

New materials for polymer electrolyte membrane fuel cell current collectors

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Abstract

Polymer Electrolyte Membrane Fuel cells for automotive applications need to have high power density, and be inexpensive and robust to compete effectively with the internal combustion engine. Development of membranes and new electrodes and catalysts have increased power significantly, but further improvements may be achieved by the use of new materials and construction techniques in the manufacture of the bipolar plates. To show this, a variety of materials have been fabricated into flow field plates, both metallic and graphitic, and single fuel cell tests were conducted to determine the performance of each material. Maximum power was obtained with materials which had lowest contact resistance and good electrical conductivity. The performance of the best material was characterised as a function of cell compression and flow field geometry. Crown Copyright © 1999 Published by Elsevier Science S.A. All rights reserved.

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1. Introduction

The polymer electrolyte membrane fuel cell (PEMFC) is one of the most widely researched of the fuel cell technologies [1,2] because it offers several advantages for transport and a number of other applications. Its low temperature operation, high power density, fast start-up, system robustness, and low emissions have ensured that the majority of motor manufacturers are actively pursuing PEMFC research and development [3].

Research has involved a number of fundamental aspects of the PEMFC including membrane [4], catalyst [5], and electrode [6] development which has resulted in a number of alternatives to Nafion™ membrane technology with low load, high utilisation catalysts yielding significantly higher power density than was achievable a few years previously. Improvements in cell design and manufacturing have further increased power, while reducing manufacturing costs—which is essential if the fuel cell is to compete effectively with the internal combustion engine [7].

For a given membrane/electrode assembly, the power density of a fuel cell stack can be significantly increased by reducing the profile of the bipolar plates. Traditionally

fuel cells have been constructed from Poco™ graphite, which is resistant to corrosion in the fuel cell environment but suffers from being brittle, expensive, bulky, and difficult to machine.

Clearly these properties make it unsuitable for use in automotive applications, where it must have very high power density while being extremely rugged and corrosion resistant over the lifetime of the vehicle.

This paper is concerned with identifying a number of alternative materials with which the Poco™ graphite may be replaced and assessing their performance and suitability in the fuel cell environment. A number of construction techniques are suggested and single cell testing has been performed. Although a fuel cell ‘engine’ would almost certainly use air as the oxidant source, all tests presented in this paper were performed with pure oxygen to eliminate effects of stoichiometry and humidification on performance. This would additionally accelerate any corrosion effects which might be observed in the test material.

2. Experimental

A single cell design was employed for this work which was based upon a commercial cell (Electrochem) with a 50

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cm² active area. The fuel cell was connected in parallel to a Hewlett Packard 6050A load unit and in series with a TCR power supply (150 A) or two, series connected lead-acid batteries (Chloride VH51, 1500 A h) to provide the additional voltage required for control. A digital voltmeter (Solartron 7151) and shunt resistor were used to measure voltage and current, respectively. Each fuel cell was operated in a test station, which housed stainless steel gas manifolds, with needle valves on the exhaust lines. Product water was cleared by periodic gas purging through a water-trap and the cells were operated with near closed output valves. The input gases were not humidified.

A fuel cell was typically constructed with a Gore Select Primea™ membrane/electrode assembly, which has previously been tested under a number of operating conditions [8], sandwiched between a layer of Carbel™ micro-porous diffusion media and Toray carbon paper (E-Tek). This assembly was placed between the flow-field plates under test and silicone rubber gaskets were employed where necessary. Copper sheets were placed either side to provide external electrical circuit connections and the whole cell was compressed between aluminium end-plates, held together with tie-rods.

After assembly of a new fuel cell, it was operated potentiostatically (0.5 V) until it reached maximum operating temperature, then allowed to cool. This was repeated several times until consistent performance was obtained. After collecting data under a specific set of conditions the cell was allowed to cool to near ambient temperature before embarking upon another experiment to allow for identical warm-up procedures between each.

3. Results and discussion

Prospective materials for production of fuel cell current collectors should satisfy a number of different criteria: the material should have a good electrical conductivity, it must also be impermeable to hydrogen, be corrosion resistant, able to withstand shock and vibration, of minimal thickness, and easily manufactured.

Given that commercial fuel cell stacks generally contain Poco™ graphite, this material was thoroughly investigated in single cells in order to provide a baseline performance. These plates were obtained commercially and incorporated a flow-field comprised of parallel tracks. This material is impermeable, has a reasonable electrical conductivity, is corrosion resistant, but suffers from being very expensive, difficult to machine, and very brittle.

The new materials that were tested may be classified as metallic and non-metallic.

3.1. Metallic current collectors

3.1.1. Gold plated aluminium

Current collectors were machined from aluminium to the exact dimensions of the graphite plates, then coated with gold by a solution process. These plates were used in a fuel cell and during the initial warm-up procedure the data indicated performance very similar to graphite (1.2 A cm⁻² at 0.5 V). However, very quickly the performance degraded (60 mA cm⁻² at 0.5 V). Post-mortem revealed that some of the gold layer had lifted from the plate and become embedded in the membrane. The fact that an

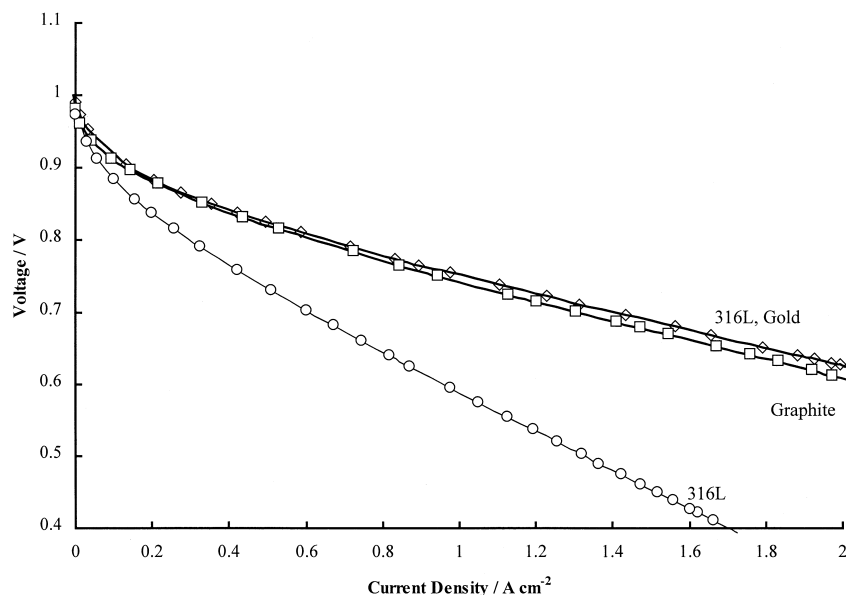


Fig. 1. Performance of stainless steel collectors.

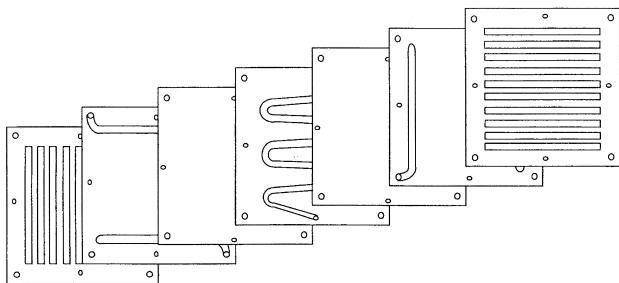


Fig. 2. Construction of titanium foils.

open-circuit voltage was still observed suggests the metal had not penetrated the membrane so it is likely that it had become contaminated with aluminium.

3.1.2. Stainless steel

Current collectors were fabricated from 316L stainless steel and the flow field machined into it. Some of these plates were then gold coated. Test data for these plates were collected on a larger cell (200 cm^2) than used for the majority of this paper and were subsequently normalised to allow direct comparisons to be made. Performance in comparison to other materials and in coated and bare form is shown in Fig. 1. This material benefits from being inexpensive, robust, and easily fabricated, but it is also dense, so the gravimetric power density suffers as a result.

3.1.3. Titanium

Titanium is a good candidate material for current collectors since it is lightweight compared to stainless steel, it is rugged, easily machined, and has good electrical conductivity, however, pure titanium (like stainless steel) forms a passive oxide layer in air which is electrically insulating. This oxide layer will increase interfacial resistance be-

tween the fuel cell components so it is necessary to etch and coat the surface to prevent this.

To form these plates, a series of foils were diffusion bonded [9] (Fig. 2). These foils were cut by spark erosion which allows large numbers of foils to be manufactured simultaneously. Diffusion bonding allows complex flow fields to be built which could not be produced by conventionally machining from a single block, and additionally, it allows the incorporation of water cooling channels integral to the plate, obviating the need for separate cooling plates within a stack.

Diffusion bonding is a technique which allows the formation of large area joints, which are indistinguishable from the parent material and distortion free. It is achieved hot pressing suitably prepared metal surfaces. Titanium is particularly suitable for diffusion bonding since it absorbs its own oxide above $600\text{--}700^\circ\text{C}$ leaving an atomically clean surface, but this also means the process must be performed under vacuum in order to prevent embrittlement. When titanium surfaces are brought together at $>700^\circ\text{C}$, creep brings the two surfaces into intimate contact and diffusion effects minimum bond line porosity.

It was found that deformation of the internal channels during the bonding process was dependent on the number of foils in the plate and on the width of the tracks. Since the bonding is geometry specific, the bonding parameters are unique to these plates and could not be inferred from bonding solid pieces of titanium. For these plates the best joints were achieved at 870°C and 6 MPa for 6 h. These bonds exhibited only 3% porosity at the interfaces, which was sufficient for a gas-tight seal. The bonded foils were skimmed flat to remove any embedded boron nitride release agent, and ion implanted with nitrogen to provide corrosion resistance and to prevent formation of an oxide layer.

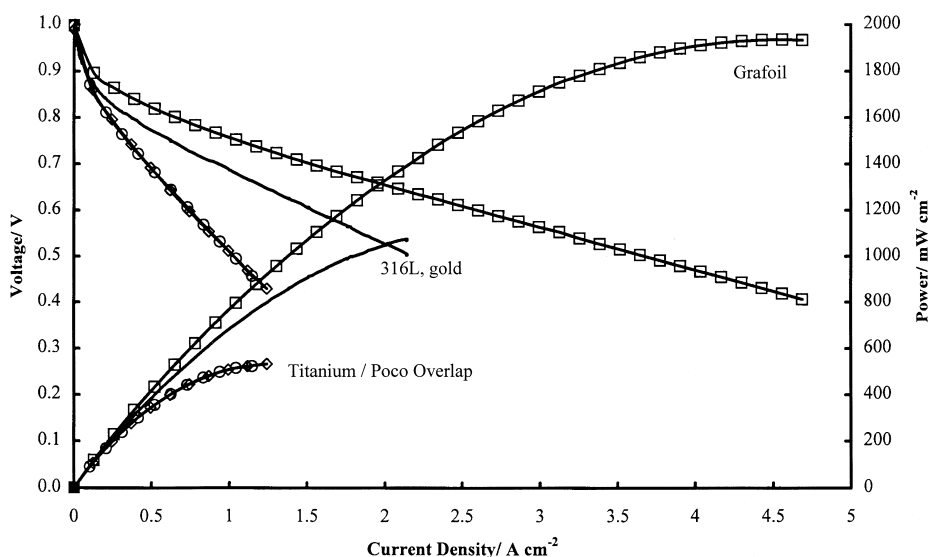


Fig. 3. Performance comparison of materials.

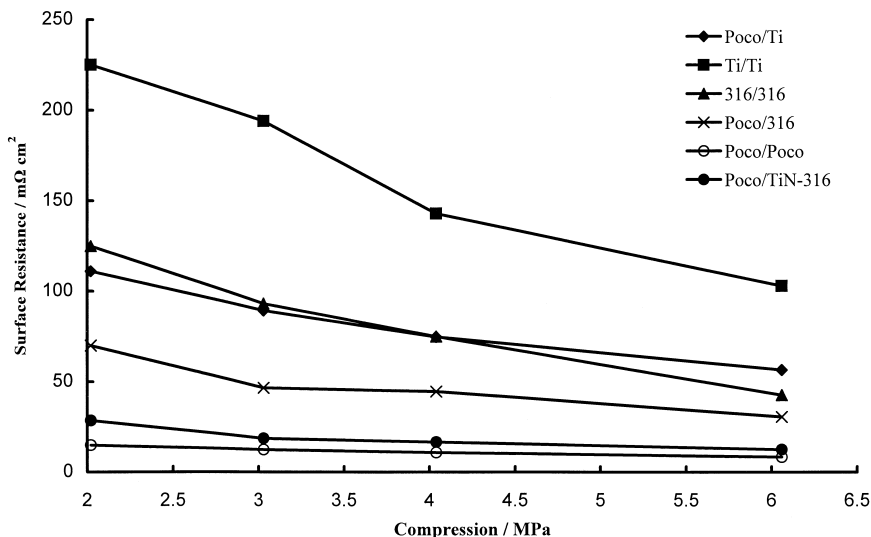


Fig. 4. Contact resistance of metallic plate materials.

During construction of the single cell for testing it was found that any non-planarity in the plates made sealing of the fuel cell difficult and it was very easy to crush the membrane/electrode assembly when tightening the tie rods. Performance of the cell under load was broadly similar to graphite (Fig. 3) but the plate itself was thinner so volumetric density was correspondingly higher.

As mentioned previously, one disadvantage in the use of self-passivating materials such as stainless steels and titanium, which form oxide coatings to achieve corrosion resistance, is that these coatings are usually electrically resistive. These coatings can result in high voltage losses across the plate/macrodiffuser interface. To determine the extent of this problem the contact resistance between the plates was measured for a current of 20 A at different

levels of cell compression (Fig. 4). The plates were separated by two sheets of conducting carbon diffuser paper (Toray 120).

Contact resistance losses from the metal/metal plates were considerably higher than that observed with Poco™ graphite. At higher compression this discrepancy was minimised, but the passive layer present on 316L and titanium still exerted an influence. Coating the steels with titanium nitride reduced the voltage loss to almost that of graphite. Gold coatings have a similar effect.

3.2. Non-metallic current collectors

3.2.1. Exfoliated graphite

This material is used principally in high temperature gaskets. It is readily available, inexpensive, and available

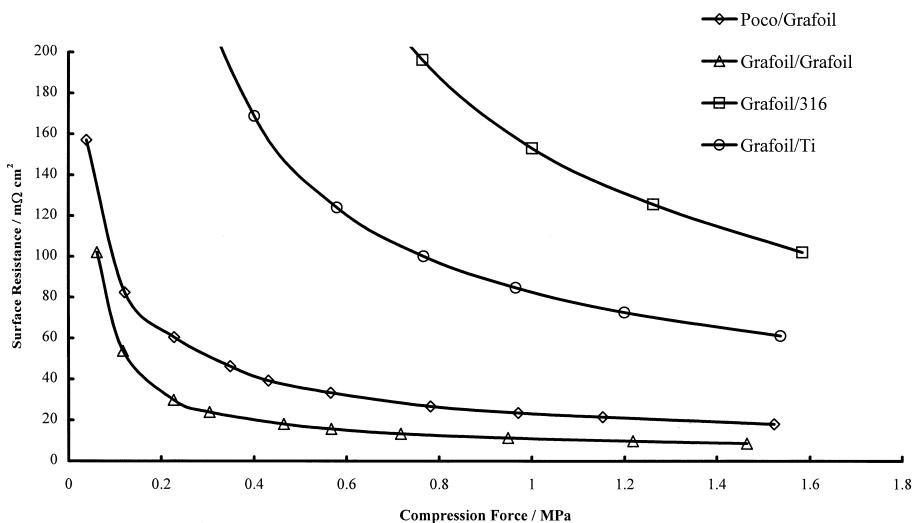


Fig. 5. Contact resistance of graphitic materials.

in several forms (this paper discusses the use of Grafoil™). It is electrically conducting, corrosion resistant, and is self-sealing, which obviates the requirement for separate gaskets. However, it is not mechanically robust so a stack built from this material would have to be protected from impact.

Current collectors were produced by cutting foils and assembling them in a similar manner to titanium, with the exclusion of water cooling foils. This foil construction method is particularly suitable since the material is easily cut to form the channels and the individual foils form a gas-tight seal when the stack is compressed.

Performance of the Grafoil™ current collectors is shown in Fig. 3. It was immediately apparent that the performance achieved in this cell was greater than for any other

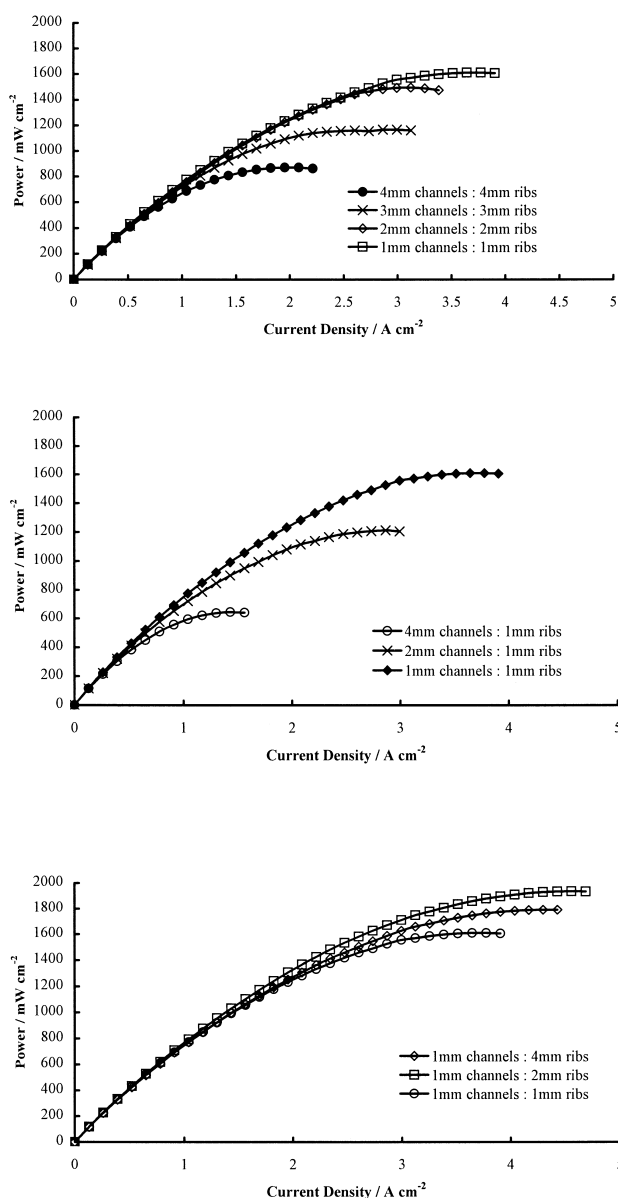


Fig. 6. Comparison of Grafoil performances with flow field geometry.

material under test. It is likely that this is principally due to the compressibility of the Grafoil™ which allows it to form an intimate interface with the membrane/electrode assembly and thus minimise interfacial resistance (Fig. 5). Comparison with contact resistance of the metallic materials shown on Fig. 4 highlights the benefit of using a compressible material since Grafoil™ has an order of magnitude less contact resistance than metallic plates and reaches an optimum value with a lower compression force. This phenomenon cannot be explained solely in terms of the electrical conductivity of the material since it is worse than that of the metal current collectors.

To determine the contribution that track dimensions make towards overall performance of the Grafoil™ plates, a series of single-cell experiments were performed (Fig. 6) in which the width of the gas channels and the current collecting ribs were varied while keeping all other parameters constant (that is, using the same MEA, end-plates, load unit, and instrumentation). These experiments represent a sequential change in the width of the gas tracks, the current collecting rib, and the ratio of the two.

The performance of cells with altered track and rib width (but keeping the ratio constant) clearly show that decreasing the size of both was advantageous since the power output was increased from 871 mW cm⁻² (4:4 mm) to 1610 mW cm⁻² (1:1 mm). This broadly followed expectations as the increased gas track width ensured a smaller number of tracks in total, and increasing rib width would hinder gas diffusion through the electrode, rendering areas of the cell inactive.

The performance of cells in which the ribs were kept to 1 mm (the optimum identified from the previous experiments) and the gas channels were altered, showed that a minimum track size was optimal. Power output was increased from 645 mW cm⁻² (4:1 mm) to 1610 mW cm⁻² (1:1 mm). Once again this was almost certainly due to the increased density of tracks which resulted in higher utilisation of the active area of the cell.

The performance of cells in which the gas channels were kept to 1 mm (the optimum identified from the previous experiments) and the ribs were altered show a smaller effect. Performance was increased to a maximum with 2 mm ribs (1930 mW cm⁻²) so it appears that the increased contact area offered to the MEA by the thicker ribs offset the reduction in channel density by reducing internal resistance. Further increasing rib width to maximise contact was not beneficial since the negative effect of reducing the number of gas tracks became dominant. Overall, the maximum power in this cell, with this geometry, and without humidification, was obtained with 1 mm gas channels and 2 mm ribs (1930 mW cm⁻²).

To investigate the effects of compression on the performance of a fuel cell constructed from Grafoil™ a single cell was held horizontally in a hydraulic press (0–3.5 MPa) and operated at 1 bar (gauge) and 50°C. Polarisation data were obtained for a range of compression pressures

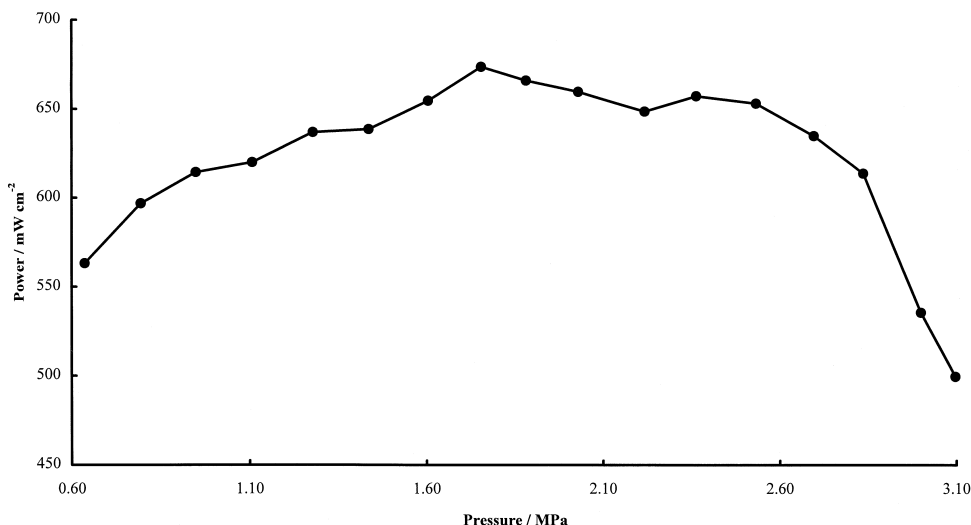


Fig. 7. Compression dependence of a cell using Grafoil.

and peak power density was compared for each. These data (Fig. 7) clearly show an optimum compression range of 1.5 to 2.6 MPa for peak performance with significant loss outside of this range. The compressibility of Grafoil™, which is responsible for its remarkable performance, requires that force exerted by the end-plates and tie-rods in a stack be carefully managed to optimise performance. During the experiments it was also noted that the cell expanded as it warmed up, which suggests an optimised fuel cell should utilise end-plates with pneumatic compression which can react to expansion within the cell.

All the above results have been compared in terms of power per unit area but volumetric and, to a lesser extent, gravimetric power density is of prime importance for automobile applications. Therefore, volumetric power densities have been calculated for the different materials on the basis of a single cell, with end-plates and MEA discounted. The current collectors were not optimised as the active area was not maximised on each, so the data in Table 1 do not represent the best that could be achieved, but are useful for comparison. The greater volumetric power density found for 316L compared to titanium is because the test data and dimensions were taken from a much larger single cell (200 cm² compared to 40 cm²) which allows for much more efficient operation. It is

expected that titanium plates of a similar size would have similar volumetric power.

4. Conclusions

A variety of metallic and non-metallic materials have been investigated for use in the fabrication of current collector plates for use in fuel cells. Single cell testing using oxygen has revealed that Grafoil™ offers significant performance gains over standard graphitic materials, probably because of its compressibility which enables it to form an intimate contact with the electrode, minimising interfacial resistance. Cells were formed from this material with different flow field dimensions to determine the optimum tracks sizes for this particular geometry and compression experiments determined the optimum force that needs to be exerted on the Grafoil™ for good performance. This material is ideally suited to production as it is inexpensive and simple to cut into foils but it suffers from being prone to impact damage and its compressibility will hinder the manufacture of multiple cell stacks.

Metallic plates have been manufactured from aluminium, titanium, and 316L stainless steel. Aluminium has proven reactive towards the membrane, even when coated. This material poses a high risk since the coating would need to be completely pore-free in order to prevent contamination of the membrane. Titanium, coated with nitride, exhibited similar performance to Poco™ graphite, but it is more easily manufactured, very robust, water cooling can be incorporated into the plate, and plate volume is lower. Gold-coated stainless steel offered superior performance to Poco™ graphite and it is less expensive than titanium. However, it has a higher density and it is more difficult to diffusion bond since its passive surface layer is stable at bonding temperatures.

Table 1
Power densities of materials used for current collectors

Material	Volumetric power density (mW cm ⁻³)	Gravimetric power density (mW g ⁻¹)
Poco™ graphite	131	71
Titanium	500	112
316L, gold coated	800	74
Grafoil™	1235	1545

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