

Mitigation of Fuel Cell Degradation Through MEA Design

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ABSTRACT

Hydrogen PEM fuel cells offer a viable way of providing the electrical energy to power a vehicle. With rapid refueling and acceptable range on a tank of fuel, they provide a complementary technology to battery-powered EVs that will ultimately offer a route to decarbonising transport.

However, the demands on an automotive fuel cell stack provide a challenging environment for key components within the membrane electrode assembly (MEA). Frequent start-up shut-down events and freeze starts can create conditions that cause corrosion within the fuel cell. The risk of fuel starvation to individual cells within a large stack of several hundred cells is also a potential cause of corrosion which will inevitably lead to degradation and reduced stack lifetime. While there are system-level mitigation strategies that can be employed in terms of design, controls and interventions, the most efficient solution is to improve the intrinsic stability of the key cell components themselves.

Many of the mechanisms that lead to degradation can be addressed through the design of the MEA. Potential excursions that drive corrosion of cathode catalysts layers have been found, perhaps surprisingly, to be reduced by design changes in the anode catalyst. Anodes can be protected from corrosion caused by cell reversal through the incorporation of additional oxygen evolution reaction functionality built into the catalyst layer. We have demonstrated significant improvements to MEA stability and durability through such design changes. In particular, significant improvements in cell reversal tolerance of MEAs with novel anodes are described.

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INTRODUCTION

PEM fuel cells can be deployed in a range of applications from small scale consumer electronic devices requiring a few watts through to stationary power plants delivering hundreds of kilowatts. The maximum power output of a fuel cell stack will be dependent on the total surface area of the membrane electrode assemblies of which it is built up. Typical automotive fuel cell stacks are required to deliver in the order of 80 to 100 kilowatts of power and to achieve this would comprise a few hundred MEAs each with an area of a few hundred square centimetres.

The demands on an automotive fuel cell stack are usually much greater than those on a stationary system. An automotive fuel cell is expected to start rapidly from sub-zero temperatures with minimal energy input; function at a wide range of ambient temperatures and humidity and deliver load following the power demands of the vehicle which could be anything from a few watts to the maximum power of around 100 kilowatts. These requirements, together with the durability expectations of over 100,000 miles and tens of thousands of start-ups put a high demand on the components of the MEA.

There are many degradation mechanisms that can affect the life expectancy of an MEA which in-turn can be accelerated by the specific demands of an automotive system. Membrane degradation through chemical corrosion and mechanical stress limited the life expectancy of MEAs in the early years though recent improvements in membrane technology has gone a long way to addressing this issue. However, the drive to use thinner membranes in order to improve power density may require further improvements.

Further, there are a number of requirements of automotive fuel cell stacks that can significantly affect the stability of the catalytic electrodes. For example, there are specific conditions that can occur during start-up and shut-down that can cause corrosion of the cathode electrode. When a stack is shut down and isolated from the fuel supply hydrogen in the anode will slowly diffuse out or be oxidised by oxygen that diffuses through the membrane. Thus, over time the anode will contain some oxygen instead of hydrogen; this is then displaced by hydrogen at start up. However, during the short time that the anode contains both hydrogen and oxygen it is possible to set up an internal cell that in turn creates a high potential on the opposing cathode. Under these conditions severe corrosion of the carbon of the cathode catalyst can occur. To mitigate this degradation mechanism,

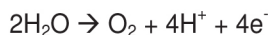
there is a drive to find catalyst supports that are resistant to the corrosion mechanism. There are other ways to help mitigate against this degradation mechanism which are shown later in this paper.

Cell reversal is another mechanism that can cause severe corrosion damage to catalyst layers. This effect is caused when there is insufficient fuel available at the anode of some of the cells of a stack to support the current that is being drawn. When this occurs the potential of the fuel starved anodes will increase until they reach a level at which a reaction can occur that will provide the protons to support the current being drawn. With conventional anodes the reaction will corrode the carbon in the electrode as shown below:



With the standard types of carbon used in anode catalyst layers the carbon corrosion reaction will begin to take place below 1.4 V and becomes fast above that potential. By using a more corrosion resistant carbon the corrosion reaction can be delayed until a higher potential but without another mitigation strategy the higher potentials are reached and the carbon still corrodes.

To reduce or prevent the carbon corrosion reaction requires the facilitation of an alternative reaction that can generate the protons that are needed at a potential at or below the potential for carbon corrosion. Water electrolysis (or oxygen evolution) is such a reaction:



For this reaction to occur in preference to carbon corrosion the anode layer must contain an oxygen evolution reaction (OER) catalyst; the platinum catalysts used for hydrogen oxidation are not particularly active for this reaction. Ruthenium Iridium oxides are known to be active for water electrolysis¹ and such catalysts have been proven to impart cell reversal tolerance to anode electrodes. However, it is also known that ruthenium can dissolve at elevated potentials and if this occurs in the anode layer, not only will the anode lose its reversal tolerance but the ruthenium can migrate to the cathode where it can decrease the activity of the oxygen reduction catalyst^{2, 3} and thus lower the performance of the fuel cell stack.

In this paper we will show the advantage of improved cell reversal tolerant anodes using new test methods that are designed to show the relative differences in stability between various anode designs.

REVERSAL TEST METHOD

The amount of time an anode electrode will spend under reversal over the lifetime of an automotive stack is not known, but various OEMs have made estimates which can equate to tens of hours. From such estimates various targets have been proposed and from these specific tests applied. Often these tests involve forcing a fixed current through a fuel starved anode for a specific period of time which can be up to the target of many hours. Whilst this method can demonstrate the stability of a particular design it doesn't necessarily represent what will happen in a real system; reversal events are usually of short time duration and many such short events will not have the same effect as one long reversal event.

We have developed a series of protocols that allow us to monitor the change in performance after a number of short reversal events and measure the loss in carbon due to corrosion during the test.

Tests were carried out in a single cell hardware with an active area of 217 cm² connected to a Hydrogenics test stand with a load bank capable of driving a current. The anode and cathode exhausts were equipped with Vaisala CARBOCAP IR-based CO₂ probes to monitor the products of carbon corrosion. Before each test, a new MEA would be conditioned by operating at 500 mA/cm² at 100% relative humidity (RH). MEAs all comprised JMFC proprietary membranes and cathodes were all a standard JMFC design.

6 Second Reversal Events

A polar curve is measured under specific conditions to determine beginning of life performance. The anode is then purged with nitrogen to remove all the hydrogen fuel. A current of 200 mA/cm² is then forced through the cell for 6 seconds; during this process the cell voltage, resistance and anode and cathode CO₂ levels are recorded. After the reversal event we continue to flow nitrogen across the anode whilst recording the CO₂ levels to ensure we capture all the corrosion products created during the reversal event. The hydrogen is then restored to the anode and a polarisation curve recorded. The reversal cycles are then repeated until a significant performance loss is determined.

5 Minute Reversal Events

The above procedure is repeated using a fresh MEA except this time each reversal event is maintained for five minutes. The procedure is repeated until significant performance loss is determined.

45 Minute Reversal Events

The above procedure was repeated using a fresh MEA except this time each reversal event lasted 45 minutes.

START UP / SHUT DOWN (SU/SD) TEST METHOD

The MEA is initially conditioned using standard current density-hold methods and polarisation data obtained. The load is then removed such that the cell moves to OCV. The anode gas feed is switched from H₂ to synthetic air (79:21 N₂:O₂) and so any CO₂ subsequently monitored is solely from carbon corrosion without the background level of 'standard air'; (the cathode is also switched to synthetic air). The anode air flow is maintained for 4 minutes before returning the MEA to normal H₂/air conditions with the immediate re-introduction of load. The cell performance is monitored at medium and a high current density points and the cycle repeated. After each set of 10 SU/SD cycles, the MEA is reconditioned under full RH, 1 A/cm² conditions to ensure adequate hydration of the MEA.

RESULTS AND DISCUSSION

The 6 second cell reversal tolerance test was first carried out on a standard MEA with no specific inbuilt cell reversal tolerance. The anode catalyst comprises platinum supported on a Ketjen EC300J carbon.