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**Title:** DESIGN AND TESTING CRITERIA FOR BIPOLAR PLATE
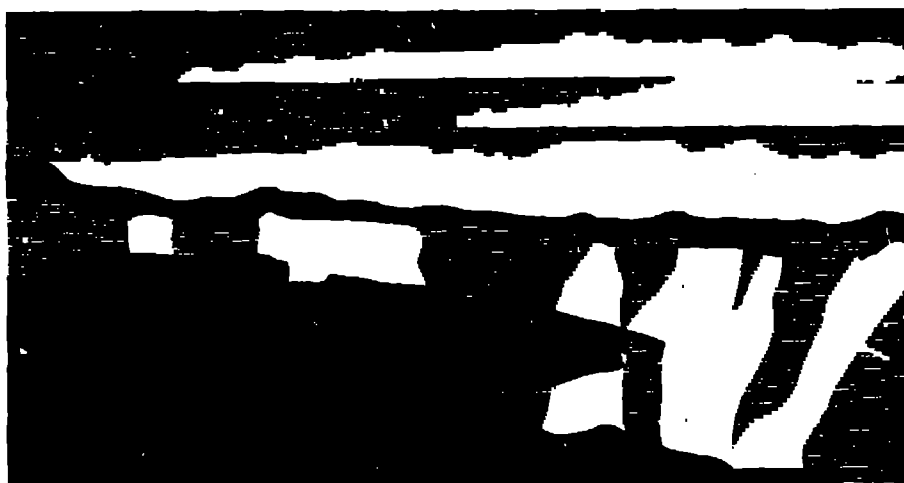MATERIALS FOR PEM FUEL CELL APPLICATIONS

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# DESIGN AND TESTING CRITERIA FOR BIPOLAR PLATE MATERIALS FOR PEM FUEL CELL APPLICATIONS

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## ABSTRACT

Bipolar plates for proton exchange membrane (PEM) fuel cells are currently under development. These plates separate individual cells of the fuel cell stack, and thus must be sufficiently strong to support clamping forces, be electrically conducting, be fitted with flow channels for stack thermal control, be of a low permeability material to separate safely hydrogen and oxygen feed streams, be corrosion resistant, and be fitted with distribution channels to transfer the feed streams over the plate surface. To date, bipolar plate costs dominate stack costs, and therefore future materials need to meet strict cost targets.

A first step in the bipolar plate development program is an assessment of design constraints. Such constraints have been estimated and evaluated and are discussed here. Conclusions point to promising advanced materials, such as conductive, corrosion resistant coatings on metal substrates, as candidates for mass production of fuel cell bipolar plates. Possible candidate materials are identified, and testing procedures developed to determine suitability of various materials.

## INTRODUCTION

A fuel cell stack consists of some number of single cells interconnected in series to result in a high, required voltage. Many motive applications require > 200 V DC as the stack output, so most designs require > 300 cells. Although 'edge collection' is one possible stack design approach, because of high current densities within these devices (> 1 amp/cm$^2$), 'bipolar' designs are more useful. Bipolar designs position conductive materials between adjacent cells. The anode (hydrogen or fuel) reaction occurs on one side of that plate while the cathode (oxygen) reaction occurs on the other. Bipolar plates must be strong enough to sustain clamping forces, be electrically conducting, be fitted with features that promote stack thermal control, be formed from material of low permeability to safely separate the hydrogen and oxygen feeds, be corrosion resistant, and be fitted with features that allow uniform reactant gas distribution and product removal. Obviously materials are selected to operate in stack operating environments. PEM stacks, the focus of this paper, perform between 80-100 °C, under conditions that are essentially "acidic", with quantities of liquid water present. Plate materials historically have been metals coated with conductive layers or graphite. Current graphite plates are sealed so that hydrogen and oxygen demonstrate low permeability rates. Like metal designs, manufacture of graphite plates can require extensive machining and post processing, resulting in hardware costs far more expensive than the costs for raw materials alone.

Earlier fuel cell systems were designed for defense markets that dictated performance and reliability as primary requirements. The current emphasis is on broader civilian markets that work today using established, competing technology. Consequently, fuel cell developers are focused on new systems approaches for this clean, efficient energy conversion technology. Performance, reliability and cost are the emphases. The major constraints include:

| | |
|---|---|
| 1. Electronic Conductivity | 6. Low Weight |
| 2. Gas Diffusivity | 7. Low Volume |
| 3. Corrosion | 8. Strength |
| 4. Chemical Compatibility | 9. Thermal Control |
| 5. Cost | 10. Manufacturability |

This report estimates bipolar plate design parameters, and evaluates possible material routes for useful bipolar plates. The relevant reactive conditions for bipolar plates evaluation are defined, and appropriate testing parameters established. The design constraints are used to estimate materials that could be useful for current, large scale markets, such as those required for transportation applications.

## DESIGN CONSTRAINTS

1. Electronic Conductivity: The bipolar plate conducts electricity with minimum voltage lost. Operating at a current of 1 amp/cm$^2$, voltage loss of < 10 mV/plate is minimally acceptable for high efficiency. Thus the plate resistance must be less than 0.01 $\Omega\cdot$cm$^2$ for each plate, independent of plate thickness. For example, a thickness of 0.100 cm (0.040 inch) sets bulk material resistivity of less than $1.0 \times 10^{-1}$ $\Omega\cdot$cm. This value is readily met with metals and some semiconductors. For a thin coating; assuming that the substrate is a conductive metal (R @ 0), then for a coating thickness of 25 $\mu$m (0.001 inch), the coating resistivity must be less than 4 $\Omega\cdot$cm.

2. Corrosion: The sulfonic acid cation exchange membranes utilized in PEM fuel cells foul when contaminated by most cations and by some organic compounds. Metal cations exchange with protons resulting in increased membrane resistance and mobile aqueous acids. Corrosion processes that yield halide ions, such as Cl$^-$, poison electrochemical catalysts. Corrosion processes also can result in formation of resistive surface layers, reducing the plate conductivity. For example, aluminum plates are covered by resistive alumina. In graphite hardware, slow carbon corrosion results in gaseous CO$_2$, which exhausts from the device with no adverse effect. Consequently, zero corrosion rates are not the constraints. Rather the task is to design materials that present no adverse consequences of corrosion processes.

One consideration is the number of metal ions that can be allowed to adsorb into the proton exchange membrane before performance loss is evident. For a 5,000 hour operating life an acceptable bipolar corrosion rate is approximately 0.016 mA/cm$^2$. If 99% of the metallic ions generated by this corrosion rate exhaust the cell as part of the product water, then a corrosion current as high as 1 mA/cm$^2$ may be acceptable. Corrosion which leads to ions or molecules that do not adversely affect the fuel cell, such as CO$_2$, mentioned above, are permissible. Thus the corrosion products may need to be analyzed via a technique such as XRF or atomic absorbance spectroscopy to determine elemental composition so that detrimental corrosion products are identified.

3. Gas Diffusivity: Each plate separates reacting hydrogen and oxygen streams. High leakage of either reactant presents an immediate safety concern as well as an efficiency loss. At 1 A/cm$^2$ current density, each cm$^2$ of active fuel cell electrode area processes $2.1 \times 10^{-5}$ moles/second of hydrogen. At 90°C and 2 atm, this corresponds to a volume of 0.31 cm$^3$ hydrogen processed each second. Assuming a leakage rate of 0.5% could be acceptable, the maximum average plate gas permeability is $1.0 \times 10^{-4}$ cm$^3$/s-cm$^2$. This bulk permeability can not be compromised by localized 'holes'.

4. Chemical Compatibility: The bipolar plate, although separated by graphite current collectors, is essentially in chemical contact with either the anode side or cathode side of the fuel cell. The anode and cathode have different chemical and electrochemical environments—the anode has a reducing atmosphere of H$_2$ and CO$_2$, with dissolved CO$_2$ forming carbonic acid, with a potential from 0.0 to possibly 0.6 V$_{RHE}$; the cathode has an O$_2$ oxidizing atmosphere, and potentials of up to 1.23 V$_{RHE}$. The two surfaces of the bipolar plate experience dissimilar chemical environments and most probably require different materials for the cathode and anode. The anode face cannot be susceptible to degradation by the hydrogen environment. One important consideration is chemical hydriding. Formation of disruptive hydride layers is of concern. However, the relatively

low temperature and low pressure of contemporary fuel cell designs, as well as the carbon dioxide constituents feed as part of the fuel stream (fuel processing of methane or methanol generates hydrogen-carbon dioxide mixtures) simplifies hydriding concerns. The cathode face must not passivate and become non-conductive due to the oxidizing environment of the cathode or otherwise degrade.

5. Cost: One contemporary emphasis for fuel cell development is large market automotive applications. It is clear that other stationary applications (off-grid power, etc.) are less demanding. Clearly, however, this transportation market sets the most demanding application for cost targets.[1] For a power system cost target of \$60/kW for which the stack costs 50% of the system, and the bipolar plate costs represent 25% of the fuel cell stack costs, each plate must cost less than \$0.0045/cm$^2$, including both material and fabrication costs. For plates with a surface area of 400 cm$^2$, this sets cost to about \$1.35 / plate. Milling of individual plates is inevitably expensive—the milling costs alone would exceed the target cost. Aluminum materials, at \$0.007/cm$^3$, a 0.10 cm thick, with a surface area of 400 cm$^2$ costs \$0.30 per plate. Forming, coating, and other allied processing costs can only cost \$1.00 for each plate. These price constraints are long term considerations. Bulk raw material costs may be fixed, thus most technology advances will be in forming and surface coating.

6. Low Weight: The bipolar plate component is repeated throughout a stack. Individual plates add in weight to become the major factor in device mass. Near term design weight for the fuel cell system is 4 kg/kW. If the stack component is given 30% of that budget, each bipolar plate (or anode/cathode plate set) must be no heavier than about 200 gm. This low mass dictates thin materials. For plates that are about 0.10 cm thick (0.040 inch), with a surface area of 400 cm$^2$, this requires the plate density be less than 5.0 g/cm$^3$. Aluminum and titanium appear to be the only acceptable cost metals whose densities approach this (2.7 and 4.5 g/cm$^3$ respectively).

7. Low Volume: The volume of the fuel cell power system must compete with existing electricity generating technology. Engine generator sets now are built at about 3 liters/kW. If the stack is 33% of the entire system volume, this allocates the stack to a volume about 1 l/kW. The bipolar plate component again results as the major contributing factor in the fuel cell stack volume. The cross-sectional area of the stack will be determined by the current density and the total current output of the stack. The length of the stack will be determined by the repeat distance between each cell. An important consideration in fuel cell stack design is the volume assigned to manifolds and thermal management. In general, low volume designs dictate that the fuel cell active area is a large fraction of the total stack area. Stack designs with a ratio of active to total area < 0.75 probably cannot meet the volume target.

8. Strength: Fuel cells operate under pressurized conditions. Seals and gaskets restrain reactant gas flows. Bipolar plates must be sufficiently strong to support clamping forces that exceed 200 lb/in$^2$ and show negligible creep rates. Long term creep resistance is important so that the clamping geometry remain constant.

9. Thermal Control: Reaction heat and resistance heating must be removed. The bipolar plates must include heat transfer features that facilitate heat removal. Materials must be compatible with projected heat transfer liquids and exhibit adequate conductive heat transfer rates. Although existing PEM designs use water as the heat transfer agent, other heat transfer fluids will likely be used in the future, and the bipolar plate materials need to be compatible with the heat transfer fluid. Because heat transfer fluids contact plates which operate at different potentials, shunt currents (electrical current flow within the cooling manifold), can result unless coolants with low electrical conductivity are utilized. Many current corrosion inhibitors add excessive conductivity to available heat transfer fluids.

10. Manufacturability: Materials must be selected so that stamping, embossing, joining, and other processing steps are low cost, high yield processes. Likewise, high

vclume materials selection must consider options to recycle products into future process input streams. Alternatively, materials must be selected with low-cost disposal options.

## FUEL CELL STACK OPERATING CONDITIONS

For proper design and testing of candidate bipolar plate materials, an evaluation of the operating conditions in the fuel cell, and the relevant chemical and electrochemical environments are required. Corrosion rates and mechanisms of the bipolar plates and degradation of other fuel cell materials are determined by the pH and concentration and type of ions present in the solution, the gaseous atmosphere (reducing or oxidizing) and the potential to which the materials are exposed. Expected PEM fuel cell stack operating conditions are summarized in Table 1.

The fluoride ion concentration in the fuel cell environment is important for at least two reasons: the amount of fluoride in solution indicates degradation rates of the fuel cell membrane and gives an indication of the expected life span of the membrane,[2] and fluoride ions help induce corrosion of the fuel cell materials as do other halide ions such as $Cl^-$. The exact source of fluoride is not known, but it is suspected that the sulfonic acid side chai i, during polymer degradation, oxidizes to form a carboxylic terminal group, releasing fluoride ion to solution. Carbonic acid, present on the anode side is the result of $CO_2$ dissolution. This carbonic acid is high enough in concentration to be a major determining fac r to the solution pH.

The cathode plate will be exposed to an $O_2$ (oxidizing) containing environment. The cathode plate will experience potentials of up to 1.23 $V_{RHE}$. The anode plate will be exposed to a $H_2$ containing, reducing environment. The plate will experience smaller anodic potentials—at open circuit the anodic plate will be near 0.0 $V_{RHE}$, but could see potentials up to 0.6 V as CO or COH poisoning species are oxidized, if anodic pulsing were used for CO control.

## MATERIALS

Possible bipolar plate materials are being evaluated to meet these design constraints. In the long term, mass production dictates inexpensive and readily available materials. Candidate materials include molded conductive polymers and coated metal plates. A possible manufacturing route for metal substrates, such as aluminum, could be cutting and forming, followed by a corrosion resistant coating. Possible metal substrates include: aluminum, titanium, iron / stainless steel and nickel.

Corrosion resistant coatings require conductivity and adhesion to protect the substrate from the environment. Classes of viable coatings materials include carbon-based and metallic:

| Carbon Based | Metallic |
|---|---|
| graphite | inert metals |
| conductive polymer | metal nitrides |
| diamond, diamond like carbon (DLC) | metal carbides |
| organic self-assembled monolayers[3] | noble metals |

## TESTING

Corrosion testing of any coated metal plates must be done emulating conditions similar to those projected during use of that material. Because these fuel cell plates will be exposed to constant potentials, the galvanostatic corrosion rate at relevant potentials is of interest. During usual operation, the potentials for the anode and cathode are expected to be closer to 0.1 and 0.8 $V_{RHE}$, respectively. Anodic polarization and cyclic polarization are techniques used to determine passive/transpassive properties, and what occurs to test materials during the first polarization.

Fig. 1 shows electrochemical polarization curves for three materials, aluminum, a carbon coated aluminum and a titanium alloy. The steady state operating potentials for the anode and cathode plates have been labeled, as has the allowable corrosion rate, based on the above criterion. As can be seen, carbon coating on aluminum has reduced the corrosion rate by more than two orders of magnitude. The titanium alloy has excellent corrosion characteristics, but will passivate and become non-conductive in an oxidizing environment.

The electrochemical measurements need be conducted at fuel cell operating conditions, replicating both pressures and temperatures. A reducing hydrogen (anode) or an oxygen atmosphere (cathode) is required to simulate either cathode or anode conditions. The electrical resistance of materials must be measured and should not increase during exposure to the fuel cell environment. For plate materials in which gas permeability could be a concern, gas diffusion properties also need to be evaluated.

## CONCLUSIONS

Design constraints for bipolar plates materials have been established. These constraints suggest that advanced materials, such as conductive coatings on metal substrates may be required for mass production of bipolar plates for PEM fuel cell applications.

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2. R. Baldwin, M. Pham, A. Leonida, J. McElroy, and T. Nalette, NASA Conf. Publ. (1989), 3056 (Space Electrochem. Res. Technol.) 127.
3. For example, see DeQuan Li, C. T. Buscher and B I. Swanson, Materials, 1994, 6, 803.

## ACKNOWLEDGMENTS

## DISCLAIMER

**Table 1. Fuel Cell Operating Conditions for Bipolar Plate Material Design.**

| | |
|---|---|
| Temperature | 70 - 100 °C |
| Pressure | 2 - 3 atmospheres |
| Anode Potential (long term) | 0.1 $V_{RHE}$ |
| Anode Potential (peak) | 0.6 $V_{RHE}$ |
| Anode water pH | 3.60 |
| Anode fluoride concentration | 1.8 ppm |
| Anode Chemical Environment | reducing ($H_2$) |
| Cathode Potential (long term) | 0.8 $V_{RHE}$ |
| Cathode Potential (peak) | 1.23 $V_{RHE}$ |
| Cathode water pH | 4.02 |
| Cathode fluoride concentration | 1.1 ppm |
| Cathode Chemical Environment | oxidizing ($O_2$) |
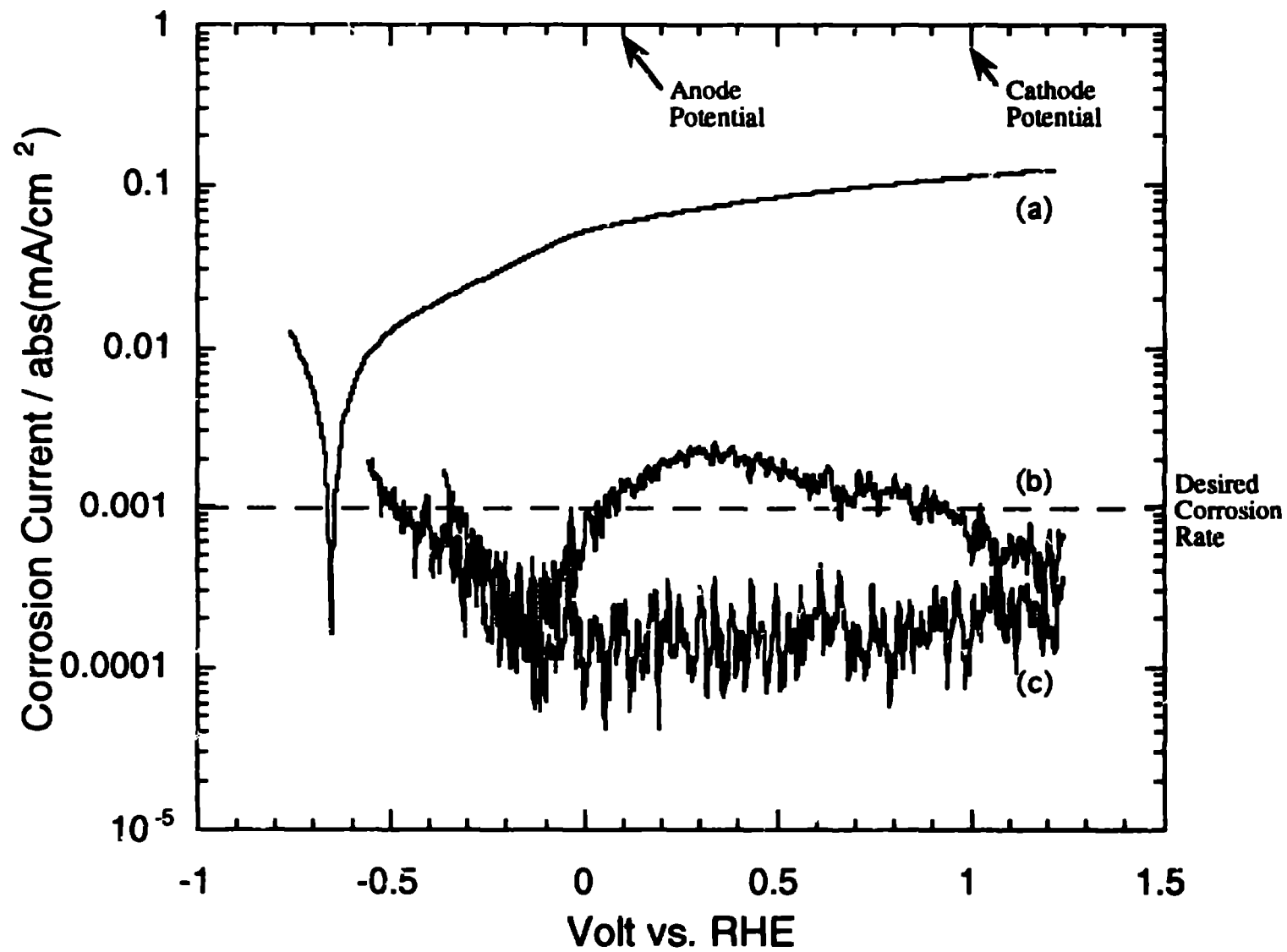
Fig. 1: Electrochemical Polarization Curves for (a) aluminum, (b) carbon coated aluminum and (c) titanium alloy. 1 mV/sec sweep rate. Solution pH = 4.