steel as a function of pH. A huge influence both on corrosion rate and composition of the oxide layer as a function of pH was found. At pH in the range of 1.2 – 3.3, the surface consisted of mainly chromium

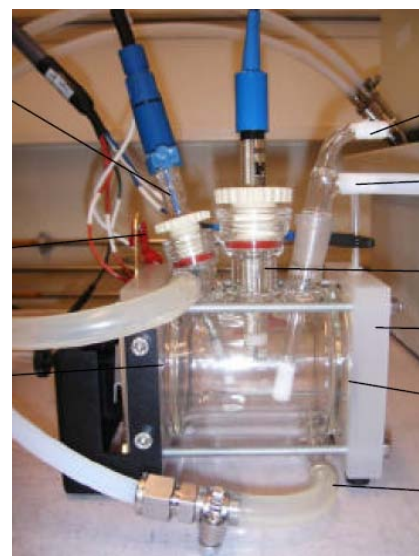


Figure 21: Example of three electrodes electrochemical cell for corrosion experiments ^[17]



oxide but at pH 4.3 and 5.5 the surface was mainly iron oxide. As expected, the corrosion rate in 0.05 M SO_4^{2-} + 2 ppm F^- at 80 °C decreased with increasing pH in the range 1.2 to 5.5.

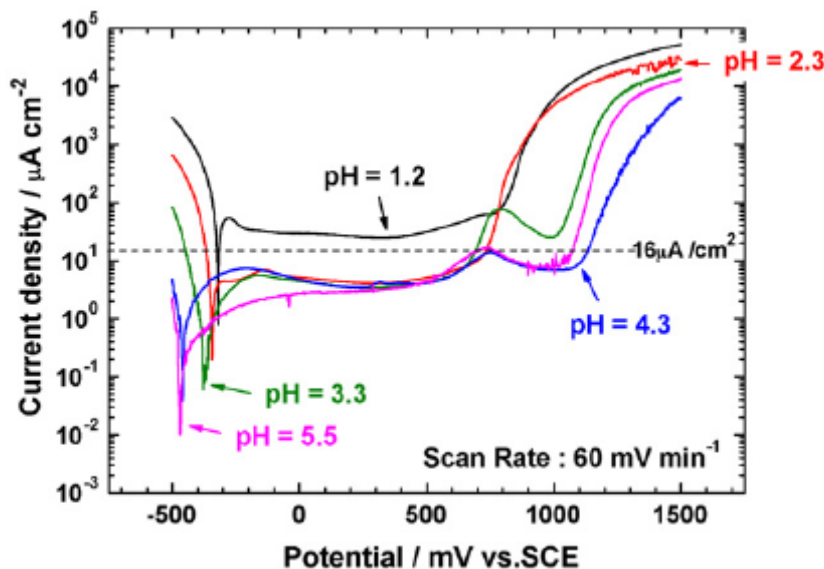


Figure 22: Anodic polarization curves for type 310S stainless steels in deaerated 0.05M SO_4^{2-} (pH 1.2–5.5) + 2 ppm F^- solutions at 353 K ^[72].

From analysis of surface oxides after fuel cell operations it was suggested that pH in an operating fuel cell was in the range of 3.3 to 5.5.

As pointed out by Mele and Bozzini ^[73], crevice corrosion has to be taken into consideration because of a crevice is formed between the gasket and the bipolar plate material.

J. André et al. ^[74] analyzed water exhausted during 1000 h single cell tests with graphite bipolar plates to define electrolytes representative of PEFC cathode and anode environments. Composition of them is given in the following table.

Table 2 – Electrolyte composition [43].							
Ion	F^-	Ca^{2+}	Na^+	Br^-	Cl^-	SO_4^{2-}	NO_3^-
Concentration in anode solution (mol/L) (pH = 3.5)	$5, 7 \cdot 10^{-4}$	$1, 26 \cdot 10^{-5}$	$2, 1 \cdot 10^{-5}$	$8, 1 \cdot 10^{-5}$	$2, 7 \cdot 10^{-6}$	$1, 3 \cdot 10^{-6}$	–
Concentration in cathode solution (mol/L) (pH = 3.5)	$4, 1 \cdot 10^{-4}$	$1, 6 \cdot 10^{-5}$	$1, 4 \cdot 10^{-5}$	$3, 2 \cdot 10^{-6}$	$2, 1 \cdot 10^{-6}$	$7, 9 \cdot 10^{-6}$	$1, 5 \cdot 10^{-6}$

Table 5: Electrolyte composition for electrochemical tests ^[18]



IV.1.2 Testing protocol

- Cyclic voltammetry

Electrochemical tests should be performed in a three electrodes electrochemical cell with a Hg/Hg₂SO₄/K₂SO₄ reference electrodes (0.650 V vs. SHE) in order to prevent chloride contamination.

After one hour of stabilization at OCV in anodic electrolyte at 60°C, with gas bubbling (nitrogen, oxygen or hydrogen). Polarization curves are recorded by cyclic voltammetry from -150 to 100 mV vs. SHE at 10 mV min⁻¹ and return to -150 mV at the same sweep rate.

- Zero Resistance Ammetry

Zero Resistance Ammetry tests consisted in 5 min stabilization of each component voltage at OCV, followed by ZRA measurement (measuring voltage and current with both components in short circuit) during 5 h.

- Impedance spectroscopy (Mott-Schottky)

Flat band potential V_{fb} and doping density (N_A or N_D) of the semiconductor surface oxide can be extracted from Mott-Schottky plots on the whole frequency range of acquisition of impedance spectra. Electrochemical Impedance Spectroscopy (EIS) should be performed in the whole potential range by steps of 100 mV. Each spectrum should be acquired twice between 0.1 Hz and 2 kHz with a peak-to-peak 14 mV sinusoidal signal after a waiting period of 8 min to ensure steady conditions (eight points per decade and five measures per frequency) ^[75].

The model used to represent the interface metal/electrolyte can be limited to a resistor R1 in series with a constant phase element (CPE) and another resistor R2, placed in parallel with this the CPE. R1 is generally attributed to ohmic drop in the electrolyte, while R2 is linked to resistivity properties of the passive film (charge transfer resistance) and the CPE, which can be represented as the association in parallel of a resistor and a capacitor both variable in frequency, can originate from surface roughness, distribution of reaction rates on the electrode surface (if polycrystalline), surface heterogeneities in the passive film composition or thickness, or current repartition (edge effects).



$1/C^2$ vs $f(E)$ could be traced on the whole frequency spectrum. V_{fb} was deduced from the intersection of $1/C^2$ with x-axis, almost independent on frequency, while N_D was extracted from the whole frequency range for each sample referring to the method proposed by Antoni et al. [76].

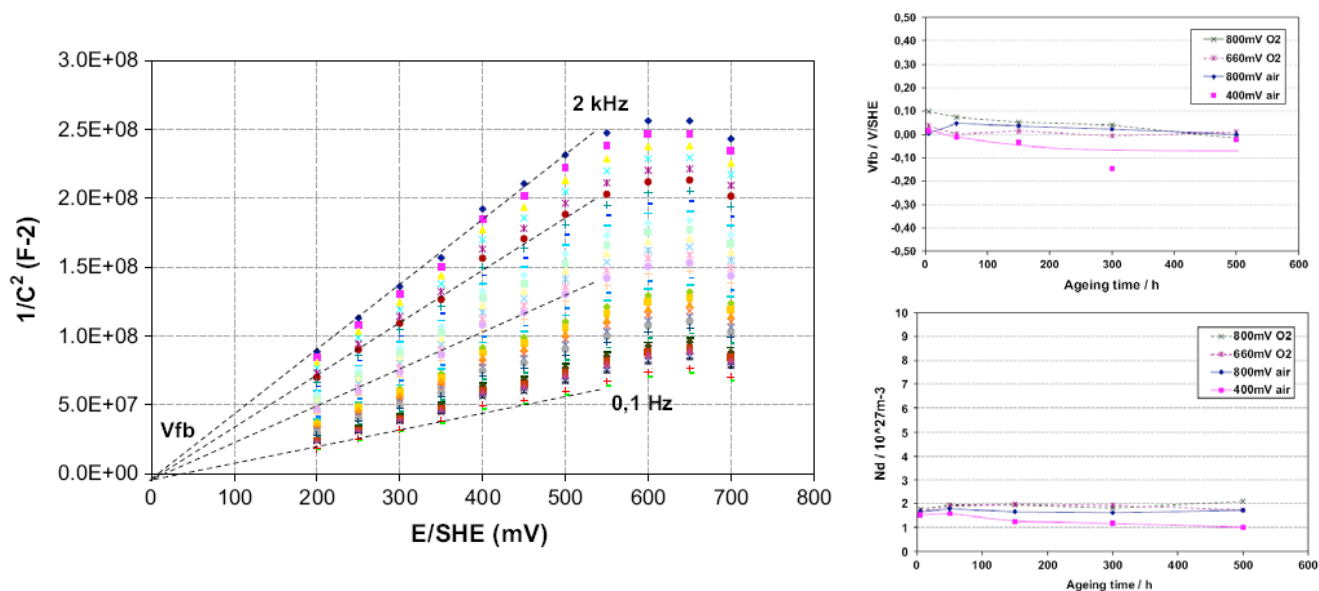


Figure 23 : Typical Mott–Schottky plot on aged 316L BA in cathodic environment: $1/C^2$ vs. $f(E)$, 800 mV/SHE, air bubbling. Flat band voltage evolution and donor density evolution with ageing time on 316L BA in cathodic environment, air bubbling [75].

Due to the semiconductor behaviour of passive films, associated to a charge carrier density inferior than in metals, a space charge layer of capacitance C_{SC} , thickness about some nanometers, where almost all interfacial voltage is established, is developed into the passive layer. Therefore, experimental accessible data, i.e. the global differential capacitance C_d of the electrode/solution interface, is assimilated to C_{SC} .

- Ageing tests

Ageing tests could consist in 500 h ageing at a fixed voltage chosen as representative as possible of electrolysis conditions at the temperature of 60°C.



IV.2 Electrical interface resistance measurements

IV.2.1 Experimental setup

Bulk resistance of materials can be deduced from 4-probe measurements using Van Der Pauw method. Contact resistance was measured between the metallic sample and a carbon felt with a 2-probe device. The metallic sample is sandwiched between two pieces of carbon felt, and compressed with two copper plots as shown below.

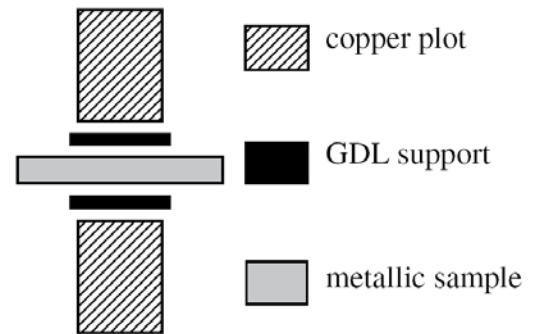


Figure 24: Schematic representation of the configuration used to determine contact resistance.

IV.2.2 Testing protocol

Experiments ^[18,77,78] were conducted while recording the electric resistance vs. mechanical pressure applied from 0 to 3 MPa at a constant compression speed of 0.2 kN/min. First measurement performed with a pair of GDL supports should systematically be always left apart to improve precision because of irreversible packing of carbon fibres.

$$ECR = R_{\text{measured}} - 2R_{C/Cu}$$

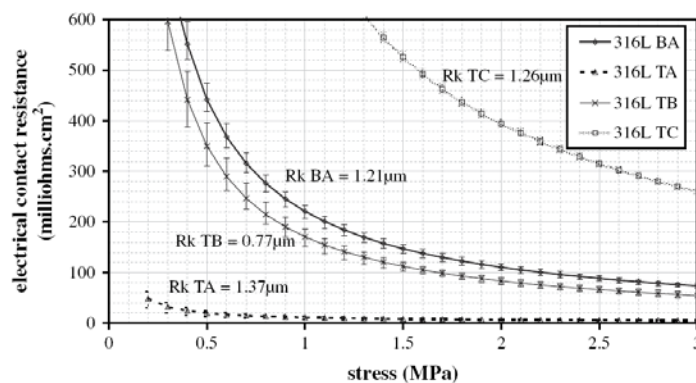


Figure 25 : Electrical contact resistance vs. stress for as received and treated 316L samples ^[18].



V. Conclusions

Bipolar plates for PEM electrolyzers are a lot more challenging than for PEM fuel cells. Chromium nitride, titanium nitride or carbon does not withstand the high anodic potentials. Titanium plates oxidizes and form electrically insulating TiO_2 at the surface.

The only viable way to solve this problem from the literature is probably to either use precious metals or tantalum. However, only a very small extent of research has been carried out.

Another way to go is probably to use conducting oxides, as used in the electrowinning industry. Lead anodes are used when electrowinning is performed in sulphate media and dimensional stable anodes (DSA) in chloride containing media. Lead oxide coatings could be evaluated as protective layers ^[79]

Porous current collectors are subject to the same problems of corrosion and electrical conductivity. Coated materials such as grid, mesh or fibre can be used to replace sintered titanium powder. We can also imagine sintering core-shell particles. The cost of the processes involved should be the main parameter to take into account.

One interesting way would be to produce porous layer directly grown on the surface of the bipolar plate. Such a layer should, obviously, be conductive and resistant to corrosion. Slurry method ^[80,81] could be evaluated as well as more "exotic" processes such as electroforming ^[82] or dissolution of space-holders ^[83].



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