



Low-Platinum Group (PGM) Metal Catalysts

Cooperative Research and Development Final Report

CRADA Number: CRD-16-649

NREL Technical Contact: Shaun Alia

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Contract No. DE-AC36-08GO28308

Technical Report
NREL/TP-5900-74569
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Suggested Citation

Alia, Shaun. 2019. *Low-Platinum Group (PGM) Metal Catalysts: Cooperative Research and Development Final Report, CRADA Number: CRD-16-649*. Golden, CO: National Renewable Energy Laboratory. NREL/TP-5900-74569. <https://www.nrel.gov/docs/fy19osti/74569.pdf>.

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This work was authored by the National Renewable Energy Laboratory, operated by Alliance for Sustainable Energy, LLC, for the U.S. Department of Energy (DOE) under Contract No. DE-AC36-08GO28308. Funding provided by the U.S. Department of Energy Office of Energy Efficiency and Renewable Energy Fuel Cell Technologies Office. The views expressed herein do not necessarily represent the views of the DOE or the U.S. Government.

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Cooperative Research and Development Final Report

Report Date: 5/6/2019

In accordance with requirements set forth in the terms of the CRADA agreement, this document is the final CRADA report, including a list of subject inventions, to be forwarded to the DOE Office of Science and Technical Information as part of the commitment to the public to demonstrate results of federally funded research.

Parties to the Agreement: Oorja Fuel Cells

CRADA Number: CRD-16-649

CRADA Title: Low-Platinum Group (PGM) Metal Catalysts

Joint Work Statement Funding Table showing DOE commitment:

Estimated Costs	NREL Shared Resources a/k/a Government In-Kind
Year 1	\$100,000.00
TOTALS	\$100,000.00

Abstract of CRADA Work:

High catalyst loadings and relatively high over-potential losses have limited the commercial viability of direct methanol fuel cells (DMFCs). Platinum-based catalysts are used in DMFCs with a loading of 4.5 mg cm⁻²; the catalyst layer is a significant contributor to the membrane electrode assembly (MEA) cost, which accounts for 60% of the system cost. The large-scale commercial viability of DMFCs is dependent on a significant (~ 50%) cost reduction. If these cost goals can be reached, the current market can be extended from 100's of units to 10,000's of units.

Currently, Oorja is using a platinum-ruthenium catalyst for methanol oxidation, but does not have access to a supplier able to develop low-platinum group (PGM) metal catalysts to reach DMFC cost reduction targets. Oorja has recently developed a small lab scale capability in fabrication and testing of DMFC membrane electrode assemblies (MEAs), but does not have access to synthesis and characterization of advanced electrocatalysts. The materials, equipment, and expertise at the National Renewable Energy Laboratory (NREL) are of significant value to Oorja. NREL recently develop platinum-nickel nanowires as catalysts in hydrogen fuel cells. These materials have also shown promise in DMFC applications as a potential replacement for standard platinum-ruthenium catalysts; in ex-situ testing, these materials have shown one order of magnitude higher mass activity and can avoid ruthenium crossover contamination effects. These combined properties are exceptionally appealing to Oorja, and can result in significantly decreasing the capital costs of DMFCs.

Summary of Research Results:

The NREL work scope for this activity include multiple tasks listed below:

- Fabrication of MEAs
- Test station verification and baseline performance from commercial MEAs and in-house made MEAs
- Different DM comparison
- Catalyst coated membrane (CCM) vs Gas diffusion electrode (GDE)
- PtNi performance for oxygen reduction
- PtNi performance for DMFC system
- MEA Diagnostics: anode polarization curve
- Reinforced PtNi to make more robust wires

Fabrication of MEAs included both CCMs and GDEs. The key fabrication details are given below for both approaches:

The following 2 sets of results encompass the two tasks listed below.

Task 1: Develop anode and cathode ink formulation using existing platinum-nickel nanowire catalyst compositions.

Task 2: Fabrication of MEA's using the above-optimized ink formulations.

Fabrication of CCM MEA (25 cm²)

- Nafion 115 (127 μ m)
- DM: Toray carbon paper TGP 060
- MEA spraying with the Johnson Matthey catalysts
 - Anode loading (Pt-Ru) = 3 mg/cm²
 - 50% Pt-25% Ru/HSC
 - Cathode loading (Pt) = 1.5 mgPt/cm²
 - Cathode: 60% Pt/HSC

Fabrication of GDE MEA (5 cm²)

Nafion 115 (127 μ m)

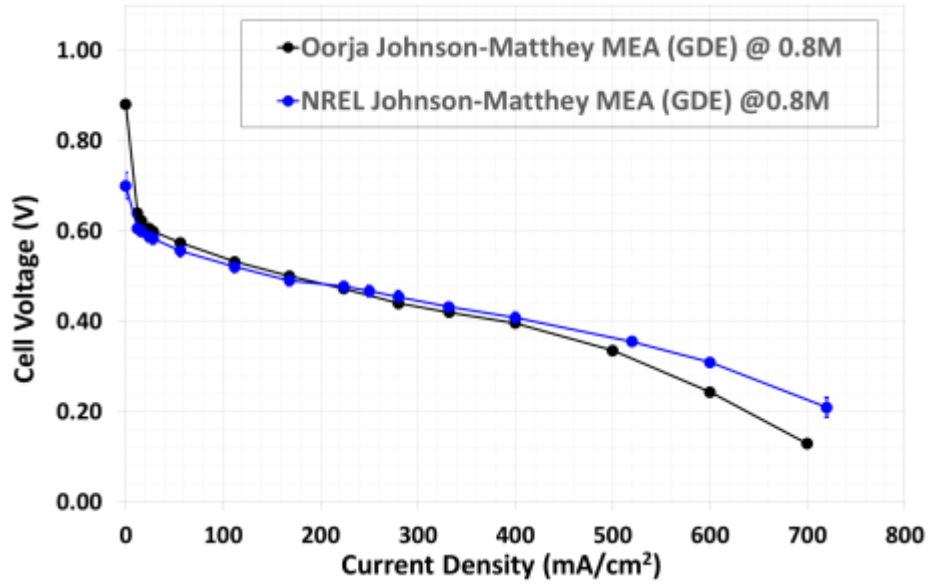
DM: Toray carbon paper TGP 060

Direct spraying on DM with the Johnson Matthey catalysts

- Anode loading (Pt-Ru) = 3 mg/cm²
 - 50% Pt-25% Ru/HSC
- Cathode loading (Pt) = 1.5 mgPt/cm²
 - Cathode: 60% Pt/HSC
- Applied an ionomer overspray between the electrode and membrane (1 wt%, 0.014g/ml)
- Hot-pressed the MEA

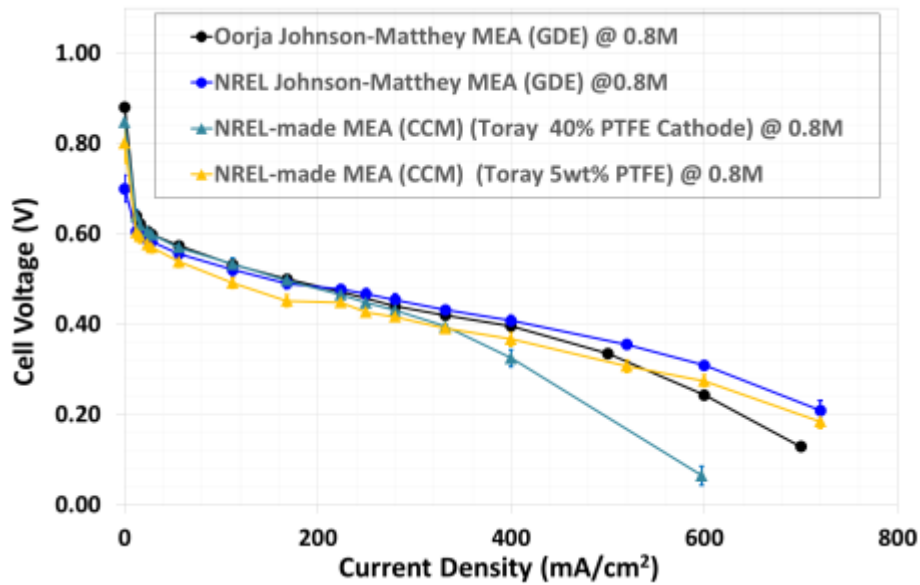
Task 3: Generate single cell test data at Oorja and correlate with RDE and half-cell data generated at NREL.

NREL baselined performance with Oorja to validate test stand performance to ensure relevant comparisons. The Figure below shows that reasonable performance agreement between the two locations was achieved.

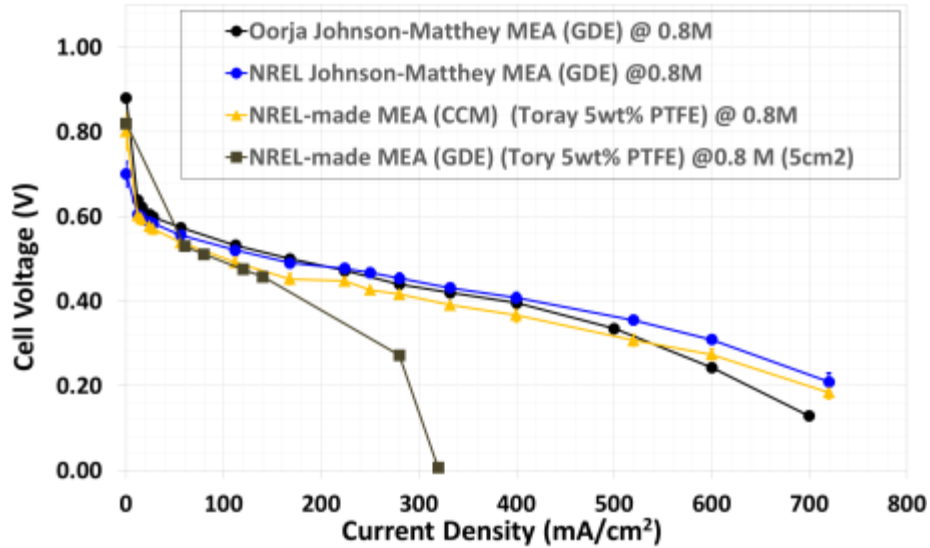


NREL fabricated MEAs were then investigated to ensure similar performance to commercial MEAs. The Figure below shows that 5% Teflon coated gas diffusion layer (Toray paper) allowed for similar performance to be achieved to commercial MEAs.

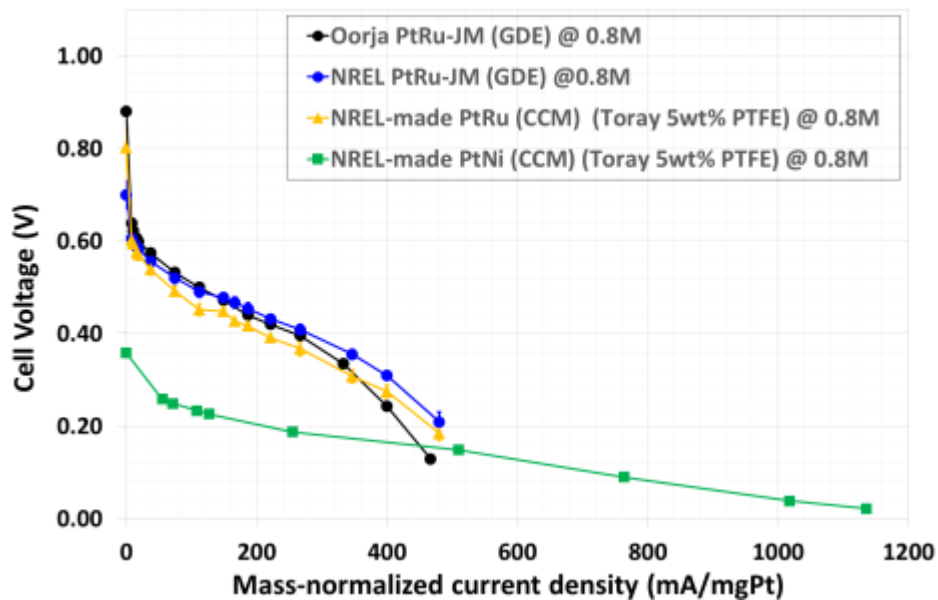
Task 4: Compare the performance and durability of Pt-Ni nanowire catalyst based MEA with current state of the art DMFC MEA used in Oorja power system and recommend a pathforward.



MEA fabrication route was also investigated showing that CCMs exhibited higher performance than GDEs as shown in the Figure below.



Having decided on CCM MEAs with 5 wt% PTFE Toray paper backing, NREL fabricated multiple MEAs from PtNi nanowires to explore DMFC performance, results shown in Figure below. The performance of the PtNi cells were much lower than that of PtRu based cells.



The performance of PtNi in these systems was similar to Pt and suggested the Ni was being leached from the surface, preventing the catalytic improvements in the bifunctional mechanism that are achieved with Pt alloying with Ru or Ni that have been observed. This is likely due to the Ni stability in the Pt surface being improved in ex-situ testing relative to in cell testing. In order to try to improve the stability of PtNi oxidation of nanowires was investigated, however the results from these tests led to even poorer performance, perhaps because oxidized Ni also isn't active in the bifunctional mechanism or because it is still prone to dissolution. At this point no specific approach to maintain the half cell performance advantage in functioning cells has been identified.

Summary/Conclusions:

- PtNi performance for oxygen reduction is reasonable.
- PtNi performance in DMFC system is poor.
- Based on anode polarization curve, it was obtained that PtNi has high overpotential ~ 0.5V than PtRu ~ 0.3V.
- The pre-leached PtNi wires does not show bi-function mechanism that we see in PtRu catalysts.
- Over oxidized PtNi wires to stabilize the wires, making them more robust. But MEA performance is very poor. No current drawn in MeOH operation.

Subject Inventions Listing:

None

ROI #:

None

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DOE Program Office:

Office of Energy Efficiency and Renewable Energy Fuel Cell Technologies Office (FCTO)