

Final Technical Proposal

Award number: N00014-18-1-2650

Title of proposal: Oxygen Generation and Extraction from Seawater

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Period of performance: 1 August 2018–31 December 2020

Distribution Statement

Approved for public release: distribution unlimited.

Major Goals

The major goal for the project is to explore the basic science behind producing breathable oxygen from an ocean environment by water electrolysis. The first project period was devoted to Aim 1 of the proposal: Construction of a DEMS Instrument to Assess Oxygen Generation from Seawater. We constructed a differential electrochemical mass spectrometer (DEMS), which allows for a quantitative determination of the faradaic efficiency for oxygen generation versus chlorine, bromine and other extraneous oxidation products.

With the DEMS experiment constructed, attention turned to the main aims of the project, Aim 2: Design of Self-Healing Water Electrocatalysis in Seawater. We sought to develop metallate oxygen evolving catalysts (M-OECs) for oxygen evolution by seawater electrolysis. The workplan focused on cobalt phosphate (CoP_i) and nickel borate (NiB_i) catalysts. The self-healing properties were proposed to be useful in stabilizing these catalysts in seawater.

The final major aim of the proposal was also targeted, Aim 3: Design of Mixed Metal Structure-Function Oxygen Evolving Catalysts. The idea here was to decouple oxygen evolution activity from catalyst stability such that each property is achieved by use of distinct metals. In this way, oxygen evolution activity may be optimized independently from catalyst stability. We proposed to use a stable oxide framework (PbO_x) to house the CoP_i and NiB_i self-healing catalysts. We believed that the anionic nature of the PbO_x framework would lead to even higher selectivity for oxygen generation from seawater because the anionic PbO_x matrix would reject halide ions,

During the project period, major accomplishments were achieved for Aims 1– 3.

Accomplished Goals

Aim 1 Accomplishments

A home-designed DEMS system was constructed that has a detection limit of ~ 0.1 nmol. The DEMS setup consists of two differentially pumped chambers (ionization chamber and analysis chamber) and a quadrupole mass spectrometer (PrismaPlusTM QMF 110, Pfeiffer-Vacuum). The ionization and analysis chambers were pumped to high vacuum by two Pfeiffer 65 L/s turbomolecular pumps backed by a Pfeiffer dry diaphragm pump, in order to avoid contamination by oil vapors. The PrismaPlusTM quadrupole mass spectrometer was connected to the analysis chamber and equipped with electron multiplier/faraday cup dual detecting units. The time constant of the mass spectrometer was in the millisecond regime. Mass spectrometric data was collected with Quadera software, with three selective channels recording m/z of 32, 70, and 160 in real time during the electrochemical CV experiments. A dual thin layer flow electrochemical cell made of Kel-F was connected to the ionization chamber via an angle valve. The upper chamber, which

houses the electrochemical reaction, is connected to the lower chamber, which is under high vacuum and in line with the mass spectrometer, by 6 capillaries. In the upper compartment, the working electrode is pressed against a ~100 mm thick Teflon gasket with an inner diameter of 6 mm. This leaves an exposed area of 0.28 cm² and results in an electrolyte volume of ~3 μL. In the lower compartment, a porous Teflon membrane (Gore-Tex) supported on a stainless-steel frit serves as the interface between the electrolyte and vacuum. It is pressed against a ~100 mm thick Teflon gasket with an inner diameter of 6 mm. The Gore-Tex Teflon membrane has a thickness of ~75 μm, a mean pore size of 0.02 μm and a porosity of 50%. A leak-free Ag/AgCl reference electrode is connected at the inlet side of the flow cell by insertion into a capillary, and a Pt wire counter electrode is connected in a similar fashion at the outlet of the cell. Electrolyte was purged with argon for 1 h before being transferred to a syringe pump (Harvard Apparatus PHD 2000 Infusion). Electrolyte flow into the electrochemical cell was then controlled by the syringe pump, at 60 mL/h, which ensured fast transport of the species formed at the electrode to the mass spectrometric compartment where the volatile products were evaporated into the vacuum system of the DEMS via the porous Teflon membrane.

Accomplishment for Aim 2: Design of Self-Healing Water Electrocatalysis in Seawater

Aim 2 Accomplishments

Two M-OEC catalysts were prepared, CoP_i and NiB_i. Experiments were performed in NaCl solutions at concentration (0.5 M) of the salt found in seawater collected from the Fort Point Channel location of Boston Harbor. The work has since been published in *ACS Omega*, and a pdf of the published manuscript has been uploaded under the Products section.

For both catalysts, as determined by DEMS, no chlorine (Cl₂) production is observed over the entire potential range examined (0.5 V to 1.3 V vs Ag/AgCl) for saltwater. Chlorine (Cl₂) may also react with water in neutral or basic solutions to form HClO/ClO⁻ and thus we also analyzed for these products. Electrolysis was performed at an OER overpotential of 490 mV for ~12 hours and hypochlorite (HClO/ClO⁻) were spectroscopically analyzed using a N,N-diethyl-p-phenylenediamine (DPD) assay. A faradaic efficiency for HClO/ClO⁻ production was 3.2 ± 1.1 % and 0.4 ± 0.1 % for CoP_i and NiB_i, respectively.

We also examined the oxygen generation selectivity of CoB_i and NiB_i catalysts in seawater. Again, no chlorine was detected by DEMS from seawater oxidation over all potentials examined (0.5 V to 1.3 V vs Ag/AgCl) (see Figure 1, uploaded in Product section). An additional byproduct to consider when electrolyzing seawater is bromine (Br₂), which can be produced from the oxidation of bromide (Br⁻) anions present in natural seawater. No Br₂ was produced upon seawater electrolysis, as determined by DEMS (see Figure 1A, uploaded in Product section). Analogous to Cl₂, Br₂ may react with water in neutral or basic solutions to form hypobromite (HBrO/BrO⁻). Using the same procedure as was used for the NaCl electrolysis, we determined that the faradaic efficiency for the combined production of HClO/ClO⁻ and HBrO/BrO⁻ was 1.4 ± 0.5 % and 4.3 ± 0.1 % for CoB_i and NiB_i, respectively.

Aim 3 Accomplishments

Although the accomplishments listed in Aim 2 were quite extraordinary with respect to catalyst

stability in seawater and to the generation of oxygen with an absence of chlorine or bromine production, hypohalous (HOCl and HOBr) acid was observed to be produced in extremely low percentages (1-4%). Though low in concentration they must be eliminated totally for breathable oxygen, as these acids entrained in an oxygen stream would be dangerous to the diver. On this count, a major accomplishment was achieved in the previous project period. We perfected rotating-ring disk electrochemistry (RRDE) to measure halogen products (e.g., hypohalous acids) in solution. Figure 1B (top panel, uploaded in Product section) shows the total current at the disk (reduction of O₂ and halide oxidation products of HOCl and HOBr) for CoP_i in solutions of high salt concentrations. Solution-based halide oxidation products may be quantified by subtracting the ring current (determined at lower reduction potentials) from the overall disk current. This data combined with DEMS data, allows the overall efficiency for O₂ production vs halide oxidation to be determined. As observed in Aim 2, some HOCl/HOBr is produced by the CoP_i catalyst. We posited that if we embedded CoP_i in a negative oxide matrix, like PbOx, the negatively charged chloride and bromide ions would be rejected from the catalyst layer. This idea has worked spectacularly well. As shown in Figure 1B (bottom panel, uploaded in Product section), a CoP_i/PbOx catalyst does not produce and halogen *or* hypohalous (HOCl and HOBr) acid. This catalyst exclusively generates breathable oxygen from seawater.

Training Opportunities

- Specific Training for Past Project Period

A fifth-year graduate student Thomas Keane has performed the research during the project period. He made extremely good progress towards his Ph.D. and is graduating in April 2021. He was assisted by an undergraduate, Jing Jing Chang. Jing Jing learned to synthesize catalysts and electrochemistry.

- General Training

Graduate and undergraduate students who participate in the program become expert in several important sub-disciplines. Materials chemistry is at the heart of the program—studies proposed here involve the design and preparation of catalysts tailored to support the multielectron reaction chemistry of water splitting. However, making the catalysts is only the beginning. All proposed work involves extensive spectroscopic and electroanalytical characterization, as well as the examination of reaction kinetics.

Students receive extensive experience in oral research presentations through their participation in regular research group meetings and the weekly seminar series. In addition, students are encouraged to attend and make presentations at regional, national, and international scientific conferences, especially the national American Chemical Society and Materials Research Society meetings and Gordon Research Conferences, which provide great opportunities for networking. On the Harvard campus, students are part of the Harvard Graduate Consortium on Energy and Environment, for which water splitting is a featured topic (as a solar fuels strategy). This consortium fosters a community of doctoral students who are well versed in the broad,

interconnected issues of energy and environment while maintaining their focus in their primary discipline.

High value comes from one-on-one interactions with the PI, who meets with students to discuss his or her preferred career path. Those who have chosen to enter academia have prepared drafts of their research proposals, which are reviewed by the PI who then provides the researcher with feedback and comments. Training in written presentation of research results is provided by the process of preparing manuscripts for publication. The prepared drafts of manuscripts describing their results are critiqued with detailed comments, suggestions and corrections. They then learn how to submit their manuscripts to journals and respond to comments by reviewers.

As one measure of the training and mentorship success of the PI, 72 graduate and postdoctoral students have entered academics from the PIs program (at schools including Amherst, Berkeley, Birmingham (UK), Boston College, U Colorado Boulder, Caltech, Case Western, Colorado State, Cornell, Delaware, El Paso, Erlangen, Florida, Georgia Tech, Glasgow, Harvard, Houston, Humboldt-Berlin, Illinois Chicago, Indiana, Irvine, Johns Hopkins, Kansas State, Lehigh, Michigan, Michigan State, MIT, Nante, U North Carolina Chapel Hill, Northwestern, Ohio State, Oregon, Penn State, South Dakota, Stanford, South Carolina, U Texas El Paso, UCLA, UC Santa Barbara, Wayne State to name a few). In all cases, of those students eligible for tenure, all have received it. Similar success stories follow for students entering industry and the private sector. This is an indicator that the students are trained well in the rigors of beginning a career and are able to hit the ground running in their independent careers.

Results Dissemination

Project accomplishments have been reported in a published manuscript in *ACS Omega*. The PI also presented work from the project at the:

- (1) 2019 ONR Undersea Medicine and NAVSEA Deep Submergence Biomedical Development Program Review at Duke University in May 2019
- (2) GILS Workshop held in Panama City, FL in October 2018
- (3) ONR Distinguished Lecture Series in Arlington, VA on April 30, 2019
- (4) Plenary Lecture, SUNRISE Workshop; European Union; Brussels, Belgium; 18 June 2019.
- (5) Keynote Lecture; 47th IUPAC World Chemistry Congress; Paris France; 10 July 2019.
- (6) 23rd International Symposium on the Photochemistry and Photophysics of Coordination Compounds; City University of Hong Kong, Hong Kong, China; 16 July 2019.
- (7) Plenary Lecture, North East Centre for Energy Materials (NECEM) Conference; Newcastle University; Newcastle. England; 29 July 2019.
- (8) 258th ACS National Meeting; Sustainable Energy and the Environment Symposium; San Diego, CA; 26 April 2019.
- (9) Honda-Fujishima Lectureship Award; Japanese Photochemistry Association; Nagoya University; 11 September 2019.
- (10) CCB Lecture Series; RIPPLE Effect; Department of Chemistry; Harvard University; Cambridge, MA; 25 October 2019.
- (11) NGFM10-nanoGe Fall Meeting; Berlin; Germany; 4 November 2019.

- (12) Next Generation Materials for Energy Applications; iCHEM Cell Symposium; Xiamen University; Xiamen, China; 17 November 2019.
- (13) Industrial Technology Research Institute (ITRI); Taipei City, Taiwan; 10 December 2019.
- (14) Plenary Lecture; 18th Asian Chemical Congress (18th ACC); Taipei City, Taiwan; 11 December 2019.
- (15) 29th Inter-American Photochemical Society (IAPS) Meeting; Sarasota, FL; 3 January 2020.
- (16) Presidential Lecture, Sabanci University; Istanbul Turkey; 17 January 2020.
- (17) Harvard Law School; Harvard University; Cambridge, MA; 12 February 2020.
- (18) Harvard Club of Miami; Harvard Alumni Association; Miami, FL; 22 February 2020.
- (19) Syngenta Global; Webinar; 2 June 2020.
- (20) SynBio Oxford University; Webinar, 24 August 2020.
- (21) International School of Chemistry - WEB edition 2020 (ISC on the WEB 2020); Webinar, 5 September 2020.
- (22) Office of Naval Research; Webinar1; 5 October 2020.
- (23) 24 Hours of Harvard; David Rockefeller Center for Latin American Studies; Harvard University; 7 October 2020.
- (24) Office of Naval Research; Washington DC; Webinar2; 8 October 2020.
- (25) Office of Naval Research; Washington DC; Webinar3; 8 October 2020.
- (26) Air Force Office of Scientific Research, Webinar; Washington DC; 13 October 2020.
- (27) NORA Meets BASF Challenges, BASF, Webinar; 21 October 2020.
- (28) Graduate School of Design; Harvard University, Cambridge MA, 11 November 2020.
- (29) Columbia Business School, Webinar; Columbia University, NY, NY; 11 December 2020.
- (30) ARPA-E Webinar; Department of Energy; Washington DC; 28 December 2020.
- (31) Bio-Manufacturing Solutions Workshop, Webinar; Boston University; Boston, MA; 10 February 2021.
- (32) Reducing the Health Impacts of the Nitrogen Problem; National Academy of Sciences and National Academy of Engineering; Washington DC; 11 February 2021.
- (33) iGEM SYnBio, Webinar; Harvard University; 28 February 2021.
- (34) RENEWS Enerchem, Webinar; Italian Chemical Society; 4 March 2021.
- (35) Columbia Energy Symposium, Webinar; Columbia Business School; 19 March 2021.

In addition to the presentation of research in peer-reviewed journal publications, all scholarly work resulting from this project is made freely available to the public in digital form in Harvard's DASH (Digital Access to Scholarship, <http://dash.harvard.edu>) repository. DASH is an open-access repository of scholarly work administered by the Office for Scholarly Communication (OSC) and the Office for Information Systems (OIS). The repository has the institution of Harvard standing behind it to ensure its longevity and functionality. DASH is meant to promote openness in general, and especially to the public. It makes the scholarship emanating from this program freely available to everyone, everywhere in the world. The DASH system provides a comprehensive view of research publications and connections within the Harvard University research community, indexes faculty, and supports automated embargo "lift dates," so that a work can be deposited as "dark" and then automatically switched to open access once a publisher's embargo has expired. DASH is also synchronized with tools that store bibliographic information, provide open access to full text, and control established subject repositories that are already used by scholars to disseminate their work.

Finally, as allowed by individual publishing companies, publications and supplementary information from this project is freely available on the PI's laboratory website.

Honors and Awards

- (1) Honda-Fujishima Award from the Japanese Photochemical Society
- (2) Presented (5) honorary lectureships during the project period
- (3) Was elected a member of the American Philosophical Society, the oldest learned society in the United States, founded by Benjamin Franklin in 1743. The A.P.S. is the most selective society in the U.S. – only ~25 resident members across all fields of humanities, economics, law, medicine, engineering and the sciences are elected each year.

Technology Transfer (patent applications, inventions, licenses, interaction with DoD laboratories)

The PI has had extensive interactions with Navy laboratories. As a participant of the 2019 ONR Undersea Medicine and NAVSEA Deep Submergence Biomedical Development Program Review in May 2019 at Duke University, the PI interacted with personnel from NAVSEA (civilians and Navy personnel in the areas of submarine rescue, decompression sickness, hyperbaric physiology, diver performance and medicine) and from ONR (civilians and Navy personnel in the areas of GILS, Oxygen Toxicity, Decompression Sickness Hyperbaric physiology, diver performance and medicine). The PI also had significant interactions during October 2019 with personnel from the Diving and Life Support Enterprise and Naval Surface Warfare Center in Panama City Division and Maritime Mission Systems Division.

Participants

Undergraduate and graduate STEM participants:

Thomas Keane (g)

Kay Xia (ug)

Number of participants that received a STEM degree:

Kay Xia, B.S. in Science, Undergraduate Senior Thesis: *On the Culture of Chemistry*

Thomas Keane, Ph.D. in Chemistry, PhD Thesis: *Development and Study of Heterogeneous Earth-Abundant Oxygen Evolving Catalysts for Use in Diverse Electrolyte Environments*

Products

1. Publications

Title: Selective Production of Oxygen from Seawater by Oxidic Metallate Catalysts

Journal: ACS Omega

Authors: Thomas P. Keane, Daniel G. Nocera

Keywords: Seawater, Electrolysis, Water-Splitting, Catalysis, Oxygen Generation

Distribution Statement: There is no restriction to distribution of this article. The journal was chosen for publication because it is an Open Access journal. Thus, the work is available to the public.

Publication Status: published

Publication Identifier: 10.1021/acsomega.9b01751

Publication Date: 2019

Volume: 4

Issue: 7

First Page Number: 12860

Publication Location: United States

Acknowledgement of Federal Support? Yes

Peer Reviewed? Yes

2. Thesis

- a. Kay Xia, B.S. in Science, Undergraduate Senior Thesis: *On the Culture of Chemistry*
- b. Thomas P. Keane, Ph.D Thesis: *Development and Study of Heterogeneous Earth-Abundant Oxygen Evolving Catalysts for Use in Diverse Electrolyte Environments*

3. Website

- a. Title: Daniel G. Nocera
Website: <https://chemistry.harvard.edu/people/daniel-g-nocera>
Description: Faculty website for the Department of Chemical biology at Harvard University
- b. Title: Nocera lab
Website: [https:// http://nocera.harvard.edu/Home](https://http://nocera.harvard.edu/Home)
Description: Research group website

4. Other Products: Identify any other significant products that were developed under this project. Describe the product and how it is being shared.

- a. Description: DEMS Instrument (as described in Accomplishments section under Aim 1)
Product Type: instruments or equipment