

## V.D.2 Highly Dispersed Alloy Catalyst for Durability

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- Texas A&M University, College Station, TX
- Brookhaven National Laboratory, Upton, NY

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### Fiscal Year (FY) 2012 Objectives

- Develop structurally and compositionally advanced supported alloy catalyst system with loading  $\leq 0.3$  mg platinum group metal (PGM)/cm<sup>2</sup>.
- Optimize catalyst performance and decay parameters through quantitative models.
- Demonstrate 5,000 cyclic hours below 80°C with less than 40% loss of electrochemical surface area and catalyst mass activity.

### Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4.4) of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (A) Durability
- (B) Cost

### (C) Performance

### Technical Targets

**TABLE 1.** DOE technical targets for electrocatalysts and the current status of this project

Electrocatalyst Targets	Units	Current Status	DOE 2010 Target	DOE 2017 Target
PGM (total content)	g/kW	0.50	0.3	0.125
PGM (total loading)	mg/cm <sup>2</sup>	0.40 <sup>a</sup>	0.3	0.125
Mass activity @ 900 mV	A/mg <sub>PGM</sub> at 900 mV (iR-free)	0.20 (in MEA) 0.30 (in liquid cell)	0.44	0.44
Specific activity	μA/cm <sup>2</sup> at 900 mV (iR-free)	940 (in MEA) 612 (in liquid cell)	720	720
Cyclic durability At T $\leq 80^\circ\text{C}$	h	2,050 <sup>b,c</sup>	5,000	5,000
At T $> 80^\circ\text{C}$	h		2,000	5,000
ECA Loss	percent	30 <sup>d</sup>	<40	<40
Cost	\$/kW at \$51.55/g	~26 <sup>e</sup>	5	3
Electrocatalyst Support mV after 400 hours @ 1.2 V	mV	92 <sup>f</sup>	<30	<10

iR – internal resistance; MEA – membrane electrode assembly; ECA – electrochemical area

<sup>a</sup> Based on current scaled-up 30% Pt<sub>2</sub>IrCr/C MEA; anode/cathode loading – 0.1/0.3 mg/cm<sup>2</sup> (PGM).

<sup>b</sup> Under an accelerated vehicle drive cycle protocol in a short stack; 40% mass activity loss under UTC-defined accelerated single-cell test after 270 hours at 70°C and 120 hours at 80°C.

<sup>c</sup> Primary degradation mechanism in the alloy catalyst due to transition metal alloy dissolution.

<sup>d</sup> Durability data measured after 30,000 cycles under UTC-defined accelerated test protocol.

<sup>e</sup> 5-year average PGM price \$51.55/g (Pt = \$1,234.33/troy oz.; Ir = \$369.06/troy oz.); costs not projected to high volume production.

<sup>f</sup> 40 mV iR-free O<sub>2</sub> performance loss at 1.5 A/cm<sup>2</sup> after 360 hours at 1.2 V.

### FY 2012 Accomplishments

- Completed the scale up and MEA optimization of down-selected dispersed catalyst, 30% Pt<sub>2</sub>IrCr/C for performance at high current densities in a full-size fuel cell. A mass activity of 0.17 A/mg (PGM) was achieved compared to the previous status of 0.14 A/mg (PGM) with a 53 mV improvement in performance at 1 A/cm<sup>2</sup> in H<sub>2</sub>/air.
- Completed the durability testing of 30% Pt<sub>2</sub>IrCr/C in a short stack under an accelerated vehicle drive cycle protocol. The stack accumulated 2,050 hours of uninterrupted operation at 70°C in H<sub>2</sub>/Air. Completed

stack teardown to understand degradation mechanism for Pt<sub>2</sub>IrCr alloy: primary durability loss in the alloy catalyst was due to transition metal dissolution.



## Introduction

For the proton exchange membrane fuel cell (PEMFC) technology to become commercially viable, the production cost of the components in a fuel cell must be reduced and, more importantly, the durability of the MEA must be improved. This project focuses on two distinct approaches to the DOE 2010 durability and performance targets. The first approach is the development of conventional but high performance highly dispersed Pt alloy electrocatalyst on a carbon support. The second system utilizes a novel “Pt monolayer core-shell” approach capable of achieving very high Pt mass activities [1-3]. Under the former concept, the main objectives are to improve the high current density performance and durability towards cycling of the cathode catalyst by optimizing the MEA fabrication methods.

## Approach

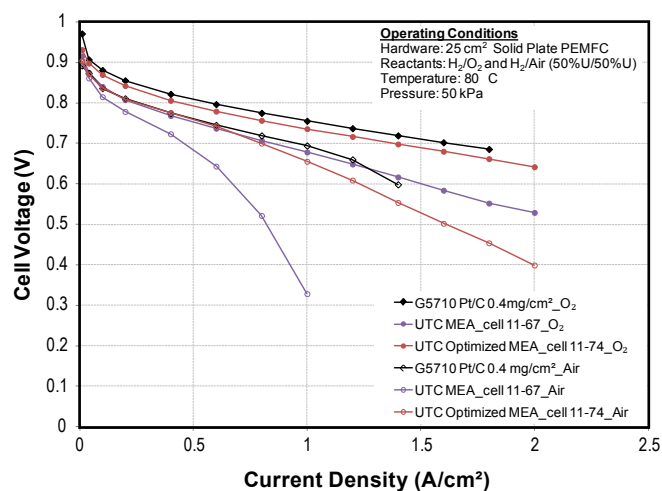
To achieve the objectives on this project, UTC Power (UTCP) has teamed with Brookhaven National Laboratory (BNL), Texas A&M University (TAMU) and Johnson Matthey Fuel Cells (JMFC). The research focus and the role of all partners were reported previously [4]. BNL's role on the project focuses on the development of Pt monolayer “core-shell” systems on various cores including ideal surfaces such as single crystals. In addition, BNL leads our efforts to understand the effect of electronic properties, crystal structure and particle size on activity and durability of this class of electrocatalysts. TAMU focuses on development of computational atomistic models to study parameters that influence the activity and durability of core shell and dispersed catalyst systems. The overall scope of JMFC activities in the project encompasses development of (i) dispersed Pt alloy catalysts including scale up on conventional and advanced carbon supports, (ii) novel synthesis methodologies to scale up Pt monolayer core-shell catalysts and (iii) MEA optimization and fabrication. Apart from overall project management, UTCP primarily focuses on the development of advanced dispersed Pt-based binary and ternary alloy catalysts. UTCP activities also include electrode modeling for MEA optimization, carbon support corrosion studies, fuel cell testing on full-size (410 cm<sup>2</sup>) MEAs, and fabrication and testing of a 20-cell short stack for verification.

## Results

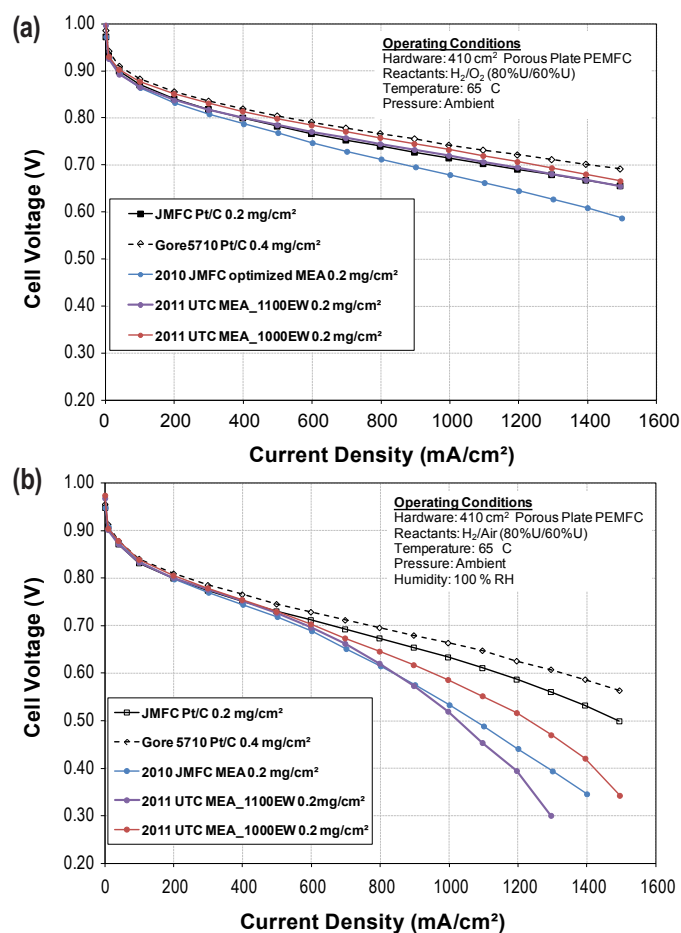
### Dispersed Pt Alloy Catalyst

Many factors such as structure, particle dispersion, particle size, type of carbon support, etc, influence the electro-catalytic activity of Pt and Pt alloy nanoparticles. Previously, within this project, a 30 wt% Pt<sub>2</sub>IrCr cathode (0.3 mg<sub>PGM</sub>/cm<sup>2</sup> loading) showed higher durability in both active electrochemical area (ECA) and mass activity (MA) under potential cycling. This catalyst showed much lower loss (~30% ECA and MA) compared to the standard Gore Pt/C (0.4 mg<sub>PGM</sub>/cm<sup>2</sup> loading) which showed ~50% loss and was down-selected for further development and scale up into full size MEAs [4]. In the past year, a significant amount of effort was focused towards development and optimization of the cathode catalyst layer in an MEA with 30% Pt<sub>2</sub>IrCr alloy catalyst to improve the catalyst utilization in electrodes keeping low PGM loading and enabling good performance at high current densities. This involved an elaborate investigation to identify key parameters such as catalyst ink formulations, ionomer equivalent weight and content, to produce an optimum cathode electrode capable of achieving good fuel cell performance in wide range of current densities.

Figure 1 shows the sub-scale (25 cm<sup>2</sup>) solid plate fuel cell performance curves in H<sub>2</sub>/O<sub>2</sub> and H<sub>2</sub>/air at 80°C for the 30% Pt<sub>2</sub>IrCr/C MEA with two different ionomer equivalent weights during the optimization process compared to a baseline Gore 5710 Pt/C MEA. The performance at 100 mA/cm<sup>2</sup> is 0.87 V for the electrode with 1000 equivalent weight (EW) (cell 11-74) compared to 0.84 V for the electrode with 1100 EW (cell 11-67) for a loading of 0.3 mg<sub>PGM</sub>/cm<sup>2</sup>. Figures 2a and 2b show the



**FIGURE 1.** Polarization curves of H<sub>2</sub>/O<sub>2</sub> and H<sub>2</sub>/air performance for the preliminary optimization of JM 10-112 (30% Pt<sub>2</sub>IrCr/C<sub>KB</sub>) MEAs compared to the Gore Pt (0.4mg/cm<sup>2</sup>) MEA in sub-scale solid plate cells at 80°C, 50 kPa backpressure operation



**FIGURE 2.** Polarization curves of (a) H<sub>2</sub>/O<sub>2</sub> and (b) H<sub>2</sub>/air performance for the optimization of JM 10-112 (30% Pt<sub>2</sub>IrCr/C<sub>KB</sub>) MEAs compared to JMFC Pt (0.2 mg/cm<sup>2</sup>) MEA in full-size porous plate cells at 65°C, 0 kPa backpressure operation

performance in H<sub>2</sub>/O<sub>2</sub> and H<sub>2</sub>/air, respectively, for the (30% Pt<sub>2</sub>IrCr/C<sub>KB</sub>) in a porous plate cell at 65°C using various EW Nafion<sup>®</sup> ionomer solutions in the cathode catalyst layer after optimizing the MEA for suitable solvents, ionomer/carbon ratio and fabrication methods. The performance curves for a baseline JM Pt/C and the 2010 JMFC optimized 30% Pt<sub>2</sub>IrCr/C<sub>KB</sub> MEA is also included for comparison. Table 2 summarizes the performance of all the MEAs. As shown in Figure 2, the MEAs using different ionomer solutions in the catalyst layer of the cathode electrode results in higher performance than the 2010 JMFC optimized MEA in both oxygen and air at low current density regions. Moreover, the electrode with 1000 EW shows significant improvement in the mass activity (0.17 A/mg<sub>Pt</sub>) and the corresponding H<sub>2</sub>/air performance for the 2011 UTC-optimized MEA shows a 53 mV improvement at 1 A/cm<sup>2</sup> compared to the 2010 JMFC-optimized MEA. This improvement in activity and performance is primarily due to the better utilization of the catalyst and improved mass transport resistance in the MEA.

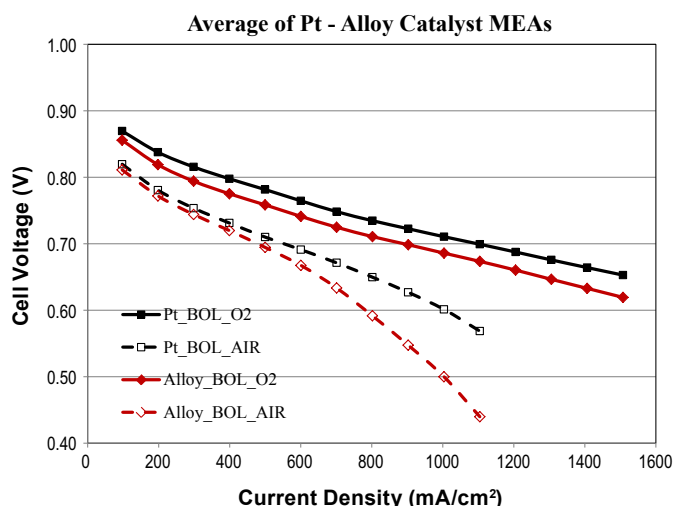
**TABLE 2.** Summary of H<sub>2</sub>/O<sub>2</sub> and H<sub>2</sub>/air performance of the 30% Pt<sub>2</sub>IrCr/C alloy catalyst MEAs compared to a commercial Gore Pt/C (0.4 mg<sub>Pt</sub>/cm<sup>2</sup>) and JMFC Pt/C (0.2 mg<sub>Pt</sub>/cm<sup>2</sup>) MEA

Cell	Voltage at 0.1A/cm <sup>2</sup> in H <sub>2</sub> /O <sub>2</sub> (V)	Voltage at 1A/cm <sup>2</sup> in H <sub>2</sub> /Air (V)	iR at 1A/cm <sup>2</sup> in H <sub>2</sub> /Air (V)
JM Pt/C (0.2)	0.871	0.634	0.079
Gore5710 Pt/C (0.4)	0.883	0.664	0.062
JMFC MEA	0.864	0.533	0.093
UTC MEA 1100EW	0.866	0.520	0.076
UTC MEA 1000EW	0.886	0.586	0.084

### 20-Cell Stack Validation

In FY 2011, a 20-cell short stack built at UTC containing the 30% Pt<sub>2</sub>IrCr/C<sub>KB</sub> MEAs completed 2,000 hours of cycling using the accelerated lifetime test conditions developed under a DOE-funded project at UTC Power titled “Improved Accelerated Stress Tests Based on Fuel Cell Vehicle Data”. The short stack contained four Pt MEAs as references and sixteen alloy catalyst 30% Pt<sub>2</sub>IrCr/C<sub>KB</sub> MEAs. All MEAs were manufactured by JMFC with a cathode Pt loading of 0.2 mg<sub>Pt</sub>/cm<sup>2</sup> and anode Pt loading of 0.1 mg<sub>Pt</sub>/cm<sup>2</sup>. After conditioning, beginning-of-life (BOL) performance was tested in both oxygen and air. Cell resistance was measured by the H<sub>2</sub>-pump method.

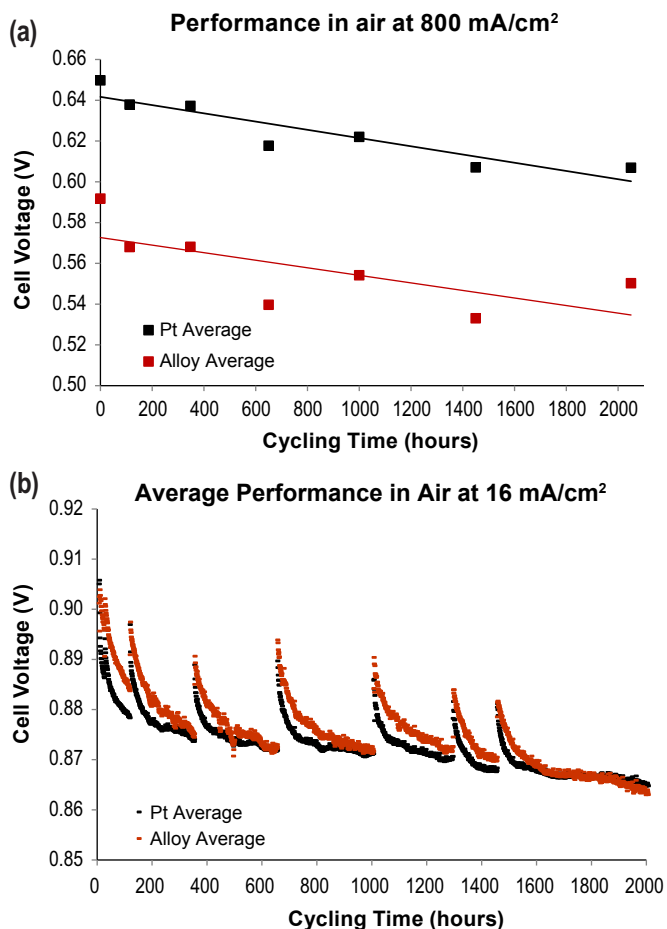
The average performance of the cells in O<sub>2</sub> and air with the alloy catalyst was lower than the Pt catalyst cells as shown in Figure 3. The resistance of 79±5 mΩ·cm<sup>2</sup> in the alloy catalyst cells was similar to that of Pt catalyst cells (73±3 mΩ·cm<sup>2</sup>). In general, the Pt catalyst outperformed the alloy catalyst by 100 mV in air at 1 A/cm<sup>2</sup>. This performance gap is ascribed to oxygen permeability and proton concentration losses in the cathode due to Cr ion contamination in the 30% Pt<sub>2</sub>IrCr/C<sub>KB</sub> MEA. Figure 4a shows the average voltage at 800 mA/cm<sup>2</sup> in air for both Pt/C and the alloy catalysts decrease with load cycles at an average voltage decay rate of 20 μV/h and 19 μV/h (or μV/cycle) respectively. Previously, a higher rate of activity and performance loss was observed for the Pt-alloy compared to the pure Pt under a load cycling test in the full-scale water transport plate cells (85 μV/h compared to 36 μV/h). In terms of the catalyst activity, no current density steps lower than 100 mA/cm<sup>2</sup> were measured during the polarization curve measurement and hence mass activity cannot be determined from the 20-cell stack data. Although from the BOL oxygen curves in Figure 3, the Pt/C cells show slightly higher average voltage than the alloy catalyst cells at 100 mA/cm<sup>2</sup>,



**FIGURE 3.** BOL performance of Pt/C and the alloy catalyst (30% Pt<sub>2</sub>IrCr/KB) in the 20-cell stack

during the load cycling, the alloy catalyst shows a higher performance compared to the Pt/C at a lower current density of 16 mA/cm<sup>2</sup> (Figure 4b). After periodic diagnostic tests, both Pt and Pt alloys show partial performance recovery. This was mostly due to the removal of Pt oxides on catalyst surfaces at high current density. During subsequent load cycles following the diagnostic tests, it's noticeable that the alloy catalyst had initial lower voltage or activity decay than Pt/C, which was mostly due to the slower surface Pt oxidation. However, with continued load cycling, the alloy performance decreases slowly while the Pt/C catalyst quickly reaches a steady-state voltage. This difference is attributed to alloy catalyst compositional changes with the loss of Cr as discussed below.

Post-test observations including catalyst composition and electrode structure were conducted on the degraded MEAs after the stack tear down. Figure 5 shows the presence of Pt, Ir, and Cr in the MEA as measured by electron microprobe analysis (EMPA) from one of the cells from the 20-cell stack after 2,000 hours of cycling. The EMPA image shows a significant amount of Cr in the membrane and the anode electrode after durability cycling. Table 3 shows the ratio of Pt, Ir and Cr in the cathode electrode before and after cycling as determined by energy dispersive spectroscopy. A significant reduction (~50%) in Cr concentration in the electrode is comparable to the EMPA elemental analysis shown in Figure 5. Transmission electron microscope image analysis of the cathode catalyst particles did not show significant increase in particle size for the alloy catalyst before (5 nm) and after cycling (5.6 nm). However, a pure Pt catalyst from a baseline MEA with Pt/C in the cathode electrode showed a significant increase in particle size before (~2 nm) and after (5.6 nm) cycling for 2,000 hours in the 20-cell stack. Based on the post-test analysis shown



**FIGURE 4.** 20-cell short-stack performance decay during load cycles for Pt/C and the alloy catalyst (30% Pt<sub>2</sub>IrCr/C<sub>KB</sub>) in air at (a) 800 mA/cm<sup>2</sup> and (b) 16 mA/cm<sup>2</sup>

**TABLE 3.** Ratio of Pt, Ir and Cr in the cathode electrode before and after durability cycling in the 20-cell stack as determined by energy dispersive spectroscopy

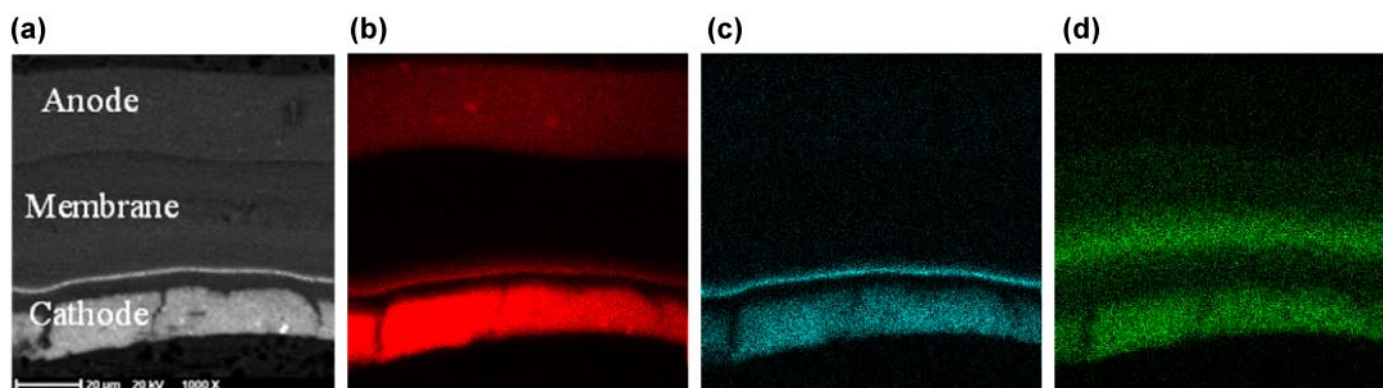
30% Pt <sub>2</sub> IrCr alloy composition	Pt	Ir	Cr
Initial wt.%	61.4	30.4	8.2
Initial atomic ratio	1.0	0.50	0.50
Final wt.%	71.0	24.2	4.8
Final atomic ratio	1.0	0.35	0.25

above, it is concluded that the primary durability loss in the 30% Pt<sub>2</sub>IrCr/C alloy catalyst is due to the transition metal dissolution (~50% loss) from the alloy catalyst.

### Conclusions and Future Directions

The effects of MEA compositions were studied for the scaled-up 30% Pt<sub>2</sub>IrCr/C in full-size water transport plate fuel cells. The electrode optimization studies clearly





**FIGURE 5.** (a) Representative electron microscopy image of the MEA cross section and EMPA elemental map in the MEA after 2,000 hours of accelerated cycling in the 20-cell stack (b) Pt, (c) Ir and (d) Cr

show that MEA ink formulations and processing methods significantly impact the electrode structure in an MEA and their performance under high current density operations. A short stack containing the Pt-alloy was built and the durability of 30% Pt<sub>2</sub>IrCr/C alloy catalysts under an accelerated vehicle drive cycle protocol showed that the durability loss was primarily due to the transition metal dissolution (~50% loss) from the alloy catalyst. Although some progress was made to overcome key barriers for the incorporation of the 30% Pt<sub>2</sub>IrCr in an MEA such as low catalyst utilization in electrodes, the transition metal stability under operating conditions remains a concern. It is now recognized that a focus on MEA optimization during the early stages of catalyst development is essential to identify

and understand the limits of alloy catalysts and their impact on the high current density performance.

## References

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