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Recent Work

Title

Solar conversion of CO₂ to formate

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Report on CRADA #FP00004002**AWD#00001924****LBNL-Toyota Central Research and Development Laboratory****PI: Frances Houle****Period of Performance 10/28/2016 – 10/27/2018****Introduction**

The Statement of Work for this CRADA was initially focused on optimization of a photoelectrochemical device, to be constructed using expertise in the Joint Center for Artificial Photosynthesis (JCAP) at LBNL, for transformation of CO₂ into formate using a new catalyst developed by TCRDL. The work was to be jointly performed by LBNL and TCRDL at LBNL, and to involve an 18 month stay by a TCRDL researcher, Dr. Takeo Arai, at LBNL. Due to a family emergency this plan had to be cancelled after 6 months, and was replaced by a new work plan involving synchrotron studies that could be performed without requiring exchange of personnel.

Progress on original plan

The first approximately 6 month period of performance was focused on demonstrating a 10% efficient, 75% selective solar CO₂ device for generation of formate. The formate-specific tasks worked on were

- A. Optimize TCRDL formate-generating catalyst loading for use with JCAP semiconductor platform. TCRDL and JCAP jointly developed the research plan, and TCRDL performed the work.
- B. Develop designs for formate-generating devices including alternatives for catalyst supports. JCAP and TCRDL worked together on this task.
- C. Construct working formate devices, characterize performance, identify and make improvements. TCRDL led this work with participation by JCAP.

Tasks A and B were completed and Task C was in progress when the plan was cancelled.

New work plan: An Operando-XAS investigation of β -FeOOH:Ni surface-decorated with amorphous Ni(OH)₂: reversible Ni-state change and Ni-Fe interaction during electrocatalytic OER

The revised Statement of Work shifted to a new topic in the general area of solar fuels that took advantage of the partnership between TCRDL and LBNL and LBNL's unique expertise in in situ and operando electrochemical studies. The technical lead for the new topic was Dr. Junko Yano. The research results are presented here.

The water oxidation reaction which referred to as the oxygen evolution reaction (OER) extracting electrons from water molecules is a crucial step in generating useful chemicals, such as hydrogen by proton reduction or organic compounds from CO₂, as part of the drive toward a sustainable society which makes use of natural energies from sunlight, wind, etc. with an uphill reaction (energy storage reaction). High catalyst activity, cost, and long-term durability are important for future

implementation of catalysts in society using these energy conversion reaction systems. Oxides, oxyhydroxides and hydroxides of earth-abundant metals are considered to be one of best choices from viewpoints of the cost and long-term durability. There also has long been a need for cost-effective OER catalysts for use in alkaline water electrolysis, electrochemical and photoelectrochemical cells and photocatalysis. Currently the catalyst cost is considered to be not a major factor in the total cost of the proton exchange membrane (PEM) electrolysis system, while at a large scale, earth-abundant catalysts which are only stable in neutral-to-alkaline conditions will be necessary. To this end, nickel oxyhydroxide OER catalysts such as NiOOH and Fe-doped NiOOH have recently been reported. Ni-rich oxides and oxyhydroxides exhibits high OER activity together with low overpotential, but mechanistic insight is under debate.

Under this project, we have carried out X-ray absorption spectroscopy of β -FeOOH nanorods for the oxygen evolution reaction (OER) at Stanford Synchrotron Radiation Lightsource (SSRL) at beamline 7-3. The rate and the overpotential of OER over stacked hyperfine β -FeOOH nanorod (ϕ 3 x 13 nm) catalyst were enhanced by doping with Ni ions ($\text{Ni/Fe} < 1\%$), and the OER rate was further lowered by additional surface decoration with amorphous Ni(OH)₂ ($\text{Ni/Fe} \sim 20\%$), which exhibited highest level OER current at a low potential among Fe-rich oxides and oxyhydroxides in aqueous alkali solution (10 mA/cm² at an overpotential of 430 mV containing iR drop, in 1 M KOH) (**Fig. 1**). It is strongly suggested that Fe-Ni interaction is crucial to the very high OER activity. In this study, we used operando XAS in the aqueous solution (**Fig. 2a**) to understand oxidation states and local atomic structure motifs under catalytic potential. We showed that that nearest neighboring structure and valence of Fe³⁺ under electrically-biased OER condition were identical to those under non-biased condition. In contrast, Ni showed 2nd nearest neighbor ordering to beta-Ni(OH)₂ and electrons of Ni²⁺ were withdrawn to shift toward Ni³⁺ under the catalytic condition, which were reversible depending on the electrical bias change for OER (**Fig. 2b**). This finding, the improvement of OER with reversible structural change of Ni species while irreversible Fe under catalytic potential, could contribute to further understanding of detailed mechanism of these Fe-rich oxide OER catalysts which have a contact with Ni species.

(manuscript under preparation, and plan to be submitted in January, 2019)

Fig. 1: β -FeOOH:Ni nanorods on carbon paper. Ni coverage of 1% and 20 % was used in this study.

Fig. 2: (a) Experimental setup of operando XAS data collection, and (b) the EXAFS spectra of FeOOH:Ni nanorods of as it is (Dry), open circuit (OC), and under applied potentials. β -Ni(OH)₂ spectrum is shown as reference.