

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 all of the aims above. We have also extended the project to electrocatalysis in general including OER catalysts and hydrogen evolution reaction HER catalysts and new types of batteries including the invention of Al ion batteries. Below we summarize the works that have been published recently. Other projects related to the aims above are in progress and some are being prepared for publication.

1. Photoelectrochemical (PEC) electrocatalysis.

Photoelectrochemical (PEC) water splitting is a promising approach to harvest and store solar energy. Silicon is widely investigated for PEC photo-electrodes due to its suitable band gap (1.12 eV) matching the solar spectrum. However, Si is problematic in terms of limited chemical stability in electrolyte solutions under PEC conditions for both OER and HER. Recently, we investigated employing nickel both as a HER catalyst and protecting layer for p-type silicon photocathode for photoelectrochemical hydrogen evolution in basic electrolytes for the first time. The silicon photocathode was made by depositing 15 nm Ti on a p-type silicon wafer followed by 5 nm Ni. The photocathode afforded an onset potential of ~ 0.3 V vs. RHE in alkaline solution (1 M KOH). The stability of the Ni/Ti/p-Si photocathode showed a 100 mV decay over 12 h in KOH, but the stability was significantly improved when the photocathode was operated in potassium borate buffer solution (pH \approx 9.5). The electrode surface was found intact after 12 h of continuous operation at a constant current density of 10 mA/cm² in potassium borate buffer, suggesting better protection of Ni in borate buffers for Si based photocathodes. This is the first time Ni metal film is used for Si based PEC for HER, and the work was published in **Nano Research** with acknowledgement to GCEP.

2. Water splitting with novel OER and HER electrocatalysts using a single AAA battery.

Hydrogen is a clean and renewable energy resource, has been intensely investigated as an alternative to the diminishing fossil fuel. An effective way of producing high purity hydrogen is to electrochemically split water into hydrogen and oxygen in an electrolyzer. The state-of-art hydrogen evolution HER catalyst is platinum (Pt) and its alloys, but the scarcity and cost of Pt limit its large-scale application for electrolysis. It has been difficult to achieve both high activity and stability matching those of Pt. For oxygen evolution OER catalyst, Ir metal is the most active but is also expensive and not stable.

Recently we developed a nickel oxide/nickel (NiO/Ni) hetero-junction like structure attached to mildly oxidized carbon nanotube (NiO/Ni-CNT) exhibiting high HER catalytic activity close to commercial Pt/C catalysts in several types of basic solutions (pH=9.5-14). The high catalytic activity of NiO/Ni-CNT towards HER was combined with a highly active NiFe LDH catalyst (reported to GCEP last year) to enable a high performance electrolyzer with ~20

mA cm⁻² at a voltage of 1.5 V (**Figure 1** below), which sets a low voltage record for water electrolysis using non-precious metal catalysts. This work was the first time anyone can split water by electrolysis under 1.5 V using non-precious metal catalysts. It generated high impact to the energy community and general public. Stanford's press release and Mark Schwartz's Youtube video received record viewing numbers among all his videos. This work was published in **Nature Communications** with acknowledgement to GCEP.

3. Invention of a rechargeable aluminum ion battery.

The development of new rechargeable battery systems could fuel various energy applications from personal electronics to grid storage. Due to the low cost, low flammability and 3-electron redox properties of aluminum, rechargeable Al-based batteries could offer cost-effectiveness, high capacity and safety, leading to a breakthrough in energy storage technology. However, rechargeable Al battery research over the past 30 years has failed to compete with other battery systems. These efforts have been plagued by problems such as cathode material disintegration, low cell discharge voltage (~0.55 V), capacitive behavior without discharge voltage plateaus (1.1–0.2 V or 1.8–0.8 V), and insufficient cycle life (<100 cycles) with rapid capacity decay (by 26%–85% over 100 cycles).

We made a breakthrough recently by developing a high-performance rechargeable aluminum battery with high-rate capability using an aluminum (Al) metal anode and novel graphitic materials for the cathode. The battery operates through electrochemical deposition/dissolution of Al and intercalation/de-intercalation of chloroaluminate anions in graphite using a safe, non-flammable ionic liquid electrolyte (**Figure 2** below). The cell exhibited well-defined discharge voltage plateaus near ~2 V, a specific capacity ~70 mAh g⁻¹ and ~98% Coulombic efficiency. A novel three-dimensional (3D) graphitic foam cathode was found to enable fast anion diffusion and intercalation, affording unprecedented charging times (~1 minute) with high current densities ~4,000 mA g⁻¹ (~ 3,000 W kg⁻¹), which can withstand > 7,500 cycles without capacity decay. The aluminum battery has the potential for cost effectiveness, high safety and high charging speed, making it a promising new energy storage system. This work was published in **Nature** with acknowledgement to GCEP and generated significant interest.

Publications in which GCEP support is acknowledged.

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3. Meng-Chang Lin, Ming Gong, Bingan Lu, Yingpeng Wu, Di-Yan Wang, Mingyun Guan, Michael Angell, Changxin Chen, Jiang Yang, Bing-Joe Hwang, and Dai. "An ultrafast rechargeable aluminium-ion battery", *Nature*, 520, 324-328, 2015.
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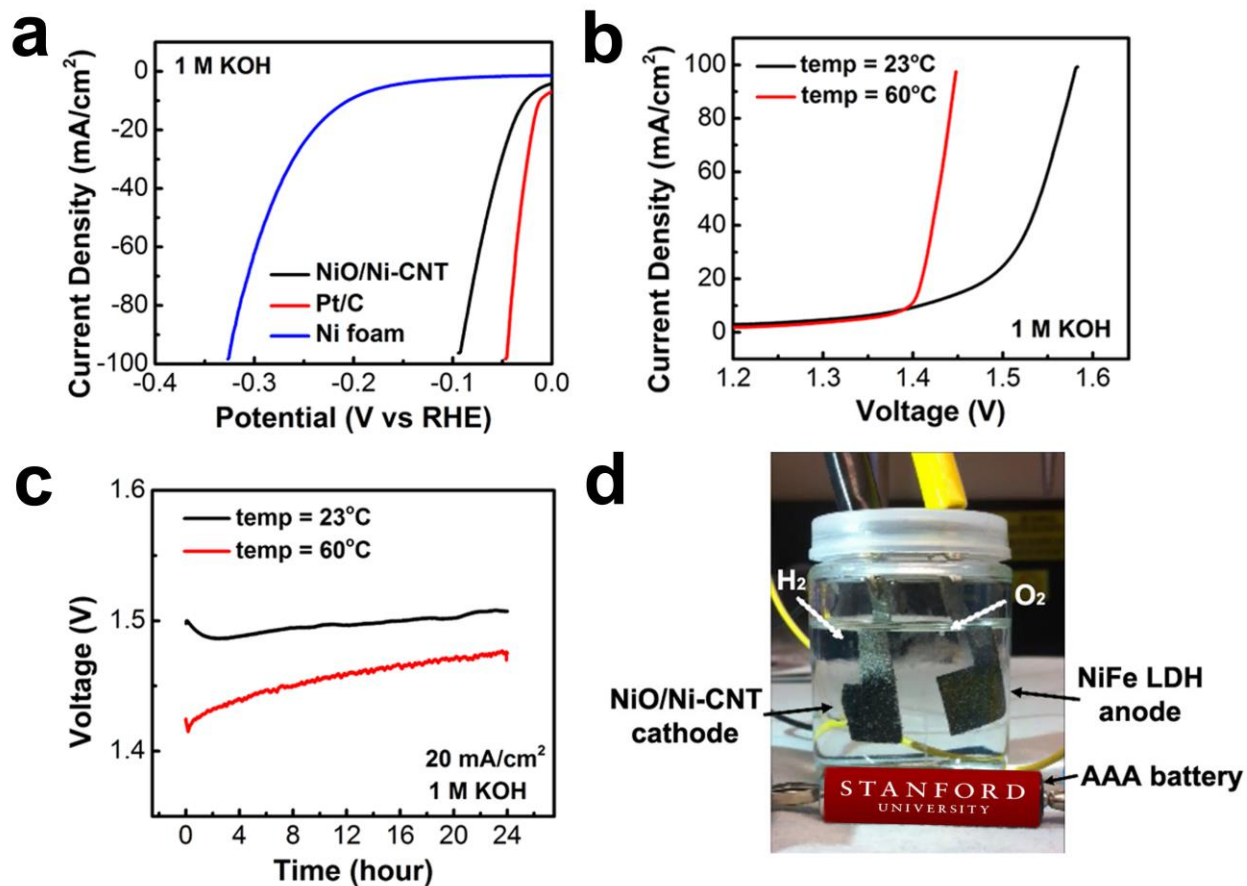


Figure 1. High performance NiO/Ni-CNT cathode for water splitting with a single battery. (a) Linear sweep voltametry of NiO/Ni-CNT, Pt/C deposited on Ni foam and pure Ni foam at a scan rate of 1 mV/s under the loading of 8 mg cm⁻² in 1 M KOH. For uncompensated curve, please refer to Figure S10. (b) Linear sweep voltametry of water electrolysis using NiO/Ni-CNT as HER catalyst and NiFe LDH as OER catalyst (both loaded into Ni foam at a loading of 8 mg cm⁻² based on the active mass) in 1 M KOH under different temperature. (c) Chronopotentiometry of water electrolysis using NiO/Ni-CNT and NiFe LDH at a constant current density of 20 mA cm⁻² in 1 M KOH. (d) Demonstration of water splitting device powered by an AAA battery with a nominal voltage of 1.5 V.

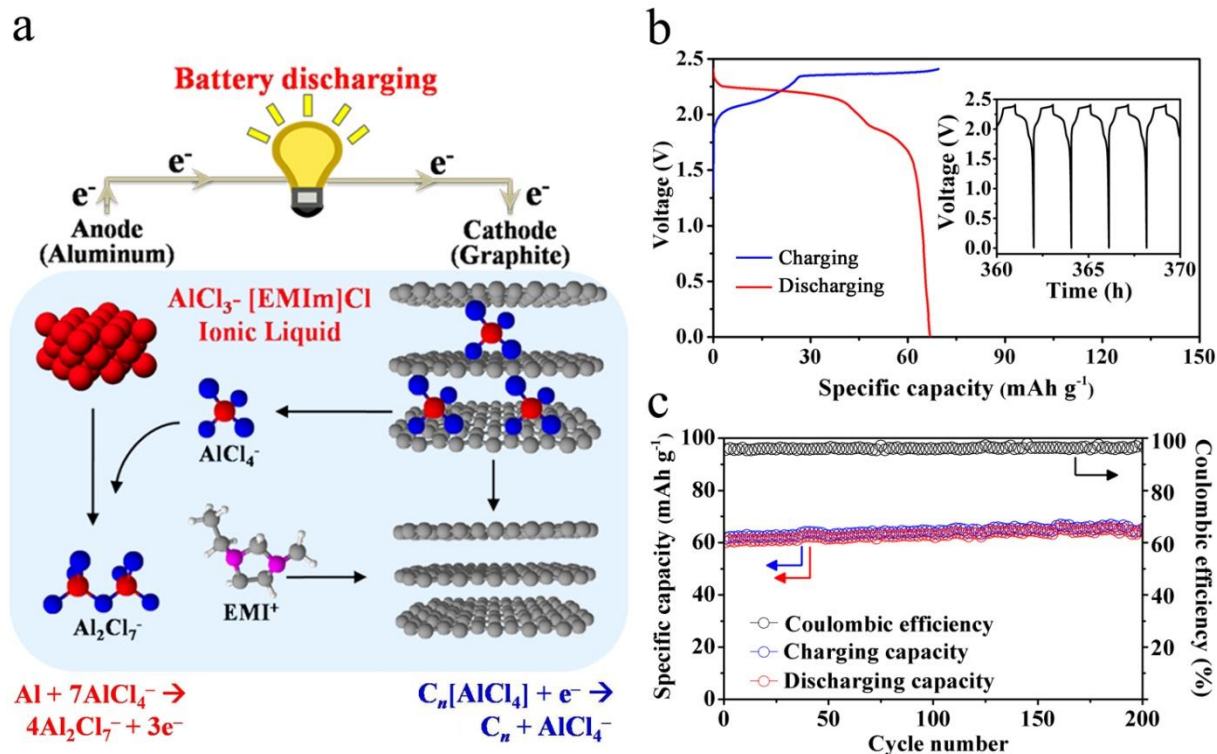


Figure.2 Birth of a rechargeable Al battery. **a**, A schematic drawing of the Al/graphite cell during discharge. An aluminum foil was used as the anode and a pyrolytic graphite foil or a 3D graphite foam was used as the cathode in an optimal ratio of AlCl_3 /[EMIm]Cl ionic liquid electrolyte. In the anode side, metallic Al, AlCl_4^- and Al_2Cl_7^- were active species during charge and discharge reactions, respectively. In the cathode side, predominantly AlCl_4^- was intercalated and de-intercalated in the space between graphite layer planes during charge and discharge reactions, respectively. **b**, Galvanostatic charge and discharge curves of Al/pyrolytic graphite cell at a current density of 66 mA g^{-1} . Inset shows that charge and discharge cycles of the cell. **c**, Long-term stability test of Al/pyrolytic graphite cell at 66 mA g^{-1} . The cells can be cycled to $\sim 100\%$ depth of discharge for at least 200 cycles and exhibited with $>97\%$ Coulombic efficiency. The electrochemical studies were performed in a 1.3:1 (in mole ratio) AlCl_3 :[EMIm]Cl ionic liquid electrolyte in a Swagelok-type cell (see SI).