

V.D.3 Advanced Catalysts and Membrane Electrode Assemblies (MEAs) for Reversible Alkaline Membrane Fuel Cells

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(OER) cathodes for reversible alkaline fuel cells. The new materials will achieve the following targets at the end of the project for viable applications.

- In a rotating disk electrode, demonstrate ORR activity >1 mA/mg at internal resistance (IR)-free 0.9 V; and OER activity >15 mA/mg at IR-free 1.6 V.
- Achieve reversible current density of 600 mA/cm² at 0.55 V for fuel cell and 2.0 V for electrolyzer.
- Achieve fuel cell and electrolyzer life of 500 h with less than 10% performance decay.

FY 2017 Accomplishments

During this period, we have achieved the following accomplishments.

- Bifunctional ORR and OER catalysts with various compositions have been successfully synthesized at Giner and SUNY Buffalo.
- MEA fabrication and operation have been optimized by varying bifunctional catalysts, ionomer dispersion content, and introduction of diluted liquid electrolyte.
- Fuel cell and electrolyzer performance have been improved simultaneously, reaching 700 mA/cm² at 0.55 V in fuel cell mode and 850 mA/cm² at 2.0 V in electrolyzer mode, which exceeded the milestone targets.



Fiscal Year (FY) 2017 Objectives

- To develop highly efficient bifunctional electrocatalysts related to the heteroatom doped carbon/graphene nanotubes.
- To optimize regenerative fuel cell MEAs using developed bifunctional catalysts and selected alkaline membranes.
- To test the fabricated MEAs in a reversible fuel cell system under both fuel cell and electrolyzer modes to demonstrate their performance and to meet the reversible fuel cell targets.

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 Plan.

- (A) Durability (catalysts, electrode layers)
- (B) Cost (catalyst, MEAs)
- (C) Performance (catalysts, electrodes, MEAs)

Technical Targets

This project is developing novel bifunctional oxygen reduction reaction (ORR) and oxygen evolution reaction

INTRODUCTION

The primary goal of this project is to design advanced bifunctional non-platinum group metal catalyst-based MEAs for a reversible alkaline membrane fuel cell. Water is split into H₂ and O₂ to be stored in electrolyzer mode, and reversibly, the gases can be utilized in fuel cell mode to produce electricity. The performance of the innovative reversible alkaline membrane fuel cell technologies greatly relies on a bifunctional oxygen electrode capable of high activity for the ORR and the OER. The development of highly efficient bifunctional cathode catalysts derived from earth-abundant elements faces two grand challenges. The first is that the optimal active sites for the ORR differ from those for the OER. The second is stability during the high potential/voltage (>1.6 V) of the OER. As a result, most of the studied traditional carbon catalysts likely suffer from significant performance loss during ORR–OER dual-

operation modes. In FY 2016, Giner and SUNY Buffalo developed transition metal-based oxide nanocomposites and heteroatom doped graphene tube catalysts with high ORR and OER activities and limited durability. In the past year, the stability of nano-carbon catalysts has been tremendously enhanced by doping Mn into the nanocarbon. The newly developed catalysts were integrated with selected anion-exchange ionomers and membranes. The MEAs were tested under both fuel cell and electrolyzer operating modes.

APPROACH

The stability of nano-carbon composite catalysts was further enhanced via Mn doping into the graphene tubes. The graphitic feature and thickness influences on

the catalyst stability were analyzed. The best-performing ORR–OER bifunctional catalysts, which include transition metal oxide–carbon composites (cobalt oxide supported on carbon nanotubes, $\text{Co}_3\text{O}_4/\text{CNT}$, Giner), binary transitional metal oxides (nickel cobalt oxide, MO_x , SUNY Buffalo), and metal nanocarbon composites (FeCoNiMn-derived N-doped graphene tube, NC-FeCoNiMn_4 , SUNY Buffalo), were screened using rotating disk electrode experiments. These catalysts were incorporated into MEAs for cell performance tests. Ionomer and membrane materials, ionomer and catalyst ratios, electrode configurations, and testing protocols were optimized to maximize the cell performance. The synthesis of $\text{Co}_3\text{O}_4/\text{CNT}$ and MO_x catalysts are illustrated in Figure 1. Both catalysts were derived from metal precursors and

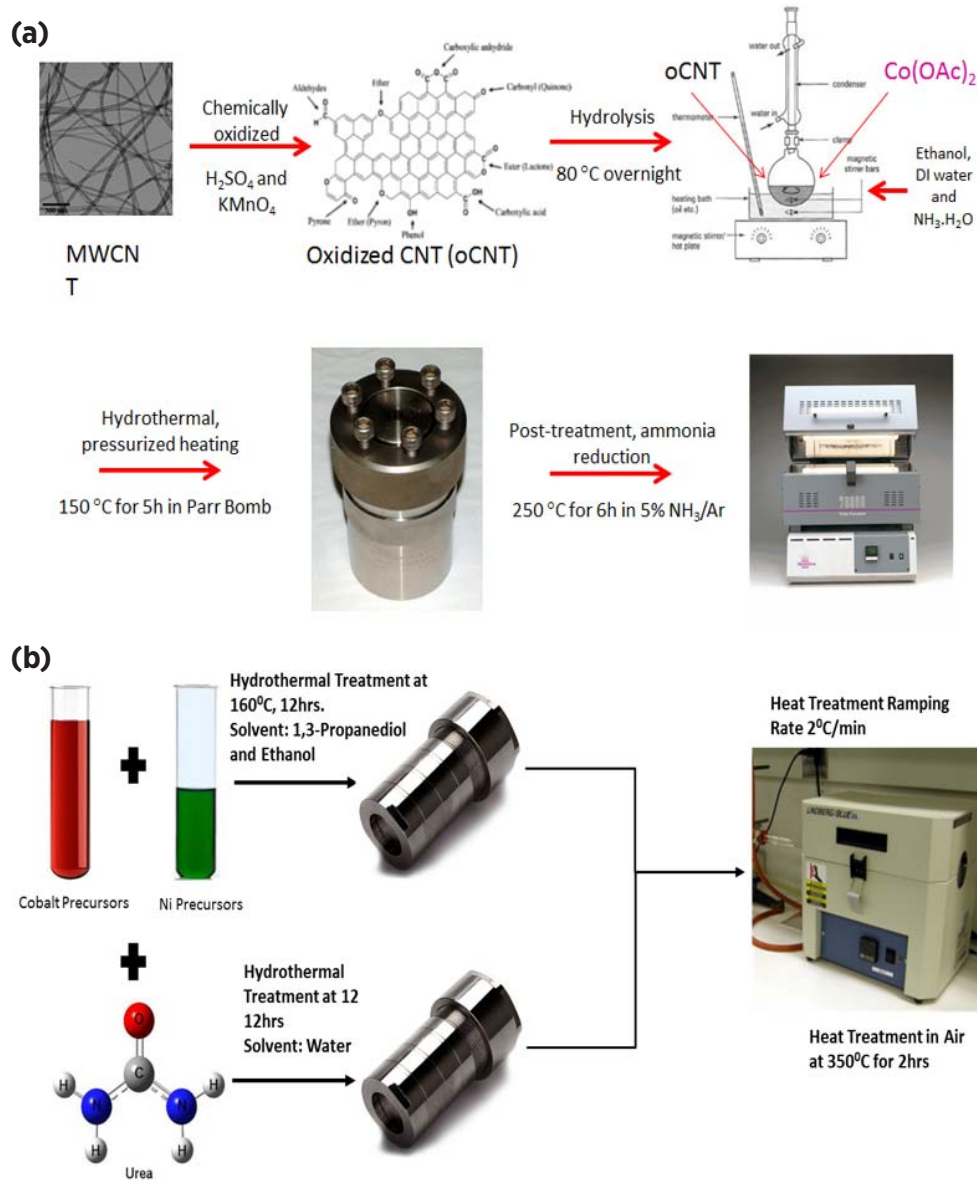


FIGURE 1. The synthesis routes for Giner $\text{Co}_3\text{O}_4/\text{CNT}$ and SUNY Buffalo MO_x catalysts

synthesized using a scalable and cost-effective hydrothermal approach.

RESULTS

The above catalysts were incorporated into MEAs that were tested in both fuel cell and electrolyzer operating modes. Figure 2 demonstrates the steady progress that was made towards improved cell performance. The initial fuel cell and electrolyzer performances were very poor as the maximum current density was less than 60 mA/cm². However, the current densities were significantly increased to above 1,000 mA/cm² with reasonably low overpotentials. The performance improvements were due to electrode configuration changes (from catalyst-coated membrane [CCMs] to gas diffusion electrodes [GDEs]), ionomer category and content optimization, and introduction of diluted liquid electrolyte.

The optimization of electrode design and operation using Giner Co₃O₄/CNT catalysts is elaborated in Figure 3. Figures 3a and 3b show that the electrode fabrication approach impacts electrolyzer performance more noticeably than fuel cell performance. For fuel cell operation, the GDE achieved slightly better performance at high current density, but both the GDE and the CCM met the milestone 0.55 V at

600 mA/cm². For electrolyzer operation, the GDE achieved significantly better performance than the CCM. Therefore, all the following tests were conducted using the GDEs. The ionomer content was varied to find the optimal amount in the electrode (Figure 3c); the electrode with a lower ionomer content (20 wt%) exhibited a much better performance due in part to a lower high frequency resistance and mass transport resistance. The same cell was tested when flowing 0.1 M KOH solution into both the anode and cathode to improve the membrane conductivity and to enable intimate contact between the catalyst and OH⁻ ions. The performance with the addition of diluted KOH improved significantly, reaching 850 mA/cm² at 2 V, which exceeded the milestone: 600 mA/cm² at 2 V (Figure 3d).

For the SUNY Buffalo MO_x catalysts, focus was placed on optimization of the MO_x-based O₂ electrode at a fixed 3 mg/cm² catalyst loading, ionomer percentages were varied from 18 wt% to 22 wt% (Figure 4). As shown in Figure 4a, the electrolyzer performance improved with decreasing ionomer content; the electrodes containing 18 wt% ionomer performed much better than that with 22 wt% ionomer. The influence of feeding diluted KOH was also investigated and again the performance was tremendously boosted with the addition of dilute KOH solution. A short durability test (up to 7 h) is shown in Figure 4b; the voltage at a constant current

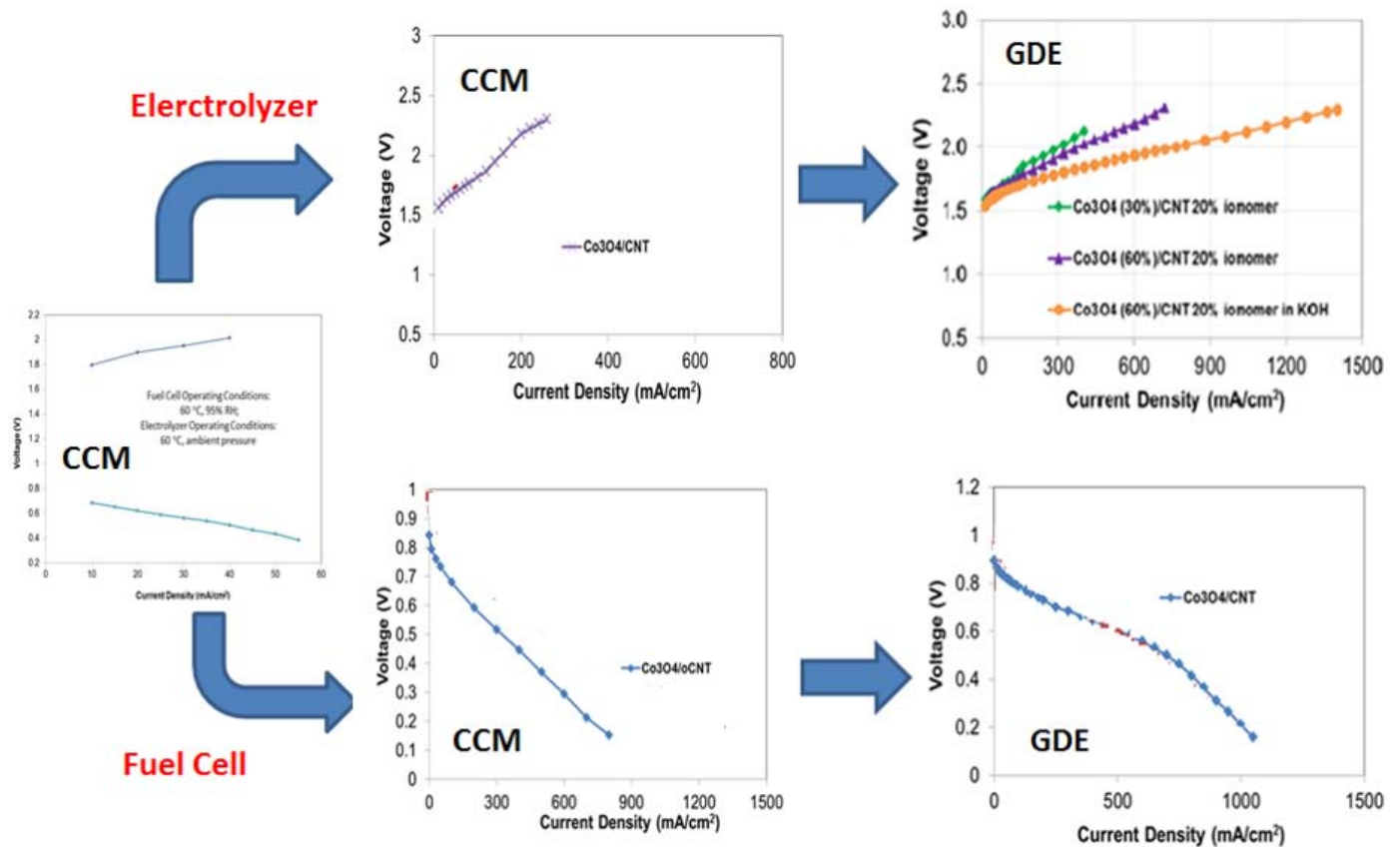
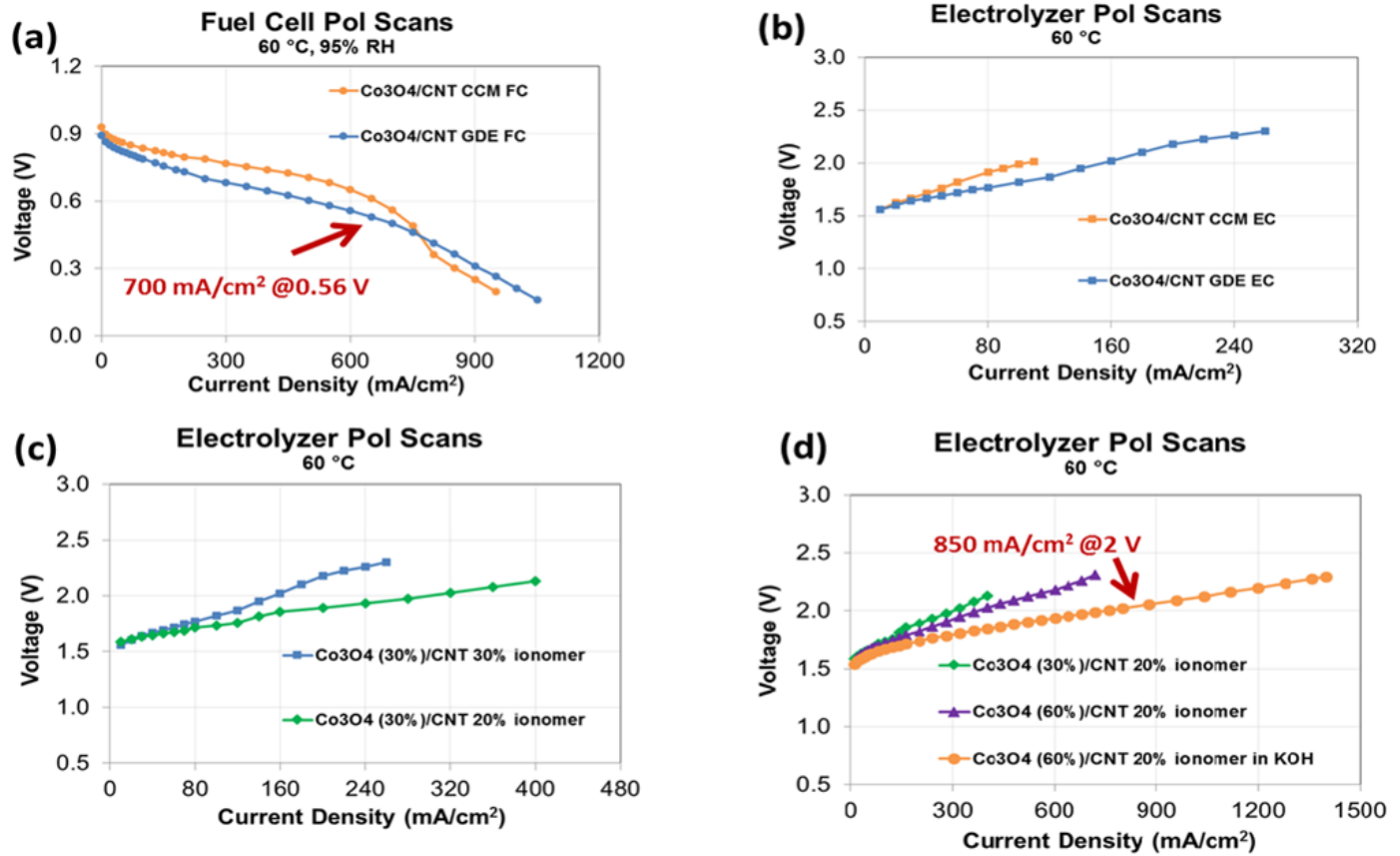


FIGURE 2. Cell performance progress for both fuel cell and electrolyzer operations



RH - relative humidity; FC - fuel cell; EC - electrochemical capacitance

FIGURE 3. Fuel cell and electrolyzer performance using Giner Co₃O₄/CNT catalysts: (a) and (b) impact of electrode fabrication; (c) ionomer concentration influence; (d) introduction of diluted KOH solution. Fuel Cell Test conditions: H₂/O₂ flow rate 1,000 ccm/min, temperature 60°C. The membrane was Tokuyama A201 and ionomer was National Renewable Energy Laboratory Gen 2. The H₂ electrode for all the following non-platinum group metal catalyst MEA tests are identical: PtRu/C (0.7 mg_{PtRu}/cm², ionomer to catalyst ratio = 0.8).

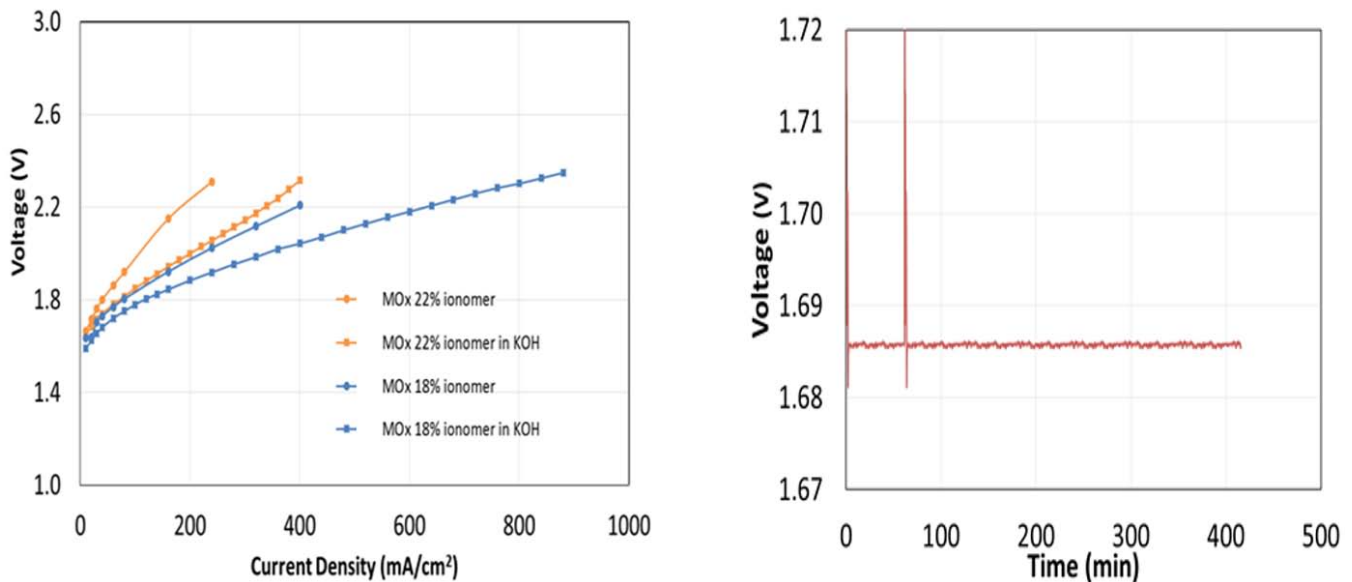


FIGURE 4. Electrolyzer performance and durability using SUNY Buffalo MO_x catalysts. (a) Impact of ionomer concentration and introduction of diluted KOH solution; (b) 7-hour durability test. Test conditions: H₂/O₂ flow rate 1,000 ccm/min, temperature 60°C. The membrane was Tokuyama A201 and ionomer was National Renewable Energy Laboratory Gen 2. The H₂ electrode for all the following non-platinum group metal catalyst MEA tests are identical: PtRu/C (0.7 mg_{PtRu}/cm², I/C = 0.8).

density of 100 mA/cm² remained very stable over the course of the durability test. Operation with lower concentrations of KOH will be investigated later.

CONCLUSIONS AND UPCOMING ACTIVITIES

Conclusions

- A variety of bifunctional OER–ORR catalysts (Giner Co₃O₄/CNTs and SUNY Buffalo NC-FeCoNiMn/NiCo₂O₄) have been synthesized with improved activity and durability in the MEA.
- The factors contributing to improved cell performance have been identified:
 - Electrode fabrication (CCM vs. GDE).
 - Ionomer content optimization.
 - Introduction of diluted liquid electrolyte.
- Both fuel cell and electrolyzer MEAs using Co₃O₄/CNT surpassed the milestones of 0.55 V at 600 mA/cm² and 2.0 V at 600 mA/cm².

Upcoming Activities

- Test the reversible alkaline membrane fuel cell at elevated temperature (>90°C) using a more advanced membrane and ionomer from a selected collaborator.
- Complete dual-operation durability test up to 500 h after integration of the fuel cell and electrolyzer test station.

FY 2017 PUBLICATIONS/PRESENTATIONS

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4. Osgood, H.; Devaguptapu, S.V.; Xu, H.; Cho, J.P.; Wu, G., “Transition Metal (Fe, Co, Ni, and Mn) Oxides for Oxygen Reduction and Evolution Bifunctional Catalysts in Alkaline Media.” *Nano Today* 2016, 11, 601–625.
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