DOE-Final Report

Multi-Hybrid Power Vehicles with Cost Effective and Durable Polymer Electrolyte Membrane Fuel Cell and Li-ion Battery

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Submitted by

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Executive summary: Anima Bose, the principal investigator of the project, originally proposed to develop composite membranes to operate PEMFCs at much higher temperatures than 80 °C and to alleviate the flooding problems often encountered in Nafion membrane containing fuel cells. The PI has successfully created composite membranes by blending small quantities of octasilane-poss (OSP) with Nafion. The composite membranes exhibited temperature tolerance up to 110 °C without sacrificing cell performance as determined by polarization curves and proton conductivity measurements. These membranes also exhibited superior water management performance as evident from the lack of flooding. Furthermore, these fuel cells performed well under reduced humidities. Structural and thermal analyses revealed that these Nafion-octasilane composite membranes are homogenous at concentrations up to 3 wt% of the OSP and that the siloxane offers additional thermal stability. The representative Figure 1 below compares the cell performance of the composite membrane and neat Nafion membranes at 90 °C, and illustrates the proposed composite membrane structure.

Figure 1: (Left) Comparison of single cell performance of composite membrane (purple curve) with those of neat Nafion membranes (blue curve, commercial Nafion membrane and yellow curve, in-house prepared Nafion membrane); (Right) proposed structure of the (a) composite membrane consisting of (b) Nafion and (c) OctaSilane-POSS.

Potential Intellectual Property: Potential intellectual properties (IP) have emerged from this DOE funded project.

The invention relates to the efficient mitigation of flooding/water management issues by incorporating hydrophobic cage filler in electrode structure for electrochemical cells like PEMFCs. A mechanism related to this invention will be proposed soon on water management for low temperature electrochemical cells such as fuel cells (FCs). Details invention is described in this report. This invention also includes the nature of pore structure generated by incorporation the cage-structured additive. Hydrophobic nature of cage-structured additive created a unique electrode environment to push out water from cell and nano-pores allow reactants breathe freely in and out of electrode matrix.

In addition to the above mentioned potential, a porous electrode fabrication technique has been described for quick solvent evaporation resulting uniform porous electrode. This technique demonstrated reproducible MEA fabrication in a significantly shorter time compared to conventional spray MEA fabrication techniques. This method of electrode fabrication helps to maximize the catalyst utilization thereby lowering the catalyst use in preparing porous electrode through fast solvent evaporation from the electrode matrix.

List of potential Intellectual property developed from the grant

1. Hydrophobic-cage structured materials in electrodes for mitigation and efficient management of water flooding in Fuel/Electrochemical Cells: Inventor, Anima Bose; US Provisional Application SN: 61/879,412; Filed on September 18, 2013

List of Articles Published

1. A. Bose, P. Babburi, R. Kumar, D. Myers, J. Mawdsley, "Performance of individual cells in PEMFC Stack under load cycling conditions", J. Power Sources, 243 (2013) 964-972.

List of Papers Presented in Meetings/Conferences

1. C. K. Perera, A. B. Bose. D. J. Bayless, "Fuel Cell Losses: The Invisible Presence in Electrochemical Impedance Spectroscopy (EIS) Measurements Fuel Cell Seminar & Exposition. Orlando, FL. October 31 2011.
2. A.B. Bose and S. Gopu, "Assessment of Performance Losses in PEMFCs by Polarization Models", Fuel cell Gordon Research Conference, August 5 2012.
3. A. B. Bose and S. Gopu, "Remarkable Performance Enhancement of Polymer Electrolyte Membrane Fuel Cells (PEMFCs) by Creating Modified Electrode with Phosphotungstic Acid", Hydrogen and Fuel Cells Zing Conference, July 12 2013.

Introduction: The final report summarizes the accomplishments of Task 1, Hybrid composite membrane stack design and evaluation in vehicle load cycling. The report provides the summary

of earlier findings and details of composite membrane characterization, single cell performances and durability under the vehicle load cycling conditions, and structural integrity of the composite membranes after the durability tests.

As rationalized in the proposal, Nafion containing membrane electrode assemblies function optimally at 80 °C, but platinum oxygen reduction catalyst increases its catalytic efficiency by increasing temperatures. Furthermore, catalyst poisoning can be reduced by functioning PEMFCs at higher temperature. Hence, there is a need for creating high-temperature membranes to increase PEMFC efficiency. Through this funded project by the Department of Energy, the PI has successfully created composite membranes by blending various concentrations of OctaSilane-POSS (OSP, from 1 to 10% by weight) with Nafion.

The earlier reports include the highlights:

- Composite membranes can be easily prepared by simply blending octasilane-poss up to 5 wt% with Nafion polymer without any visible phase separation
- These composite membranes show considerable shelf lives, up to 26 months
- Fabricated MEAs exhibited acceptable performance up to 110 °C
- MEAs performances implied good water management properties
- MEAs exhibited very good performance under reduced humidity

These earlier reports were solely concentrated to determine cell performance at various octasilane concentrations without detailed characterization of the composite membranes. In this report, we evaluated the membrane morphology and thermal stability of different composite membranes, and conducted durability of select single cells based on the structural information of the composite membranes as detailed below. Furthermore, the water management properties of a select composite membrane were fully investigated.

Membrane characterizations: The membranes were characterized with various imaging tools including SEM, EDX, TEM, TGA and others. Table 1 lists the composition of composite membranes some of which were fully characterized.

Figure 2 and 3 show optical and microscopic morphology of some selected membranes. These images clearly show the variation of morphology based on casting conditions of temperature profile and modes of preparation. D₂ and D₃ membranes show more uniform optical and microscopic morphology than D₁, indicating protocols II and III are better than protocol I to manipulate more homogeneous octasilane distribution inside the membrane. The highest concentration in the composite membranes was optimized as 3.0 wt% based on optical and SEM techniques, which indicate the maximum capacity to accommodate the siloxane polymer based on this set of data. Optical and SEM images suggest non-uniformity could occur with higher percent of OSP in the membrane, observed micro-phase separation and cracking with 7.5% OSP in Nafion blend. Though optical image displayed foggy or cracking nature in the membrane with

higher OSP additive in membrane, and phase separation and wrinkle support the evidence in SEM images. However, author plans to conduct further study for impregnating optimal percent of OSP in the polymer blend.

Table 1: A Series of composite membrane (OSP-Nafion) designated as (D_x) prepared by varying OSP content in Nafion blend under different curing conditions. Protocol of curing and percent of OSP listed in table. Three different curing protocols are: I. 12 hours = 2 h at 80 °C + 10 h at 140 °C; II. 12 hours = 4 h at 60 °C + 4 h at 80 °C + 2 h at 100 °C + 2 h at 140 °C; III. 16 hours = 8 h at 60 °C + 4 h at 80 °C + 2 h at 100 °C + 2 h at 140 °C. Heating rate was maintained 8 °C/min for all membrane casting.

Membrane Code	over Nafion solid	Drying Protocol	Comments
D ₀	0	I	SEM/EDX, Stained TEM
D ₁	7.5	I	
D ₂	7.5	II	
D ₃	7.5	III	SEM/EDX, Stained TEM
D ₄	5	III	Stained TEM
D ₅	1	III	SEM/EDX, Stained TEM
D ₆	1	III	
D ₇	5	III	
D ₈	3	III	SEM/EDX
D ₉	0	III

Figure 2: Optical Images of membrane D₁ (Left), D₂ (Middle), and D₃ (Right) appearances with 7.5 wt% OSP.

Figure 3: SEM images of membrane D₁ (left and medium) and D₂ (right) surface morphology, with magnifications of 35, 100 and 100 times, with scale bar of 100, 50, and 100 μm , respectively.

Figure 4: SEM images of the cross-sections of membrane D₀ (Nafion®), D₅ (1.0 wt%), D₈ (3.0 wt%) and D₃ (7.5wt%).

Figure 5: SEM images of the surfaces of membrane D₀ (neat Nafion®), D₅ (1.0 wt%), D₈ (3.0 wt%), and D₃ (7.5 wt%) with varied magnification.

Composite membranes showed various micro-morphology and element distributions. As indicated above, SEM coupled with EDX technique and lead ion stained TEM was used were employed to characterize the membrane surface and cross-section micro morphologies to identify the OSP distribution at nanometer scale. These studies provided first-hand knowledge in mechanical strength improvement of OSP-Nafion blend. Figure 4 shows the SEM images of

membranes with two different OSP contents. With increasing OSP concentrations from 1.0 to 7.5 wt%, the cross-section of membranes showed increased breaking wrinkles nature of the membrane. Cross-sectional images of membrane D₅ and D₈ were more smoother and long wrinkles, similar to that of membrane D₀ (pure Nafion®), rather than rigid and short wrinkles of membrane D₃. These observations suggest homogeneous or near homogenous OSP distribution occurred in membrane D₅ and D₈ during membrane casting process.

As can be seen from Figure 5, membrane D₃ images at various magnifications (left column) show the inhomogeneous distribution of OSP relative to smoother surfaces of membrane D₀, D₅ and D₈, which are consistent with those of cross-sectional images displayed in Figure 4. Both surface and cross-section SEM images illustrate the homogeneous distribution of OSP in the membranes with concentration below 3.0 wt%, in contrast to inhomogeneous distribution with that of 7.5 wt%.

Figure 6: EDX mapping images of C, O, F, Si, and S elements of the cross-section of membrane D₃, with SEM image (top left) to show the position.

Figure 6 shows the EDX elements distribution mapping images of C, O, F, Si, and S. Since light elements are not easily detectable, in particular, with lower concentration by EDX, EDX images tabulated here are considered more accurate of those membranes with highest percent of OSP. Sulfur element mapping is not shown but shown in element concentration calculation listed in Table 2. A characteristic of silicon distribution represents an enriched silicon corresponds to OSP distribution in membrane D₃ at the surface relative to the inner membrane. This is consistent with the observations in optical and SEM images of Figure 2, 3, and 5.

Table 2: EDX element concentration analysis of membranes D_x^* ($x = 0, 5, 8$, and 3).

D_x^*	SP / Nafion mass ratio	Measured mass concentr.		Measured ratio of Si/S		Calculated mass concentr.		Calculated ratio of Si / S	
		S	Si	mass	molar	S	Si	mass	molar
D_0	0.00%	1.60%	0.00%	0.00	0.00	3.17%	0.00%	0.00	0.00
D_5	1.00%	1.27%	0.36%	0.28	0.31	3.14%	0.44%	0.14	0.16
D_8	3.00%	0.74%	0.39%	0.53	0.61	3.08%	1.29%	0.42	0.48
D_3	7.50%	0.97%	1.28%	1.32	1.49	2.94%	3.08%	1.05	1.20

* Nafion® D 2021: EW = 1010 g/mol-SO₃H; OSP (C₁₆H₅₆O₂₀Si₁₆): Mw = 1017.99; silicon: Mw = 28.085; sulfur: Mw = 32.065.

Figure 7: Lead ion stained TEM images of membranes D_x ($x = 0, 5, 4$, and 3 ; from left to right), corresponding to OSP concentrations of 0%, 1%, 5%, and 7.5%, respectively. The scale bars represent 100 nm and 20 nm, respectively, of top row and bottom row images. The inset of the bottom right image shows small dark dots (ionic clusters) in the area between the blue and red circles.

As can be seen from Table 2, measured sulfur and silicon mass and molar concentration values are lower than those of theoretically calculated. The measured sulfur mass concentration was only half to the calculated because of the light element sulfur with low concentration in Nafion

membrane as mentioned above. Interestingly, D₀, D₅, D₈ and D₃ membranes with the increase in OSP concentration, show the ratio values of measured sulfur mass concentration to calculated, reduced from almost 1/2 to 1/3. Although the absolute values of sulfur and silicon elements concentrations were not accurately determined by EDX, it should be noted that the measured mass and molar ratio values of Si/S of membranes D₃ and D₈ are fairly consistent with those of calculated. However, membrane D₅ with the lowest OSP concentration showed the measured mass and molar ratio values of Si/S, almost twice those of D_x (x = 3 and 8). This observation for membrane D₅ is similar to that of neat Nafion D₀ where the measured sulfur concentration was obtained half of the calculated value.

Figure 7 shows the TEM images of membranes D_x (x = 0, 5, 4, and 3; from left to right) with the increasing OSP concentrations. The black dots with a size around 20 nm in the images at top row could cause from the aggregated OSP in the composite membranes. Where as a relatively homogeneous distributed dots appears with 1%OSP containt membrane. Non-uniformty of dark spots detected with increased OSP wt% the membranes, for example with 5 wt% and 7.5 wt% OSP contained membrane. Combined TEM and SEM result suggest that OSP concentration should be lower than 5 wt% and higher than 1 wt% of OSP in polymer blend for better OSP distribution in the membrane. The bottom row images are the higher resolution images of the top row. It can be seen that black dots with sizes of 1–4 nm uniformly distributed in all the membranes. The dots represent the hydrophilic domains of Nafion ionomer, *i.e.*, the ionic clusters, of which the H⁺ ions are replaced by lead ions. The addition of OSP does not significantly affect the distribution of the hydrophilic domains of Nafion ionomer.

The octasilane is in nano cage-structure, ca. around 1.2 nm of molecule and Figure 7 shows about a 20 nm of aggregation. The source and mechanism of this aggregation is required further investigation by comparing with controlled experiments. The distribution and interface of OSP with polymer in it's network is expected to different from regular inorganic particles such as silicon oxide.because octasilane not only have inorganic filler function, but also the unique nanometer scale cage is anticipated to promote reinforcement within polymer. Based on the observations summarized above, we propose a homogenous blend of the siloxane with Nafion as schematically shown in Figure 8.

Figure8: (a) Proposed structure of the composite membrane consisting of (b) Nafion ($x, y, z = 6, 1, 1$; EW = 1100) and (c) OctaSilane POSS®.

The proposed structure of this composite revealed an interlinked polymer network that reinforces each other. This unique reinforcement of polymer network upholds polymer chain weaving through or wrapping around the additive cages. It is also proposed that the cage-structured additives not only strengthen the polymer networks but also protect membranes from excess swelling during operations. Moreover, this composite membrane possibly can enhance mechanical stability of membranes as in PEMFCs. Based on proposed hypothesis, cage-structured additive functions very differently than standard inorganic fillers. Hence, these enforced membranes can improve the durability of PEM cell/stack when simultaneous swelling and drying occurs in membrane during cell/stack operation. This is a significant improvement in membrane technology, especially for membrane fuel cell technology, and is applicable in enforcing any polymer network with cage structure additives. Further investigation is in plan to uncover the novel crossing point of OSP with polymer in OSP-Nafion network.

Mechanical, thermo-mechanical and physicochemical properties of membranes were characterized through Thermogravimetry Analysis (TGA). Tensile stress is also planned to further investigate the membrane mechanical stability. Further, thermo-mechanical and water sorption properties are also in interest, if DMA and Dynamic Vapor Sorption (DVS) facilities become available for additional information related to membrane structure.

TGA experiments were conducted on dry (dried overnight at 100 °C) samples under 20 ml/min Argon, 10 °C/min conditions. Figure 9 shows the octasilane decomposition at temperature ranging from 150 to 235 °C. Membrane D₅ shows better thermal stability at temperature up to 310 °C, relative to 265 °C of membrane D₀ and D₈. At 318 °C, D₈ membrane showed more weight loss than D₀, which might be due to the presence of octasilane. At temperature up to 150 °C, temperature ranging from 265 to 383 °C, and temperature ranging from 383 to 530 °C, D₀

membrane weight loss is ascribed to that loss of water, side chain decomposition and backbone decomposition, respectively. Since octasilane contains silicon element, it might accelerate the weight loss at temperature above 318 °C of perfluorinated sulfonic acid (PFSA), which also was shown with earlier backbone decomposition temperature profile possibly due to Si and F existence to form SiF_4 gas. With an increased octasilane concentration, membrane D_8 showed more weight loss than membrane D_0 due to the silane decomposition. More interestingly, membrane D_5 with least octasilane but with highest thermal stability was shown at temperature before 310 °C, which also showed less weight loss at temperature below 150 °C. This might be due to the less water sorption effect. Residual weight of octasilane was around 7.0 wt%, however, that of composite membranes with PFSA was around 0%, which might indicate the silicon element contributing to the acceleration of PFSA decomposition at temperatures above 318 °C.

Figure 9: TGA analysis of membranes D_x ($x = 0, 8$, and 5) and OSP (Left), and magnified plot (Right),

Evaluation of Membrane Performance

To evaluate the membrane performance, two types of MEAs with 3.0 wt% OSP over Nafion in both membrane and catalyst layers, and pure Nafion ionomer in membrane and catalyst layers were prepared and tested in single cells followed by 250 hours dynamic stress test. The selection of 3.0 wt% OSP was based on the fact that the highest siloxane concentration of 3.0 wt% exhibited near homogenous distribution. Linear scanning voltammetry (LSV), cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were utilized to analyze MEA components. In order to analyze MEAs degradation and durability, the F^- ion leaching in the water collected at anode and cathode outlets and to be measured by ion selective electrode (ISE) through water condenser trap, Norgren® Stainless Steel Filter (f22-405-M2DA). The preparation of MEA was somewhat modified compared to that reported earlier. A brief description is provided below.

To prepare the catalyst inks, desired amounts of 20 wt% Pt/C (Vulcan XC-72) and 20 wt% Nafion D2021 were mixed and stirred for half an hour, sonicated by horn sonication for 10 minutes, and sprayed onto both sides of the membranes. Catalyst loadings for anode and cathode were 0.2 and 0.25 mg_{Pt}/cm², respectively. According to the geometric area calculation, real loading values were 0.13 and 0.17 mg_{Pt}/cm², respectively. Mass ratio of the ionomer to carbon was 0.81. SGL 10 BC was used as the GDL and hot-pressed with catalyst coated membrane (CCM) at 145 °C, 2500 lb for 5 cm² of MEA active area. Single cells (Fuel Cell Technologies) were assembled and connected with fuel cell testing system (850e and 890CL, Scribner Associates, Inc.) to evaluate MEAs. Prior to dynamic stress testing (DST), polarization curves under the voltage scan mode were recorded. Single cells were operated at 80 °C, 80% RH, and 0.2/0.2 L/min flows of H₂/O₂ at ambient pressure.

In describing the MEA performance, FCD₀ and FCD_{0a} MEAs consisted of neat recast Nafion D2021 membrane while FCD₈ MEA contained 3.0 wt% OSP and Nafion D2021 in place of Nafion ionomer in membrane and electrodes. In FCD_x MEA code, FC stands for fuel cell and D_x has chosen as membrane code used earlier sections. Details of DST protocol are shown below.

Cell Start-up (Pre Conditioning):

1. Set purge gas / (fuel and oxidant) flow rate to 0.2 L/min and start sending purging gas.
2. Set cell operation temperature at 80 °C and start heating up cell.
3. Maintain the system (heating up the cell while purging the cell) for five minutes.
4. Set humidifier temperatures at 75 °C and start heating up humidifiers.
5. Maintain the system under this condition for two minutes.
6. Start sending the fuel (H₂) and oxidant (O₂) through anode and cathode, respectively.
7. Maintain the system under this condition for one minute.
8. Operate the cell at 0.65 V for two minutes.

During 12 Hours Operational Period:

During 12 Hours Operational Period:

DST program with 367 seconds per cycle and 118 cycles were used, which is equivalent to around 12 hours of total duty on operation. Single cells were operated at 80 °C with around 80% relative humidity (humidifiers at 75 °C) with 0.2 L/min H₂ and O₂ as the fuel and oxidant, respectively.

The cell was operated at 16 different constant current conditions over a period of 367 seconds, as shown in Figure 9, during a single cycle of DST.

Cell Shutdown (Prior to Cell off Period):

1. Turn off fuel and oxidant flow to the cell and start sending purging gas.

2. Turn off humidifier heaters.
3. Maintain the system for three minutes.
4. Turn off cell heaters.
5. Maintain the system under this condition for seven minutes.
6. Turn off purging gas.

During Off Period:

The cell was isolated from all the gases, loads and heating for a period of 700 minutes. The time of 700 minutes with other non-operational time, during shutdown and start-up, makes total non-operational time equal to 12 hours.

Table 3: Dynamic stress test (DST) protocol and current and voltage values as functions of time for FCD₀, FCD_{0a}, and FCD₈ MEAs.

Items		Steps of single cycle															
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Time /S		15	25	20	15	24	20	15	25	20	15	35	20	35	8	35	40
Current /A		0.00	0.45	1.10	0.045	0.45	1.10	0.045	0.45	1.10	0.045	0.45	5.50	3.65	0.045	1.10	0.045
Voltage /V	FCD ₀	0.97	0.79	0.73	0.87	0.78	0.73	0.87	0.78	0.72	0.87	0.78	0.42	0.54	0.88	0.72	0.87
	FCD _{0a}	0.96	0.77	0.68	0.87	0.76	0.68	0.88	0.76	0.68	0.87	0.76	0.38	0.47	0.88	0.68	0.87
	FCD ₈	0.86	0.74	0.67	0.82	0.73	0.67	0.82	0.73	0.67	0.82	0.73	0.42	0.52	0.83	0.68	0.81

Figure 10: Single cycle of FCD₈ MEAs in 367 seconds.

Figure 10 shows single cycle of a typical MEA (FCD₈) within 367 seconds. The data in Table 3 were extracted from the cycles. As shown in Table 3 and Figure 10, FCD₈ MEA showed very similar DST single cycle performance. FCD₀ and FCD_{0a} MEAs exhibited with very identical performance, suggesting excellent MEA reproducibility. Since FCD₀ MEA was tested and flooding phenomenon was observed, MEA FCD_{0a} was prepared for repeating experiments to replace FCD₀ MEA. However, FCD_{0a} also showed the same flooding issue at current density of 1100 mA/cm₂. Within one single cycle, no obvious performance change was observed. In order

to investigate MEA durability, in particular, under DST conditions, those MEAs were conducted up to 250 hours with duty on 12 hours and duty off 12 hours per day.

Figure 11: Areal resistance and proton conductivity of membranes in FCD₀, FCD_{0a}, and FCD₈ MEAs during 250 hours DST experiments.

Figure 11 shows areal resistance values of FCD₀, FCD_{0a} of neat Nafion membrane and FCD₈ of 3.0 wt% OSP/Nafion in MEAs, ranging from 0.09 to 0.19 $\Omega \cdot \text{cm}^2$, corresponding to proton conductivity values ranging from 25 to 52 mS/cm. Due to non-proton-conductive component of OSP presence, FCD₈ MEA containing D₈ membrane showed a bit higher areal resistance and a lower proton conductivity values observed compared to those of FCD₀ and FCD_{0a}. According to the profile during 250 hours, it did suggest that the membrane resistance and proton conductivity of FCD₈ did not change much. However, the pure Nafion membranes of FCD₀ and FCD_{0a} MEAs resistance and proton conductivity values did change and approached that of 3.0 wt% OSP/Nafion contained FCD₈ MEA. Most importantly, those two values demonstrate the single cells performance drop of FCD₀ and FCD_{0a} MEAs, ascribed to the mass transport issue rather than membrane degradation, which are illustrated in additional DST experiments shown in Figures 12 to 19. A noticeable voltage drop in FCD₈ MEA observed in initial cell testing, resulted from the mixed potential generated from relatively high H₂ cross-over that accelerated H₂ cross-over result on tremendous OCV loss over the DST testing period of FCD₈ MEA.

Table 4: Parameters of FCD₀ (neat Nafion), FCD_{0a} (neat Nafion-2nd cell) and FCD₈ (3.0 wt% OSP/Nafion) MEA single cells under normal conditions at 80 °C, 80% RH, at flow rate of 0.2/0.2 L/min H₂/O₂ at ambient pressure.

	Cell operation conditions (Anode/Cell/Cathode) Temperature					
	80 °C_80%RH_H ₂ /O ₂ _PreDST			80 °C_80%RH_H ₂ /O ₂ _After DST		
	FCD ₀	FCD _{0a}	FCD ₈	FCD _{0_48 h}	FCD _{0a_250h}	FCD _{8_250h}
E_{Theoretical}⁰ / V	1.168	1.168	1.168	1.168	1.168	1.168
OCV / V	0.968	0.987	0.968	0.972	0.957	0.81
Ohmic resistance / mΩ·cm²	0.101	0.109	0.159	0.0985	0.13	0.175
Tafel slope / mV/dec (£/ §)	84 / 79	57 / 85	60 / 97	99 / 84	83 / 96	112 / 56
i₀ / A/cm²	1.4E-6	6.00E-06	3E-6	2E-6	1.4E-6	2.2E-6
M / V	0.02865	0.04048	0.00306	0.02202	0.02922	0.01029
n / cm²/mA	0.00183	0.00184	0.00216	0.00294	0.01041	0.00236
Peak power density / W/cm²	0.44	0.366	0.604	0.33	0.11	0.36
Current density at 0.7 V / mA/cm²	278.2		314.4		71	84
		238.5		237.19		
Power density at 0.7 V / W/cm²	0.193	0.166	0.209	0.164	0.048	0.07
Current density at 0.9 V / mA/cm²	9.07		1.65		4.8	-
		11.67		11.91		
H₂ crossover / mA/cm²	0.5	1.14	5.5	0.88	0.65	-

£: obtained from Tafel slope plot simulation, §: obtained from the equation simulation, equation of $E = E_{oc} - r \cdot I - A \log(i) - m \cdot \exp(n \cdot i)$, where i , E , E_{oc} , r , A , m , n are current density, potential, OCV, membrane resistance, m and n parameters, respectively, as shown in table 4.

Data presented in Table 4 were extracted from Figure 11, 12, 13, and 14. Figure 12 shows the FCD₀ MEA with regular performance before DST testing, but obvious flooding at current density above 1000 mA/cm² after DST running only for 48 hours was observed. For a better understanding of flooding behavior, FCD₀ was replaced by another cell, FCD_{0a} same composition as FCD₀. Also, a set of performance parameter of FCD_{0a} and FCD₈ MEAs before and after DST experiments are summarized in Table 4 for comparing the performance losses and operational behavior in vehicle application. The performances of FCD_{0a} and FCD₈ MEAs before and after DST experiments were shown in Figure 13 and 14, respectively.

Figure 12 top left and top right, shows FCD₀ MEA after 48 hours DST experiment with higher concentration loss, similar ohmic loss and identical activation loss, in contrast to those prior to DST testing.

Figure 12: Polarization curves of raw data, concentration-free, ohmic resistance-free + concentration-free and power density curve (top left), polarization curve with that with non-linear fitting curve (bottom left) of single cell employing FCD₀ MEA prior to DST and those (top right and bottom right) after under normal conditions at 80 °C, 80% RH, 0.2/0.2 L/min H₂/O₂ at ambient pressure. DST experiments for FCD₀ MEA continued for 48 hours until flooding issue was observed.

Figure 13, top left and top right, indicate FCD_{0a} MEA after 250 hours under DST test effect severely and contributed in all major overpotentials: concentration loss, ohmic loss and similarly in activation loss. Variation of parameters contacted from performance losses are listed in Table 4 where OCV loss occurred only 3% for FCD_{0a} with peak power loss 67%, compared to a significant 16% OCV loss noticed with FCD₈. A reasonable explanation of OCV loss associated with FCD₈ cell majorly due to huge H₂ crossover and an incremental growth of fuel. However, drop in peak power density of FCD₈ happened to 40% compared to 67% in FCD_{0a}. It indicates that though cell FCD₈ losses catalytic activity compared to neat Nafion but holds much better overall stability in long run operation than FCD_{0a}.

Figure 13: Polarization curves representing concentration-free, Ohmic resistance-free + concentration-free and power density curve (top left), polarization curve with non-linear fitting curve (bottom left) of single cell employing FCD_{0a} MEA prior to and after DST (top right and bottom right) under conditions, 80 °C, 80% RH, 0.2/0.2 L/min H₂/O₂ at ambient pressure. DST experiments for FCD_{0a} MEA continued for 250 hours even after flooding was observed.

Figure 14 (top left and top right) showed that FCD₈ MEA after 250 hours DST experiment with relatively increased concentration loss, ohmic loss and activation loss, in contrast to those prior to DST testing. Those losses of FCD₈ MEA are much less than those of FCD₀ and FCD_{0a} MEAs, which is ascribed to normal voltage drops during 250 hours DST experiments. All these data of areal resistances are summarized in table 4. From Figure 12, 13, and 14, it can be demonstrated that mass transport and related water management are big problems for FCD₀ and FCD_{0a} MEAs, but alleviated for FCD₈ MEA with 3.0 wt% OSP. It might be attributed to lower water content of the membrane with OSP in FCD₈ MEA, which could allow pushing water out more easily than pure Nafion with higher water content. Therefore, with 3.0 wt% OSP, it alleviated MEA mass transportation and water flooding issues as established from DST protocol.

Figure 14: Polarization curves repressing, concentration-free, ohmic resistance-free + concentration-free and power density curve (top left), polarization curve with non-linear fitting curve (bottom left) of single cell employing D₂ MEA prior to and after DST (top right and bottom right) under conditions, 80 °C, 80% RH, 0.2/0.2 L/min H₂/O₂ at ambient pressure. DST experiments for D₂ MEA continued for 250 hours even after flooding was observed.

Comparison of single cells performances using FCD_{0a} and FCD₈ MEAs can be seen in the top left panel of Figures 13 and 14. It is apparent that FCD₈ MEA shows more humidity managing ability than that of FCD₀ and FCD_{0a}, which might be due to the less water content property of the cell. With OSP addition, the membrane areal resistance measured by AC impedance prior to DST was 0.159 Ω·cm² under OCV condition (rather than constant current discharging model), which was a little greater than 0.101 and 0.109 of Ω·cm² FCD₀ and FCD_{0a}, respectively. In terms of impedance analysis, FCD₈ MEA is more sensitive to water status in MEA in comparison to FCD_{0a} MEA. Therefore, we hypothesized that OSP addition might slightly reduce proton conductivity of the membrane, but may improve mechanical property, and exhibit better water management. In fact, no flooding was observed for FCD₈ resulting more durable performance under DST conditions. The simulated parameters from Figure 12, 13, and 14 are shown in Table 4. Though, it showed 4 to 5 times higher hydrogen crossover (possible reasons are given

elsewhere) of FCD₈ MEA with OSP, than that of FCD_{0a} MEA, but Figure 14 (top left) shows a better performance of FCD₈ MEA with a little higher areal resistance value than that of FCD_{0a} shown in Figure 13 (top left). Thus, these results suggest that OSP reinforced membrane exhibits better mass transport and water management properties, two dominant factors in the DST experiments for those three MEAs.

Figure 15: Voltage profile as a function of time of FCD₀ MEA under normal conditions of 80 °C, 80% RH, and 0.2/0.2 L/min H₂/O₂ at ambient pressure for 48 hours. Number inserted in plot is the current in ampere by the program.

At low current of 0.0, 0.045, 0.45, 1.1 and 3.65 A (Figure 15) for FCD₀ MEA, voltage values were stable, but voltage fluctuation appeared at current of 5.5 A during the 1st duty-on 12 h, but worsen during the second duty-on 12 h with notable flooding. The vertical points shown in this figure represent fuel starvation before fuel completely supplied to single cells. Water flooding issue is recognized as horizontal data points at potential of near 0 V.

In order to confirm the flooding problem observed in FCD₀ MEA, FCD_{0a} MEA was repeated after FCD₀ MEA running for 48 hours. The voltage profile for FCD_{0a} is shown in Figure 16.

Figure 16: DST experiment voltage profile as a function of time of FCD_{0a} MEA under normal conditions of 80 °C, 80% RH, and 0.2/0.2 L/min H₂/O₂ at ambient pressure. Number inserted in plot is the current applied in ampere by program.

It is consistent that FCD_{0a} MEA showed very similar fluctuation of voltage values at current above 3.65 A. The flooding issue appeared during the 1st duty-on 12 h, and became even progressively worse after than that of FCD₀ MEA. Moreover, the voltage values at current lower than 3.65 A were relatively stable than the rest during the DST measurements for 250 hours. Voltage profile of FCD_{0a} MEA during 250 hours DST experiment did show voltage drops. Estimated voltage drop rate values at current of 1.1, 0.45, and 0.045 A were 0.72, 0.64, 0.32 mV/h, respectively.

Due to water flooding initiated mass transport issue, single cell voltage dropped until constant current load was applied. The program will reduce the current load if voltage is lower than potential limitation of fuel cell testing system. Therefore, it would be more desirable to confirm the voltage profile with applied/desired current load, as shown in Figure 17.

Consistent with Figure 16, the load at current of 3.65 and 5.5 A could not be applied, which was shown in the 1st and 2nd duty-on 12 h of Figure 17. Even during the first two duty-on 12 h, the current at 5.5 A was not stable and fluctuated, which means water flooding was present causing mass transport issue.

To compare FCD₀ and FCD_{0a} MEAs DST measurements (shown in Figures 15, 16 and 17), experiments on FCD₈ MEA was conducted in parallel, as shown in Figure 18.

Figure 17: DST experiment current profile as a function of time of FCD_{0a} MEA under normal conditions of 80 °C, 80% RH, and 0.2/0.2 L/min H₂/O₂ at ambient pressure. Number inserted in plot is the current applied in ampere by program.

Figure 18 shows DST of FCD₈ MEA during 250 hours. It showed less fluctuation voltage profile than those of FCD₀ and FCD_{0a} MEAs. FCD₈ MEA did not show any water flooding at even highest current of 5.5 A for 250 hours DST experiments. The vertical drop points under 0.2 V are ascribed to fuel starvation before fuel completely stopped. The voltage profile of FCD₈ MEA during 250 hours DST experiment did not show obvious degradation. Estimated voltage drop rate values at current of 5.5, 3.65, 1.1, 0.45, and 0.045 A were 0.36, 0.3, 0.32, 0.28, and 0.27 mV/h, respectively.

Consistent with Figure 18, the load at current of 3.65 and 5.5 A could be applied as shown in Figure 19, which means that the current applied is as desired and the voltage profile in Figure 18 corresponding to the current profile in Figure 19. Compared with very noisy profiles of voltage and current for FCD₀ and FCD_{0a} MEAs shown in Figure 15, 16, and 17, very neat voltage and current profiles of FCD₈ MEA were observed, as shown in Figure 18 and 19, suggesting that water flooding and thus mass transport issue does not exist with the OSP addition in the membrane and electrodes of FCD₈ MEA.

Figure 18: DST experiment voltage profile as a function of time of FCD₈ MEA under normal conditions of 80 °C, 80% RH, and 0.2/0.2 L/min H₂/O₂ at ambient pressure. Number inserted in plot is the current applied in ampere by program.

Figure 19: DST experiment current profile as a function of time of FCD₈ MEA under normal conditions of 80 °C, 80% RH, and 0.2/0.2 L/min H₂/O₂ at ambient pressure. Number inserted in plot is the current applied in Ampere by program.

Figure 20: Photograph of flow-field (left) of hard-wear used in FCD0a (does not contain OSP) 250 hours DST measurement and GDL facing FCD0a (right) with drops of water in GDL pores and swollen membrane at the edge GDL. Photograph was taken immediately after disassembling the cell from 250 hours DST operation.

Figure 21: Photograph of flow-field (left) of hard-wear used in FCD8 (contains OSP) 250 hours DST measurement, and GDL facing FCD8 (right) with only few tiny drops of water standing on GDL. Photograph was taken immediately after disassembling the cell from 250 hours DST operation.

Furthermore, evidence of standing water in various components of cell from visual inspection is shown in Figures 20 and 21. Huge water mark and water accumulation can be observed in the flow-field (left) of Figure 20, confirming the flooding occurred during 250 hours of DST operation on FCD0a. It is well established that flooding is a serious issue in PEMFCs (low temperature fuel cells in general), causes water accumulation between GDL and flow-field layers, and block the pores of GDLs and electrodes as expected. In contrast, there was no sign of water either in flow-field or on GDL surface observed in Figure 21. In both cases photographs were taken immediately after disassembling cells after completing 250 hours DST operation.