V.D.6 Advanced Catalysts and Membrane Electrode Assemblies (MEAs) for Reversible Alkaline Membrane Fuel Cells

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Project End Date: May 31, 2017

Overall Objectives

- Develop highly efficient bifunctional platinum group metal free electrocatalysts and optimize them to meet the rotating disk electrode (RDE) activity targets for the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER).

- Supply perfluorinated anion exchange membranes (AEM) and ionomers with an aim to improve the performance of alkaline membrane fuel cell (AMFC) relative to commercial membranes (Tokuyama).

- Fabricate regenerative fuel cell membrane electrode assemblies (MEAs) using as developed bifunctional catalysts and perfluorinated AEMs (after their optimization).

- Test the fabricated MEAs in a regenerative fuel cell system under both fuel cell and electrolyzer modes to demonstrate its performance and to meet the reversible fuel cell targets.

Fiscal Year (FY) 2016 Objectives

- Develop highly efficient bifunctional electrocatalysts related to platinum group metal free perovskite, spinel oxides, and heteroatom doped carbon nanotubes.

- Optimize these bifunctional catalysts to meet the RDE activity targets for ORR–OER as set by DOE.

- Develop perfluorinated AEM and ionomers with an aim to improve the performance of AMFCs relative to commercial membranes (Tokuyama).

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 [1].

(A) Durability (catalysts, electrode layers)

(B) Cost (catalyst, MEAs)

(C) Performance (catalysts, electrodes, MEAs)

Technical Targets

This project will develop novel bifunctional ORR and OER catalysts and MEAs for reversible alkaline fuel cells. The new materials will achieve the following targets at the end of the project for viable applications.

- In RDE, demonstrate ORR activity >1 mA/mg at 0.9 V (internal resistance [IR]-free); and OER activity >15 mA/mg at 1.6 V (IR-free).

- Achieve reversible current density of 600 mA/cm^2 at 0.55 V for fuel cell mode operation and 1.6 V for electrolyzer mode operation.

- Achieve fuel cell and electrolyzer life of 500 hr with less than 10% performance decay.

FY 2016 Accomplishments

- Identified that multi-walled carbon nanotubes (CNTs) are much more stable during potential cycling (0.0–1.9 V), when compared to amorphous carbon black and graphene (reduced graphene oxide).

- Synthesized spinel oxide (e.g., Co_3O_4) supported on N-doped advanced carbon materials via three routes. The activity of Co_3O_4 supported on carbon nanotubes (Co_3O_4/CNTs) met the first year no/no-go milestone of ORR activity >1 mA/mg oxide at 0.9 V (IR-free); and OER activity >15 mA/mg oxide at 1.6 V (IR-free) in RDE testing.

- Discovered that the activity and stability of the spinel on CNT catalysts are largely impacted by the size, oxidation state, and functional groups attached to the CNTs.

- Developed a low cost and scalable synthesis approach to preparing novel graphene tubes. Integrating $CoNiO_x$ with active graphene tubes led to enhanced ORR and OER activity exceeding Pt and Ir, respectively. OER and ORR activity determined by RDE has met the first year's go/no-go milestone.

- Synthesized core-shell Pt-Ni nanowires as bi-functional hydrogen oxidation reaction (HOR) and hydrogen evolution reaction (HER) catalysts. The high catalytic activity was achieved by lowering the Pt content to 10 wt% and via hydrogen annealing at >250°C.

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INTRODUCTION

The primary goal of this project is to design advanced bifunctional platinum group metal free catalyst MEAs for a reversible electrochemical energy storage and conversion device. The single device can either operate in one direction as an electrolyzer to generate H_2 and O_2 from water, or operate in reverse by utilizing H_2 and O_2 as an AMFC to produce electricity. The performance of the innovative reversible AMFC technology greatly relies on a bifunctional oxygen electrode capable of high activity for the ORR and OER. Our overall approach is to prepare transition metal-based oxide nanocomposites and heteroatom doped graphene tube catalysts with optimal chemical formulation, surface defects, and morphology in order to maximize the ORR–OER activity and stability. The best performing catalyst will then be integrated with selected anion-exchange ionomers and membranes. The constructed MEAs will be operated as reversible AMFCs for stationary energy storage. In the first year, we will primarily focus on the synthesis of novel nanocomposite catalysts capable of catalyzing both the ORR and OER in alkaline media.

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. This incubator project addresses these catalyst challenges by developing non-platinum group metal catalysts coupled with novel AEMs and

ionomers. Therefore, special emphasis is given to exploring highly stable oxides and graphitized nanocarbons under appropriate accelerated stress tests.

APPROACH

Our overall approach is to prepare transition metal-based oxide nanocomposites and heteroatom doped graphene tube catalysts with optimal chemical formulation, surface defects, and morphology in order to maximize the ORR–OER activity and stability. One of the grand challenges in developing bifunctional ORR–OER catalysts is likely due to different active sites for corresponding ORR and OER. By tuning the electronic structures of oxide catalysts, an enhancement of ORR activity is often accompanied with a reduction of OER activity. We explored robust nanocarbon components that maintain stability over the wide potential range spanning from 0–1.9 V vs. reference hydrogen electrode (RHE). Such a material could be the ORR component and integrated with OER active oxide catalysts to form a bifunctional nanocomposite.

As shown in Figure 1a, our overall approach is to integrate active transition metal-based oxides with highly active and stable graphitized nanocarbons to maximize the
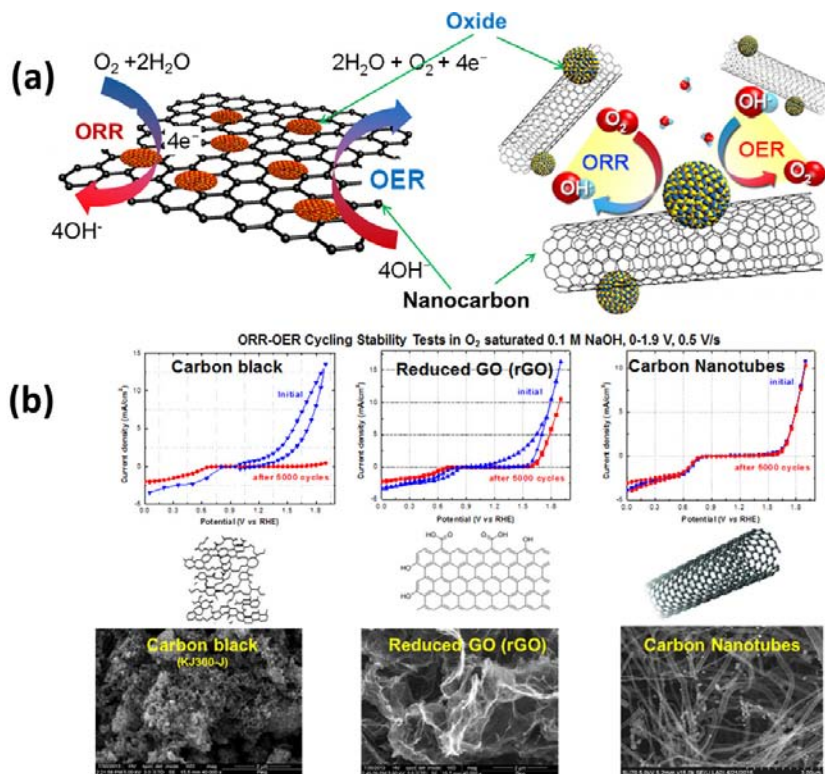

FIGURE 1. (a) Proposed schemes of ORR–OER bifunctional cathode catalysts consisting of active oxide nanocrystals onto highly stable graphene (left) and carbon tubes (right). (b) Identification of nanocarbons in terms of their potential cycling stabilities in 0.1 M NaOH electrolyte (0–1.9 V vs. RHE, 500 mV/s at room temperature).

ORR–OER activity and stability in alkaline media. The best performing catalyst will be integrated with selected anion-exchange ionomers and membranes to construct a MEA that helps to revive reversible AMFCs in stationary energy storage. As shown in Figure 1b, we identified that multi-walled CNTs are much more stable during potential cycling (0–1.9 V), thanamorphous carbon black and graphene (reduced graphene oxide). This interesting finding suggests the stability of carbon materials is greatly dependent on their nanostructure and morphology. The remarkable stability enhancement is likely due to the closed-tube morphology.

RESULTS

Commercially available nitrogen-doped carbon nanotubes (N-CNT) were integrated with metal oxides to design bifunctional catalysts at Giner due to the good stability of the N-CNTs. The cobalt oxide (Co_3O_4) was supported on oxidized CNTs (oCNTs), forming a Co_3O_4/oCNT hybrid structure as shown Figure 2a. X-ray diffraction patterns for Co_3O_4/oCNT before and after NH_3 treatment are shown in Figure 2b. The five major characteristic peaks of the well-defined face-centered cubic Co_3O_4 (red pattern) corresponded to the (220), (311), (400), (511) and (440) reflections (JCPDS 43-1003, red triangles), respectively. Two peaks appeared at 26.2° and 43.2° corresponding to the (002) and (100) planes of the multi-walled CNTs, respectively. After NH_3 treatment (blue pattern), the Co_3O_4 character decreased, indicated by the disappearance of the (511) and (440) peaks. Among all of the studied samples, the best performing NH_3-treated cobalt oxide Co_3O_4/oCNT was compared with Pt/C (50 wt%) and Ir in terms of their ORR and OER activities, respectively. (Figure 2c and 2d). Both the ORR onset and half-wave potentials of Co_3O_4/oCNT were about 0.1 V less than those of the commercial Pt/C. The OER onset potential for Co_3O_4/oCNT was only 0.05 V higher than that of Ir black. Both the ORR and OER activity of Co_3O_4/oCNT were much enhanced relative to oxide-free N-CNT as shown in Figure 2e, and they both approach or exceed the first year's go/no-go milestone. Moreover, the durability test of NH_3 treated Co_3O_4/oCNT was conducted in O_2-saturated 0.1 M KOH electrolyte for 2,000 cycles (0–1.9 V) at a

scan rate of 500 mV/s. Intermediate polarization curves were collected at 1,600 rpm, 20 mV/s (Figure 2f), demonstrating insignificant changes for both ORR and OER activities even after 2,000 cycles in this harsh oxidizing environment.

In the project, University at Buffalo-SUNY has developed an approach to prepare a new type of large sized and few-layered nitrogen-doped graphene nanotube (N-GT). The synthesis (Figure 3a) is low-cost and easily scalable via a simple one step thermal treatment using inexpensive carbon and nitrogen precursors (i.e., dicyanadiamide, ~$2/kg). During the catalyst development, we discovered the type of transition metal used is able to tune the chemical and physical properties of the resulting graphene tubes. This allows us to engineer the doping, tube morphology and structure to yield maximum performance for bifunctional applications. The best performing N-GT(FeCoNi) achieved an outstanding
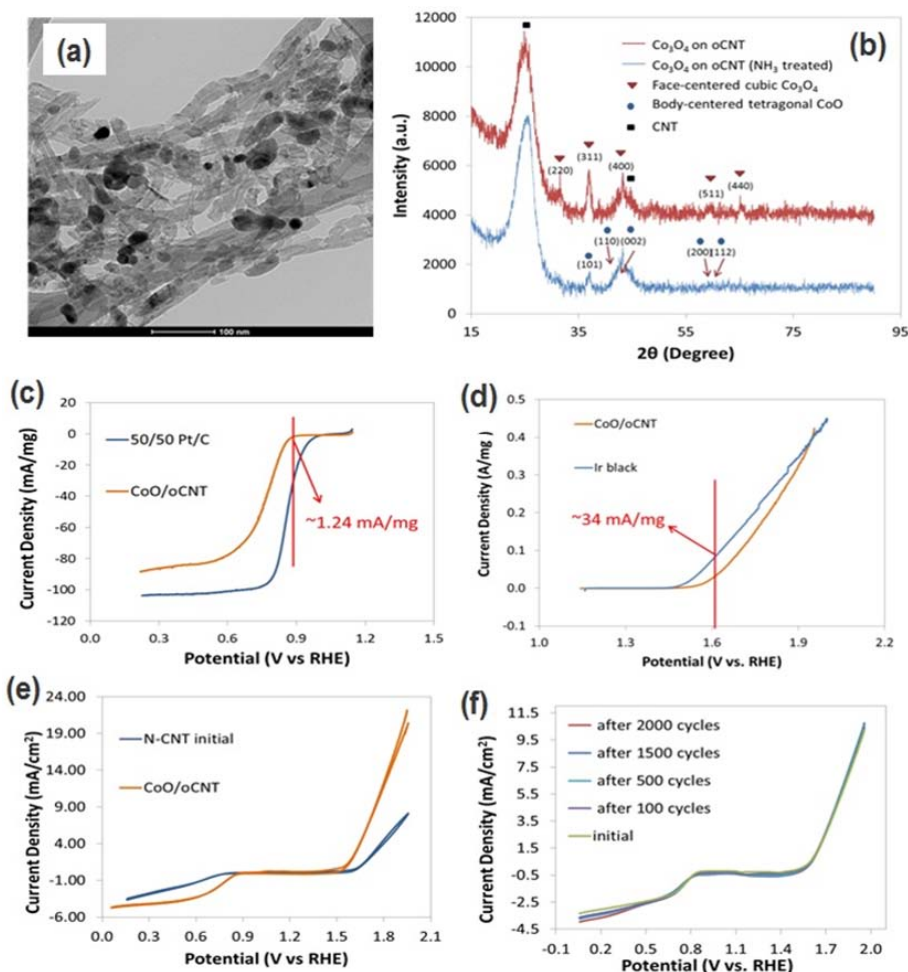

FIGURE 2. (a) Transmission electron microscopy image of the best performing Co_3O_4/oCNT after NH_3 treatment with Co ($C_2H_3O_2$)·4H_2O to oCNT weight ratio of 5:3. (b) X-ray diffraction patterns of Co_3O_4/oCNT (red) and NH_3 treated Co_3O_4/oCNT (blue). (c) ORR and (d) OER activity of NH_3 treated Co_3O_4/oCNT compared to Pt/C and Ir black, respectively. (e) OER–ORR activity comparison between the NH_3 treated Co_3O_4/oCNT sample and as received N-CNT. (f) durability test of NH_3 treated Co_3O_4/oCNT for 2,000 cycles.

current density of 29.6 mA/cm^2 (28 mA/mg catalyst) at 1.6 V during the OER (Figure 3b). This result is around four times higher than that obtained for commercial Ir catalyst and has exceeded the first year go/no-go decision milestone (15 mA/mg catalyst). With respect to the ORR, the onset potential for the N-GT(FeCoNi) catalyst is 1.05 V vs. RHE, which is similar to that of Pt (1.10 vs. RHE), suggesting the nature of active sites on the N-GT catalysts is intrinsically active for the ORR in alkaline media. Half wave potential, which corresponds to the total number of active sites, is as high as 0.89 V vs. RHE at a catalyst loading of 0.60 mg/cm^2. This value is only 10 mV lower than that of Pt/C catalyst

at a loading 60 µg$_{Pt}$/cm^2. In addition, its diffusion limiting current density was greater than that for platinum, suggesting higher mass transport of O$_2$ through its pores as a result of its exceptionally high electrochemically active surface area. Importantly, the current density generated at 0.9 V is 1.31 mA/mg catalyst and successfully met the first year go/no-go decision point (Figure 3c).

Apart from excellent bifunctional performance of N-GT(FeCoNi), extensive electrochemical durability tests were also performed to evaluate durability of the catalysts in 0.1 M NaOH in a potential window covering both
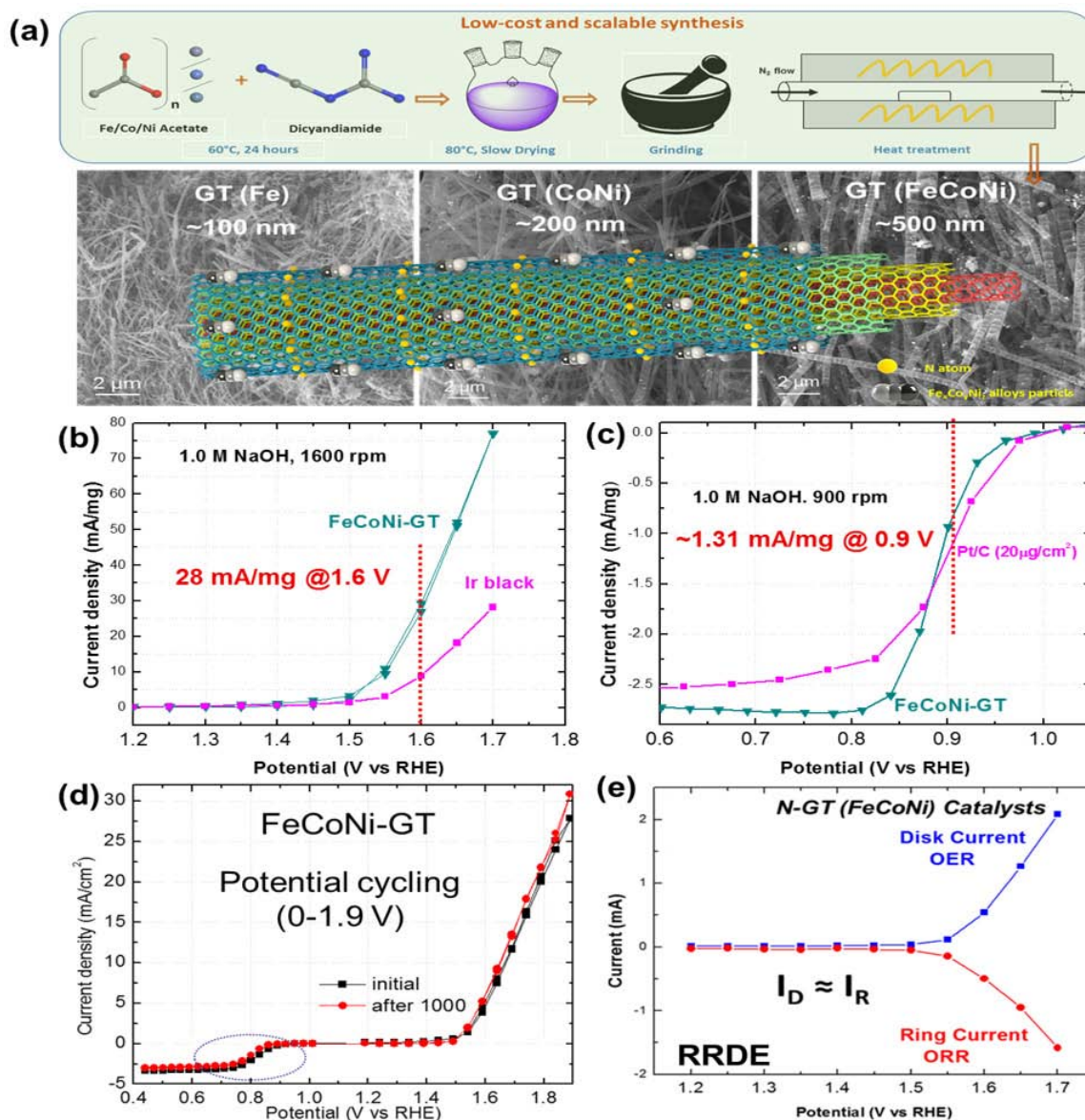
RRDE – Rotating ring disk electrode

FIGURE 3. Graphene tube catalysts: (a) low-cost and scalable synthesis; (b) OER activity; (c) ORR activity; (d) potential cycling stability; and (e) rotating ring disk electrode tests to verify O$_2$ evolution rather than carbon oxidation during the OER.

ORR and OER reactions (0.0–1.9 V). After 1,000 cycles, N-GT(FeCoNi) exhibited exceptional durability during the harsh potential cycling tests, showing only 17 mV decay in ORR half-wave potential, along with 30.7% enhancement in the current density measured at 1.6 V during the OER (Figure 3d). Combined with the rotating ring disk electrode test in Figure 3e, these results provide strong evidence that the active sites for ORR and OER on N-GT(FeCoNi) are highly stable. Generation of a mixed metal catalyst, i.e., FeCoNi during the graphitization process is the key factor to yield improved activity and durability.

National Renewable Energy Laboratory has worked on the development of platinum (Pt) catalysts in the HOR and HER for reversible AMFCs. Although this work involves the use of precious metal catalysts, the work seeks to reduce the amount of Pt in the catalyst layer to reduce cost and to improve upon slower HOR–HER kinetics in the AEM environment. Pt/Ni nanowires (Figures 4a and 4b) were formed by the spontaneous galvanic displacement of Ni nanowires with Pt. Lower levels of displacement appeared to thin the Pt layer and improve Pt utilization, leading to higher catalytic activity (Figure 4c). Post-synthesis annealing of the nanowires in hydrogen served to integrate the previously segregated Pt and Ni zones, compressing the Pt lattice and improving the site-specific exchange current densities (Figure 4d). Annealed Pt-Ni nanowires exceeded the HOR–

HER mass exchange current density of Pt/HSC by 10 times in a 0.1 M potassium hydroxide electrolyte.

CONCLUSIONS

- Integration of active transition metal-based oxides with highly active and stable graphitized nanocarbons leads to bifunctional ORR–OER catalysts in alkaline media.

- NH_3 treated Co_3O_4 spinel type catalysts on CNTs demonstrated superior ORR– OER activity; activity and stability of the spinel on CNTs catalysts are largely impacted by the size, oxidation state, and functional groups attached to the CNTs.

- FeCoNi-derived N-GT catalysts also demonstrated high ORR activity (28 mA/mg catalyst @ at 1.6 V IR-free), and OER activity (1.31 mA/mg catalyst ORR activity at 0.9V IR-free) in the same catalyst, comparable to the baseline catalyst Pt and Ir, respectively.

FUTURE DIRECTIONS

- Explore MEA fabrication for bifunctional catalysts and optimize test conditions for both fuel cell and electrolyzer mode.
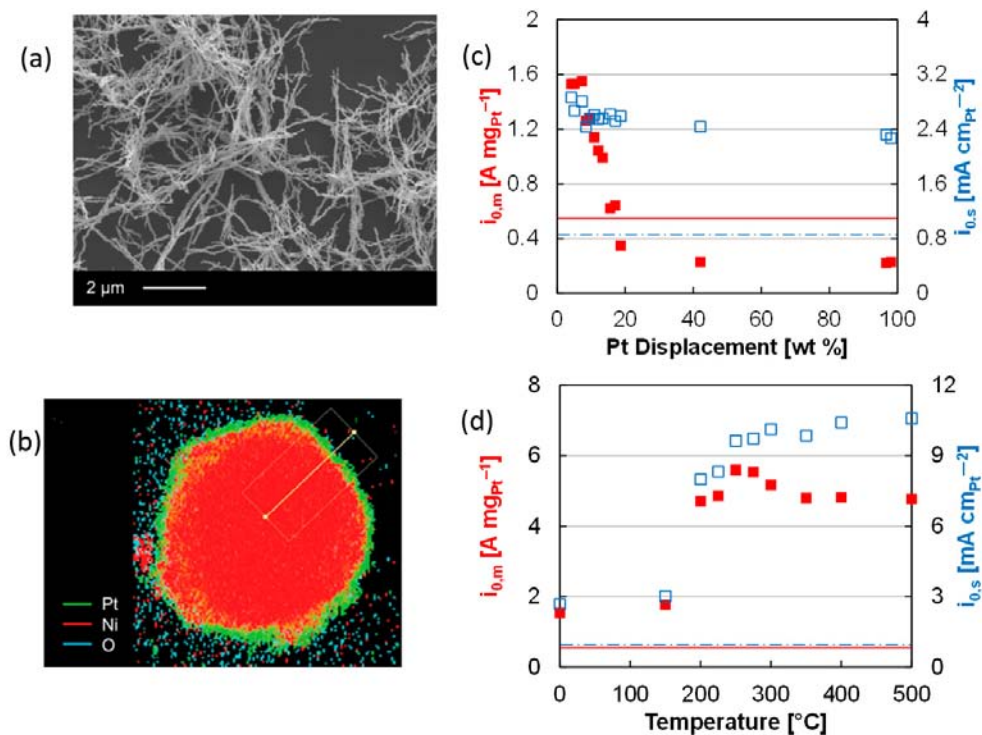

FIGURE 4. (a) Synthesized core-shell Pt-Ni nanowires as bi-functional HOR–HER catalysts and (b) morphology and structure of the Pt-Ni nanowire catalyst. (c) Effect of Pt loading on the catalyst activity. (d) Effect of H_2 annealing temperature on the catalyst activity.

- Modify fuel cell configuration and test station to operate fuel cell (discharge) and electrolyzer (charge) intermittently.

SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

1. Prof. Gang Wu was appointed as an Associate Editor for *RSC Advances*, published by Royal Society of Chemistry in the United Kingdom, and was selected as one of the Editorial Board Members for *ChemistrySelect* (Wiley-VCH, Germany) and *Scientific Reports* (Nature Publishing Group).

FY 2016 PUBLICATIONS/PRESENTATIONS

Peer-Reviewed Publications

1. Gupta, S.; Kellogg, W.; Xu, H.; Liu, X.; Cho, J.; Wu, G.; "Bifunctional perovskite oxide catalysts for oxygen reduction and evolution in alkaline media," *Chemistry–An Asian Journal,* **11**(1), 10–21, 2016.

2. Wu, G.; Santandreu, A.; Kellogg, W.; Gupta, S.; Ogok, O.; Zhang, H.; Wang, H.-L.; Dai, L., "Carbon nanocomposite catalysts for oxygen reduction and evolution reactions: from nitrogen doping to transition-metal addition," *Nano Energy,* doi:10.1016/j.nanoen.2015.12.032, 2016.

3. Osgood, H.; Devaguptapu, S.V.; Xu, H.; Wu, G., "Transition metal (Fe, Co, Ni, and Mn) oxides for oxygen reduction and evolution bifunctional catalysts in alkaline media," *Nano Today*, *minor revision*, 2016.

4. Gupta, S.; Qiao, L.; Zhao, S.; Devaguptapu, S.V.; Xu, H.; Swihart, M.T.; Wu, G., "Highly active and stable graphene tubes decorated with FeCoNi alloy nanoparticles via a template-free graphitization for bifunctional oxygen reduction and evolution," *Advanced Energy Materials*, accepted, 2016.

Presentations at International Conferences

1. Zhao, S.; Rasimick, B.; Mustain, W.E.; Xu, H., Metal oxides supported on carbon nanotubes as bifunctional eectrocatalysts for reversible alkaline membrane fuel cells, 229th ECS meeting, San Diego, CA, May 29, 2016.

2. Wu, G., Bifuncational nanocomposite catalysts for reversible electrochemical energy applications, 229th ECS meeting, San Diego, CA, May 29, 2016.

3. Gupta, S.; Wang, X.; Wu, G., Large-size and few walled graphene tube catalyst for electrochemical energy storage and conversion, 2016 International Carbon Conference, State College, PA, July 10–15, 2016.

REFERENCES

1. *Multi-Year Research, Development, and Demonstration Plan: Section 3.4 Fuel Cells*, Fuel Cell Technologies Office, 2011. http://www1.eere.energy.gov/hydrogenandfuelcells/mypp/pdfs/fuel_cells.pdf