
High-Performance Polymer Electrolyte Membrane Fuel Cell Electrode Structures

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Contract Number: DE-EE0007652

Subcontractors:

- Ion Power Inc., New Castle, DE
- University of Arkansas at Little Rock, Little Rock, AR

Project Start Date: October 1, 2016

Project End Date: June 30, 2020

- Fabricate sufficient thin-film catalyst to fabricate an MEA with a cell active area of $\geq 12.5 \text{ cm}^2$.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan¹:

- (A) Durability (improved understanding of initial transport losses is required to mitigate)
- (B) Cost (MEAs with ultra-low PGM loadings have relatively large transport losses)
- (C) Performance (reduced transport losses are required to meet high power density targets).

Technical Targets

This project is ultimately focused on developing high-performance MEAs with ULCLs. To date, the team has focused on MEAs with Pt-only catalysts (i.e., not Pt-alloy catalysts that have higher activities), because these MEAs are less complex, are inherently more stable, and exhibit similar transport losses at ULCLs using Pt particles that are similar in size to those used with Pt-alloy catalysts. Analogously, the team is utilizing MEAs that do not utilize SOA catalyst loadings for the anodes (e.g., $\leq 0.025 \text{ mg-PGM/cm}^2$), because the key remaining barrier is improving cathode performance with ULCLs.

FY 2018 Accomplishments

- Developed and demonstrated MEAs with improved transport losses with CCLs that meet the 2020 target (i.e., MEAs with 0.1 mg-Pt/cm^2 on the cathode exhibited superior performance to the team's FY 2017 MEAs with 0.2 mg-Pt/cm^2 on the cathode at high current densities).
- Completed the development of a new hierarchical model of the CCL, which was

Overall Objectives

- Develop improved understanding of the various transport losses in polymer electrolyte fuel cell (PEFC) cathode catalyst layers (CCLs) with state-of-the-art (SOA) ultra-low catalyst loadings (ULCLs) of platinum-group metals (PGMs).
- Obtain this fundamental understanding by developing and validating a detailed microstructural CCL model.
- Utilize the validated CCL model to develop and demonstrate membrane electrode assemblies (MEAs) that potentially can meet all of DOE's 2020 technical targets for MEAs.

Fiscal Year (FY) 2018 Objectives

- Complete development of microstructural CCL model, and implement this key component model into the Fuel Cell Performance and Durability Consortium (FC-PAD) model of a complete PEFC.
- Validate this new CCL model using data from MEAs with ULCLs and SOA performance.

¹ <https://energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22>

successfully validated using both the team's data and multiple data sets in literature on ULCL MEAs.

- Completed an extensive assessment of how various CCL models compare with experimental data. Results show that the United Technologies Research Center (UTRC) hierarchal model provides the best physical representation of an SOA CCL, and the most

quantitatively reasonable predictions for transport resistances.

- Fabricated a complete MEA with a novel thin-film catalyst that demonstrated reasonable performance for a first-of-a-kind MEA with ULCL (0.096 mg-PGM/cm² on cathode).

Table 1. Progress Toward Meeting MEA Technical Targets for Transportation

Characteristic	Units	DOE 2020 Targets	Project Status (Differential Operating Conditions)
PGM total loading	mg-PGM/cm ² _{geo}	≤0.125	≈ 0.2 total (≈ 0.1 per electrode)
MEA performance	mA/cm ² _{geo} @ 0.8 V	≥300	304 (Pt-only catalyst)
MEA performance	mW/cm ² _{geo} @ 0.675 V	≥1,000	805 (Pt-only catalyst)

INTRODUCTION

MEAs with ULCLs of highly active Pt-alloy catalysts already have been demonstrated to exceed DOE's 2020 high-efficiency target of $>0.3 \text{ A/cm}^2$ at 0.8 V [1]. Meeting the rated-power target of 1 W/cm^2 with these MEAs, however, has been far more challenging because mass-transport losses in conventional PEFC CCLs increase as the amount of catalyst is decreased [2]. Therefore, what primarily is needed to fully realize DOE's 2020 targets is mitigation of these transport losses, which is the focus of this project.

The initial focus of this project is to improve the fundamental understanding of transport losses in PEFC CCLs, because the sources of these losses historically have not been sufficiently understood, as evidenced by disagreement about the key mechanisms [3]. Subsequently, this improved fundamental understanding shall be used to design advanced MEAs that have significantly reduced mass-transport losses. This ultimately should enable the achievement of simultaneous requirements of high mass activity, low PGM loading, and high power density.

APPROACH

The project objective will be realized by first developing and validating a detailed microstructural CCL model. CCLs are complex structures and there are many constituents and mechanisms within this critical layer that may make significant contributions to the observed transport losses [4]. Further, the relative importance of processes could vary with operating conditions. To discern transport-loss mechanisms, it is necessary to first differentiate between the wide variety of possible microstructures and phases within the electrodes with sufficient geometric detail. A sufficiently detailed geometric model of the CCL can be used to uniquely determine what components and mechanisms are major contributors to transport losses in the CCL. This model and its performance-prediction capabilities then can be validated using a variety of CCL-characterization methods to measure the key geometric details included in the model, as well as by testing a variety of MEAs under various operating conditions.

The core project team has the capability to fabricate SOA MEAs using conventional carbon-support catalysts. Additionally, the University of Arkansas at Little Rock (UALR) has unique capabilities to fabricate thin-film catalyst architectures, which can be used to fabricate CCLs with alternative electrocatalyst structures. Therefore, the team can make and test both SOA MEAs and novel catalyst materials. These capabilities are being used to design innovative catalyst-layer morphologies to achieve high performance at both high and low power densities. Discerning the sources and magnitudes of the various losses requires testing a matrix of CCLs that provide sufficient variations in the underlying parameters to highlight the different losses. Each CCL variant must be subjected to a battery of diagnostic tests that help to quantify the different overpotentials. An iterative process is used to develop high-performance MEAs (depicted in Figure 1). In addition to the core team, the world-class material-characterization capabilities of FC-PAD are being used to help the team measure key geometric details of the CCLs.

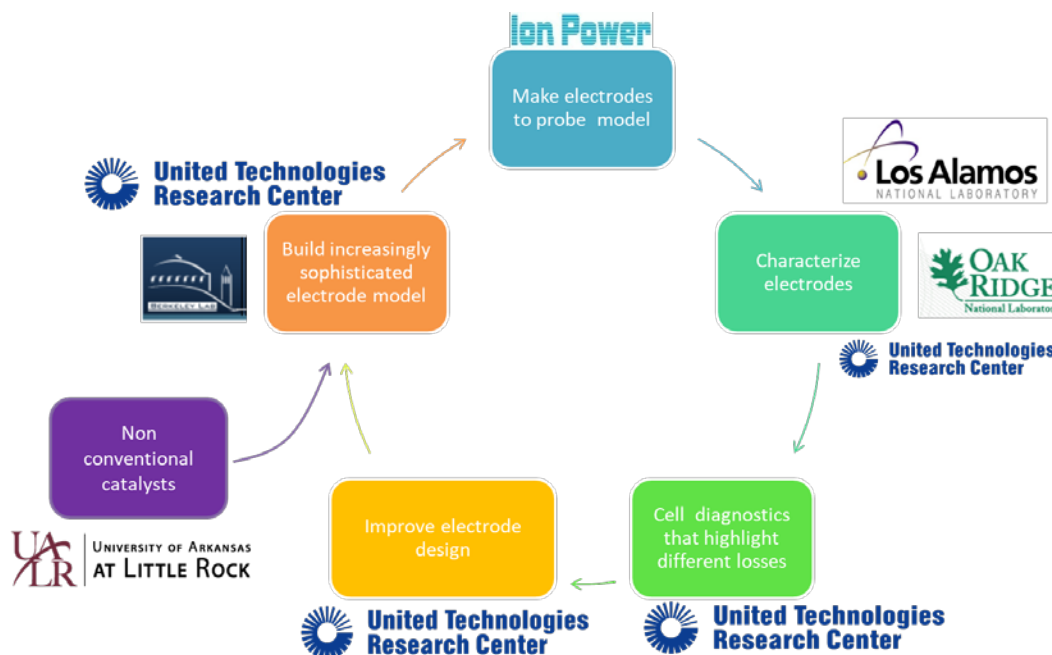


Figure 1. Simple graphical summary of the team's approach to achieving the project's objectives

RESULTS

UTRC has developed and validated a new type of hierarchal CCL model [5]. Conceptually, the model treats the catalyst layer as an assembly of representative spherical volume elements (i.e., agglomerates) that contain supported catalyst particles and are flooded with electrolyte as depicted schematically in Figure 2. Uniquely, this hierarchal model includes both spherical diffusion losses at the scale of platinum particles, as well as transport processes at the scale of the agglomerates—which is the only scale normally considered in many CCL transport models. This hierarchal approach was motivated by the realization that very large fluxes occur on catalyst particles near the outer surface of agglomerates at high overpotentials. The agglomerate in Figure 2 (not to scale) contains an interior core comprised of platinum (light grey) on carbon (dark grey) separated by ionomer (dark blue), and an exterior ionomer film (light blue). Relatively large pores between agglomerates—often called secondary pores—are available for gas transport.

The structure is largely determined by the morphology of the carbon black support. Carbon blacks in fuel cells typically contain significant amounts of micro-, meso-, and macroporosity. Electrolyte occupies the mesoporosity, and the macroporosity remains open for gas transport. It is interesting to note that, historically, fuel-cell modelers have found it very beneficial to utilize agglomerate models to effectively treat the complex processes that occur in gas-diffusion electrodes over two different length scales that vary by approximately 20X (i.e., the electrode thickness and the agglomerate diameter). A somewhat analogous treatment of the agglomerate and catalyst particles had not been done previously, however, even though the ratio of these two length scales is twice as large (i.e., approximately 42X using the dimensions shown in Figure 2). UTRC's hierarchal-agglomerate model incorporates—for the first time—spherical diffusion losses at the scale of the platinum particles to the processes at the scale of the agglomerate that are normally considered in a conventional agglomerate model.

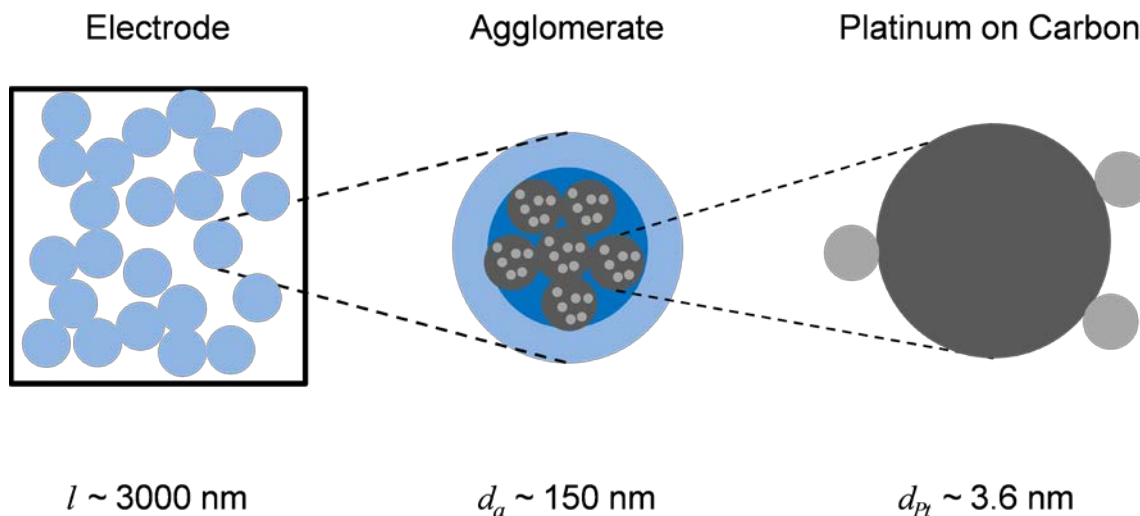


Figure 2. From left to right: schematic representations of agglomerates in a gas-diffusion electrode; an individual agglomerate consisting of a core containing platinum, carbon, and ionomer surrounded by an ionomer film; and platinum on a primary carbon particle

Predictions from this hierarchal model agree semi-quantitatively with published experimental investigations into the effect of platinum loading on cell performance. One example of this agreement is shown in Figure 3; more examples can be found in Darling et al. [5], which compares transport resistances as introduced by researchers at General Motors [6] predicted for agglomerate diameters ranging from 50 nm to 200 nm, to the experiments of Owejan et al. [7], Ono et al. [8], and Nonoyama et al. [2], as summarized by Weber and Kusgolo [9], along with the data fit of Greszler et al. [10] at 150 kPa. All resistances were calculated at 80°C and 90% relative humidity. Qualitatively, the model and experiment show similar trends of decreasing transport resistances with increasing platinum loading. Quantitative comparisons are only appropriate for the data of Owejan et al. and Greszler et al. because they used Pt on Vulcan, which is what has been modeled by UTRC to date. Nonoyama et al. did not disclose their carbon support, and Ono et al. used a high-surface-area support (TKK's TEC10E50E). The model simulations with agglomerate diameters in the range of 100 nm to 150 nm compare quite favorably with the data reported by Greszler et al. In general terms, the model appears to effectively explain why transport losses increase as platinum content decreases.

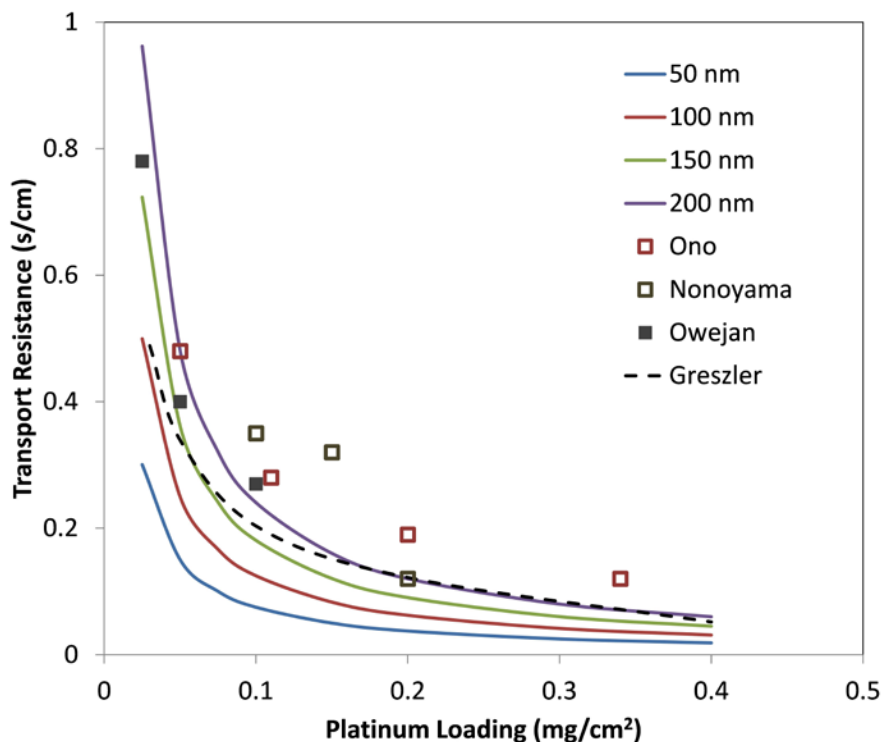


Figure 3. Measured and predicted transport resistances as functions of catalyst loading. Predictions are shown for agglomerate diameters ranging from 50 nm to 200 nm.

Using cell performance data, UTRC also has successfully validated this hierarchical model on both the ULCL MEAs fabricated and characterized by the project team, and multiple data sets reported in the literature on MEAs with ULCLs [5]. Although UTRC's model is only a CCL model, it can be used to predict complete polarization curves by doing the following.

1. Use methodology developed by General Motors to isolate the transport resistance of the gas-diffusion layer (GDL) via experiments with dilute O₂/N₂. We used a transport resistance of 0.65 s/cm to describe the GDL when comparing to UTRC's polarization curves at the specified operating conditions.
2. Subtract the resistance of the membrane to convert the measured voltages to cathode voltages.
3. Use UTRC's CCL model to predict the current as a function of cathode voltage and oxygen content.

An example of the results from this analysis are shown in Figure 4. With minimal fitting parameters, the model successfully predicts performance of an Ion Power MEA tested at UTRC on oxygen, air, and "half air" (10.5% oxygen in nitrogen). The project's first year go/no-go milestone was for the model to predict the current density of polarization curves to within 50% at 0.8 V and 0.6 V. The measured current density at 0.8 V (IR-free, as modeled) was 35 mA/cm² and the model value was 40 mA/cm², which is 14% larger. The measured current density at 0.6 V (IR-free) was 1.145 A/cm² and the model value was 1.130 A/cm², which is 1.3% smaller. The agreement between the model and the data therefore exceeded the go/no-go milestone criteria.

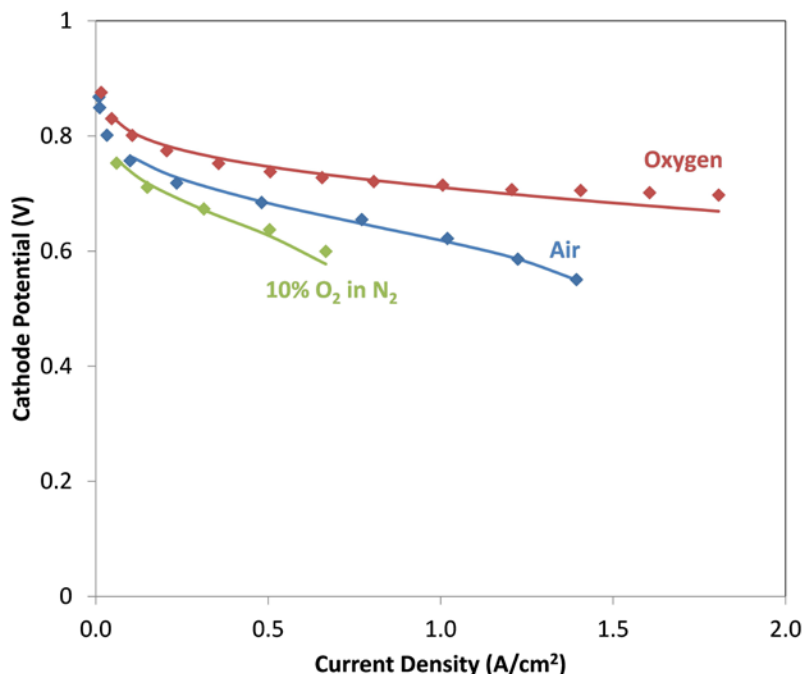


Figure 4. Comparison of model (solid lines) to polarization data measured by UTRC on an Ion Power MEA with a CCL catalyst loading of 0.046 mg/cm² Pt. The ORR activity on air was increased to 2.5 A/m² from 1.9 A/m² on oxygen to fit low current data; no other model parameters were fit.

Other commonly applied models do not qualitatively match all of the empirically observed trends. This is an important point and is worth emphasizing rigorously for this new model to gain broad acceptance within the fuel-cell community. Therefore, during the past quarter, UTRC completed an extensive comparison of various CCL-transport models; a very brief summary of the results is presented here (these different transport models are fully described in Weber et al. [5] and are beyond the scope of this report). Table 1 summarizes how the different expressions for the transport resistance (R_{Pt}), described in 11 different models of transport in the CCL, vary with three electrode descriptors L_{Pt} , M_{Pt} , and I/C , as well as the overpotential $U-V$. Where $R_{Pt} = \Gamma_{Pt} * R_{CL}$, is a convenient derived quantity that should not vary with platinum loading; R_{CL} is the transport resistance (s cm⁻¹); Γ_{Pt} is the platinum area divided by macroscopic area of electrode; L_{Pt} is the amount of platinum in electrode (mg/cm²), M_{Pt} is the mass fraction of platinum in a supported catalyst, and I/C is the ionomer to carbon ratio (by mass). The next-to-last column summarizes whether a particular model is in directional agreement with all relevant experimental observations summarized in Table 2, and the final column gives quantitative estimates for R_{Pt} . Unfortunately, experimental observations regarding how R_{Pt} varies with M_{Pt} , and I/C are sparse and, in the case of I/C , are inconsistent. Nevertheless, it is possible to conclude that many of the simplest and most common models for transport in a CCL cannot correctly describe the experimental data.

Table 2. Qualitative Comparisons of Different CCL Models to Experimental Results

Case	How does R _{Pt} respond to increases in:	L _{Pt}	M _{Pt}	I/C	U-V	Match	R _{Pt}
–	Experiment	↔	↑	↑	↔	–	12
1	Through electrode thickness	↑	↓	↑	↓	✗	2.3
2	To isolated catalyst nanoparticles	↔	↔	↔	↔	✗	2.2
3	Diffusion through thin ionomer film	↔	↓	↑	↔	✗	0.8
4	Adsorption onto platinum from ionomer	↔	↔	↔	↔	✗	12.0
5	Dissolution, primary carbon particles	↔	↑	↔	↔	✗	?
6	Dissolution, agglomerates	↔	↑	↓	↔	✗	?
7	Diffusion in film around agglomerates	↔	↑	↑	↔	✓	4.6
8	Diffusion inside agglomerates	↔	↑	↔	↓	✗	0.02
9	Agglomerate core + shell	↔	↑	↑	↔	✓	1.2
10	Agglomerate core + shell + nanoscale	↔	↑	↑	↔	✓	15.0

Only three of the ten models in Table 2 match the experimentally observed dependencies on L_{Pt} , M_{Pt} , I/C , and $U-V$. Of the three directionally correct models, the model incorporating nanoparticle limitations associated with either localized diffusion to or adsorption on the platinum particles (i.e., Case 10, UTRC’s hierarchal model) provides the best fit to the experimental data. One example of this is the R_{Pt} values shown in Table 2.

In conclusion, the sensitivities of different analytical models for transport resistances in the air electrode of PEFCs were qualitatively and semi-quantitatively compared to empirical data. Seven of the ten models examined do not qualitatively reproduce the experimentally observed responses to changes in mass fraction of platinum and ratio of ionomer to carbon. Of the three qualitatively correct models, the model incorporating both nanoscale transport effects to the agglomerate plus external diffusion gives the best physical representation of a CCL, and provides quantitatively reasonable predictions for transport resistances.

The team also demonstrated the capability to fabricate MEAs using unique thin-film electrocatalysts produced by UALR. UALR has developed the capability to make density-modulated platinum-thin-film (Pt-TF) catalysts using high-pressure sputtering deposition. Change of working gas pressure of the sputtering system results in various Pt-TF catalysts with different densities and porosities. UALR also has developed the capability to deposit Pt-TF catalysts directly onto either GDLs or membranes. UTRC tested an MEA that was fabricated by using a GDL with an MPL (SGL-25BC), which UALR had coated with Pt-TF catalyst, and integrating this gas-diffusion electrode with “half MEA” that had a conventional catalyst layer on only one side of the membrane. The results successfully demonstrated that the team can fabricate and test functional MEAs with thin-film catalysts, which will be a focus of both experimental and modeling work going forward.

CONCLUSIONS AND UPCOMING ACTIVITIES

The first objective of this project has successfully been completed; specifically, a detailed microstructural model has been successfully developed and validated. UTRC’s hierarchal model matches the experimentally observed responses of conventional MEAs with ULCLs in a manner that is clearly superior to other CCL-transport models. The team now is using this hierarchal CCL model to guide the development of advanced MEAs which utilize conventional carbon-supported catalysts. The team also has developed the capability to fabricate and test MEAs with thin-film electrocatalysts. UTRC also plans to develop a microstructural model for these types of CCL architectures—which are very different than MEAs with conventional carbon-supported catalysts. This work should lead to the development of improved PEFCs, which ultimately can meet both the cost and performance targets established by DOE for transportation applications.

FY 2018 PUBLICATIONS/PRESENTATIONS

1. R.M. Darling, “A Hierarchical Model for Oxygen Transport in Agglomerates in the Cathode Catalyst Layer of a Polymer-Electrolyte Fuel Cell,” *J. Electrochem. Soc.* 165 (2018): F571.

2. R.M. Darling, “A Hierarchical Model for Oxygen Transport Within Agglomerates in the Cathode Catalyst Layer of a Polymer Electrolyte Fuel Cell,” Presented at FC PAD Meeting at NREL, April 2018.
3. R.M. Darling, “High Performance PEFC Electrode Structures,” Presented at Fuel Cell Tech Team Meeting, Detroit, Michigan, September 2018.
4. M.L. Perry, “High Performance PEFC Electrode Structures,” Presented at FCTO AMR Meeting, Project ID FC157, June 2018.

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