In-Situ Monitoring of Interfacial Contact Resistance in PEM Fuel Cells

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Abstract Text

A new in-situ method for measuring the interfacial contact resistance between the bipolar plate and gas diffusion layer of an operating PEM Fuel Cell has been developed. This method involves the insertion of probe wires, supported by a printed circuit board, between the catalyst-coated membrane and cathode side gas diffusion layer. Initial results suggest that the probe has no significant impact on fuel cell performance and produces real-time contact resistance measurements that are sensitive to changes in relative humidity and cell temperature, thus allowing the investigation of phenomena such as the oxidation of bipolar plate coatings during real operation.

Introduction

Bipolar plates (BPPs) serve five main functions in a fuel cell: i) to separate individual electrochemical cells in a stack, ii) to distribute gas flow evenly across the active area of the membrane electrode assembly (MEA) *via* the flow field, iii) to conduct electricity and heat iv) provide mechanical stability and v) facilitate water removal. As such, it is crucial that BPPs exhibit high mechanical strength, and good electrical and thermal conductivity.

Stainless steel is an attractive BPP material owing to its low-cost, favourable physical properties, and well established high throughput manufacturing techniques.[1–3] In the oxidising environment of a proton exchange membrane fuel cell (PEMFC), stainless steels rapidly form a protective oxide layer on their surface. While this oxide layer protects the steel from corrosion it also leads to an increased interfacial contact resistance (ICR) between the bipolar plate and

the gas diffusion media. With every 1 mΩ cm^2 of contact resistance resulting in 1 mV cell voltage loss per 1 A cm^{-2}, even small increases in contact resistances can lead to large cell inefficiencies. A solution that simultaneously increases the corrosion resistance of the stainless steel and lowers the ICR of the BPP is to apply a surface treatment or coating.[4] Examples include metal nitrides,[5] carbides,[6] noble metals,[7] carbon-based coatings,[8] and conductive polymers.[9]

Ex-situ ICR measurements have been used to evaluate surface modifications on stainless-steel BPPs,[10–12] however, while these types of measurements allow for screening of BPP materials, they only provide data on BPPs at the beginning and end of life. *In-situ* measurements allow the ICR to be monitored during fuel cell operation, allowing correlation with operating conditions and evaluation over time. To date, few examples of *in-situ* ICR measurements exist in the literature,[13–18] and reported techniques require either highly specialized cell designs or significant modifications to the BPP. The results are therefore often collected in fuel cells with designs and operating conditions that do not well reflect commercial PEMFCs. Additionally, the experiments can be complex and time consuming.

Herein, we report a new method for measuring the *in-situ* ICR of BPPs using thin gold sense wires supported on a printed circuit board (PCB). The flexibility in PCB design allows this technique to be applied to wide range of fuel cell configurations, irrespective of active area geometry or design. As the probes sit outside of the active area of the cell, they have little influence on the conditions and operation of the cell.

Experimental

The PCBs consisted of a 1.2 mm thick glass-reinforced epoxy laminate material (FR-4), with a silver-plated copper conductive track and a design that ensured that the PCB did not impact normal cell assembly, Figure 1. Two ~1 mm wide strips of 7 µm thick Kapton film and two 50 µm diameter gold-coated tungsten wires (Advent Research Materials, UK) were located such that they ran from the top to bottom of the cell, 2 mm to the left and right of the normal 49 cm^2 active area (purple sections in Figure 1 a). Kapton ensures no electrical short between GDL & CL. The top and bottom of each wire was soldered to separate PCB terminals to create a total of four electrical contacts. The cathode GDL and gaskets were cut 4 mm wider than normal so that the probes contacted the cathode GDL and the Kapton contacted the CCM once

the probes were assembled into a cell. The anode GDL maintained a normal width and defined the active area. This design ensured that the probes did not intrude into the active area of the cell. Full details of assembly and testing are provided in the Supplementary Information.
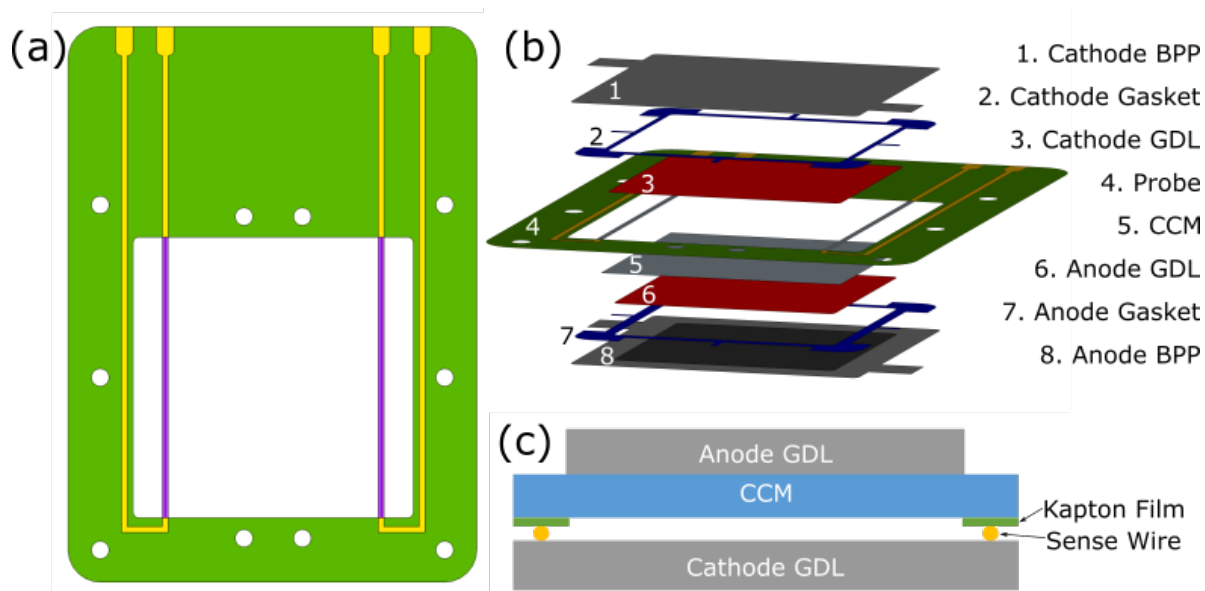

Figure 1. A schematic of (a) the PCB probe, (b) the assembly of the probe with the fuel cell components, (c) a cross-section showing the position of the probe between the CCM and cathode GDL.

During operation, a high precision voltmeter (Agilent 34970A) was used to record the potential difference between the probes, which were in contact with the GDL, and cathode side BPP. The potential difference between the GDL and BPP was divided by the cell's current density to obtain an area specific resistance. While this measure theoretically includes some component of the bulk electrical resistance of the GDL and BPP it is expected to be dominated by the ICR[19]. *Ex-situ* ICR measurements were performed before and after *in-situ* testing using a technique adapted from Wang *et al.*[11] Full details of testing are provided in the Supplementary Information.

Results and Discussion

Polarization curves were collected on an unmodified cell and with a cell featuring the *in-situ* ICR probe. The polarization curves, Figure 2a, show that there was no discernable impact of the probe on cell performance. These results are significant as they confirm that the measurements can be made on state-of-the-art cells using largely unmodified components without compromising performance. The simple and modifiable nature of the PCB design allows for this type of ICR probe to be incorporated into a wide variety of active area
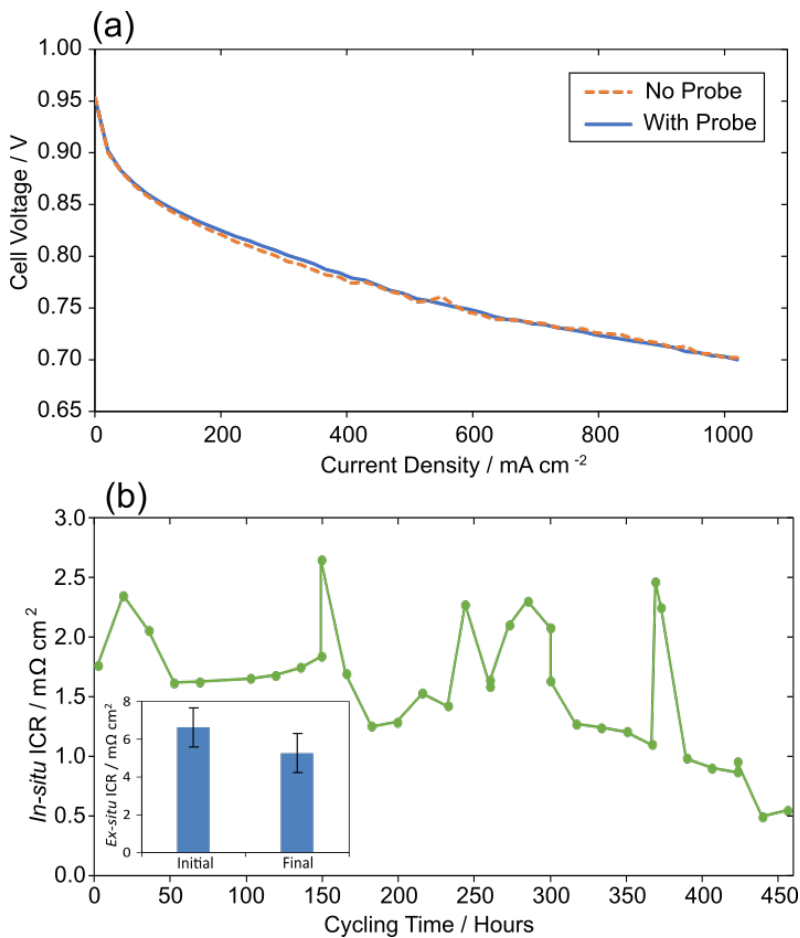
geometries or designs.

Figure 2. a) Polarization curves of cell with and without in situ probes b) Variation of ICR over 450 hours of cycling time with pre-planned cell shutdowns performed at 150 and 360 h. The inset shows a comparison with ex-situ ICR at BOL and EOL.

Long-term monitoring of the performance of the BPP is possible (figure 2 b) and has been validated for 450 hours of dynamic load cycling, following procedures outlined in the EU Harmonized Test Protocols for PEMFCs.[20] The in-situ data showed a similar trend to *ex-situ* ICR measurements, which were of a larger magnitude, as expected[11], and remained in the same range as literature values for the ICR of gold coated BPPs, which are typically around 1 - 5 mΩ cm^2, depending on the coating thickness[21–23].

Additional validation of the *in-situ* probe was performed during the measurement of a polarization curve (Figure 3a), where the change in contact resistance with current density is dependent on the type of BPP used, as observed by Ihonen *et al*.[13]
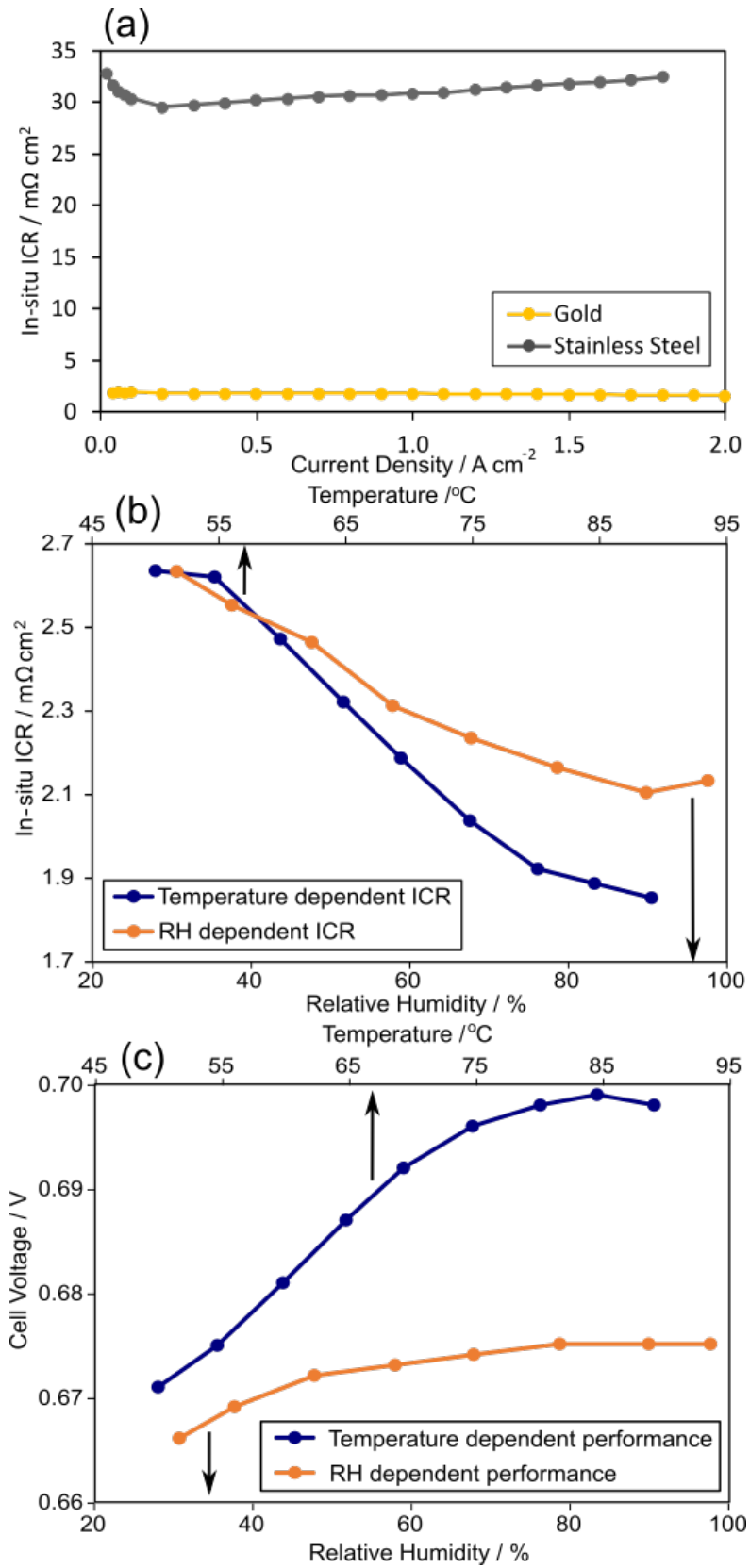
Figure 3. (a) The average in-situ ICR between the BPP and GDL as a function of current density, and dependence on temperature and relative humidity of (b) the in-situ ICR, (c) the fuel cell performance. The baseline conditions, as described in the supplementary information, were 1 A cm⁻², 80 % RH and a cell temperature of 70 °C.

Figures 3 b and c show that the *in-situ* ICR measurement is sensitive to small changes in temperature and RH, with a reduced ICR observed upon increasing the temperature or RH of the fuel cell. These results align closely with results reported by Oyarce *et al.*[16] who hypothesize that changes in ICR as a result of operating conditions are caused by mechanical changes, such as membrane swelling at higher RH, changing the effective clamping pressure inside the cell. However, it is clear that the change in ICR of the BPP/GDL interface contributes only a small amount (less than 1 mV at 1 A cm^{-2}) to the overall performance change observed when varying the operating conditions.

Further work is being undertaken to improve understanding of the reproducibility and uncertainty of the measurements but trends in ICR upon variation of coating type and operating conditions can already be elucidated. Further investigation is also underway to understand the extent of the spatial resolution afforded by the probes i.e. to what extent measurements reflect a true average of cell ICR.

Thus, the *in-situ* ICR probe is a complementary tool to other electrochemical techniques such as impedance spectroscopy and polarisation curves, aiding the deconvolution of ohmic resistances inside the cell. It is particularly well suited to investigating the behavior of BPP coatings *in situ,* allowing monitoring of the evolution of ICR over time.

Conclusions

A new method applying a simple principle for performing *in-situ* ICR measurements has been developed. Initial experiments demonstrated the ability to measure variations in ICR over time and with changes in operating conditions. In the future, this technique may be easily adapted to other fuel cell designs. Further work is being undertaken to understand the reproducibility and uncertainty associated with the measurements, as well as the impact of spatial variations in fuel cell conditions and current on ICR.

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