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CRADA Final Report

Date: _4/8/2020________________________

PI: Ahmet Kusoglu

CRADA AWD No.: AWD00003680 **CRADA FP No.:** FP00008543

LBNL Report Number: LBNL-2001301

OSTI Number: _________________________

1. Parties: Tetramer Technologies LLC

2. Title of the Project:
   New Approaches to Improved PEM Fuel Cell Catalyst Layers

3. Summary of the specific research and project accomplishments:
   Note: Final Reports and Forms containing Protected CRADA Information are to be emailed directly to the SPO close out requestor, along with a confirmation of the public release date. Do not submit via eSRA. Also, please do not include any Proprietary Information (defined below) in CRADA Final Reports and Forms.*
   Tetramer will design and develop the ionomers and provide them to LBNL for characterizing their structural and transport properties, and performance of the ionomer as the electrolyte thin films in catalyst layers. The hydration and conductivity properties of the candidate ionomers were measured and then the results were used for down selections. Selected materials were used to fabricate membrane-electrode assemblies to be tested in a fuel cell system for performance evaluation. The results showed performance variation can be achieved through material architecture modification. The preliminary results accomplished in the completion of Phase I, were going to be used for a systematic investigation and optimization of the material systems in Phase II, which was not funded.

4. Deliverables:

Deliverables met	Party (LBNL, Participant, Both)	Delivered to Other Party?
Hydration and conductivity properties of ionomers for down-selection	LBNL	Yes
Ink characterization to demonstrate stability	LBNL	Yes
Cell testing for selected materials to demonstrate improvement	LBNL	Yes

5. Identify (list below) and attach all publications or presentations at conferences directly related to the CRADA:

None

6. List of Subject Inventions and software developed under the CRADA: (Please provide identifying numbers or other information.)
   None

7. A final abstract suitable for public release:
   (Very brief description of the project and accomplishments without inclusion of any proprietary information or protected CRADA information.)
   Polymer-electrolyte membrane (PEM) fuel-cells are one of the most promising energy conversion technologies for renewable clean energy applications. A major challenge preventing their widespread commercialization is achieving high performance with low-loadings of platinum group metal (PGM) catalysts. One of the factors driving performance limitations in the cell is the mass transport losses within the cathode catalyst layers due to sluggish oxygen-reduction reactions occurring at the platinum-ionomer interface, which is believed to be linked to reduced transport of ions and oxygen. A viable solution to reduce the transport resistances in the catalyst layers is to create new ionomers that can provide good ion and oxygen transport needed to accomplish high-performing fuel cell catalysts. Characterization of transport properties of ionomers for various molecular architectures is the key step, in the effort to create and identify the optimized polymer structure with improved transport. Using this approach, Tetramer Technologies and LBNL propose improved fuel-cell catalyst ionomers based on Tetramers proprietary polymer chemistry, as highlighted under subtopic 17a *Innovative Approaches Toward Discovery and Development of Improved Ionomers for Polymer Electrolyte Membrane Fuel Cell Catalyst Layer.*

8. Benefits to DOE, LBNL, Participant and/or the U.S. economy.
   Development of materials by the participated and their demonstrated performance in LBNL improvements would be beneficial for the DOE-funded research activities and help reach DOE targets for fuel cells. Thus, the anticipated public benefits of this work include the further expansion of fuel cell technology, as a source of affordable clean energy, into the mass market. Consequences of the success of this work would include a significant reduction of US dependence on (foreign) oil and fossil fuels and an associated reduction of carbon dioxide emissions.

9. Financial Contributions to the CRADA:

DOE Funding to LBNL	$0
Participant Funding to LBNL	$35,000
Participant In-Kind Contribution Value	$871
Total of all Contributions	$35,871

** "Proprietary Information" means information, including data, which is developed at private expense outside of this CRADA, is marked as Proprietary Information, and embodies (i) trade secrets or (ii) commercial or financial information which is privileged or confidential under the Freedom of Information Act (5 U.S.C. 552 (b)(4)).*

Final CRADA Report for SBIR Phase I

New Approaches to Improved PEM Fuel Cell Catalyst Layers

Yagya Regmi, Jessica Luo, Nemanja Danilovic, Ahmet Kusoglu

LBNL SBIR Phase I

Award #	AWD00003680
Sponsor	Tetramer Technologies LLC
Period of Performance	1/3/2019 - 10/3/2019

Executive Summary:
Polymer-electrolyte membrane (PEM) fuel-cells are one of the most promising energy conversion technologies for renewable clean energy applications. A major challenge preventing the widespread use and commercialization of PEM fuel cells is achieving high performance with low-loadings of platinum group metal (PGM) catalysts. One of the factors driving performance limitations in the cell is the mass transport losses within the cathode catalyst layers (CCL) due to sluggish oxygen-reduction reactions occurring at the platinum-ionomer interface. Any resistance to transport of these ionic and gaseous species within the CCL results in mass-transport limitations and performance losses, especially at high current densities. It is known that mass-transport losses increase with reduced platinum loading, thereby creating a performance-cost tradeoff for fuel cells. A viable solution to reduce the transport resistances in the catalyst layers is to create new ionomers that can provide good ion and oxygen transport needed to accomplish high-performing fuel cell catalysts. Using this approach Tetramer Technologies and LBNL propose improved fuel-cell catalyst ionomers based on Tetramers proprietary polymer chemistry.

Results

1. Membrane/ionomer testing results

Hydration

Membrane samples made from Tetramer ionomers CL1-CL5 were evaluated with ex situ tests and compared with Nafion 211. Membranes were used for testing ionomer properties as a quick screen of basic properties in lieu of doing ionomer film specific tests which are directly representative of the ionomer in catalyst layer properties. These will be the focus of Phase 2 activities ans were circumvented due to time constraints within the exploraratory Phase 1 work.

Materials supplied Tetramer cast membranes from ionmomers CL1-CL5 without a reinforcement at thickness up to 50um. Membranes were initially tested in the as received condition. Some down-selected membranes were subsequently processed before retaking certain measurements. Summary of membrane properties is in Table 1.

Table 1. Summary Table of Ionomer/Membrane Properties

Sample	IEC	Oxygen Permeability (Barrer)	Proton Conductivity (S/cm) @100%RH (as received)	Hydration number (mol H_2O/mol SO_3H) (as received)	Proton Conductivity (S/cm) @100%RH (after treatment)	Hydration number (mol H_2O/mol SO_3H) (after treatment)
Nafion 212	1	1	85	10.5		
CL-1	3.3	0.2	62	5		
CL-2	2.3	0.3		4.5	85	
CL-3	1.8	1	5	3	swelled	
CL-4	2.3	0.4		5		
CL-5	1	4	1	2	5	5.5

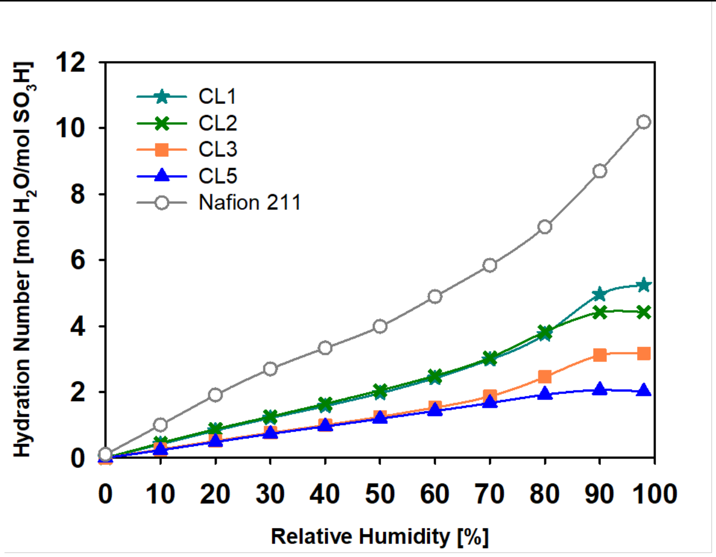

Figure 1. Membrane hydration number as a function of relative humidity at 25 °C.

Tetramer iomomers in membrane form were evaluated for water uptake under different relative humidities (RH) and compared to Nafion 211 as a baseline material. Figure 1 shows the obtained hydration curves. All Tetramer ionomers took up less water than Nafion, with the trend being CL1>Cl2>CL3>Cl5. The membranes were evaluated as received.

Conductivity

Next the conductivity of the membranes was evaluated as a function of RH. CL1 had the most appreciable DC conductivity, while CL3 and CL5 did not appreciably increase with increasing RH. When looking at conductivity versus hydration number (ratio of water versus sulfonic groups), CL1 exceeded Nafion, while CL3 followed a similar trend as Nafion and CL1.

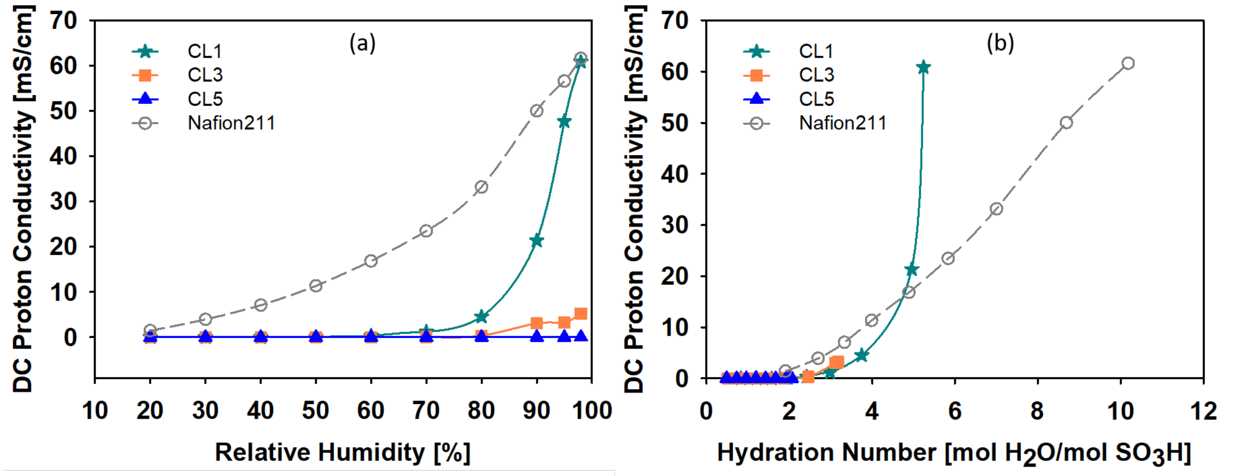

Figure 2. As-received membrane proton conductivity as a function of a) relative humidity and b) hydration number at 30 °C.

CL2, CL3 and CL5 membranes were down-selected for pretreatment and reevaluation. These were chosen because their oxygen permeabilities were high enough to warrant promoting these two membranes. Pretreatment consisted of a 2M H_2SO_4 soak, followed by heating at 80 ^oC in deionized water. CL3 was not able to withstand pretreatment conditions, and conditions were not varied in Phase 1 in order to optimize pretreatment. CL5 withstood the pretreatment condition. Figure 3 and Figure 4 show the results of the change in water uptake and conductivity before and after pretreatment. Both the water uptake and conductivity increased as a result of the pretreatment. Notably hydration was significantly affected, and conductivity at high RH noticeably increased.

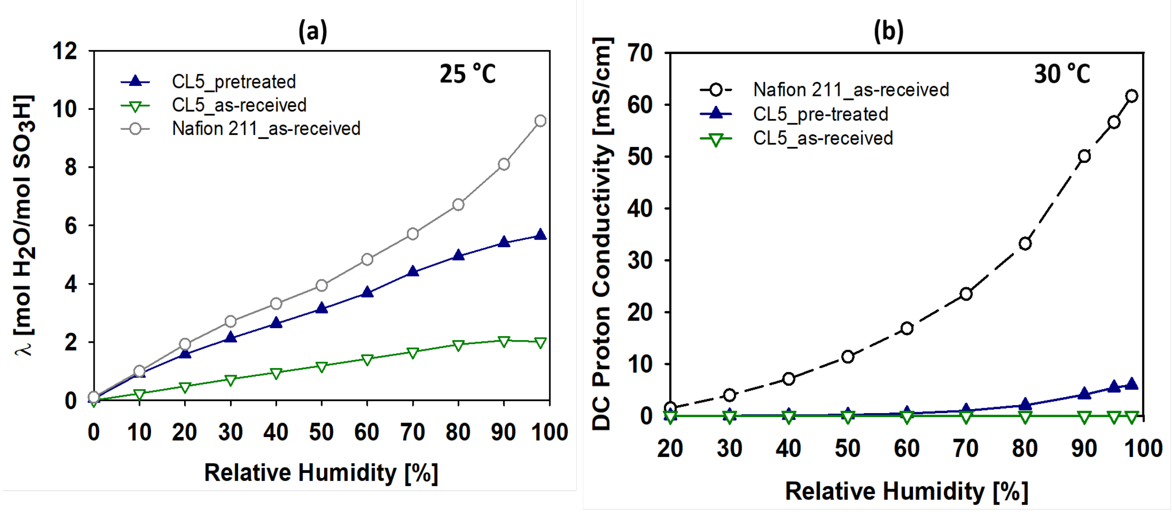

Figure 3. The impact of pretreatment on a) water sorption and b) proton conductivity as a function of relative humidity for CL5 membrane.

Lastly CL2, was also pretreated and evaluated. Its conductivity and water uptake were similar to Nafion, although the permeability was low and was not promoted to MEA testing.

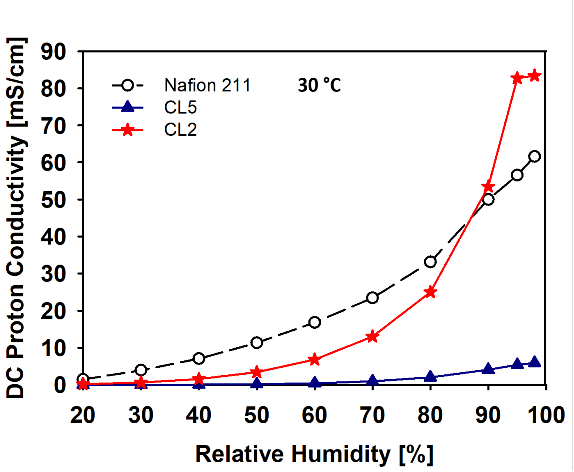

Figure 4. DC proton conductivity as a function of relative humidity at 30 °C for pretreated CL2 and CL5 membranes (as-received Nafion 211 is used as baseline).

We note that membrane measurements do not always scale well to electrode ionomer film properties. Membrane pretreatment was performed to get a true assessment of the bulk properties, but is not necessarily possible with ionomer films. Therefore, based on the ex-situ testing results of Tetramer ionomers in membrane form, CL3 and CL5 were promoted to MEA testing.

2. Fuel Cell Testing Results

Ink stability

Before depositing catalyst layers, the catalyst ink was characterized using dynamic light scattering. The ink was make using a dispersion of Tetramer ionomers (CL5 and CL3) using the same method as used for making Nafion containing inks, in the same ratio of ionomer, solvent and catalyst. The as prepared ink was sonicated and then analyzed by DLS. The results shown in Figure 5 demonstrate that the Tetramer and Nafion ink are quantitatively similar as the average diameter of the agglomerates is the similar. Most importantly over the course of 10 runs the diameters didn’t change significantly indicating a stable dispersion. This data provided confidence in proceeding with depositing the catalyst inks. Note that no attempt to optimize the ionomer to carbon ratio was done at this time in Phase 1, the optimized of which was planning to be carried out under Phase II.

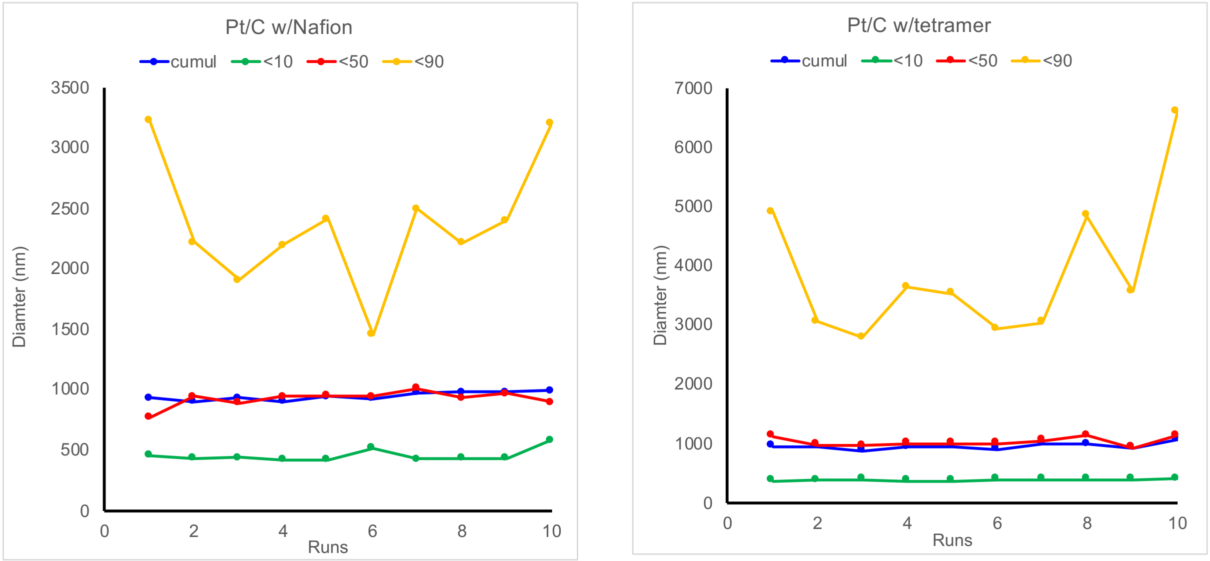

Figure 5. Dynamic light scattering (DLS) of Pt/C containing Nafion and Tetramer (CL-5) inks. The DLS measures the particles size of ionomer and Pt/C agglomerates and their stability over 10 minute run increments.

MEA Preparation and Cell Testing

Membrane electrode assemblies were fabricated as catalyst coated membranes (CCMs) on pretreated N212. The hydrogen counter electrodes were unaltered with a constant loading of 0.3mg/cm^2 and with Nafion ionomer for all MEAs. The I/C ratio for the cathode catalyst layers (CCLs) was kept constant for all tests, CL5 was fabricated at 0.3 and 0.125mg/cm^2. For the low loaded MEA no additional carbon was put in the ink to increase the thickness of the CCL.

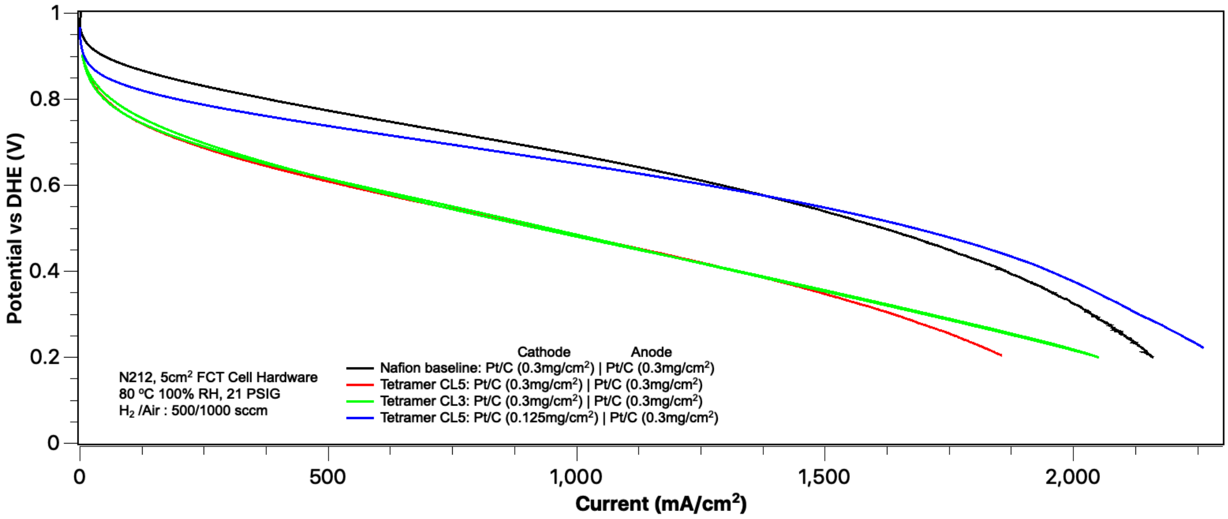

Figure 6. Polarization curves comparing Nafion and Tetramer ionomer CL5 and CL3 at standard loading of 0.3 mg/cm^2 and 0.125 mg/cm^2 in the CCL.

Using 5cm^2 Fuel Cell Technologies hardware and tests stand, all MEAs were broken in, overnight at 80 °C and 100 %RH at 0.6V. When a steady current is obtained ~20 hrs polarization curves (Figure 6) and impedance curves (Figure 7) were taken at 21 PSI back pressure and flow rates of 500 sccm H_2 and 1000 sccm air. While at standard baseline loadings both Tetramer CL5 and CL3 performed worse than Nafion CCLs, presumably due to the lower conductivity of CL5 and CL3 relative to Nafion, at low loadings with thinner CCLs the higher permeability of CL5 is accentuated and the performance is improved over the standard loaded Nafion CCL. Looking at the impedance curves of Nafion and the low loaded CL5 CCLs at 600 and 900mV the conclusion drawn is that the total resistance of the MEA is reduced and the reaction kinetics are also improved.

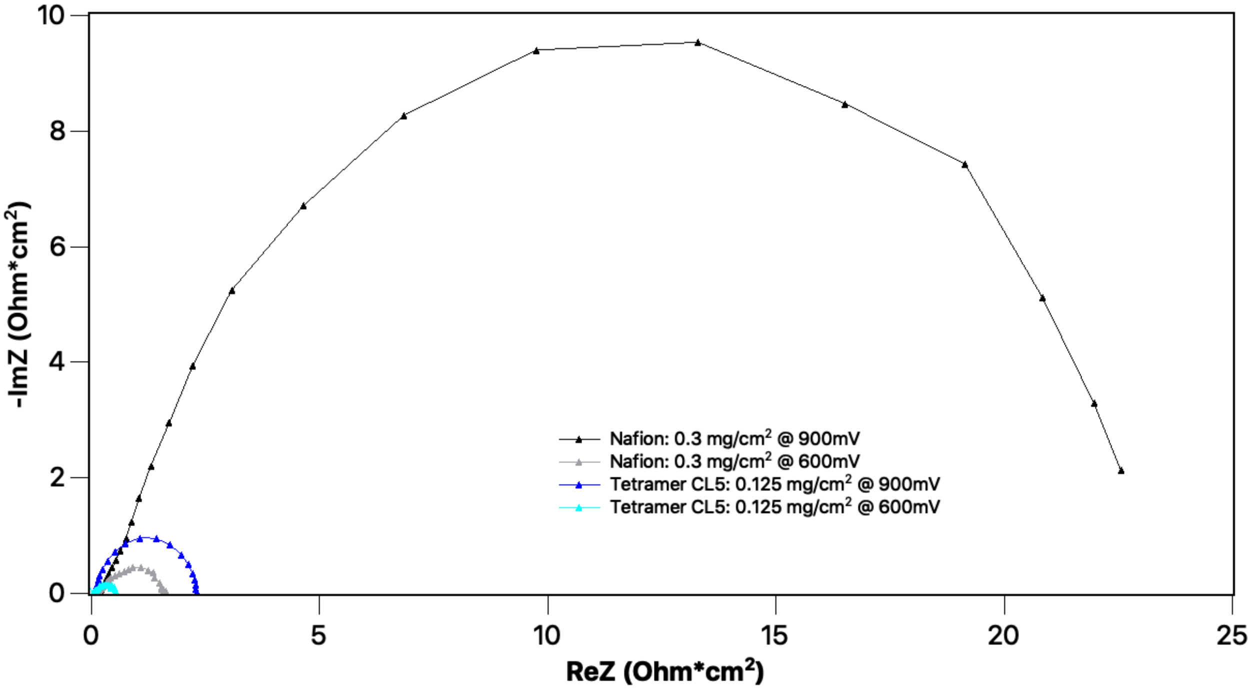

Figure 7. Impedance spectroscopy measurement of MEAs containing Nafion or Tetramer CL5 ionomer in the cathode catalyst layer at loadings of 0.3 and 0.125 mg/cm^2. High frequency intercept shows improved conductivity for Tetramer ionomer. Low frequency intercept shows improved ORR kinetics.