Title: FACTORS AFFECTING POLYMER ELECTROLYTE FUEL CELLS PERFORMANCE AND REPRODUCIBILITY

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Submitted to: 1998 Fuel Cell Seminar
Palm Springs, CA
November 1998
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Development of fuel cells is often based on small-scale laboratory studies. Due to limited time and budgets, a minimum number of cells are usually prepared and tested, thus, conclusions about improved performance are often drawn from studies of a few cells. Generally, statistics showing the significance of an effect are seldom reported. In this work a simple PEM fuel cell electrode optimization experiment is used as an example to illustrate the importance of statistical evaluation of factors affecting cell performance. The use of fractional factorial design of experiments to reduce the number of cells that have to be studied is also addressed.

Many steps are encountered when preparing fuel cells, each of which may influence the final cell performance. In this work the main steps included preparation of electrocatalytic material, application of the electrocatalytic layer to a Nafion™ membrane by spraying, and assembling single cells. Details of these steps were reported previously [1]. The electrocatalytic material for the thin film electrodes was mixed extensively (both mechanically and ultrasonically) and was thus expected to be of uniform composition. The amount of electrocatalytic material applied to the membrane was kept within ±3%.

To assess the effect of variation in single cell preparation on cell performance, three factors were analyzed using a statistically designed experiment as shown in Figure 1. The factors were i) the Nafion content and ii) the Pt-loading of the catalyst layer, and iii) the temperature at which the membrane and electrode assembly (MEA) was dried. Each factor was given two levels, hence this was a 2³-experiment, as described by Box et al. [2].

In one particular series of experiments, three ‘identical’ cells were tested to obtain an estimation of the reproducibility. Despite effort put into making the cells as identical as possible, a large deviation in performance between the cells was observed. The cells were compared, giving a standard deviation of σ=86 mV at a current density of 100 mA/cm². Factorial analysis was used to evaluate the effects of the three main factors on cell performance. The main effects of the factors were calculated as differences of the form (y⁺−y⁻), where y⁺ and y⁻ are the average cell potentials at high and low levels of the factor, respectively. Since y was an average of four values, the variance of the main effects, \( V_e \), is given by Box et al. [2]:

\[
V_e = \sqrt{(y_+ - y_-)^2} = (\frac{1}{4} + \frac{1}{4})\sigma^2
\]

where \( \sigma \) is the standard deviation for one type of cells, as given above. The standard deviation for
Table 1. Main effects on cell potential, $E^*$, and significance level of the factors in the full 2$^3$-experiment and half-fractions A and B.

<table>
<thead>
<tr>
<th>Factor</th>
<th>Full factorial 2$^3$-experiment</th>
<th>Half-fractions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Effect on $E^*$ [mV]</td>
<td>Sign. Level</td>
</tr>
<tr>
<td>Nafion (wt%)</td>
<td>+123</td>
<td>91.0%</td>
</tr>
<tr>
<td>Drying Temp. (°C)</td>
<td>-87</td>
<td>79.6%</td>
</tr>
<tr>
<td>Pt-loading (mg/cm$^2$)</td>
<td>+225</td>
<td>99.0%</td>
</tr>
</tbody>
</table>

The effects was calculated to be $\sigma_e = \sqrt{\epsilon} = 61\text{mV}$. The calculation of the effects was based on 8 measurements, however, the use of average values at high and low levels decreases the degrees of freedom by 2, leaving 6 degrees of freedom for the estimation of the effects. The level of significance of the effects was calculated from the $t$-distribution [2] and the results are shown in the left part of Table 1. Increasing the catalyst loading and the Nafion content in the catalyst layer increased cell performance, whereas high MEA drying temperatures reduced cell performance. The significance levels were all close to or over 80%, implying that the probability that the factors did have an effect on the cell potential was high. Still, there was a 20% probability that the drying temperature did not have any effect on cell performance. This uncertainty is relatively high and calls for improvements; thus, factors concerning the cell assembly, break-in procedure, and

![Graph](image-url)

Figure 2. The effect of variation in pressure over the MEA on cell performance at 70°C.
* Pressure reduced from 9.4 to 1.8 bars.
operation of the cells were examined. Operation temperatures, gas pressures and flow rates were all maintained within very narrow limits due to microprocessor control. The break-in procedure was identical for all cells. One additional factor that could cause variations in cell performance was the pressure by which the MEA was held together during performance tests. Re-torquing the fixture bolts during operation had accidentally indicated variations in cell performance. Hence, a pneumatic cylinder was fitted to the cell fixture (see Figure 4) in order to give reproducible mechanical pressures over the MEA; hereafter called the "pressure of compaction". A single cell was tested at pressures in the range of 1.8-24.9 bars showing current densities varying from 100 to 250 mA/cm² at 0.7 V, correspondingly, as shown in Figure 2. The pressure of compaction was increased progressively and had a pronounced positive effect on cell performance. After obtaining the polarization curve at 9.4 bar, the pressure was reduced to 1.8 bar. As can be seen from Figure 2, the performance was reduced correspondingly resembling the original curve at this pressure. Further pressure increase gave even better performance. After having applied 24.9 bar to the single cell, the performance did not return to the original curve upon pressure reduction. This indicated that the changes were reversible up to a certain pressure, above which the single cell was permanently altered. From Figure 2 it can be seen that the large performance improvement was primarily due to reduction in ohmic resistance in the cell. This might again be a result of reduction in contact resistance between the current collector and backing (E-TEK) and/or between the backing and catalyst layer. It was believed that the contact between membrane and catalyst layer did not change much because the electrocatalyst was sprayed directly onto the membrane. When the single cell was taken out from the cell fixture after applying this high pressure, the porous electrode backings, which had been merely inserted in between the catalyzed membrane and the current collector piston, had become adhered to the catalyst layer. The relatively high pressure of compaction was believed

![Cell data](image-url)

Figure 3. Cell data for three cells of the same composition, containing thin film electrodes with a loading of 0.1 mg Pt/cm². Cell temperature was 70°C, and gas pressures (O₂/H₂) were atmospheric. Stippled lines show a 90% confidence interval for the data. The cell area was 5 cm².
to have resembled a mild type of hot pressing. Conditions used for hot pressing are typically in the range of 70-90 bar and 125°C for Nafion membranes [3].

Reproducibility was tested again after the incorporation of the pneumatic equipment for controlling the pressure of compaction. Three new identical cells were prepared and tested using a pressure of compaction of 10 bars. The polarization data are shown along with a 90% confidence interval in Figure 3. A 90% confidence interval means that 9 out of 10 cells would fall within the stippled lines in the figure. This corresponds to a standard deviation of 31 mV at a current density of 100 mA/cm², which is less than half the former value (86 mV) when not using the pneumatic cylinder.

The factorial experiment discussed above was a full 2³-factorial experiment, meaning that all 8 combinations were studied. A more efficient approach is to apply a fractional factorial design, in which one tests a certain fraction of the full experiment. For a 2³-experiment, a half-fraction is denoted 2³-1 = 2², and thus, consists of four experiments. By selecting the four experiments following certain rules [2], one can obtain the effects of the factors without sacrificing too much reliability. The two half-fractions that may be selected for this simple example experiment are shown as black and white balls, respectively in Figure 1. For the sake of argument, the results of the two half-fractions (A and B) of the experiment were used to evaluate the main effects. The results are included in Table 1. The main conclusions are maintained, even though the significance of the results suffers somewhat from the reduction in degrees of freedom from 6 to 2. Still, the significance of all effects are 65.6% or higher.

It can be concluded that replicates should be run when testing fuel cells, and that standard deviation or significance levels should be reported along with cell performance data. When studying different factors and their influence on cell performance, fractional factorial design may significantly reduce the number of cells to be tested, while maintaining adequate result reliability. It is further recommended that the pressure over the MEA be reproducibly controlled. Otherwise, erroneous conclusions may readily be drawn from fuel cell tests.

References