
HydroGEN Seedling: Enabling Efficient Water Splitting with Advanced Materials Designed for High-pH Membrane Interface

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Subcontractors:

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- Advent North America, Cambridge, MA

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Project End Date: December 31, 2020

- Establish a requisite baseline overpotential of 150 mV at 500 mA/cm² for a supported metal/metal-oxide OER catalyst.
- Synthesize a multi-ammonium-cation side chain-based poly(aryl piperidinium) polymer (PAP-TQN) anion exchange polymer with the requisite durability (ion exchange capacity [IEC] loss of 20% or less after a 1,000-hour treatment in 1 M KOH at 95°C) and ionic conductivity (0.15 Ω-cm²).
- Initiate collaboration with Energy Materials Network (EMN) partners for subsequent determination of the physical properties of anion exchange materials and theoretical characterization of the electrode/electrolyte interface.

Overall Objectives

- Evaluate various transition metal moieties as hydrogen evolution reaction (HER) catalysts for anion exchange membrane electrolyzers (AEMELs).
- Optimize the support material for AEMEL oxygen evolution reaction (OER) catalysts.
- Develop, optimize, and characterize novel anion exchange membrane (AEM) and ionomer materials for high-temperature operation.
- Develop methods for AEMEL electrode preparation that supports high current density, efficient gas evolution, and low resistance.
- Elucidate the influence of the electrode/electrolyte interface on the kinetics of the HER and OER.

Fiscal Year (FY) 2018 Objectives

- Determine the HER activity of transition-metal catalysts. Appropriate catalysts must demonstrate an overpotential of 300 mV at 500 mA/cm².

Technical Barriers

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

- System Efficiency and Electricity Cost.

Technical Targets

The overall project goal is cell-level performance of 1.76 V at 1 A/cm², which meets the Fuel Cell Technologies Office efficiency target of ≤\$2/kg at an efficiency of 43 kWh/kg. Component performance targets have been established using a porous electrode model to support the overall cell performance target. At the modeled scale of 50,000 kg/day and operating at 1 A/cm², the hydrogen cost is \$2.15/kg, \$1.82/kg, or \$1.76/kg, respectively, for 2, 20, or 200 plants. In the low-volume manufacturing case, it is still possible to meet the cost target by operating near 1 A/cm², sacrificing some efficiency. The overall project goals described above will be achieved by meeting the component targets outlined in Table 1.

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

FY 2018 Accomplishments

- Developed a functionalized Ni HER catalyst capable of operating at 500 mA/cm² with an overpotential of 94 mV.
- Used a NiFe/Raney Ni catalyst to achieve the requisite baseline OER overpotential of 150 mV at 500 mA/cm².
- Achieved an AEM membrane electrode assembly performance of 1.92 V at 800 mA/cm².
- Synthesized a multi-cation anion exchange polymer capable of operation at elevated temperatures (<60°C).
- Leveraged the expertise in molecular dynamics and density functional theory of our EMN collaborators to gain key insights into chemical processes at the electrode surface. The main findings from this collaboration are the following.
 - A nickel oxide surface can adsorb twice as much water as a nickel metal surface. The adsorption of water and the subsequent abstraction of a proton is the rate-determining step of hydrogen production. (Sandia National Laboratories).
 - The sequestration of carbonate anions from the electrolyte (1% potassium carbonate) causes a pH shift at the OER electrode and results in the loss in voltage (Lawrence Berkeley National Laboratory).
 - Membranes exhibit amorphous nature throughout the range of ion exchange moieties and temperatures (Lawrence Berkeley National Laboratory).
 - Durability studies independently verified the go/no-go point of less than 20% loss of IEC after 1,000-h test using 1 M KOH at 90°C (National Renewable Energy Laboratory).

Table 1. Component Targets

Target	Units	End of Project	Budget Period 1
Cell voltage	V	1.76	1.92
Current density	A/cm ²	1	0.8
Operating temperature	°C	95	85
Membrane area specific resistance	Ω·cm ²	0.08	0.15
Membrane OH ⁻ conductivity	S/cm	0.1	0.076
Cathode overpotential at design point	mV	150 mV @ 0.5 A/cm ²	300 @ 0.5 A/cm ²
Anode overpotential at design point	mV	100 mV @ 0.5 A/cm ²	150 @ 0.5 A/cm ²

INTRODUCTION

Reducing the materials cost of water electrolyzers, in particular the platinum group metal (PGM) OER and HER catalysts, is a key component for meeting DOE's goal of a \$2.00/kg levelized cost of hydrogen by 2020. The relatively recent development of AEMs allows for the use of low-cost non-PGM catalysts. In terms of OER, many studies indicate that Ni-Fe mixed oxides provide a greatly increased OER activity in comparison to pure Ni electrodes or other binary mixed oxides [1]. On the HER side, enhanced HER has been reported on Ni/MO_x by Markovic et al. [2] and Gong et al. [3]—both of whom suggested that at adjacent metal/metal-oxide sites, the metal-oxide facilitates the formation of OH_{ads}, thus weakening the H-OH bond in “activated water” and reducing activation energy for the Volmer reaction.

Operating AEMs at elevated temperatures will increase the reaction kinetics and improve performance. However, the most technologically mature anion exchange polymers cannot be used at operating temperatures >60°C for extended periods of time. Novel anion exchange materials will also be developed in the course of this project that will be thermally stable and incorporate multiple ion exchange sites.

APPROACH

This project will improve the existing NiFe OER catalyst by refining the Raney Ni support. The synthetic route involved a modified impregnation method using aniline to form an MMO as a two-dimensional film on Raney-Ni support. Despite these successes, the activity is severely limited by the relatively low surface area of Raney Ni as well as the low density of active sites. We aim to address these issues by increasing the surface area of Raney Ni support via a novel metal organic chemical vapor deposition method and increasing the active site density by developing novel polymer precursors.

Three nickel-based catalysts will be synthesized and evaluated for HER activity. NiCr/C (60% metal 1:1 Ni:Cr) provides an oxophilic metal oxide surface for the adsorption of water; chromium remains oxidized at potentials relevant to AEM operation. A functionalized monometallic nickel catalyst synthesized via heat treatment of a nickel complex chelated in the presence of a carbon support has been shown to stabilize the Ni/NO_x interface under HER conditions. Metal-organic framework (MOF)-derived electrocatalysts have already been extensively explored for various applications including oxygen reduction reaction (ORR)/OER [4] and HER [5]. The sacrificial MOF support with high nitrogen content and high microporous surface area leads to high reactivity due to the combination of inherited exceptional active site density and enhanced mass transport property. We recently demonstrated a MOF-derived Fe-N-C catalyst with ORR activity approaching that of Pt/C in both rotating disk electrode and polymer electrolyte membrane fuel cells [6]. This promising result encourages further development of metal-nitrogen-carbon catalysts for HER. As a result of initial water electrolysis testing, one or more of these catalysts will be down-selected.

The chemical stability of the poly(aryl piperidinium) (PAP) AEMs is derived from the combination of the stable piperidinium cation and the ether-bond-free aryl backbone. In addition, the rigid and hydrophobic aryl backbone enables an unprecedented combination of a high IEC and a low water uptake/swelling ratio, leading to high hydroxide conductivity and mechanical robustness. Preliminary results from one member of the PAP AEM family has already shown very high chemical stability, hydroxide conductivity and water uptake of 60 mS/cm and 25 wt% in pure water, respectively, and excellent mechanical strength (160 MPa stress). These properties translate to excellent device performance: an AEM fuel cell with a PAP membrane and the corresponding ionomer showed a peak power density of 530 mW/cm² at 95°C and demonstrated stable fuel cell performance at 90°C for 60+ h. In this project, more advanced AEMs based on the PAP polymer will be developed with multi-ammonium-cation side chain to realize superior hydroxide conductivity, chemical stability, and mechanical properties.

RESULTS

Poly(aryl piperidine) triphenyl monoquaternary ammonium (PAP-TP-MQN) was synthesized through the polymerization of 1,4-diphenyl benzene, 4-piperidinone, and 2,2,2-trifluoroacetophenone in the presence of triflic acid. Monoquaternary ammonium was synthesized through alkylation of trimethyl amine by 1,6-

iodohexane. PAP-TP was alkylated with monoquatary ammonium via the Menshutkin reaction. The resulting ionomer exhibited the high temperature and chemical stability of the baseline PAP-TP-Me ionomer with an additional anion exchange site to increase the ion conductivity. PAP-TP-MQN was subjected to 1,000-hour degradation study wherein the piece of membrane was held at 90°C while submerged in 1 M KOH. Analysis of the treated membrane with ^1H nuclear magnetic resonance (NMR) spectroscopy and titration showed a loss of IEC of 2% and 8%, respectively. Conductivity measurements conducted at 40°C and 95% relative humidity yielded a value of 30 mS/cm, which translates to an area-specific resistivity of 0.1225 $\Omega\cdot\text{cm}$. Figure 1 summarizes the ^1H NMR degradation analysis and conductivity measurements. The values for IEC loss and area-specific resistivity fall below the go/no-go values of 20% and 0.15 $\Omega\cdot\text{cm}$, respectively.

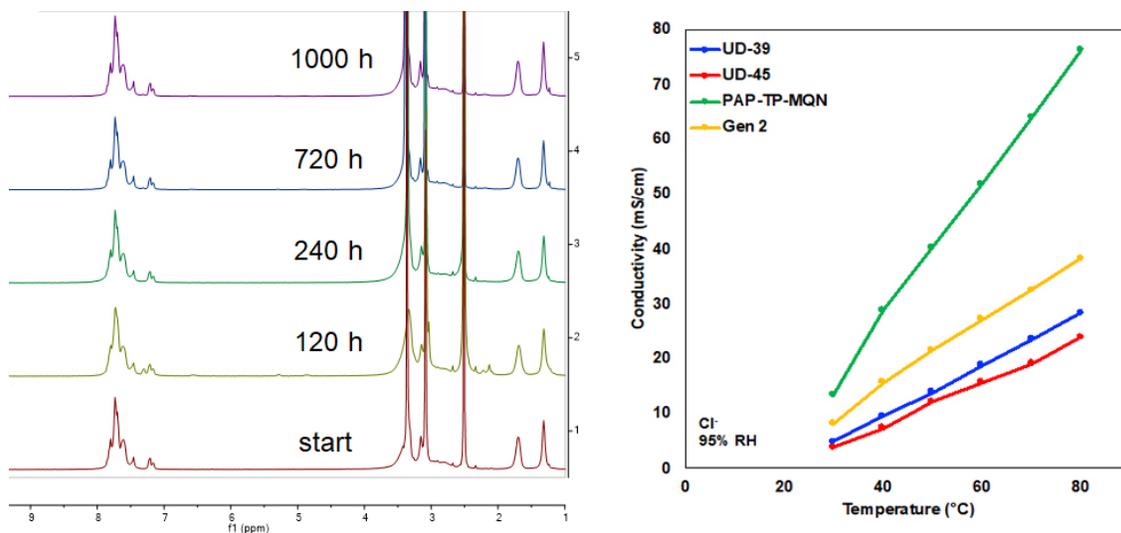


Figure 1. (Left) ^1H NMR spectra of PAP-TP-MQN after treatment in 1 M KOH at 90°C taken at various intervals. The peaks at 3.4 ppm correspond to alkyl groups bound to amines and are used to derive IEC. (Right) The conductivity of PAP-TP-MQN, PAP-TP-Me (UD-39,45), and reference data (Gen 2) taken at different temperatures at 95% relative humidity.

Three Ni-based materials were considered as possible HER catalysts for use in AEMELs for the duration of this project. Briefly, NiCr/C is a bifunctional catalyst where the chromium component remains oxidized at cathodic potentials relevant to normal AEMEL operation. The oxide moieties of this catalyst serve as favorable sites for water adsorption facilitating the breaking of the O-H bond. Preparing a functionalized nickel catalyst was another approach for HER catalysis. Here, a nickel salt was treated with an organic chelating agent, cupferron, in the presence of an appropriate carbon support and heat treated at 700°C. The heat treatment served two purposes: (1) to reduce the nickel via carbonization, and (2) form a graphitic shell around the nickel, presumably from the pyrolyzed chelating agent. The resulting catalyst, referred to as Ni-cup/C, shows high HER activity as well as anodic and cathodic stability. We hypothesize that the increased activity is a result of the graphitic shell around the Ni metal, which reduces, but does not eliminate, the formation of non-conductive metal oxide/hydroxides while retaining a certain amount of these moieties to facilitate water adsorption. Ni-MOF was synthesized via the heat treatment of ZIF-8, nickel acetate, and phenanthroline monohydrate under an ammonia atmosphere.

Of these three catalysts, NiCr/C and Ni-cup/C were tested in a hydrogen pump cell. The goal of this experiment was to assess the HER performance of these catalysts without the sluggish reaction kinetics of the OER in an AEMEL. Figure 2 (left) shows the polarization curves of these cells. Of the two, the cell equipped with a Ni-cup HER catalyst met the milestone of $\eta \leq 300$ mV at 500 mA/cm². All three catalysts were tested in an AEMEL with 1% K₂CO₃ electrolyte solution flowing over the OER catalyst and no reactant feed across the HER electrode. These cells used an iridium oxide OER catalyst and a PAP-TP-Me membrane and operated at 50°C. Based on these series of experiments (Figure 2, right), the Ni-MOF catalyst was eliminated as a viable

HER catalyst, while the NiCr/C and Ni-cup/C would be used in subsequent electrolysis studies. These activities satisfy interim milestones as well as the go/no-go milestone for HER catalysis.

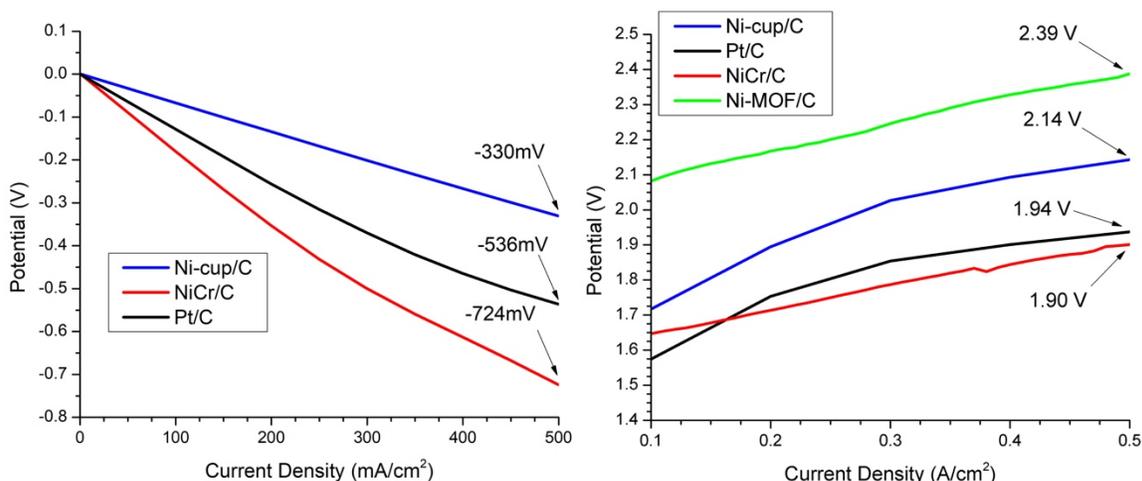


Figure 2. (Left) Polarization curves collected from hydrogen pump fuel cells each with a Pt/C OER catalyst and a Ni-cup, NiCr/C, or Pt/C HER catalysts. (Right) A comparison of polarization curves collected from AEMELs each with an iridium oxide OER catalyst and a Pt/C, Ni-cup/C, NiCr/C, or Ni-MOF HER catalyst.

The NiFe/Raney Ni was synthesized in significant quantities to satisfy the interim milestone for OER catalysis. Briefly, Ni and Fe nitrate salts were added to a slurry of Raney Ni in the presence of aniline, which served as a capping agent. A solution of NaBH₄ was added dropwise to the mixture to yield the catalyst. Figure 3 shows the polarization curve of an AEMEL cell equipped with a NiFe/Raney Ni OER electrode and Pt/C HER electrodes operating under the same conditions described in the previous paragraph. The cell required ~1.8 V to achieve a current density of 500 mA/cm². This performance is 81 mV less than that of a similar cell using IrO_x black reference OER catalysts at the same current density and satisfies the go/no-go milestone of $\eta \geq 150$ mV at 500 mA/cm². This is made on the basis of corresponding overvoltage of 450 mV on the HER electrode.

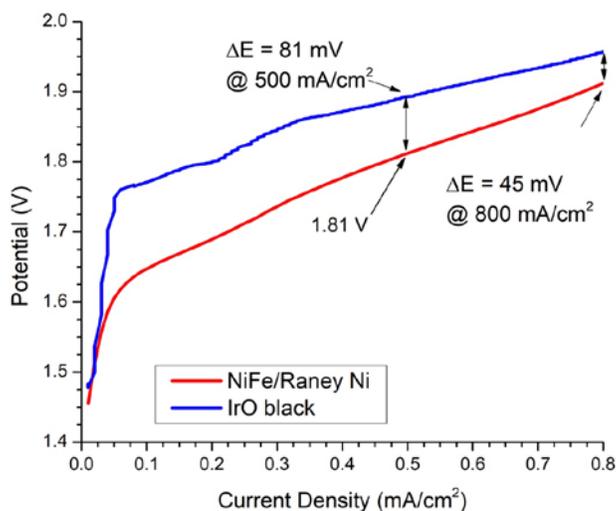


Figure 3. Polarization curves of AEMELs with NiFe/Raney and iridium oxide OER catalysts. Both cells used a Pt/C HER catalyst.

Two non-PGM membrane electrode assemblies were prepared using a NiCr/C or Ni-cup/C HER catalyst, NiFe/Raney Ni OER electrode, and PAP-TP-MQN membrane. Both were operated with 1% K₂CO₃ flowing across the OER electrode and no solution across the HER electrode. Polarization curves obtained at 50°C and 85°C are shown in Figure 4. As expected, both cells demonstrate a substantial increase in performance at higher temperatures. Sustained operation at 85°C is enabled by the ionomer materials developed for this project. At 85°C, 1.92 V and 1.95 V was required to achieve a current density of 800 mA/cm² in cells equipped with the NiCr/C and Ni-cup/C HER catalysts, respectively. This performance meets the go/no-go milestone for the non-PGM membrane electrode assembly of 1.92 at 800 mA/cm².

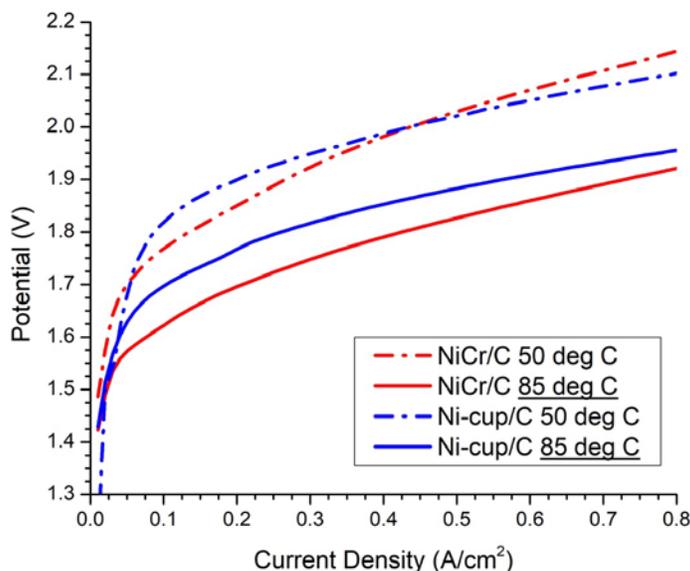


Figure 4. Polarization curves of AEMEs with NiCr/C and Ni-cup/C HER catalysts collected at 50°C and 85°C. Both cells used a NiFe/Raney Ni OER catalyst.

CONCLUSIONS AND UPCOMING ACTIVITIES

This project has met or exceeded all of the go/no-go milestones presented in Budget Period 1. In Budget Period 2 and 3, advanced electrode fabrication techniques together with further improvements in catalysts will be employed to increase the performance of the HER catalyst. Currently, commercially available Raney Ni support cannot accommodate higher loadings of NiFe. The plausibility of using chemical vapor deposition to increase NiFe loading will be investigated. The increased anion exchange sites of PAP-TP-MQN (versus baseline material) has had the unintended consequence of higher water uptake resulting in decreased mechanical stability and swelling of 22%–47%. We will seek to mitigate these negative effects by introducing various support substrates (e.g., polytetrafluoroethylene) to the membrane.

SPECIAL RECOGNITIONS AND AWARDS/PATENTS ISSUED

1. “Nitrogen Functionalized Platinum-Iridium Electrocatalyst,” U.S. patent application US180131008A1, 2018.

FY 2018 PUBLICATIONS/PRESENTATIONS

Peer-Reviewed Publications

1. Ershuhai Liu, Li Jiao, Huong Doan, Zeyan Liu, Yu Huang, Kuzhikalail M. Abraham, and Sanjeev Mukerjee, “Unifying Alkaline Hydrogen Evolution/Oxidation Reaction Kinetics by Identifying the Role of Hydroxy-Water-Cation Adducts,” Resubmitted to *JACS* (2018).

2. Qingying Jia, Ershuhai Liu, Li Jiao, and Sanjeev Mukerjee, “Current Understanding of Sluggish Kinetics of Hydrogen Evolution and Oxidation reactions in Base,” *Current Opinion in Electrochemistry* (In Press).

Presentations at National Meetings and Workshops

1. Sanjeev Mukerjee and Qingying Jia, “Fundamental aspects of regenerative hydrogen electrocatalysis in alkaline pH,” *Abstracts of Papers of the American Chemical Society* 256 (2018).
2. Sanjeev Mukerjee, Jingkun Li, and Qingying Jia, “Current Understandings of the Slow Kinetics of the Hydrogen Evolution Reaction in Alkaline Media,” *Meeting Abstracts 29* (The Electrochemical Society, 2018): 1703–1703.
3. Qingying Jia, Jingkun Li and Sanjeev Mukerjee, “Understanding the Improved Kinetics of the Hydrogen Evolution/Oxidation Reactions on Pt-Oxophilic Metal Systems in Alkaline Media,” *Meeting Abstracts 29* (The Electrochemical Society, 2018): 1710–1710.
4. Ian Kendrick, Michael Bates, Qingying Jia, Huong Doan, Wentao Liang and Sanjeev Mukerjee, “Tuning Ni Surfaces for Enhanced Oxygen Evolution Reaction,” *Meeting Abstracts 29* (The Electrochemical Society, 2018): 1702–1702.

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1. Lena Trotochaud et al., “Solution-Cast Metal Oxide Thin Film Electrocatalysts for Oxygen Evolution,” *Journal of the American Chemical Society* 134, no. 41 (2012): 17253–61; Mary W. Louie and Alexis T. Bell, “An Investigation of Thin-Film Ni–Fe Oxide Catalysts for the Electrochemical Evolution of Oxygen,” *Journal of the American Chemical Society* 135, no. 33 (2013): 12329–37.
2. N. Danilovic et al., “Enhancing the Alkaline Hydrogen Evolution Reaction Activity through the Bifunctionality of Ni (OH) 2/Metal Catalysts,” *Angewandte Chemie* 124, no. 50 (2012): 12663–66.
3. Ming Gong et al., “Nanoscale Nickel Oxide/Nickel Heterostructures for Active Hydrogen Evolution Electrocatalysis,” *Nature Communications* 5 (2014).
4. Jingkun Li et al., “Structural and Mechanistic Basis for the High Activity of Fe–N–C Catalysts toward Oxygen Reduction,” *Energy & Environmental Science* 9, no. 7 (2016): 2418–32; Shenlong Zhao et al., “Ultrathin Metal–organic Framework Nanosheets for Electrocatalytic Oxygen Evolution,” *Nature Energy* 1 (2016): 16184; Jun Wang et al., “Synergistic Effect between Metal–Nitrogen–Carbon Sheets and NiO Nanoparticles for Enhanced Electrochemical Water-Oxidation Performance,” *Angewandte Chemie International Edition* 54, no. 36 (2015): 10530–34.
5. Huilong Fei et al., “Atomic Cobalt on Nitrogen-Doped Graphene for Hydrogen Generation,” *Nature Communications* 6 (2015); Lili Fan et al., “Atomically Isolated Nickel Species Anchored on Graphitized Carbon for Efficient Hydrogen Evolution Electrocatalysis,” *Nature Communications* 7 (2016).
6. Jingkun Li et al., “Structural and Mechanistic Basis for the High Activity of Fe–N–C Catalysts toward Oxygen Reduction,” *Energy & Environmental Science* 9, no. 7 (2016): 2418–32.