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14. ABSTRACT
Lifetime DMFC performance degradation studies were performed using both single cell and high throughput catalyst screening techniques. Efforts to mitigate the degradation of the DMFC were focused on acid pre-treatment of the anode catalyst, identification of novel anode catalyst materials, load cycling techniques, and improvement of the catalyst layer deposition. Acid pre-treatment of the anode catalyst yielded no significant decrease in the time dependent performance degradation. No performance improvement was identified using the novel catalysts

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219-644-3231

Report Title

Final Report for Direct Methanol Fuel Cell Battery Replacement Program

ABSTRACT

Lifetime DMFC performance degradation studies were performed using both single cell and high throughput catalyst screening techniques. Efforts to mitigate the degradation of the DMFC were focused on acid pre-treatment of the anode catalyst, identification of novel anode catalyst materials, load cycling techniques, and improvement of the catalyst layer deposition. Acid pre-treatment of the anode catalyst yielded no significant decrease in the time dependent performance degradation. No performance improvement was identified using the novel catalysts developed or with the load cycling methods. The employment of a membrane catalyst deposition technique demonstrated superior performance over direct gas diffusion layer catalyst deposition.

List of papers submitted or published that acknowledge ARO support during this reporting period. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

1. Stanislav Stoupin, Harry Rivera, Zhengrong Li, Carlo U. Segre, Carol Korzeniewski, Dominick J. Casadonte, Jr., Hisashi Inoue and Eugene S. Smotkin, “Structural analysis of sonochemically prepared PtRu versus Johnson Matthey PtRu in operating direct methanol fuel cells” Phys. Chem. Chem. Phys., 10, 6430-6437 (2008)
2. Harry Rivera, Jamie S. Lawton, David E. Budil and Eugene S. Smotkin, “The effect of sorbed methanol, current and temperature on multi-component transport in Nafion based direct methanol fuel cells” J. Phys. Chem. B, 112, (29) 8542-8548 (2008)
3. Jamie S. Lawton, Eugene S. Smotkin and David E. Budil, “ESR Investigation of Microviscosity, Microscopic Ordering, and Local Polarity of Methanol and Water in Nafion Membranes” J. Phys. Chem. B, 112 (29) 6549-8557, (2008)
4. Zhen-Bo Wang, Harry Rivera, Xin-Peng Wang, Hong-Xin Zhang, Peter-Xian Feng, Emily A. Lewis and Eugene S. Smotkin, “Catalyst failure analysis of a direct methanol fuel cell membrane electrode assembly” Journal of Power Sources, 177, (2), pp 386-392 (2008)
5. Smotkin, E. S., “Proton spillover promoted non-Faradaic reactions at polymer electrolyte fuel cell cathodes” in Conference Proceedings of First International Conference on the Origin of Electrochemical Promotion of Catalysis, Tsiplakides, D., Balomenenou, Eds., CPERI-CERTH, ISBN 978-960-98231-0-4 Greece, pp. 14 – 19, 2008
6. James S. Cooper, Min Ku Jeon, Paul J. McGinn “Combinatorial screening of ternary Pt-Ni-Cr catalysts for methanol electro-oxidation” Electrochemistry Communications, 10 (2008) 1545-1547
7. Min Ku Jeon, James S. Cooper and Paul J. McGinn “Methanol electro-oxidation by a ternary Pt-Ru-Cu catalyst identified by a combinatorial approach” Journal of Power Sources, 185 (2008) 913–916

Number of Papers published in peer-reviewed journals: 7.00

(b) Papers published in non-peer-reviewed journals or in conference proceedings (N/A for none)

Number of Papers published in non peer-reviewed journals: 0.00

(c) Presentations

1. Hall, T.D.; Kleszyk, P.M.; Grice, C.R.; Fuccillo, M.; Russell, A.E.; Smotkin, E.S., “High-Throughput evaluation of MEA components of hydrogen-air fuel cells”, 212th Electrochemical Society Meeting, ABS#1089, Oct. 16th 2008, Hawaii, USA.
2. Hall, T.D.; Grice, C.R.; Swenson, L.R.; Smotkin, E.S., “Reversible and irreversible degradation modes of DMFC anode catalysts”, 212th Electrochemical Society Meeting, ABS#819, Oct. 14th 2008, Hawaii, USA.
3. Yuan Zhang, James Cooper, Paul McGinn “Combinatorial Screening of Fuel Cell Catalysts” 211th Electrochemical Society Meeting, Phoenix, AZ, May, 2008
4. Hall, T.D.; Grice, Corey R.; Gurau, B.; Swenson, LaSalle R.; Smotkin, Eugene S., “Power Optimization by On/Off Cycling in DMFC Fuel Cells”, 215th Electrochemical Society Meeting, May 27th, 2009, San Fransisco, CA, US.
5. Grice, C.; Hall, T.D.; Swenson, LaSalle R.; Smotkin, Eugene S., “Effect of DMFC Anode Catalyst Pretreatments on Lifetime and Durability”, 215th Electrochemical Society Meeting, May 27th, 2009, San Fransisco, CA, US.

Number of Presentations: 5.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts): 0

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Patents Submitted

Patents Awarded

Awards

Graduate Students

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period:	0.00
The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:......	0.00
The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:......	0.00
Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):	0.00
Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:	0.00
The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense	0.00
The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:	0.00

Names of Personnel receiving masters degrees

NAME

Total Number:

Names of personnel receiving PHDs

NAME

Total Number:

Names of other research staff

NAME PERCENT_SUPPORTED

FTE Equivalent:

Total Number:

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Inventions (DD882)

Scientific Progress

See attachment.

Technology Transfer

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SUBMITTED TO

Army Research Office

Final Report

Portable fuel cells with high energy density liquid fuels are an alternative to batteries for extended mission lengths. An advantage of fuel cells versus batteries is that the increase in weight required for longer mission lengths is entirely fuel weight, particularly when using collapsible methanol reservoirs. The show-stopper is membrane-electrode-assembly durability.

Toward the end of the project NuVant Systems has attempted to deliver both one-at-a-time and high throughput prepared catalysts at Northeastern and the University of Notre Dame respectively. Unfortunately, none of the catalysts produced were capable of challenging the commercially available Johnson-Matthey catalyst. In order to keep up with the stated target of delivering a better MEA and in the light of the oncoming program focused on DMFCs operating on concentrated methanol, NuVant had decided to focus on MEA optimization rather than persist with catalyst discovery and screening.

However, to show some results with the alternative catalysts under investigation the following figure is provided.

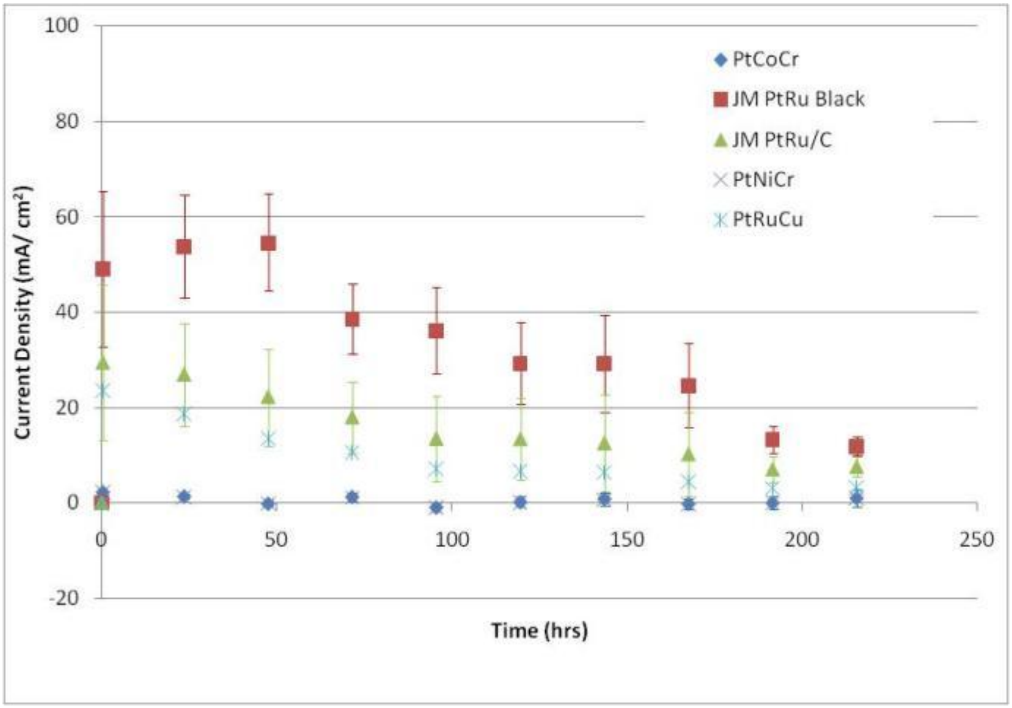


Figure 1. Life test under constant potential for various DMFC catalysts.

It can be easily noticed that the Johnson Matthey PtRu/C catalyst outperforms all the others over the entire life test. However, even that catalyst shows intense degradation over the life of the test. One reason for the decay can be attributed to the un-optimal way the MEA was prepared. NuVant has prepared the MEAs shown in the picture above by depositing the catalyst onto the diffusion layers and then hot-pressing them onto the membrane of choice (Nafion 117 in this case). The MEAs prepared in this way are known as catalyst coated diffusion layer MEAs or 5 layer MEAs. This technique is adequate for initial tests of catalyst activity but the resulting MEAs are subject to rapid degradation due to the weak bonding between the membrane and the catalyst that is deposited onto the diffusion layer. In the process of hot-pressing the pressure at which the catalyzed diffusion layer is subjected is not very high or it would collapse the porosity of the diffusion layer.

The better alternative is to deposit the catalyst directly onto the membrane. The MEAs prepared in this way are known as catalyst coated membrane MEAs (CCMs) or 3 layer MEAs. The following are the advantages and disadvantages of the two techniques:

1) Catalyst Coated diffusion layer MEAs

Advantages

- easy to employ, no special equipment needed
- easy to account for the catalyst loading
- can easily be automated

Disadvantages

- MEA prone to delamination
- high ohmic losses

2) Catalyst coated membrane MEAs

Advantages

- electrodes in intimate contact with the membrane
- lower degradation, lower ohmic losses (because of the more intimate interface)
- can be automated

Disadvantages

- more difficult to account for the catalyst loading
- requires special equipment to hold the membrane down (vacuum tables)
- longer preparation times

For more robust MEAs the CCM technique is unavoidable in spite of its somewhat more difficult implementation. Certainly, once the optimum recipe for the catalyst ink is established the process of coating the membranes can be automated using screen printing techniques. The catalyst loss that is encountered when using screen printing is significant though and the technique is suitable once a large number of MEAs is required. For the scope of this project manual painting of the catalyst onto the membrane is preferred due to the minimal loss of catalyst that is encountered. In order to be able to directly paint onto the Nafion membrane a device is required to hold the membrane down. Nafion membranes will swell when touched by liquids and that would make the painting uneven or even impossible. The most often used devices are vacuum tables. NuVant designed vacuum tables are shown in the following pictures.

It can be ……..

In order to illustrate the performance differences between MEAs prepared with the two techniques mentioned above we present first the performance of MEAs prepared with the catalyst coated diffusion layers technique.

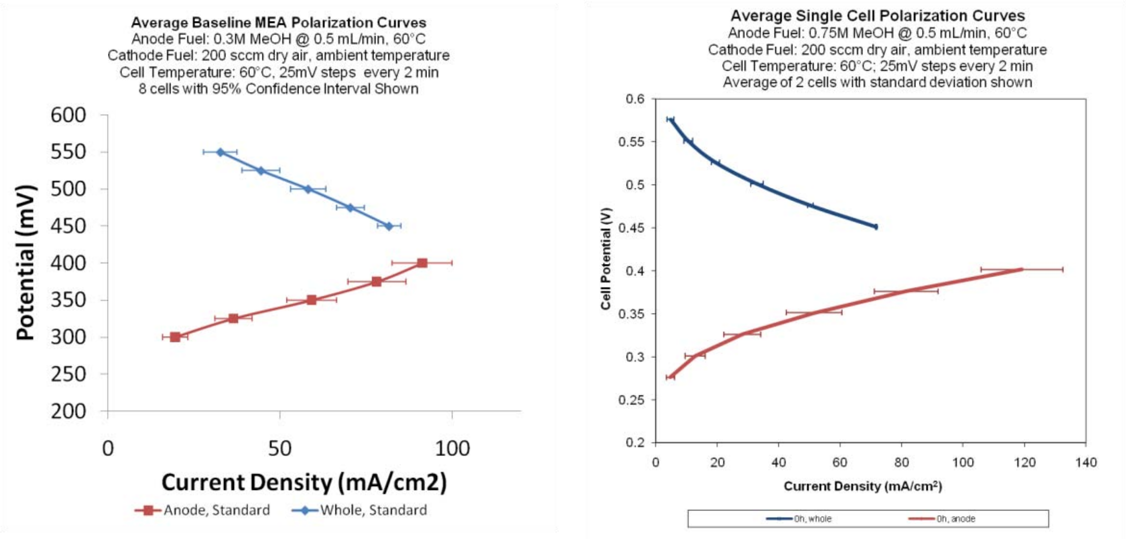


Figure 2. Baseline Legacy Cell Performance at t=0 hours. Left 0.3M MeOH, Right 0.75M MeOH

Both the anode (red) and the whole cell (blue) polarization curves are presented in figure 2. It can be noticed that when operating with 0.3M the anode becomes mass transport limited as the anode polarization curve in the left hand side graph starts curving upwards. This is normal as 0.3M is a very low concentration. Utilizing 0.75M one can extend the operating regime beyond 100 mA/cm^2.

Some of the MEAs were subjected to 1000 hr life tests and their performance was assessed after the test. The result is shown in figure 3.

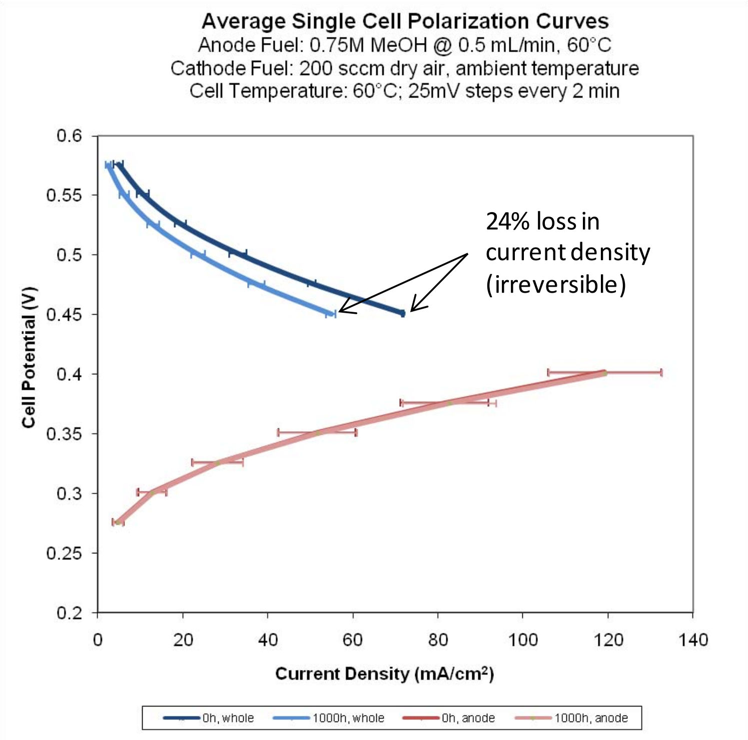


Figure 3. Polarizations of Baseline Cells at t = 0hrs and t = 1000hrs during 100mA/cm^2 soak; little anode loss but significant whole cell loss. Catalyst coated diffusion layer MEA. Red: anode polarization, Blue: whole cell polarization

It can be seen from figure 3 that the cell degrades irreversibly after 1000 hours with most of the degradation coming from the cathode. This can be from electrode delamination and/or Ru crossover. A plot of the 1000 hr life test is shown in figure 4.

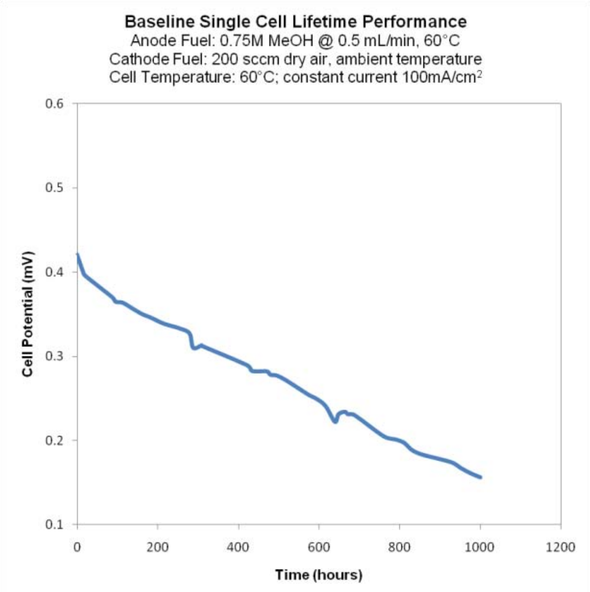


Figure 4. Baseline Legacy Cell Performance at 100mA/cm^2 for 1000hrs. Catalyst coated diffusion layer MEA.

It can be easily noticed that the degradation rate is very large. At the beginning of life the cell voltage was ca. 0.42V at 100 mA/cm^2, but by the 1000 hr mark decreased to ca. 0.16V. This equates to a degradation rate of 0.26 mV/hr. An acceptable degradation rate should be at the most a few tens of microvolts per hour.

Moving on to the CCM type MEAs and performing the same type of experiments we present by comparison in figure 5 the performance of a CCM type MEA acquired under the same conditions as the one shown in with figure 3.

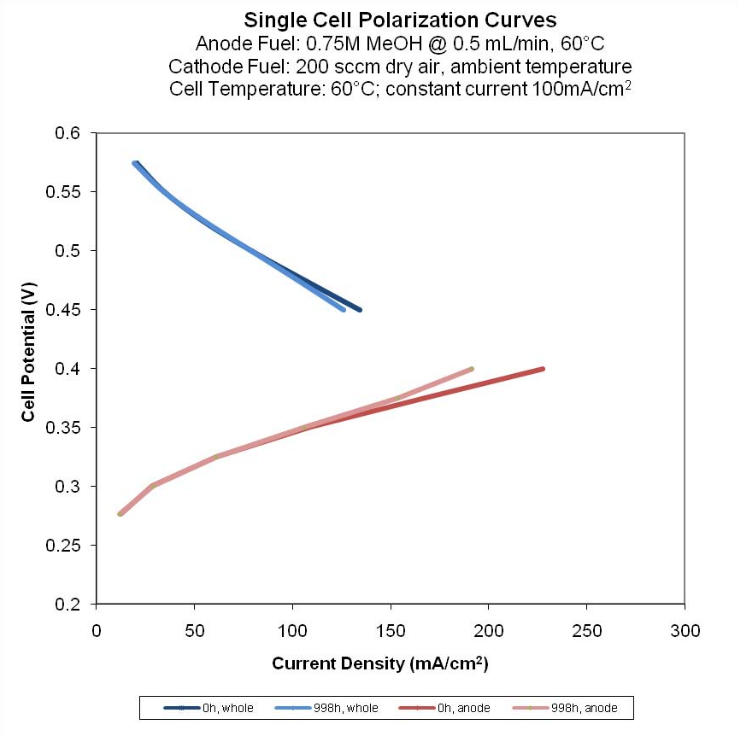


Figure 5. Polarizations of Baseline Cells at t = 0hrs and t = 1000hrs during 100 mA/cm^2 soak; almost no loss in performance. CCM type MEA. Red: anode polarization, Blue: cathode polarization

It can be easily seen that there is almost no loss in performance between beginning of life and end of life (1000 hrs). The whole cell polarization curves start to diverge around 80 mA/cm^2 but there is really minimal loss in performance. The anode polarization curves (red) diverge beyond 80 mA/cm^2 , which, again, indicates that any losses that exist come from the cathode. In the kinetic region there seems to be no loss in performance.

The same 1000 hr life test that was performed for the catalyst coated diffusion layer type MEA was performed for the CCM and the degradation rate was determined. The 1000 hr life test at a constant current of 100 mA/cm^2 is presented in figure 6.

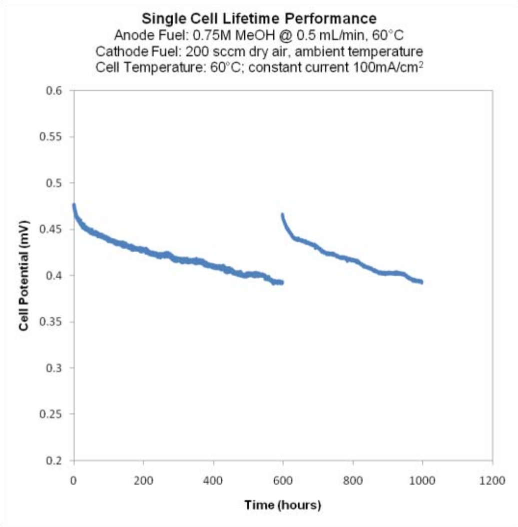


Figure 6. Baseline Legacy Cell Performance at $100mA/cm^2$ for 1000hrs. Catalyst coated membrane MEA.

It can easily be seen from the graph that the degradation rate over the 1000 hours of the experiment is much smaller than in previous case. The cell voltage at the beginning of life is ca. 0.47V and at the end of 1000 hrs is ca. 0.4V. This equates to ca. 0.07 mV/hr, which is one order of magnitude lower than in the case of the catalyst coated diffusion layer. The interruption at the ca. 600 hr mark was due to a power outage.

Not only the degradation rate proves that the coating the membrane yields a better MEA but the electrical performance in itself. The following figure proves that the performance of the CCM is much better than the performance of the catalyst coated diffusion layer.

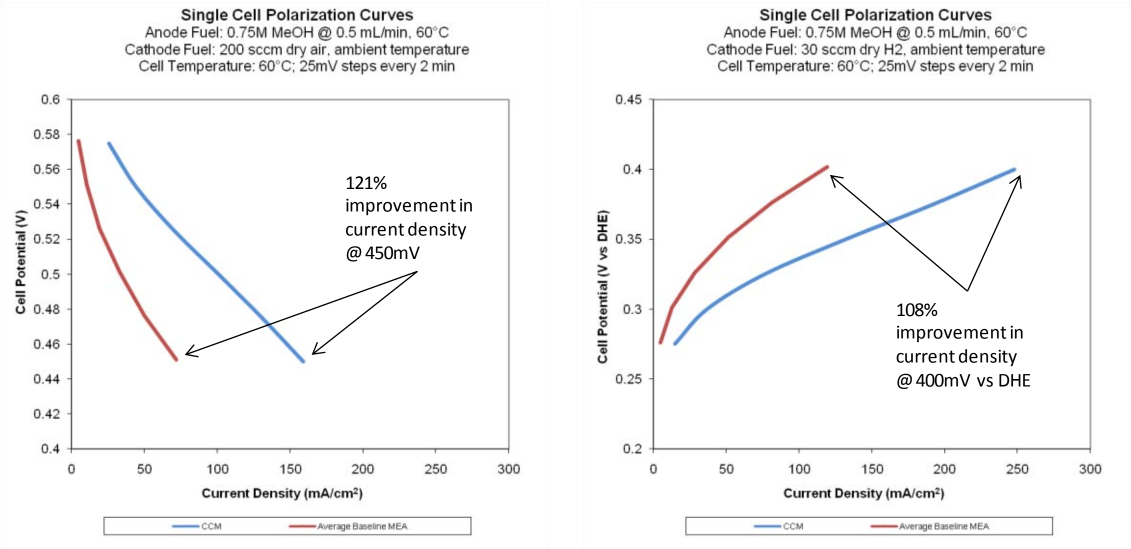
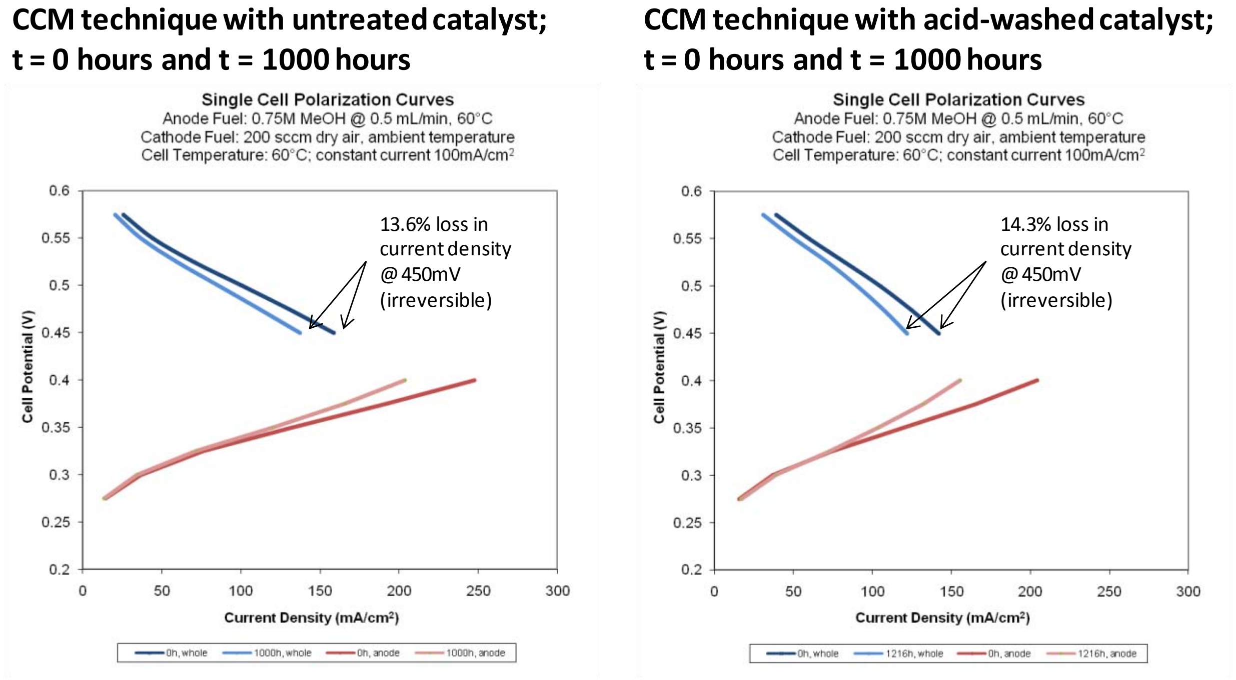


Figure 7. Performance of the catalyst coated diffusion layer MEA (red) vs. CCM MEA (blue). Left: whole cell polarization, Right: anode polarization.

The increase in performance is more than double for the CCM compared to the catalyst coated diffusion layer at 0.45V which is within the operating window of a DMFC. In the right hand side of the graph one can see that the anode carries a lot of the improvement but not all of it. It is quite clear that the application of ink to the membrane is benefic for both electrodes.

One of the recommended techniques to reduce degradation is to subject the as-received catalyst to a series of leaching experiments with the aim to remove oxidized species and stabilize the electrochemical available area of the electrode. The pretreatment of the catalyst brings it into a similar environment to that that exists in the MEA, namely corrosive acid environment at elevated temperatures. Consequently the catalyst mixed with a H_2SO_4 solution under continuous stirring at 80 deg C. We have performed the treatment of the catalyst, made the catalyst into a CCM type MEA, ran the 1000 hr life test at 100 mA/cm^2, after which we measured the polarization of the cell. We compared the polarization curves of the MEAs with untreated and treated catalyst hoping that the MEA containing the pretreated catalyst would show lower degradation. The results are shown in figure 8.



CCM technique with untreated catalyst; t = 0 hours and t = 1000 hours

CCM technique with acid-washed catalyst; t = 0 hours and t = 1000 hours

Figure 8. Polarization curves with the MEAs with pretreated (right) and as-received catalyst (left).

It can be seen that the acid-wash pretreatment did not really make much difference (if any) as far as the degradation rate is concerned. The slight difference in the percentage loss of performance is most likely within the experimental error. Perhaps better recipes for acid washing the catalyst should be investigated.

Conclusions

While we have not been able to discover novel catalysts that exceed the performance of the state-of-the-art Johnson Matthey catalysts, we have developed a new MEA preparation technique that doubled the performance of our DMFC. The degradation rate of the fuel cell was also reduced by a factor of more than 3 by employing this new CCM technique.

Our attempt to further reduce the degradation rate by acid washing the catalyst before making the MEA was unsuccessful but we suspect that better pretreatment recipes might yield better results.

We are confident that the newly developed MEA preparation will aid us in the next phase of the project where we will develop DMFCs that will operate on concentrated fuel, thus increasing the energy density of the system that they will be implemented into.