Novel Materials for Renewable Energy

Hongjie Dai

Department of Chemistry, Stanford University
Clean Energy for a Sustainable Future

Legend:
- **Hydrogen fuels**
- **Fuel cells**

Harvest solar, wind, hydro energies for:
- Electricity
- Batteries for energy storage
- Make H₂ fuel, ...
Electrocatalysts and Novel Batteries

H. Wang et. al., Chem. Rev., 2013

Y. Liang et. al., JACS (perspective), 2013


- Low cost, active and stable electrocatalysts.
- Water to H₂ with high efficiency/low voltage.
- Develop new battery concepts.
**Electrocatalysts for High Efficiency Electrolysis**

**HER:** \[ 4H^+ + 4e^- \rightleftharpoons 2H_2 \]

**OER:** \[ 2H_2O \rightleftharpoons O_2 + 4H^+ + 4e^- \]

A theoretical voltage of 1.23 V

Multi-proton/electron transfer (Large overpotential)

The best catalysts (~1.5-1.6 V)

(Pt for HER / IrO$_2$ for OER)

Industrial catalyst (> 1.8-2.0 V)

(Ni for HER / Stainless steel for OER)

Need cheap and scalable electro-catalysts with high activity and durability
NiFe Layered Double Hydroxide (LDH) for OER in Base

\[ \text{OER: } 4\text{OH}^- \leftrightarrow 2\text{H}_2\text{O} + \text{O}_2 + 4\text{e}^- \]

LDH structure

- Ni\(^{2+}\) Cation
- Fe\(^{3+}\) Cation
- Charge-balancing anion

- NiFe LDH grown on carbon nanotubes

NiFe-LDH Grown on CNTs: More Active and Durable Than Ir

~ 240 mV overpotential @ 10 mA/cm²
Tafel slope of 31 mV/decade in 1 M KOH

Gratzel group:

- NiFe LDH is both OER and HER active.
- Can be used for solar driven electrolysis efficiently with perovskite solar cells.

Water photolysis at 12.3% efficiency via perovskite photovoltaics and Earth-abundant catalysts

Jingshan Luo,1,2 Jeong Hyeok Im,1,3 Matthew T. Mayer,1 Marcel Schreier,1 Mohammad Khaja Nazneenuddin,1 Nam-Gyu Park,3 S. David Tilley,1 Hong Jin Fan,2 Michael Grätzel1*

Although sunlight-driven water splitting is a promising route to sustainable hydrogen fuel production, widespread implementation is hampered by the expense of the necessary photovoltaic and photoelectrochemical apparatus. Here, we describe a highly efficient and low-cost water-splitting cell combining a state-of-the-art solution-processed perovskite tandem solar cell and a bifunctional Earth-abundant catalyst. The catalyst electrode, a NiFe layered double hydroxide, exhibits high activity toward both the oxygen and hydrogen evolution reactions in alkaline electrolyte. The combination of the two yields a water-splitting photocurrent density of around 10 milliamperes per square centimeter, corresponding to a solar-to-hydrogen efficiency of 12.3%. Currently, the perovskite instability limits the cell lifetime.
Hydrogen Evolution Reaction (HER) Electrocatalysis

**HER:** \[ 2\text{H}_2\text{O} \rightleftharpoons 2\text{OH}^- + \text{H}_2 + 2\text{e}^- \]

- HER is important to
  - Alkaline water electrolysis
  - Chloralkali catalysis
- Nickel (Ni) has been widely used
- Lower activity than Pt
Ni@NiO Grown on CNT for HER in Base

- Ni-NiO interfaces are highly active for HER
- Onset over-potential $\sim$ 0 volt

Ni-NiO HER + NiFe LDH OER:
~ 1.5 V Water Splitting

Compared to 2V:
~ 25% energy saving

Thermodynamic limit = 1.23 V

Ming Gong, et al., Nature Comm.

With Dr. Wu Zhou
S. Pennycook,
Oakridge
Stable, Active Water Splitting Driven by GaAs Solar Cells

~15% efficiency

With R. Capusta, S. Cowley
Alta Devices, Sunnyvale (Hanergy, 汉能)

(M. Gong et al., Angew Chemie, 2015)
Desk Lamp Driven Electrolysis

Split water using night light
Cobalt Oxide–Graphene Hybrid Materials for Oxygen Reduction Reaction (ORR)

1. low temp hydrolysis
2. solvothermal treatment

CoO/Oxidized-Nanotube Electrocatalyst for ORR

- Metal-oxide/Nanotube hybrid outperform metal-oxide/graphene
- Higher electrical conductivity of oxidized multi-walled nanotubes
Electrocatalysts for Rechargeable Zn Air Batteries

Anode: \( Zn + 4OH^- \rightleftharpoons Zn(OH)_4^{2-} + 2e^- \)

Cathode: \( O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^- \) (ORR/OER)

ORR: oxygen reduction reaction
OER: oxygen evolution reaction

• Zn air battery uses earth abundant/low cost materials
• Energy density is higher than lithium ion battery by 3X.
• Rechargeable Zn air batteries need more active and stable electrocatalysts for ORR & OER to increase energy efficiency
Electrocatalysts for Zn-Air Oxygen Electrodes

**ORR:** CoO/N-CNT

**OER:** NiFe LDH/CNT


(M. Gong, *JACS*, 2013)
High Performance Rechargeable Zn-Air Battery

- Low charge-discharge voltage polarization of \( \sim 0.70 \text{ V at 20 mA/cm}^2 \)
- High reversibility and stability over long charge and discharge cycles (10 h discharge time)

Y Li et al., *Nature Comm.*, 2013
Aluminum + Graphite + Salts = Al Ion Battery

\[ H_3C - \begin{array}{c} \text{N} \\ + \text{CH}_3 \end{array} \quad \text{Cl}^{\ominus} + \text{AlCl}_3 = 1 : 1.3 \]

Abundant anions in ionic liquid solution:

\[ \text{AlCl}_4^{\ominus} & \text{Al}_2\text{Cl}_7^{\ominus} \]

Mengchang Lin, Ming Gong, Yingpeng Wu, Bingan Lu, et. al., *Nature*, 2015

Collaboration with ITRI Taiwan & Prof. B. J. Hwang.
Al Redox + Graphite/Anion Redox Reactions

Battery discharging

\[
\begin{align*}
4\text{Al}_{2}\text{Cl}_7^- + 3\text{e}^- & \rightleftharpoons \text{Al} + 7\text{AlCl}_4^- & \text{C}_n + \text{AlCl}_4^- & \rightleftharpoons \text{C}_n[\text{AlCl}_4] + \text{e}^- \\
V & \sim 2.0 \text{ volt}
\end{align*}
\]
Al Ion Battery with Graphite Paper Cathode

- Cathode capacity now increased to ~ 100 mAh/g
Fast Charging of Al Ion Battery with Graphite Foam Cathode
Al Anion/Graphite Paper Intercalation

[Graph showing X-ray diffraction patterns with peaks at 3.77 Å, 3.35 Å, and 3.15 Å and annotations for 2nd cycle with 60 mAh g⁻¹ discharged, 24 mAh g⁻¹ discharged, 62 mAh g⁻¹ charged, and 30 mAh g⁻¹ charged.]

[Image of fully charged PG and Al oxide foam with text: 850°C in air]
AlCl$_x^-$ Intercalation During Charging/Oxidation of Graphite
Potential of Al Battery

- Low cost:
  - Uses earth abundant Al and C.
  - Ionic liquid: 20$/kg at large scale quoted by a chemical company.
- Safe, non flammable
- Fast charging
- Long cycle life, > 10,000
- Energy density up to ~ 62.5 wh/kg with active materials, higher than supercapacitors;
- Pb acid replacement

Applications:
- Grid storage
- Home use
- Mechanical tools
Convert wind- and solar-energy into:

- $\text{H}_2$ and methane fuels
- Energy stored in low cost, safe, high performance batteries
Acknowledgement

Nano-Bio:
Guosong Hong, KevinWelsher, Sarah Sherlock, Joshua Robinson, Shuo Diao, Alexander Antaris, Omar K. Yaghi

Nadine Wong Shi Kam, Zhuang Liu, Giuseppe Prencipe, Andrew Goodwin

Yuichiro Kato, Sasa Zaric, Zhuo Chen.

Professor Zhen Cheng
Professor John Cooke
Dr. Jeffrey Blackburn
Professor Calvin Kuo

Energy:
Ming Gong, Michael Angell
Mengchang Lin, Bingan Lu
Yingpeng Wu, Di-yan Wang
Mike Kenney, Sebastian Schneider
Hailiang Wang
Yongye Liang, Yanguang Li
Tyler Medford, Wesley Chang

Professor B. J. Hwang, C. J. Chen
Professor Stephen Pennycook, Wu Zhou
Professor Wei Fei

Stanford GCEP and PIE

INTELL
SAMSUNG