
Advanced Catalysts and Membrane Electrode Assemblies for Reversible Alkaline Membrane Fuel Cells

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- National Renewable Energy Laboratory, Golden, CO

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Fiscal Year (FY) 2018 Objectives

- To further develop highly efficient bifunctional electrocatalysts related to spinel structures.
- To test the bifunctional catalysts under both fuel cell and electrolyzer modes to demonstrate their performance and to meet the reversible fuel cell targets.
- To operate regenerative fuel cell membrane electrode assemblies (MEAs) using as-developed bifunctional catalysts and alkaline membranes.

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

- In RDE, demonstrate ORR activity >1 mA/mg at 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 hours with less than 10% performance decay.

FY 2018 Accomplishments

During this period, we have achieved the following accomplishments:

- Co_xNi_yO_z and advanced carbon-based bifunctional ORR/OER catalysts were developed for OER durability in electrolysis cell mode with diluted potassium hydroxide (KOH) solution. The electrolysis cell was operated at 500 mA/cm² and the voltage was below 2.0 V, without any performance decay for 500 hours.
- Co_xNi_yO_z and advanced carbon-based bifunctional ORR/OER catalysts were investigated for ORR durability in fuel cell mode at 200 mA/cm² for 50 hours. There was only slight voltage decay in the initial 24 hours, but it recovered after reconditioning.
- The reversibility test in KOH solution (compared with that in water system) exhibited the good reversible catalyst activity for the ORR and OER, indicating the majority of performance loss in the fuel cell test was caused by the anion exchange materials.

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

INTRODUCTION

The primary goal of this project is to design advanced bifunctional non-platinum group metal (PGM) catalysts based MEAs for a reversible alkaline membrane fuel cell (AMFC). Water is split into H_2 and O_2 to be stored in electrolyzer mode and reversibly, the gases can be utilized by fuel cell mode to produce electricity. The performance of the innovative reversible AMFC 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 have developed transition metal-based oxide nanocomposites and heteroatom-doped graphene tube (GT) catalysts with high ORR/OER activities and limited durability. In the past year, the stability of nanocarbon catalysts has been tremendously enhanced by the doping of Mn into nanocarbon. The 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 development of highly efficient bifunctional cathode catalysts derived from earth-abundant elements faces the two challenges identified above. This incubator project addresses these catalyst challenges by developing PGM-free cathodes for reversible alkaline fuel cells coupled with anion exchange membranes and ionomers. Therefore, special emphasis is given to exploring highly stable oxides and nanocarbons under appropriate accelerated stress tests. As shown in Figure 1, our overall approach is to integrate active transition-metal-based oxides with highly graphitized and stable nanocarbons to maximize the ORR/OER activity and stability in alkaline media.

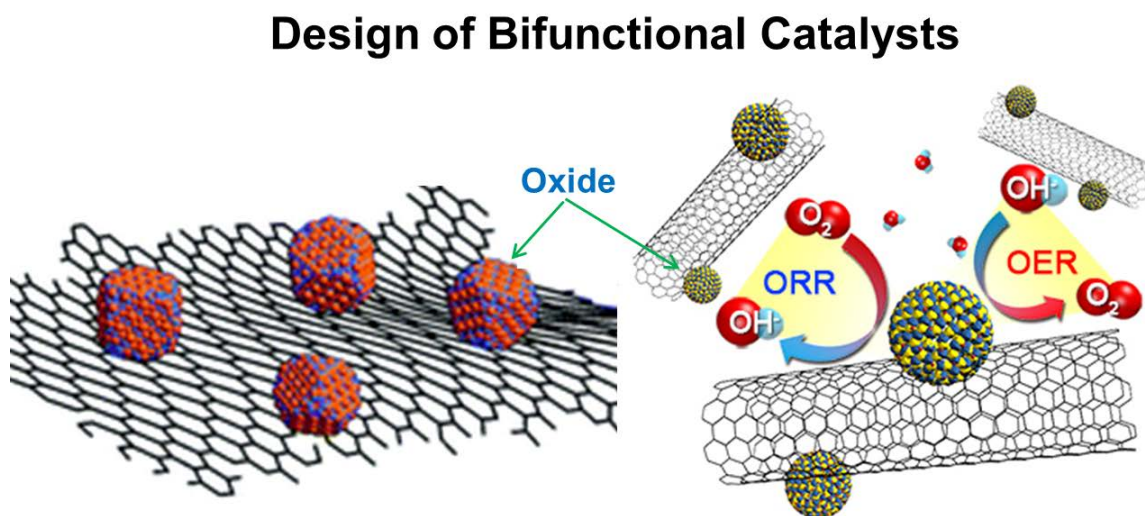


Figure 1. Proposed schemes of ORR/OER bifunctional cathode catalysts consisting of active oxide nanocrystals onto highly stable graphene (left) and carbon tubes (right)

RESULTS

As shown in Figure 2a, the core-shell structured $\text{Co}_x\text{Ni}_y\text{O}_z$ particles were prepared in situ via a hydrothermal process in the presence of the highly active and stable GTs derived from CoNi. The particle size is around 50 nm (Figure 2b) with a surface area $\sim 50 \text{ m}^2/\text{g}$. The bifunctional nanocomposite catalyst showed enhanced OER and ORR activity relative to the individual components separately (i.e., the $\text{Co}_x\text{Ni}_y\text{O}_z$ and N-GT alone), as shown in Figure 2c, in terms of the mass activity determined at 1.6 V and 0.9 V for the corresponding OER and ORR. More importantly, sufficient stability was achieved during the harsh potential cycling tests (0–1.9 V) (Figure 2d).

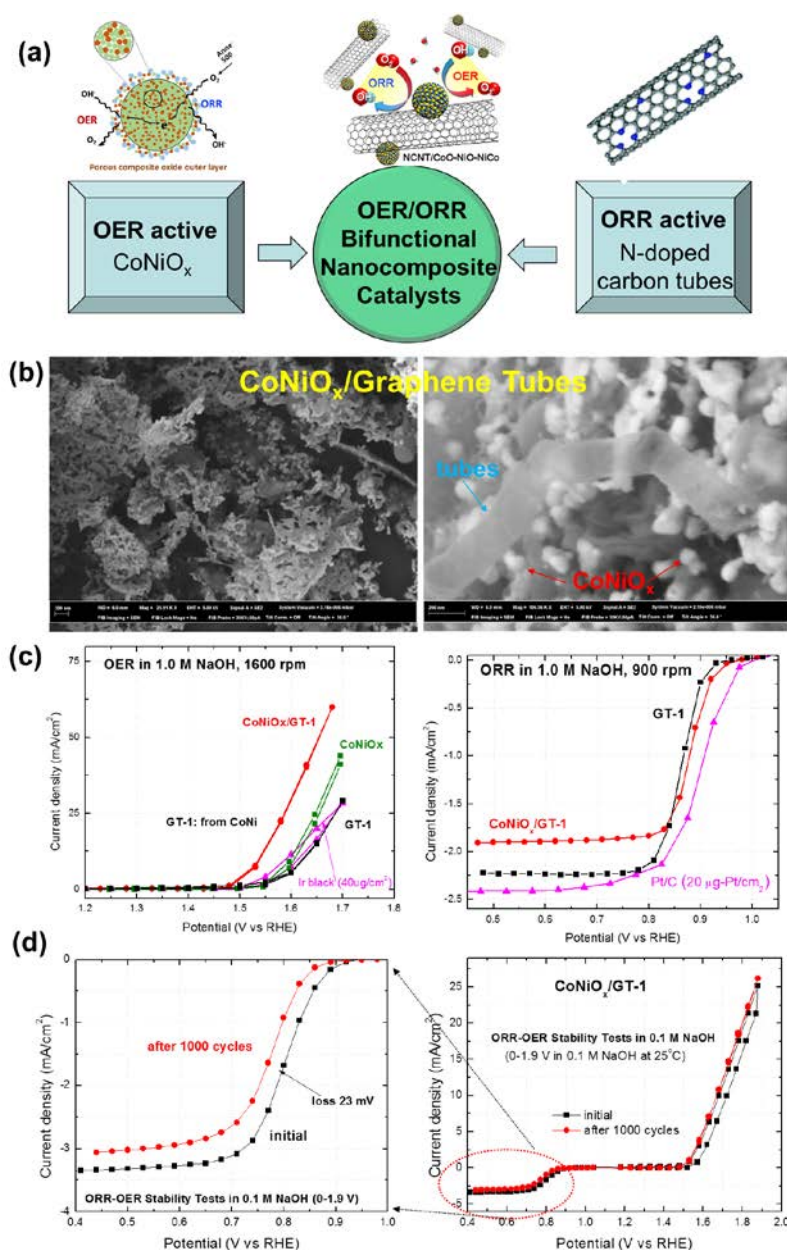


Figure 2. Design and synthesis of nanocomposite bifunctional catalysts by using GT-supported $\text{Co}_x\text{Ni}_y\text{O}_z$ and their ORR/OER activity and stability (a) integration scheme, (b) non-uniform morphology showing significant agglomeration of $\text{Co}_x\text{Ni}_y\text{O}_z$ nanoparticles, (c) ORR and OER activity in 1.0 M NaOH electrolyte, and (d) stability tests by using potential cycling stabilities in 0.1 M NaOH electrolyte, 0–1.9 V vs. reversible hydrogen electrode, 500 mV/s at room temperature

This is the first successful demonstration that nanocarbon-based catalysts can be very active and stable for ORR/OER dual-mode operation. However, scanning electron microscopy images of the $\text{Co}_x\text{Ni}_y\text{O}_z/\text{GT}$ nanocomposite indicate that oxide particles are significantly agglomerated without good dispersion onto the GTs in contrast to the ideal configuration. Therefore, our future efforts will be focused on nanocomposite synthesis with uniform oxide particle distribution onto ORR active GTs.

The $\text{Co}_x\text{Ni}_y\text{O}_z$ OER durability of the combined advanced carbon tubes and transition-metal oxide bifunctional catalyst developed by Giner was first investigated in a 0.1 M KOH-fed single electrolysis cell for 600 hours at different current densities (see Figure 3).

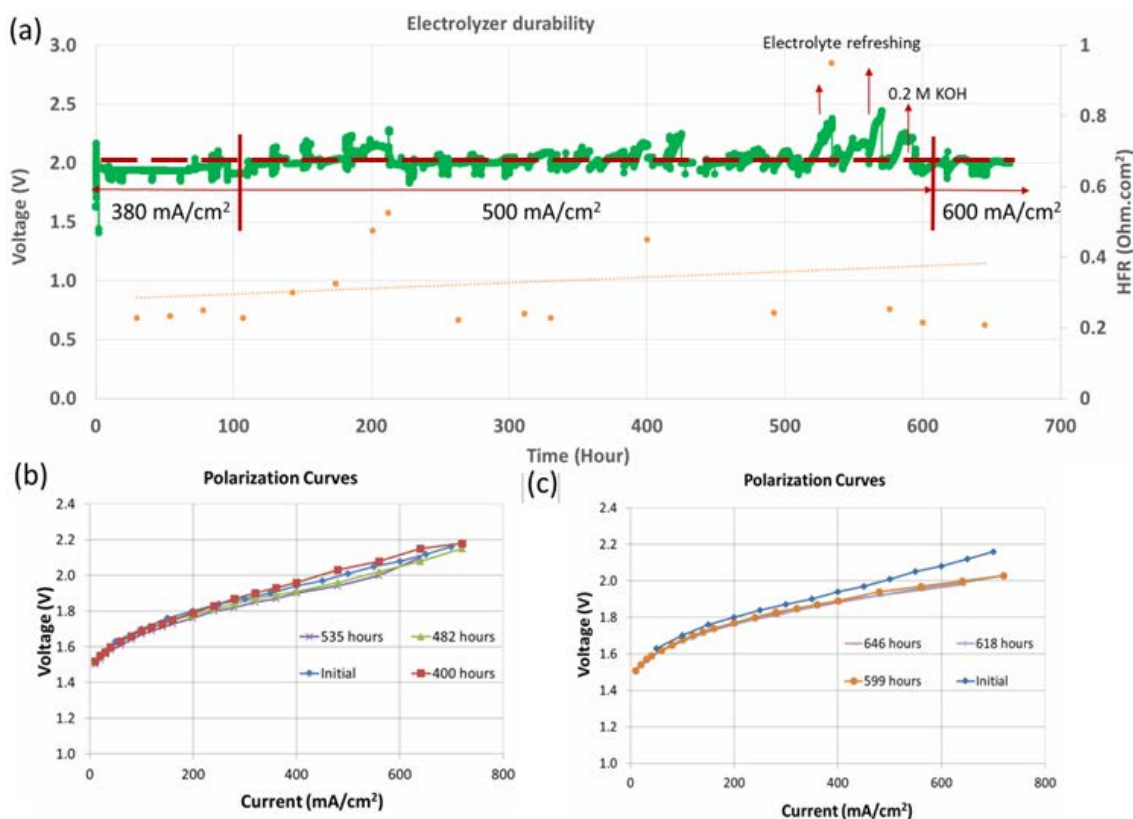


Figure 3. (a) Chronopotentiometry for 600 hours at different current densities; (b) polarization curves at different hours during durability test; (c) hydroxide solution concentration influence on bifunctional ORR/OER-based electrolysis cell. Electrolysis cell test conditions: 60 °C, 0.1 M KOH (0.2 M KOH after 500 hours) solution on both electrodes; cathode: $\text{Co}_x\text{Ni}_y\text{O}_z$ advanced carbon materials (2 mg/cm², ionomer=20 wt%); anode: PtRu/C (0.72 mg/cm², ionomer=26 wt%).

The membrane and ionomer were Tokuyama A201. The H_2 electrode for all the following MEA tests was identical: PtRu/C (0.7 mg PtRu/cm², I/C=0.8). The bifunctional catalyst loading on the O_2 electrode was 2 mg/cm², with 20 wt% ionomer. An initial screening current density of 380 mg/cm² was used for the first 100 hours in the chronopotentiometry. The performance was very stable; no frequent replenishing of the KOH solution was required to maintain the performance. From 100 hours to 600 hours, the current density was fixed at 500 mg/cm². The voltage was stable until around 200 hours, where it climbed to around 2.2 V, with the high frequency resistance (HFR) increasing from 256 to 450 mOhm-cm² for a few hours. This was likely caused by poor contact due to the gradual oxidation of the carbon paper, which was observed after opening the cell. Therefore, a piece of platinum-plated titanium paper was assembled into the original cell for continuous testing, with the HFR returning to approximately 0.25 Ohm-cm². After 300-hour operation, the membrane required a more frequent electrolyte replenishing due to increased HFR as the hydroxide ions were depleted in the recycled electrolyte. However, the catalyst performance was always recovered as shown in the polarization

curves after each electrolyte replenishing. Lastly, a higher concentration (0.2 M) of KOH was applied that helped to maintain the stable voltage after 500 hours. A much more stable voltage profile was therefore obtained as expected. The current density was increased to 600 mA/cm², without voltage increase, for an additional 50 hours. This long-term durability test proved the excellent OER activity and longevity of our bifunctional catalyst under the harsh environment and oxidizing voltage as high as 2.0 V.

To prove the reversibility of the bifunctional catalysts in reversible fuel cells, pure water (no KOH) was first used as the feedstock. First, the cell was operated in fuel cell mode; then the operation was switched to electrolyzer mode and held for 30 minutes at 2.0 V. Finally, the operation was switched back to the fuel cell operation mode. It clearly shows that the electrolyzer operation deteriorated rapidly with the pure water. More severely, when it was finally switched back to fuel cell operation, the fuel cell performance also decreased tremendously. HFRs under different operations are also compared in Figure 4. The initial HFR for fuel cell mode was 0.22 Ohm·cm² and barely changed after it was switched to the electrolyzer operation. However, the HFR increased to 0.4 Ohm·cm² only after 30 minutes, most likely due to decayed membrane and ionomer. The HFR changed little after it was switched back from electrolyzer operation to fuel cell operation. However, overall the HFR doubled from the initial fuel cell operation to final fuel cell operation. Again, this confirms that the decayed membrane and ionomer in the electrode affected not only electrolyzer operation but also fuel cell operation.

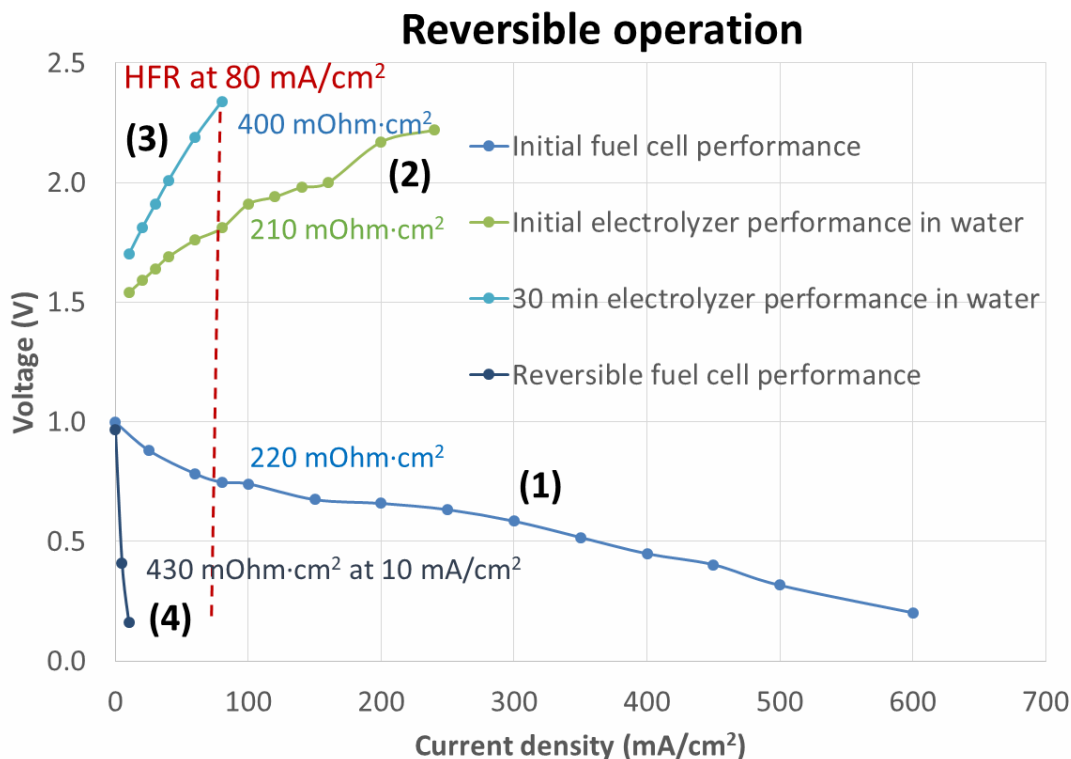


Figure 4. Reversible operation of fuel cell and electrolysis cell based on an oxygen electrode composed of Co_xNi_yO_z advanced carbon materials with Ag addition. Cathode: Co_xNi_yO_z advanced carbon materials (2 mg/cm², BP-60 ionomer=20%); anode: PtRu/C (0.7 mg/cm², ionomer=26%). Fuel cell test conditions: H₂/O₂ flow rate 1,500/3,000 ccm/min, T 60 °C, anode/cathode temperature 57 °/60 °C, and H₂/O₂ backpressure 35 psia. Electrolysis cell test conditions: 60 °C, pure deionized water on both electrodes.

CONCLUSIONS AND UPCOMING ACTIVITIES

Conclusions

- High-performance $\text{Co}_x\text{Ni}_y\text{O}_z$ /nanocarbon bifunctional OER and ORR catalysts have demonstrated remarkable reversibility and stability under harsh voltage cycling from 0.0 V to 1.9 V.
- MEA testing shows that alkaline membrane and ionomer degraded rapidly at high electrolysis voltages. Thus, hydroxide ion transfer paths across the membrane and in the electrodes were largely blocked.
- The introduction of diluted carbonate salt (e.g., NaHCO_3) or base (e.g., KOH) solutions can help to retain the electrolysis operation to some degree, although it leads to flooding and complicates the reversible fuel cell system.

Future Work

- Develop oxidation (high voltage) alkaline membrane and ionomer.
- Complete dual-operation durability test up to 500 hours after the integration of fuel cell and electrolyzer test station.

FY 2018 PUBLICATIONS/PRESENTATIONS

1. Shuai Zhao et al., “Recent Progress and Perspectives of Bifunctional Oxygen Reduction/Evolution Catalyst Development for Unitized Regenerative Anion Exchange Membrane Fuel Cells,” *Nano Energy* 47 (2018): 172–198
2. S. Zhao, B. Rasimick, W. Mustain, and H. Xu, “Highly durable and active Co_3O_4 nanocrystals supported on carbon nanotubes as bifunctional electrocatalysts in alkaline media.” *Applied Catalysis B: Environmental* 203 (2017): 138–145.
3. S. Gupta, S. Zhao, O. Ogoke, Y. Lin, H. Xu, and G. Wu, “Engineering Favorable Morphology and Structure of Fe-N-C Oxygen-reduction Catalysts via Tuning Nitrogen/Carbon Precursors,” *ChemSusChem* 10 no. 4 (2017): 774–785.
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