

Report: Photoelectrochemically Rechargeable Zn-Air Batteries

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This work aims to design photoelectrochemically rechargeable Zn-air batteries with improved energy and power density, energy efficiency and cycle life. Our plan is to solve the bottle-neck problem associated with air electrocatalysts by developing novel nanocarbon-inorganic hybrid materials for oxygen reduction and/or evolution with high efficiency and durability. Also, we are pursuing active and stable semiconductor photoanodes with proper surface engineering for photoelectrochemical (PEC) recharging of Zn-air batteries under sunlight illumination. We hope for the widespread deployment of rechargeable Zn-air batteries in all-electric vehicles and in grid storage applications, reducing our dependence on fossil fuels and mitigating global greenhouse gas emission.

The following are the specific aims for our GCEP program.

- a. Preparation of nanoscale non-precious metal hydroxide or oxide covalently linked to novel carbon supports for ORR and/or OER electrocatalysis.
- b. Detailed structural and electrochemical evaluations of the hybrids.
- c. Development of cycleable Zn electrodes.
- d. Fabrication of primary and rechargeable Zn-air batteries based on hybrid electrocatalysts.
- f. Demonstration of photoelectrochemically rechargeable Zn-air batteries.

Progress has been made in these areas especially in a, b and f:

a,b: Hybrid synthesis and characterization: Development of an advanced Ni-Fe Layered Double Hydroxide Electrocatalyst for Water Oxidation.

Oxygen evolution reaction (OER) holds a key to water splitting and rechargeable metal-air batteries. An effective electrocatalyst is needed in order to expedite the reaction, reduce the overpotential and thus enhance the energy conversion efficiency. Currently, the most active OER

catalysts are IrO_2 or RuO_2 in acidic or alkaline solutions, but these catalysts suffer from the scarcity and high cost of precious metals. We developed a NiFe layered double hydroxide-carbon nanotube complex (NiFe-LDH/CNT) with higher OER catalytic activity and stability than commercial Ir based catalysts (**Fig.1** below). The key aspects of this catalyst are the formation of ultra-thin nanoplates of a highly OER active NiFe layered double hydroxide (LDH) structure (the same structure as alpha-phase Ni hydroxide (α -phase $\text{Ni}(\text{OH})_2$) and association of the nanoplates with CNTs that can form interconnected electrically conducting networks. This was the first time that crystalline NiFe-layered double hydroxide was synthesized chemically to obtain highly active electrocatalysts for the oxygen evolution reaction in alkaline media. The turn-over frequency of the NiFe-LDH/CNT catalyst exceeded any previous Ni-Fe compounds and was comparable to the most active perovskite based catalyst. This work was published in **JACS**. The catalyst will be used as the cathode material for our Zn air battery to achieve high performance in reducing charging overpotential.

f: Towards photoelectrochemically recharging of Zn-air batteries: Development of High-Performance Silicon Photoanodes Passivated with Ultrathin Nickel Films for Water Oxidation.

Silicon is a well known photoelectrode material but its sensitivity to corrosion has hindered its use in photoanode applications. Recently we discovered that depositing a thin nickel film (~ 2 nm) on n-type silicon with the native oxide affords high-performance metal-insulator-semiconductor (MIS) photoanode for photoelectrochemical (PEC) water oxidation in both aqueous potassium hydroxide ($\text{pH} = 14$) and aqueous borate buffer ($\text{pH} = 9.5$) solutions. The Ni film acted as a surface protection layer against corrosion and as a non-precious metal electrocatalyst for oxygen evolution. The Ni/n-Si photoanodes exhibited high activity with a low onset potential in 1 M KOH (~ 1.07 V vs. RHE), high photocurrent density and durability. Remarkable stability over > 80 hours of continuous PEC water oxidation was achieved in a

mixed lithium/potassium borate electrolyte (**Fig.2** below). The high photovoltage was attributed to a high built-in potential between n-Si and the electrolyte separated by an ultra-thin, incomplete screening Ni/NiO_x layer. This work was published in Science and the photoanode will be used for PEC charging of Zn air battery in our GCEP project.

Publications:

1. Michael J. Kenney, Ming Gong, Yanguang Li, Justin Z. Wu, Ju Feng, Mario Lanza, and Dai. "High-Performance Silicon Photoanodes Passivated with Ultrathin Nickel Films for Water Oxidation" *Science*, 342 (6160) 836-840, 2013.
2. Ming Gong, Yanguang Li, Hailiang Wang, Yongye Liang, Justin Z. Wu, Jigang Zhou, Jian Wang, Tom Regier, Fei Wei, and Dai. "An Advanced Ni Fe Layered Double Hydroxide Electrocatalyst for Water Oxidation" *JACS*, 135 (23) 8452-8455, 2013

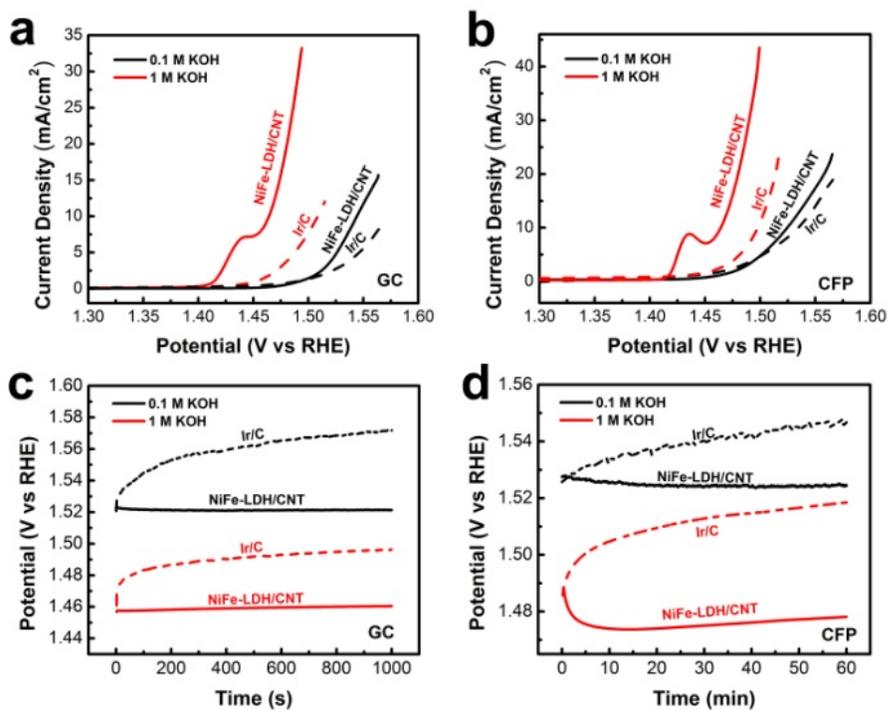


Figure 1. Electrochemical performance of NiFe-LDH/CNT hybrid OER catalyst. (a) iR-corrected polarization curves of NiFe-LDH/CNT hybrid and Ir/C catalysts on glassy carbon (GC) electrode in 0.1 M KOH and 1 M KOH respectively, measured with a catalyst loading of 0.2 mg/cm² for both NiFe-LDH/CNT and Ir/C at a continuous electrode rotating speed of 1600 rpm. (b) iR-corrected polarization curves of NiFe-LDH/CNT hybrid and Ir/C catalysts on carbon fiber paper (CFP), measured with a catalyst loading of 0.25 mg/cm². See Supporting Information and Figure S5 for details of iR correction. (c) Chronopotentiometry curves of NiFe-LDH/CNT hybrid and Ir/C catalyst on GC at a constant current density of 2.5 mA/cm². (d) Chronopotentiometry curves of NiFe-LDH/CNT hybrid and Ir/C catalyst on CFP at a constant current density of 5 mA/cm².

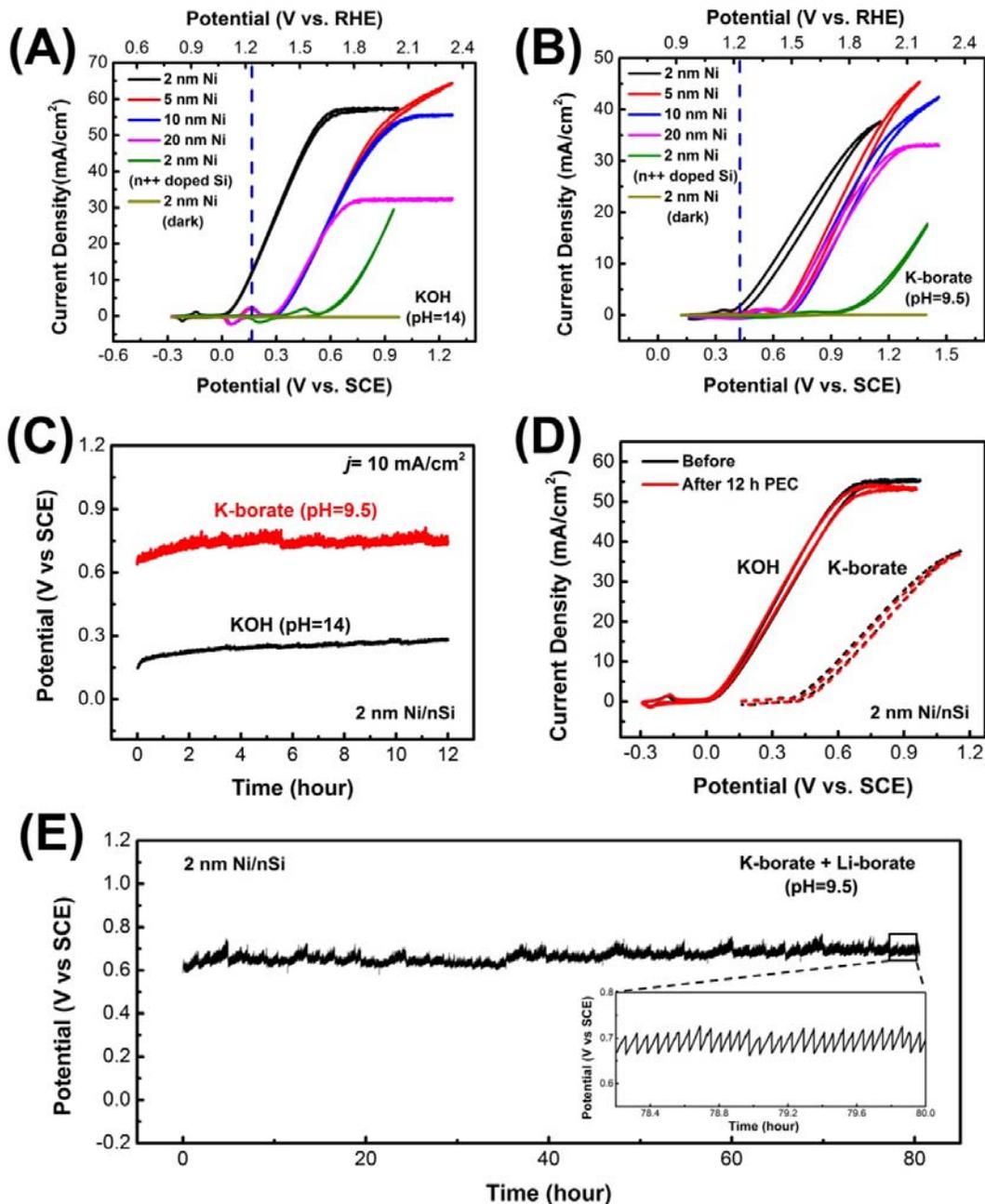


Figure 2. High performance Ni/nSi photoanode with ultra-high stability. (A) Cyclic voltammograms of 2, 5, 10 and 20 nm Ni-coated n-Si anodes in 1 M KOH under illumination with a 150 W Xenon lamp (225 mW/cm², ~2 suns) and 2 nm Ni on a metallic, heavily doped n++ silicon in 1 M KOH in the dark. (B) Cyclic voltammograms of 2, 5, 10 and 20 nm coated n-Si anodes in 1 M K-borate electrolyte under illumination. (C) Potential vs. time data under constant current of 10 mA/cm² of two 2 nm Ni/n-Si anodes in 1 M KOH and 1 M K-borate respectively for 12 hours under constant illumination. (D) Cyclic voltammograms taken before and after 12 hour stability tests in (C). All CVs were taken at 100 mV/s with no iR compensation applied. (E) Potential vs. time data under constant current of 10 mA/cm² of a 2 nm Ni/n-Si anode in 0.65 M K-borate and 0.35 M Li-borate (pH = 9.5) for 80 hours (> 3 days) under constant illumination. No PEC activity decay was observed. Inset shows details of current fluctuations caused by oxygen gas bubble release. The increased saturation current in the 5 nm Ni-coated electrodes is highly reproducible but the cause is currently unknown.