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Development of Different Metallic Bipolar plates for Proton Exchange Membrane (PEM) Fuel Cells: A review

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ABSTRACT

Bipolar plates (BPs) are a key component of Proton Exchange Membrane (PEM) Fuel Cells with multifunctional character. They uniformly distribute fuel gas and air, conduct electrical current from cell to cell, remove heat from the active area, and prevent leakage of gases and coolant. Bi-Polar Plates also significantly contributes to the volume, weight and cost of Proton Exchange Membrane Fuel Cell stacks. Hence, there are vigorous efforts worldwide to find suitable materials for Bi-Polar Plates. The materials include non-porous graphite, coated metallic sheets, polymer composites, etc. This paper reviews various types of materials, in use and proposed, for Bi-Polar Plates and critically examines their physical and chemical properties.

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Introduction

The global climate changes produced by greenhouse gases emissions such as CO2, NOx and SOx that are ongoing throughout the world pose a progressively higher demand for replacing today's fossil fuel based energy production by less pollutant technologies [1,2]. Among the alternative energies available proton exchange membrane (PEM) fuel cells have been considered to power transportation vehicles such as automobiles and buses due to their high power density, relatively quick start-up, low operating temperatures and low greenhouse gas emissions [3]. All main vehicle manufacturers like General Motors, Ford, Toyota and Peugeot are developing fuel cell cars. Honda launched the first commercial fuel cell car, the FCX Clarity, in the United States market during 2008 [4]. Nevertheless, to completely achieve the automotive industry requirements PEM fuel cells have to overcome some intrinsic limitations mainly related to durability and cost compared to conventional internal combustion engines [5].

The use of lightweight metals for fuel cell bipolar plates is attractive for automotive use. High corrosion resistance and electrical conductivity requirements for fuel cell components, however, preclude most uncoated metals from use. Careful selection of alloy coatings and their constituents can reduce or control the electrochemical corrosion potential and corresponding corrosion rate of the alloy coating. New low-cost alloy coatings are being developed for aluminum that

possess the requisite high corrosion resistance and high electrical conductivity. Our current development efforts include novel electrolytic alloys and conductive polymer coatings for aluminium to achieve desired fuel cell component lifetime goals.

Development of Corrosion-Resistant Coatings for Fuel Cell Bipolar Plates

Proton Exchange Membrane Fuel Cells are of prime interest in transportation applications due to their relatively high efficiency and low pollutant emissions. Bipolar plates are the key components of these devices as they account for significant fractions of their weight and cost. Metallic materials have advantages over graphite-based ones because of their higher mechanical strength and better electrical conductivity. However, corrosion resistance is a major concern that remains to be solved as metals may develop oxide layers that increase electrical resistivity, thus lowering the fuel cell efficiency. This paper aims to present the main results found in recent literature about the corrosion performance of metallic bipolar plates.

Fuel cell

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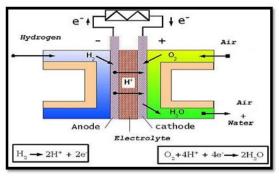
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A fuel cell is a device that converts the chemical energy from a fuel into electricity through a chemical reaction with oxygen or another oxidizing agent.^[1] Or in other words as follows.

Fuel Cells are Electro Chemical Devices consisting of an Ion Exchanging Solution, Liquid or Solid in contact with two electrodes capable of converting directly any consumable Fuels to Electrical Energy through the performance of a Chemical Reaction.



Hydrogen is the most common fuel, but hydrocarbons such as natural gas and alcohols like methanol are sometimes used. Fuel cells are different from Batteries.

In that they require a constant source of fuel and oxygen to run, but they can produce electricity continually for as long as these inputs are supplied.

Fuel Cells - Relevance and Importance

'What's so great about Fuel Cells? 'Should be a question synonymous with 'What's so great about Pollution, Changing the climate or running out of oil, natural gas and coal?'As we head into the new millennium, it is time to put renewable energy and planet-friendly technology at the top of our priorities. Dawn of this new millennium witnesses a triumphal technological march cantered on Fuel Cells! 'Clean Energy' is a technological edict that is echoing around the global.

Fuelled by concerns about environmental pollution, energy security and climate change the notion of a 'Clean Technology's moving beyond the realm of scientist and engineers and into the lexicon of political and business leaders. Energy is the lifeblood of the global economy. Getting somewhere, sharing information and producing things all

require energy. Throughout the industrial age and into the information age, energy has served as the foundation for mankind's progress.

Technology is the prime propellant of growth, modernization, progress, prosperity, power and prestige. There is no escape for us from the accelerating effect and massive impact of technology on our outlook, our life styles-social and cultural-and economic structure.

The greater the capacity of a nation to generate, transfer and utilize technology, the faster is the nation's growth. The goal is development, the tool is technology and the path is Science. Hence, Science and technologies are the chariot wheels of any development process today.

Few technologies have the potential to change the World for the better as the Fuel Cell, which offers a potentially non-polluting and renewable way to generate electricity. Fuel Cells are efficient, clean, safe and reliable. They attract increasing commercial interest for both automotive and stationary power generation. The advent of Fuel cells is powering and energy revolution.

Hydrogen represents an alternative source of energy carrier to the oil based economy. Fuel cells, harness hydrogen for energy production and thus may lead to the transition. To fully exploit the capabilities and operational advantages, the research and development of fuel cells have to confront innumerable Ichallenges and have to wait for a variety of technological breakthroughs. Fuel Cells have the potential to satisfy future energy needs.

Air and space power professionals presently review the ongoing conflicts over energy and fossil-fuel resources with the intention of making this transformation potential a reality as well as to understand the promise and limitations of fuel cell technologies, so as to take advantage of the transformation.

The attractive features of the Fuel Cells are,

- ✓ They are simple with the possibility of direct energy conversion
- ✓ They show efficiencies greater than the existing fuel burning engines and also work with a flat efficiency curve even at part loads.
- ✓ They are silent without any rotating/moving components.
- ✓ Fuel cell power plants can be constructed in modular mode to match load and increase reliability.
- ✓ Fuel and size flexibility is possible.
- ✓ Fuel cells can be exploited for Combined Heat and Power (CHP) generation with more electricity (40-45% and 35% 40% heat)
- ✓ They do not generate SOx and NOx emissions.

How fast might the energy system evolve towards Hydrogen? Energy transitions were driven by growing energy demands, local scarcities and the continual search for more abundant and accessible energy sources. the 19th century was considered to be the age of the internal combustion engine and 21st century may well come to be recognized as the age of the fuel cells.

What are Fuel Cells?

Fuel Cells are electro chemical devices consisting of an electrolyte, an ion containing solution, liquid or solid in contact with two electrodes (anode where the Oxidation of the Fuel takes place and a cathode where the reduction of Oxygen occurs) capable of converting directly any consumable fuels to electrical energy through the performance of a chemical reaction.

In the production of electricity through this mode the only by-products are Heat, Carbon Di-Oxide and Water and thus can be considered to be avoiding any of the environmental side effects. The electro chemical process in the fuel cell can be efficient converting nearly 80% of the chemical energy of the fuel into electricity in contrast to the thermal power plants which give efficiency around 40%.

In structure, Fuel Cells are similar to Batteries except that in batteries the chemical energy is stored and need to be recharged or replenished as the case may be, while in the fuel cells the fuel is constantly fed to the cell so that consistent generation of electricity is ensured.

Fuel cells can be constructed in modular form and hence fuel cell power plants can be erected to provide electricity for a number of applications ranging from electric vehicles to large grid connected utility power plants for stationary power for communities. A single cell normally produces a voltage around 1.0 V.To obtain higher voltages the cells have to be connected in series to form a stack. The heat rejected in the process can be used for different on-site thermal consumption which makes the fuel cells suitable for combined heat and power generation for building and industry.

Fuel Cells: How do they differ from Batteries?

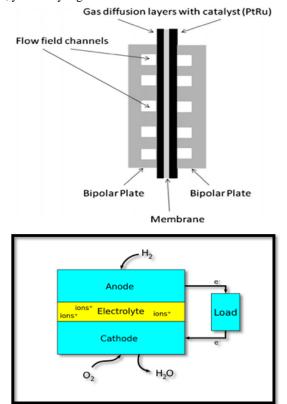
Fuel Cells have similar components and characteristics of a battery, but differ from them in several ways. A battery is an energy storage device and the extent of storage is determined by the amount of the chemical reactant stored within the battery itself. In the primary battery the maximum energy available is determined by the amount of the chemical reactant stored and will cease to produce electrical energy when the chemical reactants are consumed or discharged.

However, in a secondary battery, recharging which involves transferring energy from an external source regenerates the reactants. A fuel cell however, as stated above is energy as long as the fuel and oxidant are supplied to the electrodes. General wear and tear, electrochemical corrosion, the material stability and malfunctioning of the components may limit the life of fuel cells. Depending on the nature of the ionic species involved in the electrolytic cell, the direction of transport of these species can differ. Similarly the site of water (oxidized product) formation and removal can be different. The fuel or oxidant flows over the surface of anode and cathode and generate electrical energy by the electrochemical oxidation of the fuel (in this example hydrogen) and electrical reduction of the oxidant (usually oxygen). The electrolyte not only helps in the transport of the dissolved reactants to the electrodes but also conducts ionic charge between the electrodes and thus completes the electric circuit. The electrolyte can also act as a barrier to prevent fuel and oxidant gas streams to mix with each other, which will reduce the efficiency of the fuel cell. The functions of the electrodes in a fuel cell can be listed as follows.

The main components of a PEM fuel cell structure are bipolar plates and the membrane electrode assembly (MEA). The MEA comprises the proton exchange membrane, gas diffusion layer (GDL) and a catalyst layer. A schematic view of such structure is shown in Fig. 1.

In a fuel cell stack the bipolar plates are key elements as they account for large fractions of the total weight, volume and cost of the stack. According to Tsuchyia and Kobayashi [6] bipolar plates may reach up to 80% of the total weight and 45% of the total cost in a PEM fuel cell stack. More recent

data show that the relative cost has fallen to about 25% of the stack, yet a very significant amount.



Furthermore these components play vital functions in the stack such as to carry electric current away from each cell, to distribute fuel and oxidant homogeneously within individual cells, to separate individual cells and to facilitate the water management within the cell [8]. To perform such a number of functions a variety of materials have been proposed to the manufacturing of bipolar plates. The main properties that any material must present to be used in these devices are well established by the United States Department of Energy (DOE) as shown in Table 1. The criteria shown in this table are mustpass technical requirements that any material should be capable of achieving in order to be considered apt to a bipolar plate material.

The earlier traditional option was the use of non-porous graphite plates due to their intrinsic high electrical conductivity and chemical stability in the PEM fuel cell aggressive environment. Although the performance of graphite plates are suitable related to these properties they are brittle and lack mechanical resistance. Another drawback is the need for machining the flow field channels which raises the manufacturing cost making it prohibitive for mass production [9].Manufacturers of the next vehicle generation are targeting fuel cell power sources due to their higher efficiency operation and reduced emissions than present-day combustion processes. One of the leading candidate fuel cell systems for transportation application is the hydrogen/air proton exchange membrane fuel cell (PEMFC). Fuel cells for this application require 30 to 50 kW levels, depending on the chosen vehicle and load-levelling requirements. Attainment of such power levels is accomplished by stacking individual cells or membrane electrode assemblies (MEAs), each separated by a

The bipolar plates serve the following purposes:

- ✓ Separation of the fuel and oxidant gases,
- ✓ Rigidity for the MEA

- ✓ Electron flow through the fuel cell stack.
- ✓ To distribute the fuel and oxidant within the cell.
- ✓ To facilitate water management within the cell.
- ✓ To separate individual cells in the stack.
- ✓ To carry current away from the cell and
- ✓ To facilitate heat management.

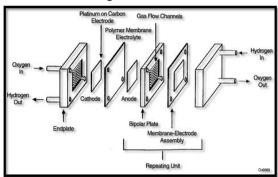
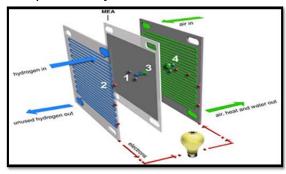


Figure 1. PEM Fuel Cell Components.

Figure 1 illustrates the components of a PEM fuel cell stack. Traditionally, these plates have been fabricated from graphite, owing to its chemical nobility, and high electrical and thermal conductivity.

The major impediments to the commercialization of PEMFCs for automotive applications are the cost, weight, and volume of the bipolar plates. State-of-the-art PEMFC stacks contain graphite bipolar plates that are either machined or moulded with a flow field arrangement for gas flow to the electrodes. To increase the structural strength and minimize gas permeation, the plates are usually relatively thick, allowing for gas channels on both sides of the plate. A typical 60-cell stack, therefore, becomes excessively large and heavy. Bipolar plates constitute the backbone of a hydrogen fuel cell power stack, conduct current between cells, facilitate water and thermal management through the cell, and provide conduits for reactant gases namely hydrogen and oxygen. In the polymer electrolyte membrane (PEM) hydrogen fuel cell design, bipolar plates are fabricated in mass production and they must be made of materials with excellent manufacturability and suitable for cost-effective high volume automated production systems.



Currently, graphite composites are considered the standard material for PEM bipolar plates because of its low surface contact resistance and high corrosion resistance. Unfortunately, graphite and graphite composites are classified as brittle and permeable to gases with poor cost effectiveness for high volume manufacturing processes relative to metals such as aluminium, stainless steel, nickel, titanium, etc. Since durability and cost represent the two main challenges hindering the fuel technology from penetrating the energy market and competing with other energy systems, considerable attention was recently given to metallic bipolar plates for their particular suitability to transportation

applications. Metals enjoy higher mechanical strength, better durability to shocks and vibration, no permeability, and much superior manufacturability and cost effectiveness when compared to carbon-based materials, namely carbon-carbon and carbon-polymer composites. However, the main handicap of metals is the lack of ability to combat corrosion in the harsh acidic and humid environment inside the PEM fuel cell without forming oxidants, passive layers, and metal ions that cause considerable power degradation. Considerable attempts are being made using noble metals, stainless steel and various coated materials with nitride- and carbide-based alloys to improve the corrosion resistance of the metals used without sacrificing surface contact resistance and maintaining cost effectiveness.

Gold-coated titanium and niobium were the materials used by General Electric in the 1960s [1] that were later replaced by graphite composites to reduce cost and weight. In recent years, due to lack of graphite durability under mechanical shocks and vibration combined with cost effectiveness concerns of its high volume manufacturability, considerable research work is currently underway to develop metallic bipolar plates with high corrosion resistance, low contact resistance, and inex-pensive mass production. Various types of metals and alloys are currently under testing and evaluation by researchers working in the field of PEM fuel cells to develop bipolar plates that posses the combined merits of graphite and metals. The ideal characteristics of a bipolar plate's material is high corrosion resistance and low surface contact resistance, like graphite, and high mechanical strength, no permeability to reactant gases and no brittleness like metals such as stainless steel, aluminium, titanium, etc.

The main challenge however is that corrosion-resistant metal bipolar plates develop a passivating oxide layer on the surface that does protect the bulk metal from progression of corrosion, but also cause an undesirable effect of a high surface contact resistance. This causes the dissipation of some electric energy into heat and a reduction in the overall efficiency of the fuel cell power stack. The key characteristics of bipolar plates material that are suitable for transportation applications are as follows:

high corrosion resistance with corrosion current at 0.1 V and H_2 purge < 16 A cm⁻²;

➤ high corrosion resistance with corrosion current at 0.6 V and air purge < 16 A cm⁻²;

- ➤ Interfacial contact resistance (ICR) @140 N cm⁻² =
- ≥ 20 m_{_} cm²;
- > does not dissolve and produce metal ions;
- ➤ possess steady low Ohmic resistance throughout the operation;
- ➤ high surface tension with water contact angle close to 90 °C, i.e. high dehydration;
- ➤ light weight;
- ▶ high mechanical strength < 200 N m⁻²;
- $\blacktriangleright \mbox{High}$ volume cost-effective manufacturability: US\$ 10 $kW^{-1}.$

Alternatives to graphite, including conductive polymers, have been explored, but with only limited success. The use of coated and uncoated metal bipolar plates has received attention recently due to the simplicity of stamping a flow field into the metal. The thin nature of the metal substrate allows for smaller stack designs with reduced weight. Table 1

lists the benefits of metallic bipolar plates, and Figure 2 illustrates this effect for an entire 33kW PEMFC stack.

From a cost perspective, inexpensive metals such as stainless steel and aluminium could easily be processed into bipolar plates. Titanium has been suggested as an alternative for the PEMFC bipolar plate material, but are better suited for aerospace applications rather than for low-cost automotive use. One of the unfortunate aspects of metallic bipolar plate materials is corrosion or oxide layer formation that lowers the electrical conductivity and severely reduces fuel cell performance. 316 stainless steel has been successfully used as a bipolar plate material by avoiding any contact with the ionexchange membrane. However, Mallant et al.1 found that PEMFCs using stainless steel bipolar plates showed about a 10% degradation in fuel cell performance over 1000 hours. Assuming, at best, a linear degradation, at least 50% of the fuel cell performance (power) would be lost over 5000 hours. Unfortunately, current design goals require greater than 5000 operating hours, as well as numerous start-stop cycles.

A few researchers have pursued coating processes to protect the metal bipolar plates. Aluminium has been coated with conductive materials by chemical vapour deposition processes and ion sputtering. These techniques require high processing temperatures, however. Low-temperature plasma spraying has been investigated, but results in severe pitting of the aluminium substrate. Both techniques require high capital equipment costs. Therefore, an effective, low-cost approach is needed to fabricate corrosion resistant coatings on aluminium bipolar plates. Below Table summarizes the anticipated cost benefit of coated metal.

Alternatives to pure graphite plates are composite bipolar plates based on the mixture of polymers and graphite particles. This class of materials allows mass production at a reasonable cost using manufacturing processes such as injection moulding for thermoplastics or BMC for thermo sets. There are several examples of graphite-based composite bipolar plates using polypropylene (PP), poly phenylene sulphide (PPS), phenolic and vinyl ester resins as matrices [10-14]. The polymer matrix gives flexibility to the bipolar plate improving its mechanical strength. The chemical stability is also not badly affected by the incorporation of polymer in graphite. On the other hand, electrical conductivity is proportionally diminished since polymers are insulating materials. Thus it is mandatory to formulate a composite bipolar plate with careful to attain mechanical performance without sacrifice electrical conductivity.

Performace requirement for proton membrane fuel cell(pem) bi-polar plates.

property	unit	value
Flexural strength – ASTM D790	MPa	>59
Electrical conductivity	S cm ⁻¹	>100
Corrosion rate	mA cm ⁻²	<1
Contact resistance	mU cm ²	<20
Hydrogen permeability	cm ³ (cm ² s)-1	<2.10-6
Mass	kg/kW	<1
Density – ASTM D792	g cm ⁻³	<5
Thermal conductivity	W (m K)-1	>10
Impact resistance	J m ⁻¹	>40,5
(unnotched) ASTM D-256		

In spite of all the advantages of graphite-based composite bipolar plates regarding to their low weight, high production and chemical stability, if one compares their overall performance with that of metal bipolar plates two major drawbacks become evident, that is, their lower mechanical resistance and electrical conductivity. Considering especially transportation applications metal bipolar plates are more resistant to mechanical shocks and vibrations that could lead to cracking and leaking of reactant gases. Cunningham [15] presented data showing that the electrical conductivity of metal bipolar plates may reach up to 1000 times that of composite ones. In addition, they present easy manufacturability at low cost which increases their competitiveness in the fuel cell market [16]. However, a significant handicap that may decrease metal bipolar plates' performance is the susceptibility to corrosion in the acid and humid environment of PEM fuel cells. Metals operating in the fuel cell with a pH of 2-4 and temperatures around 80 -C may suffer dissolution. The ions leached may poison the membrane electrode assembly (MEA), decreasing the power output of the fuel cell [17,18]. Furthermore, passive layers formed during operation increase the electrical resistivity of metal bipolar plates. Consequently, the fuel cell efficiency is also negatively affected due to the raising of interfacial contact resistance as the oxide layer grows. These effects offset the advantage of high electrical conductivity [19].

Physical and chemical properties of BP materials

Functions	Physical or chemical properties
Distribution and management of fuel	H2 permeability (dry, non-porous
and oxidants and residual gases and	plates), bubble pressure (wet,
liquids	porous plates), corrosion resistance
Conduct electrical current	Electrical conductivity
Facilitate heat management	Thermal conductivity
Separate the individual cells in the	Compressive strength
stack	

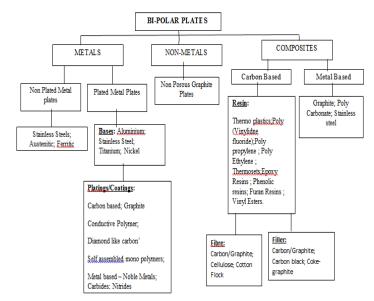


Fig 2. Classification of materials for BPs used in PEM fuel cells.

The problems outlined above may be overcome or minimized by protecting metal bipolar plates from the corrosive fuel cell operating conditions with coatings [20]. A wide variety of alternatives have been proposed in research works towards this objective. This paper aims to present major research topics and results in the corrosion protection and characterization of metal bipolar plates for PEM fuel cells. Different coating methods and substrate materials are addressed giving a comprehensive overview on this subject.

Design Criterial for Bi-Polar Plate Materials

S1.No	Material Selection Criteria	Limit	
1	Chemical Compatibility	Anode face must not produce disruptive hydride layer. Cathode face must not passivate and become non	
		conductive.	
2	Corrosion	Corrosion rate < 0.016 mA cm-2	
3	Cost	Material + Fabrication, US\$ 0.0045 cm-2	
4	Density	< 5 g cm3	
5	Dissolution	Minimization of Dissolution(For Metallic Plates)	
6	Electronic Conductivity	Plate Resistance < 0.01 ohmcm3	
7	Gas diffusivity/impermeability	Maximum average gas permeability <1.0X10-4cms-1cm-2	
8	M anufacturability	Must be low with high yield	
9	Recyclable	Material can be recycled during vehicle service, following a vehicle accident or when vehicle is retired.	
10	Recycled	Made from recycled material	
11	Stack Volume/kW	Volume < 11/kW	
12	Strength	Compressive Strength 22lb-in-2	
13	Surface Finish	>50 micro meter	
14	Thermal Conductivity	Material should be able to remove heat effectively.	
15	Tolerance	>0.05 mm	

Different low cost metals has been selected and precious and non-precious metal platins has been done and it's corrosion resistant was evaluated in order to use the same as alternate Bi-Polar Plates in PEM Fuel Cells

S1.No	Different Metals with Platings Explored as to		
	use it as Bi-Polar Plate for PEM Fuel Cell		
1	Gold Top Coat Layering		
2	Stainless Steel Layering		
3	Titanium Nitrate Layering		
4	Nickel Layering on Aluminium Substrate		
5	Nickel Layering on MS		
6	Nickel Layering on Brass		
7	(Nickel+Gold) Layering on Brass		
8	(Nickel+Gold) Layering on MS		
9	(Zinc+Gold) Layering on Aluminium		
10	(Nickel+Gold) Layering on Galvanized Iron		
11	(Nickel+Gold) Layering on SS304		

To demonstrate feasibility of replacing graphite with aluminium for PEMFC bipolar plates required Four steps:

- 1) Identification of a corrosion-resistant coating,
- 2) Confirmation of mechanical integrity of coating over the temperature range of PEMFC operation,
- 3) Fabrication of the bipolar plates, and
- 4) Operating performance evaluation and comparison with graphite. Experiments were conducted to meet these demonstration goals.

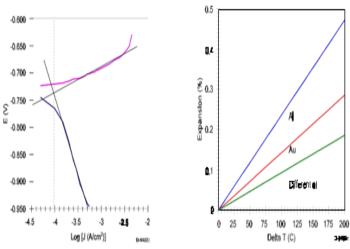
Corrosion Testing

High corrosion resistance is a necessary condition for PEMFC bipolar plate coatings since the operating environment is extremely corrosive. Typical assembly layouts require intimate contact of the bipolar plate and carbon electrodes on a solid polymer electrolyte. An abundant proton source coupled with large potential fields provides the pathway for electro-chemical corrosion. There are numerous corrosion resistant metallic and alloy coatings commercially available, which can be electrodeposited. However, few are adaptable to bipolar plate coatings since the mechanism for corrosion protection is the rapid formation of a stable surface oxide (passivation) which prevents further corrosion. Unfortunately, such oxides are usually not very conductive which departs from the high electrical conductivity requirement of PEMFC bipolar plates.

Toward the goal of identifying candidate materials for coating aluminium bipolar plates, several different metals and alloys were evaluated for corrosion resistance. Faraday's law normalized to time and exposed surface area of the material gives the corrosion rate:

Rcorr = (ja) / (nF)

Differential Thermal Expansion of Gold on Aluminium

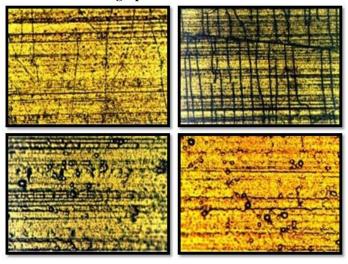


Prior to corrosion testing of the electrodeposits, pure foils of each material were obtained and corrosion tested. This screening process significantly reduced the time and expense of preparing electro- deposits of each material in-house. Following the screening tests, confirmation experiments were conducted on copper and nickel coatings plated on aluminium substrates. The corrosion rates for these electrolytic coatings matched the corrosion rates for the pure foils. Finally, electrodeposited coatings of candidate corrosion resistant materials were prepared and corrosion tested. The results of these corrosion tests are summarized in Table 3 As expected, materials such as aluminium, copper, nickel, and tin are very susceptible to electrochemical corrosion in acidic solutions, typical of PEMFC operating conditions. However, materials such as gold and phosphorous nickel show very high resistance to electrochemical corrosion, comparable to graphite, the traditional bipolar plate material. materials were selected for further study. It is important to note that while thick coatings of gold would be prohibitively expensive for vehicle PEMFCs, gold coating thickness of less than 2 µ m provides adequate corrosion protection and were re-evaluated for economic feasibility.

Corrosion	Data	for	Pure	Metals	and	Commercial
Allov Coatings						

Material	Corrosion Rate (µm/year)
Aluminum	~ 250
Copper	> 500
Gold	< 15
Graphite	< 15
Nickel	> 1000
Silver	< 15
Tin	> 10000
Titanium	< 100
Tungsten	< 100
Zinc (zincate)	> 2000
Gold-nickel	
Phosphorous Copper (electrolytic)	~ 500
Phosphorous Nickel	< 30
Stainless Steel (316)	< 100
Tin-Zinc	
Zinc-Nickel	

Photomicrographs of Gold-Plated Aluminium



Little or no micro cracking of the gold coating is seen here as with Figure 6(a). This may suggest that micro cracking of the gold is a result of internal stress. Figure 6(d) shows the surface following thermal cycle tests. Here, only a few micro cracks are present on the surface of the gold coating. A comparison of Figures 6(b) and 6(d) suggest that coating failure is preventable by controlling the CTE mismatch. Following the thermal cycle tests on these coupons, corrosion tests were performed to confirm the results of our visual inspection. Table 4 summarizes the corrosion test data for the 2 μ m thick gold deposits. It is immediately obvious from these data that the corrosion measured was that of the underlying material, and not the gold outer layer. This is likely due to the micro cracks in the gold outer layer observed during optical inspection. Such Cracks in the gold coating are apparently sufficient to allow corrosion of the preceding layer. This hypothesis can be confirmed by comparing the as-plated gold over aluminium sample (6a) corrosion rate with that of zincates (from Table 3), which was the processing step used to prepare aluminium for subsequent electro deposition steps.

The corrosion rates are very similar. The same comparison can be made for the As-plated gold over nickel over copper over aluminium sample (6c). This corrosion rate matches that

of nickel which is the coating layer preceding gold. The lower corrosion rates for the thermally cycled samples, despite the obvious mechanical degradation observed during optical inspection is likely a result of an oxide formation on the coating layer below the gold. The underlying surfaces of zinc (6a) and nickel (6c) passivate very quickly at thermal cycling temperatures near 300 C, thus providing additional corrosion protection. As previously discussed, oxide formation is the mechanism for corrosion protection for many metals and alloys.

2.1.1Bare substrates

Stainless Steel

It is generally agreed that stainless steels are prone to chemical attack in the PEM fuel cell environment. Their corrosion products may poison the catalysts in the polymeric membrane and the oxide layer grown on the metal surface increases the interfacial contact resistance decreasing the power output of the fuel cell [21]. The criterion to select stainless steels for bipolar plate applications sharply depends on the chemical composition of the material as the nature and content of alloying elements strongly influence the composition of the passive film formed on the metal surface which in turn affects its overall corrosion resistance. Hornung and Kappelt [22] used the pitting resistance equivalent (PRE 1/4 %Cr b 3.3x %Mo b 30x%N) to rank and select different iron-based materials for bipolar plates. The authors compared the performance of these alloys with nickel-based and goldcoated iron-based alloys. The alloys composition was not given in the text. Only the gold-coated alloy presented suitable contact resistance. Kim et al. [23] have also investigated stainless steels contact resistance for eleven different alloys exposed to sulphuric acid solution to simulate PEM fuel cell environment. They showed extensive results joining PRE numbers with transpassive potentials and contact electric resistance (CER) values. Chromium and molybdenum contents were found to be decisive for decreasing CER values.

The work of Wang et al. [17] compared the electrochemical behaviour of 316L, 317L, 349_ and 904L stain-less steel grades in simulating fuel cell anode and cathode environments. The authors related the Cr content with the corrosion and interfacial contact resistances of the material. The results pointed towards the following performance order 349_ >904L > 317 L > 316L. This order shows that the higher the Cr content the higher the corrosion resistance. It was verified that the thickness of the passive layer on the 349_ grade was constant with time when the material was polarized at 0.6V during 30 min. obviously this period is too short for a definite and accurate conclusion. However the results clearly allowed stating that 349_ is the best candidate for bipolar plate applications. An important fact, not mentioned in Wang's paper is the influence of both nickel and molybdenum contents on the contact resistance of the passive films formed on stainless steels.

2.12Surface treatments

Lee et al. [36,37] suggested an electrochemical surface treatment on stainless steel bipolar plates to improve their corrosion resistance and minimize the formation of a thick oxide layer that increases interfacial contact resistance during operation. The results showed an increase in the breakdown potential and a decrease in the corrosion current density after treatment.

They ascribed this superior behaviour to the Cr enrichment of the oxide layer as verified using electron spectroscopy analysis. No details on the composition of the

electrolyte used to perform the electrochemical treatment were given in the text. Cho et al. [38] evaluated the corrosion resistance of chromized 316L in PEM fuel cell simulating conditions. The chromium layer was produced by a pack cementation process. The treatment was effective with regard to the improvement of corrosion resistance of bare 316L. The lowest values of current density as shown by potentio dynamic and potentio static tests were obtained for a 2.5h period of treatment. These results were due to a Cr-rich layer with few defects. In a more recent investigation [39], the same authors used another pack cementation process to produce corrosion resistant chromized 316L stainless steel bipolar plates. They varied the Cr content in the powder mix used for the Cr pack cementation and the heating time during the chromizing treatment. The microstructure of the chromized layer was found to be strongly related to these process parameters.

2.1.3 Platings

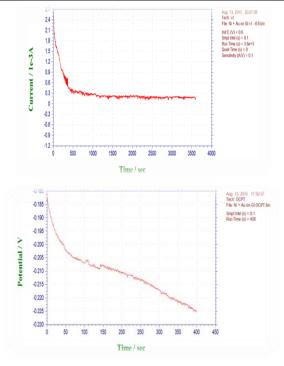
The use of corrosion resistant and high conductive coatings is another surface modification technique envisaged as a solution to the lack of corrosion resistance of metal bipolar plates. A physical vapour deposition (PVD) method was used by Li et al. [55] to deposit titanium nitride (TiN) coating on 316L stainless steel bipolar plate as an alternative to protect the materials against the corrosive electrolyte of PEM fuel cells. Potentio-dynamic polarization curves showed that the corrosion current density and passive current density of 316L were both decreased after the deposition of TiN, while the corrosion potential was shifted to nobler values. Furthermore, no signs of pitting were identified in the coated 316L specimens while in the bare specimens the polarization curves presented a breakdown potential at around 700 mV_{SCE}. Despite the Promising electrochemical performance of TiNcoated 316L one concern was pointed out by the authors. Using SEM they found that the coating was lost on small areas on the material surface after 1000 h of immersion under cathodic conditions and after 240 h of immersion under anodic conditions. Consequently larger substrate areas may be exposed to the electrolyte with the increase of immersion time. This behaviour has been ascribed to the presence of intrinsic defects on the coating layer such as pinholes and macro particles that are inherent to PVD techniques [56]. A SEM micrograph of a PVD TiN-coated 316LSS is presented in Fig. 2. The defects of PVD film are clearly seen in this image.

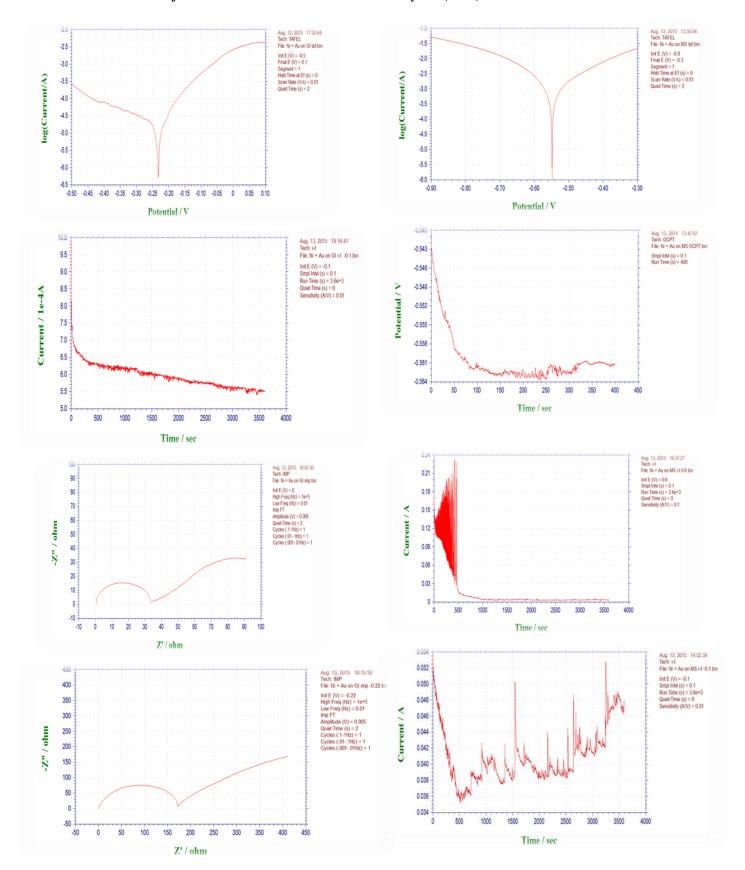
In order to avoid this effect Li et al. suggested changes in the deposition parameters to improve the coating quality. Cho et al. [57] have also found that TiN coating on 316 stainless steel substrate provided good electrochemical performance in the fuel cell environment. However, they identified a coating degradation phenomenon responsible for increasing the charge transfer resistance and, in addition, lowering the ionic conductivity of the membrane due to poisoning by Fe, Cr, Ni and Ti ions released by the 316 substrate and TiN coating. Wang and Northhwood [58] conducted potentio dynamic testes with TiN-coated 316L stainless steel specimens and verified a drastic decrease of the corrosion current density. On the other hand, under potentio static conditions there was a three-fold increase in the current density at cathode simulating operation. This behaviour was related by the authors to pitting corrosion due to the penetration of electrolyte through coating defects. The same authors [59] evaluated a TiN-coated martensitic stainless steel bipolar plate and found that the corrosion rate was decreased by two orders of magnitude in comparison with the uncoated material. Jeon et al. [60] investigated the influence of N₂ gas pressure during the

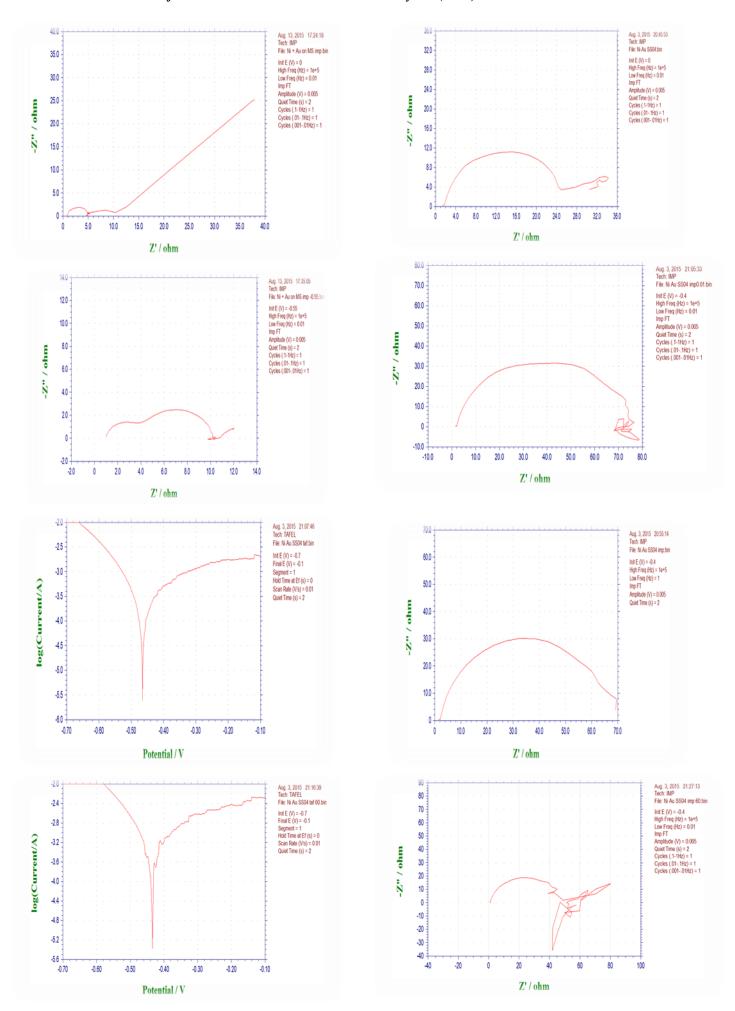
deposition process over the corrosion resistance of TiN-coated 316L stainless steel under simulating PEM fuel cell environment. They found marked differences in corrosion current density and charge transfer resistance values depending on the $\rm N_2$ pressure. The variations were ascribed to the porosity of the coatings which were dependent on the $\rm N_2$ pressure employed during the deposition process. The best performance was related to the coating with the lowest porosity percentage. This result was confirmed through SEM images of the coatings surfaces.

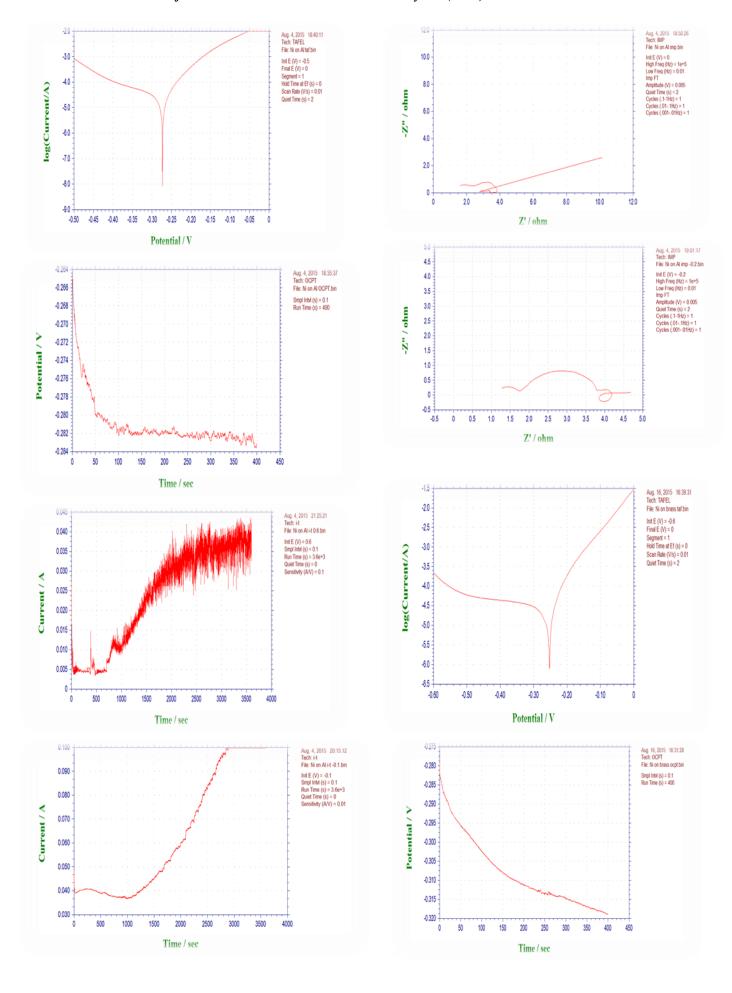
Different low cost metals has been selected and precious and non-precious metal platins has been done and it's corrosion resistant was evaluated in order to use the same as alternate Bi-Polar Plates in PEM Fuel Cells.

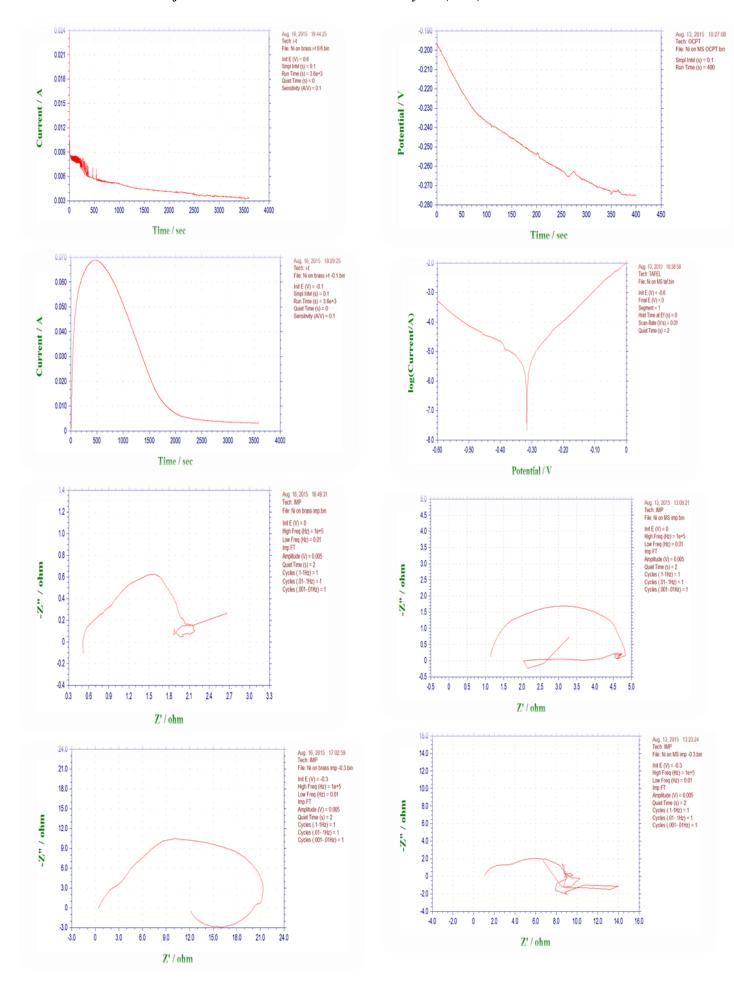
	liternate Bi-Polar Plates in PEM Fuel Cells.				
S1.No	Plating Method	Plating Processes followed			
1	Gold Top Coat	Pulse Current Electrode Deposition			
	Layering				
2	Stainless Steel	Physical Vapour Deposition (PVD)			
	Layering	(Example, Magnetron Sputtering) or			
		Chemical Vapour Deposition (CVD)			
		and Electro less Depositions for Ni-Pt			
		Alloy.			
3	Titanium Nitrate	RF-Diode Sputtering			
	Layering				
4	Nickel Layering on	Chemical Vapour Deposition (CVD)			
	Aluminium				
	Substrate				
5	Nickel Layering on	Chemical Vapour Deposition (CVD)			
	MS				
6	Nickel Layering on	Chemical Vapour Deposition (CVD)			
	Brass				
7	(Nickel+Gold)	Physical Vapour Deposition (PVD)			
	Layering on Brass	(Example, Magnetron Sputtering)			
8	(Nickel+Gold)	Physical Vapour Deposition (PVD)			
	Layering on MS	(Example, Magnetron Sputtering)			
9	(Zinc+Gold)	Physical Vapour Deposition (PVD)			
	Layering on	(Example, Magnetron Sputtering)			
	Aluminium				
10	(Nickel+Gold)	Physical Vapour Deposition (PVD)			
	Layering on	(Example, Magnetron Sputtering)			
	Galvanized Iron				
11	(Nickel+Gold)	Physical Vapour Deposition (PVD)			
11		Physical Vapour Deposition (PVD) (Example, Magnetron Sputtering)			

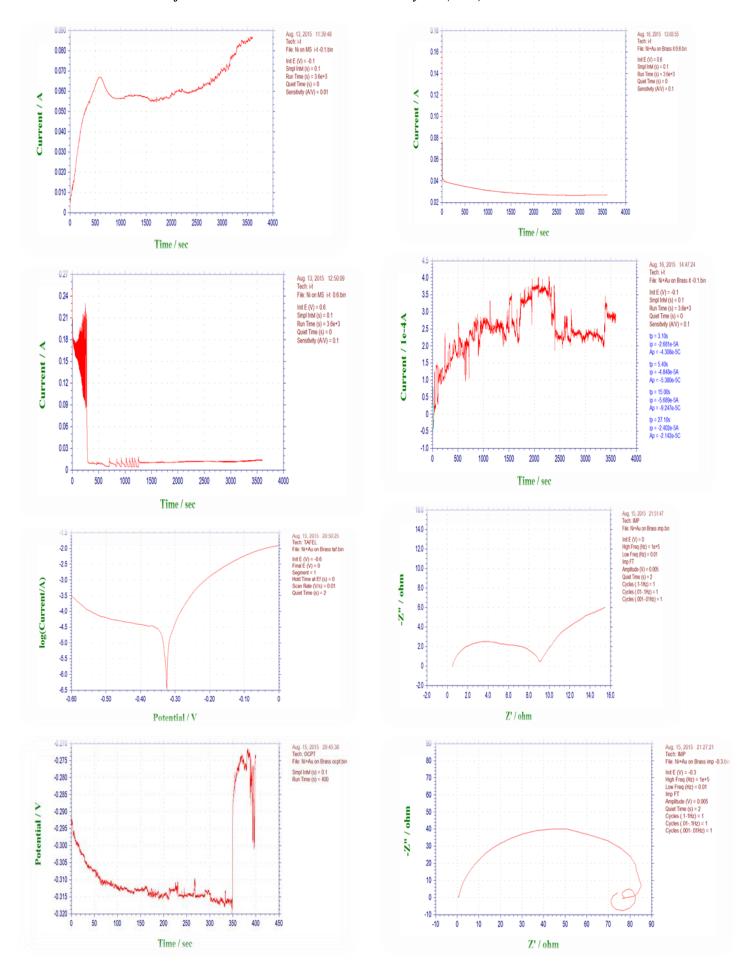


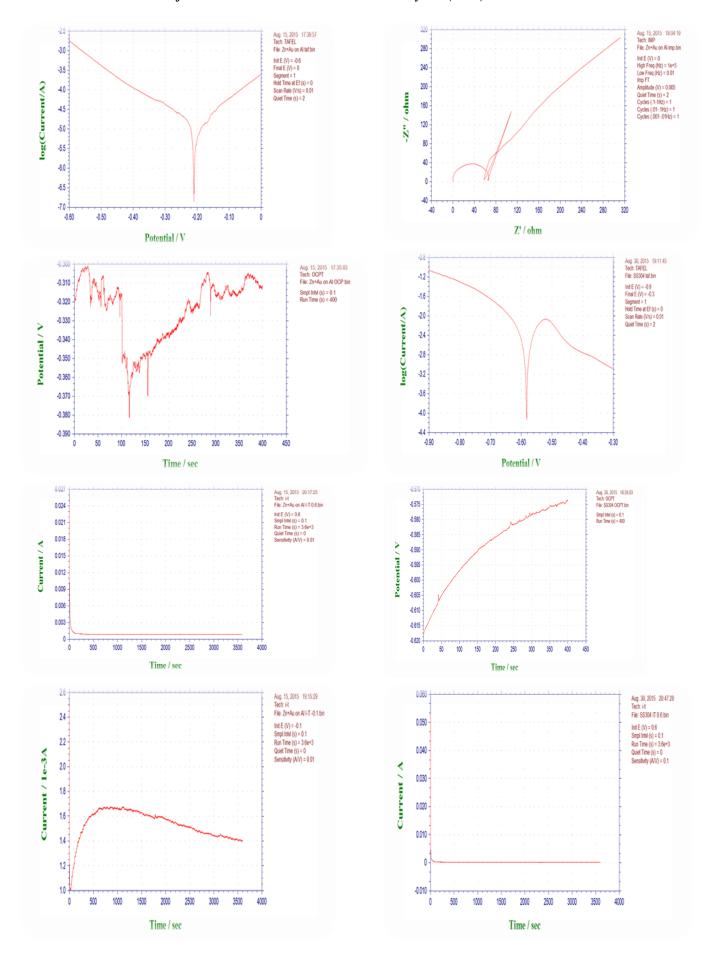


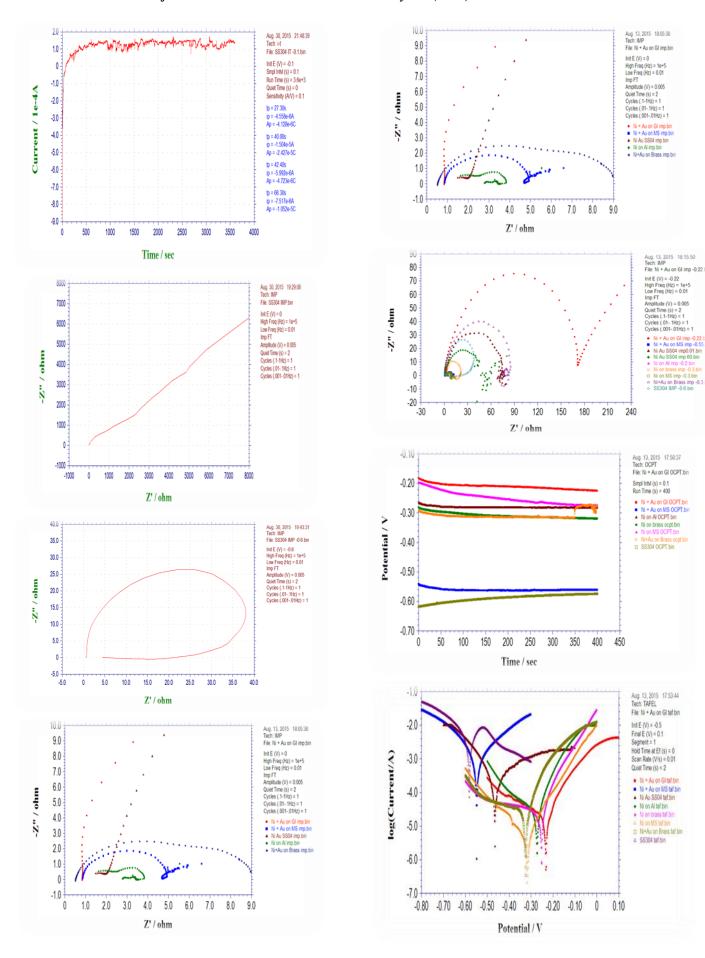












0.8

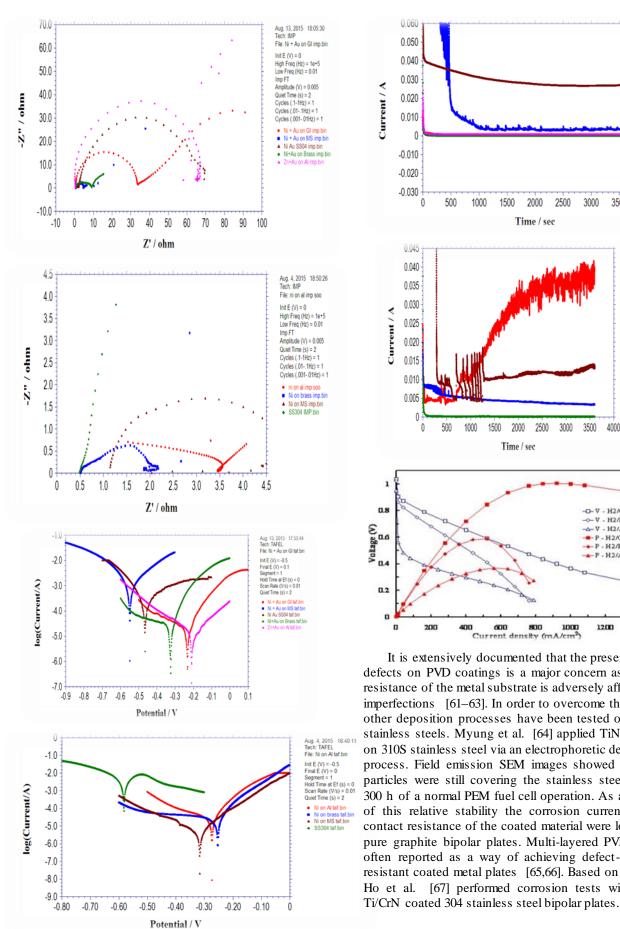
Voltage (V)

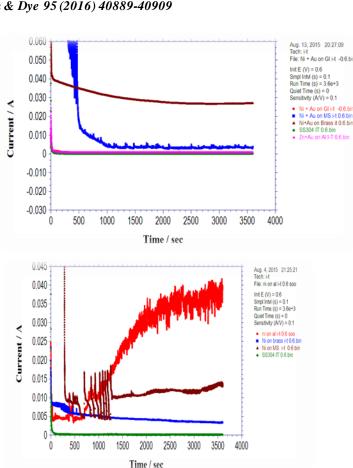
0.4

0.2

0

200





400

350

300

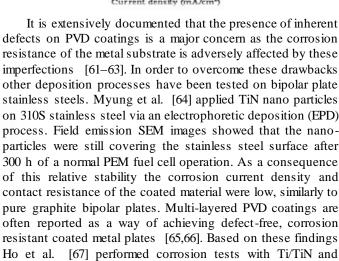
-O-V - H2/O2 H2/Pure

-- V - H2/Air

-P-H2/O2 -P - H2/Air

1200

1400



800

600

Bias Power Supply	10 KW	
Pulsed DC - Advance Energy		
Frequency	150 KHz	
Duty Cycle time	0.5 Micro Secs	
Voltage	350 to 600 Volts	
Etch Current	6.5 to 9.0 Amps	
Etching Duration	12 Mins	
Ramping Duration	4 Mins	
Argon Gas flow	300 S C C M	
Glow Vaccum	2.2 Pa	





Prototype one-cell PEM fuel cell stack with Graphite bipolar/end plates (left hand side), Aluminum Bipolar/end plates coated with Gold (Au) (middle side) and Pure Aluminum Bi-Polar/end plates (right hand side).

Scale Up Issues and Thermal Management

PEMFCs unlike other types of fuel cells show some loss of efficiency and power density with scale up of areas of electrodes and increase in no. of cells in a stack. The main reason is that remove of the product-liquid water-becomes difficult in large systems; further, a high water vapour pressure in the reactant flows, causes an increase in overpotential, especially at the cathode.

In addition, water condensation, electrode flooding and occlusion of the gas channels can occur, leading to operational failure. An issue strongly related to water management is that of thermal management in stacks; on one hand, too low temperatures cause water condensation problems, but on the other hand, even more important, is that high cell temperature(even in confined areas)leads to membrane dehydration and consequent loss of performance. The 'rule of thumb' for the evaluation of heat losses in PEMFCs is that the power dissipated as heat is approximately equal to the electrical power supplied to the external circuit(deviations from this simple rule is noticed at high current densities and low voltages).

Bi-Polar Plates for Research Work

METALLIC BI-POLAR PLATE



Pure Aluminum Bi-Polar/end plate with machined multi-parallel channel gas flow-field design designed and developed.

PEM FUEL CELL – MAJOR COMPONENTS

- ✓ Electrode –Pt catalyst used✓ Membrane-"NAFION"
- Most commonly used



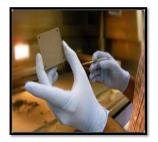




Gold Plated Aluminum

Gold Plated Aluminum Bipolar Plates Shown in Gas





GOLD PLATED ALUMINIUM BI-POLAR PLATE

DEVELOPED GOLD PLATED ALUMINUM Bi-POLAR PLATE



Gold-Plated Aluminum Bipolar/end plate with machined multi-parallel

PURE ALUMINIUM BI-

GOLD PLATED ALUMINIUM BI-





PROTO TYPE ONE CELL PEM FUEL CELL STACK WITH GOLD PLATED



Design Criterial for Bi-Polar Plate Materials.

S1.No	Material Selection Limit		
	Criteria		
1	Chemical	Anode face must not produce	
	Compatibility	disruptive hy dride layer. Cathode	
		face must not passivate and become	
		non conductive.	
2	Corrosion	Corrosion rate < 0.016 mA cm-2	
3	Cost	Material + Fabrication, US\$ 0.0045	
		cm-2	
4	Density	< 5 g cm3	
5	Dissolution	Minimization of Dissolution(For	
		Metallic Plates)	
6	Electronic	Plate Resistance < 0.01 ohmcm3	
	Conductivity		
7	Gas diffusivity/	Maximum average gas permeability	
	impermeability	<1.0X10-4cms-1cm-2	
8	M anufacturability	Must be low with high yield	
9	Recyclable	Material can be recycled during	
		vehicle service, following a vehicle	
		accident or when vehicle is retired.	
10	Recycled	Made from recycled material	
11	Stack Volume/kW	Volume < 11/kW	
12	Strength	Compressive Strength 22lb-in-2	
13	Surface Finish	>50 micro meter	
14	Thermal	Material should be able to remove	
	Conductivity	heat effectively.	
15	Tolerance	>0.05 mm	

Corrosion Data for Electrolytic Coatings on Aluminium

	Corrosion Rate
4a. Gold over aluminium, as plated	~ 3000
4b. Gold over aluminium, thermally-cycled	~ 2000
4c. Gold over nickel over copper over aluminium, as	~ 1000
plated	
4d. Gold over nickel over copper over aluminium.	~ 750
thermally cycled	

The coatings have been deposited using a cathodic arc deposition system. The good corrosion resistance of the multi-layered coatings has been confirmed as the corrosion current densities were lower for the material coated with these coatings in comparison with the bare or single layer coated one. This behaviour has been ascribed to the structure of the multi-layered coatings that inhibit the direct path between corrosive environment and the steel substrate. Choi et al. [68] showed that ternary (Ti,Cr) N_x coatings produced by

inductively coupled plasma magnetron sputtering enhance the corrosion and electrical performance of 316L stainless steel in a simulated PEM fuel cell environment. The coating prevents the formation of oxygen on the surface of the material and act as an effective barrier between the substrate and the electrolyte. Fukutsuka et al. [69] used plasma assisted chemical vapour deposition process to produce a carbon layer on 304 stainless steel bipolar plate. The corrosion rate of the coated material was less than 1 mA cm⁻² reaching therefore the US DOE technical target for bipolar plate [70]. Chung et al. [71] also evaluated the corrosion performance of a carbon coated 304 stainless steel bipolar plate. The carbon layer was produced via a chemical vapour deposition method using a C₂H₂/H₂ mixed gas as carbon source. Depending on the acetylene to hydrogen ratio the coating morphology varied from a filamentous porous layer to a continuous carbon coating. For the latter morphology the corrosion resistance was found to be high reaching the performance of commercial pure graphite bipolar plate (Poco graphite). Fu et al. [72] found that a C-Cr composite coating greatly decreased the interfacial contact resistance and corrosion rate of 316L stainless steel. They used a pulsed bias arc ion plating (PBDIP) deposition method which was chosen due to the low temperature, dense layer with few droplets that favour the final corrosion performance of the base metal. Feng et al. [73] investigated the performance of an amorphous carbon coated 316L stainless steel bipolar plate in a PEM fuel cell environment. They reported promising results of corrosion resistance under potentio dynamic and potentio static conditions and interfacial contact resistance. The dense and compact nature of the deposited film allied with the intrinsic high chemical stability and electrical conductivity of the carbon layer are responsible for the high desirable performance of the amorphous carbon coating

2.2. Aluminium

Aluminium may be considered for bipolar plate applications in PEM fuel cells due to the low manufacturing cost [89]. It is well propelled, though, that aluminium and its alloys do corrode in the fuel cell environment leaching ions that contaminate the membrane, decreasing the cell output [90,91]. Regardless this limitation, coated-aluminium bipolar plates may reach DOE technical targets [92]. Joseph et al. [93] found that PANI-coated 6061 Al alloy showed very good corrosion resistance compared to the uncoated substrate. The corrosion rate was up to 10^{-8} A cm⁻² for a 40mm thick layer. However, no information about coating degradation in longterm immersion tests is reported in this paper. PPy coating, on the other hand, presented a corrosion current density of the same order of magnitude than that of the bare alloy. According to the authors the lack of corrosion resistance in this case was due to the pinholes on the polymer layer after deposition.







PEM FUEL CELL – MAJOR COMPONENTS

- ✓ Electrode –Pt catalyst used
- ✓ Membrane-"NAFION" Most







Gold Plated Aluminum

Gold Plated Aluminum

Effects of ion contamination on PEM fuel cell performance

Notwithstanding the crucial role of corrosion processes over the increase of the interfacial contact resistance of metal bipolar plates the effects of the resultant cationic contaminants on membrane conductivity should not be neglected. It is very probable that, in real PEM fuel cell systems, contaminants originated from several different sources pois on the membrane decreasing the overall power output. Cheng et al. outlined all these sources of membrane contamination in a recent review paper [107]. Cationic impurities are released after corrosion of bipolar or end plates and even of the fuel cell piping system. Collier et al. [108] cited the presence of Fe^{3b}, Cu^{2b} and other cations in a unit cell MEA after 10,000 h of operation. According to Cheng et al. [107] almost all cations exhibit higher affinity for the sulfonic groups in the polymeric membrane than H^b. Hence, when other cations exchange for protons in the polymer structure, the amount of water in the cell is reduced

3. Conclusions

There is a wide variety of materials and surface modification methods available for metal bipolar plate development. It is evident that the major challenges regarding to a successful commercial use in PEM fuel cells are related to increasing corrosion resistance and decreasing contact resistance at a reasonable cost. Table 2 summarizes the literature findings on the corrosion data found on all the papers reported in this review. Few materials present a suitable combination of corrosion current density and contact resistance according to DOE targets. Depending on the reference consulted different values of corrosion current density have been found for the same material, especially for 316LSS. These values may vary as a function of electrolyte composition, pH and temperature, specimen surface finishing and small variations on the composition of the material itself. Although there is a plenty of information on the corrosion resistance of metal bipolar plates, long term results are often missing on most part of the literature reports. Prospective materials for BPs of PEM fuel cells have been reviewed. From the utilitarian point of view, the benefits and drawbacks of each type of BP material are summarized.

Sustainable Energy Development:

The quality of life is dependent on access to a bountiful supply of cheap energy. For a sustainable future, energy should be derived from non-fossil sources; ideally, it should also be reliable, safe, flexible in use, affordable and limitless. Energy resources have always played an important role in the development of the human society. Technological developments and consumption of energy and increase of the world population are interdependent.

It is known fact that,

✓ 8 countries have 81% of the global crude oil reserves;

- ✓ 6 countries have 70% of all natural gas reserves and ✓ 8 countries have 89% of all coal reserves.
- It must be considered too that even if the bipolar plate presents corrosion current density slightly higher than the DOE target of 1 mA cm⁻² it is not necessarily true that its behaviour will not be acceptable during long term operation. The overall performance must take into account the fuel cell output which, in turn, depends also on interfacial contact resistance and contamination of the membrane with metal ions produced by the corrosion processes. The search for coatings or surface modification treatments that are capable of increasing bipolar plate corrosion resistance simultaneously decrease contact resistance is a very well established trend. Interesting results have been reported on nitriding, PVD or CVD coatings and passive film modification. The main challenges are to produce defect-free coatings, stable passive films or nitride layers that are able to protect the metallic substrate from the fuel cell harsh environment.

Different low cost metals has been selected and precious and non-precious metal platings has been done and it's corrosion resistant was evaluated in order to use the same as alternate Bi-Polar Plates in PEM Fuel Cells. Among all the low cost metals, Aluminum playing a vital role and Gold Plated Aluminium Substrate provides higher corrosion resistance and the same can be used as a Metallic Bi-Polar Plate for PEM Fuel Cells.

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