Novel Materials for Renewable Energy

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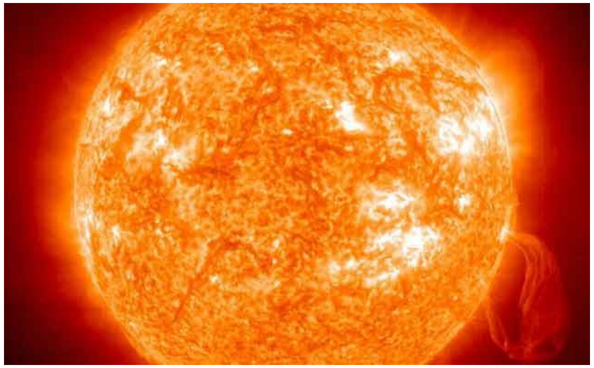
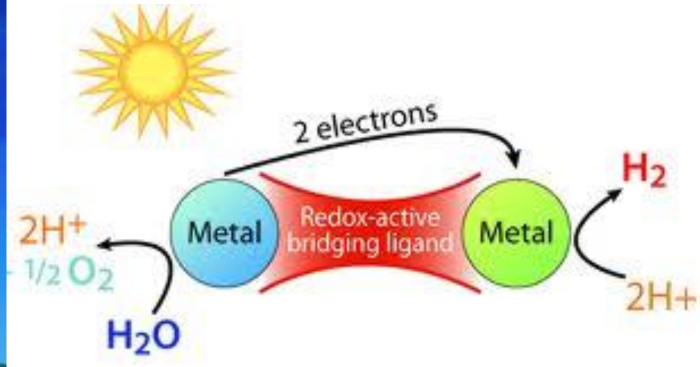
Clean Energy for a Sustainable Future



Hydrogen fuels



Fuel cells

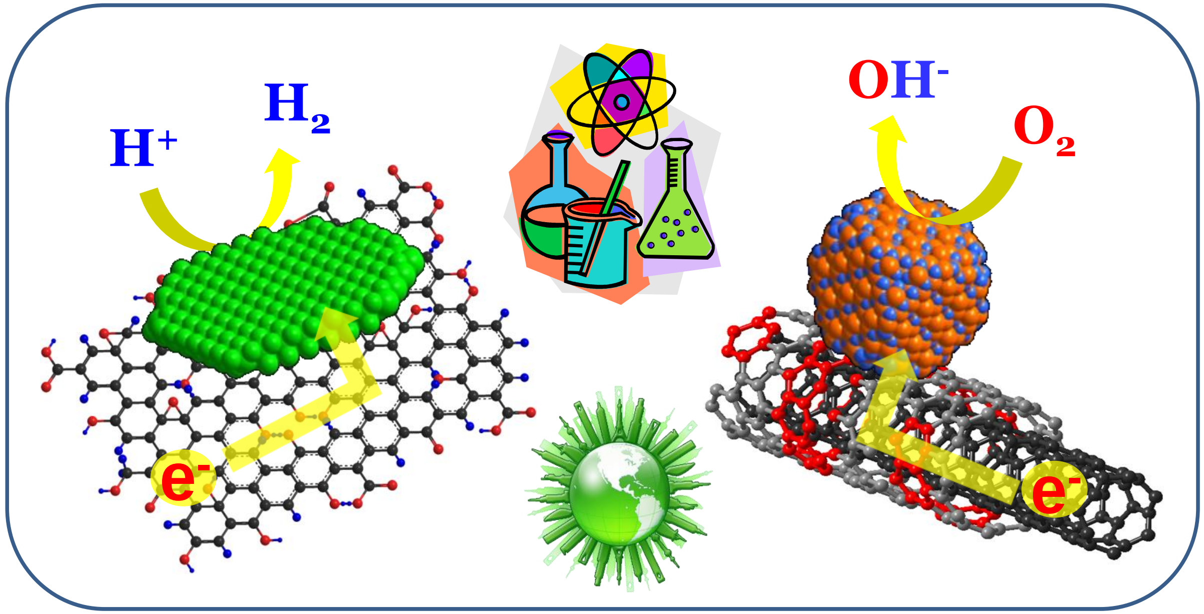
Harvest solar, wind, hydro energies for

- Electricity
- Batteries for energy storage
- Make H_2 fuel, …

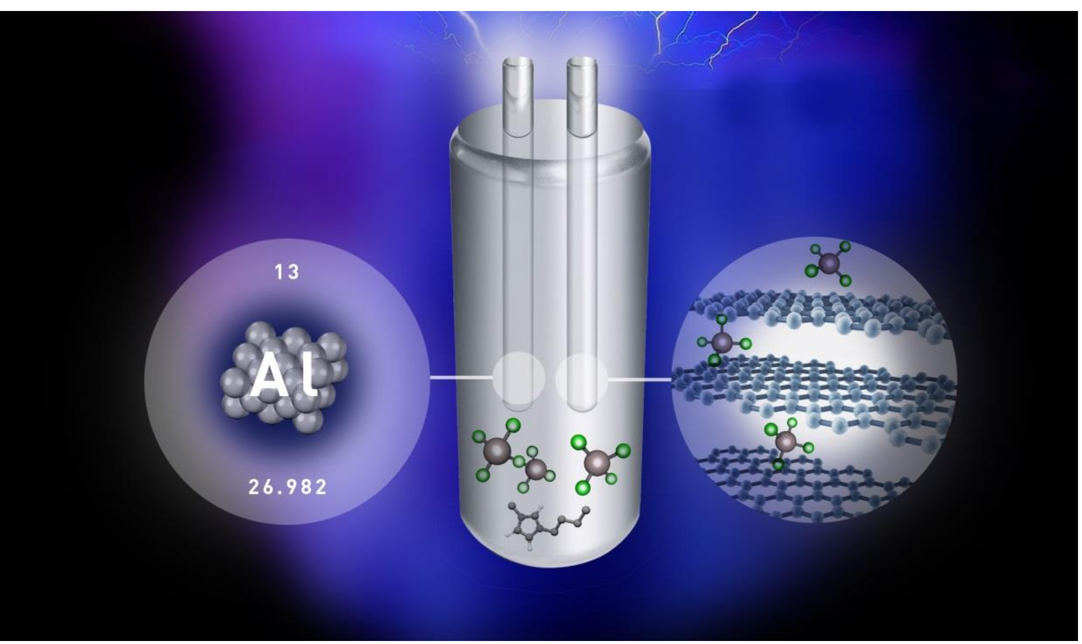
Electrocatalysts and Novel Batteries

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

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

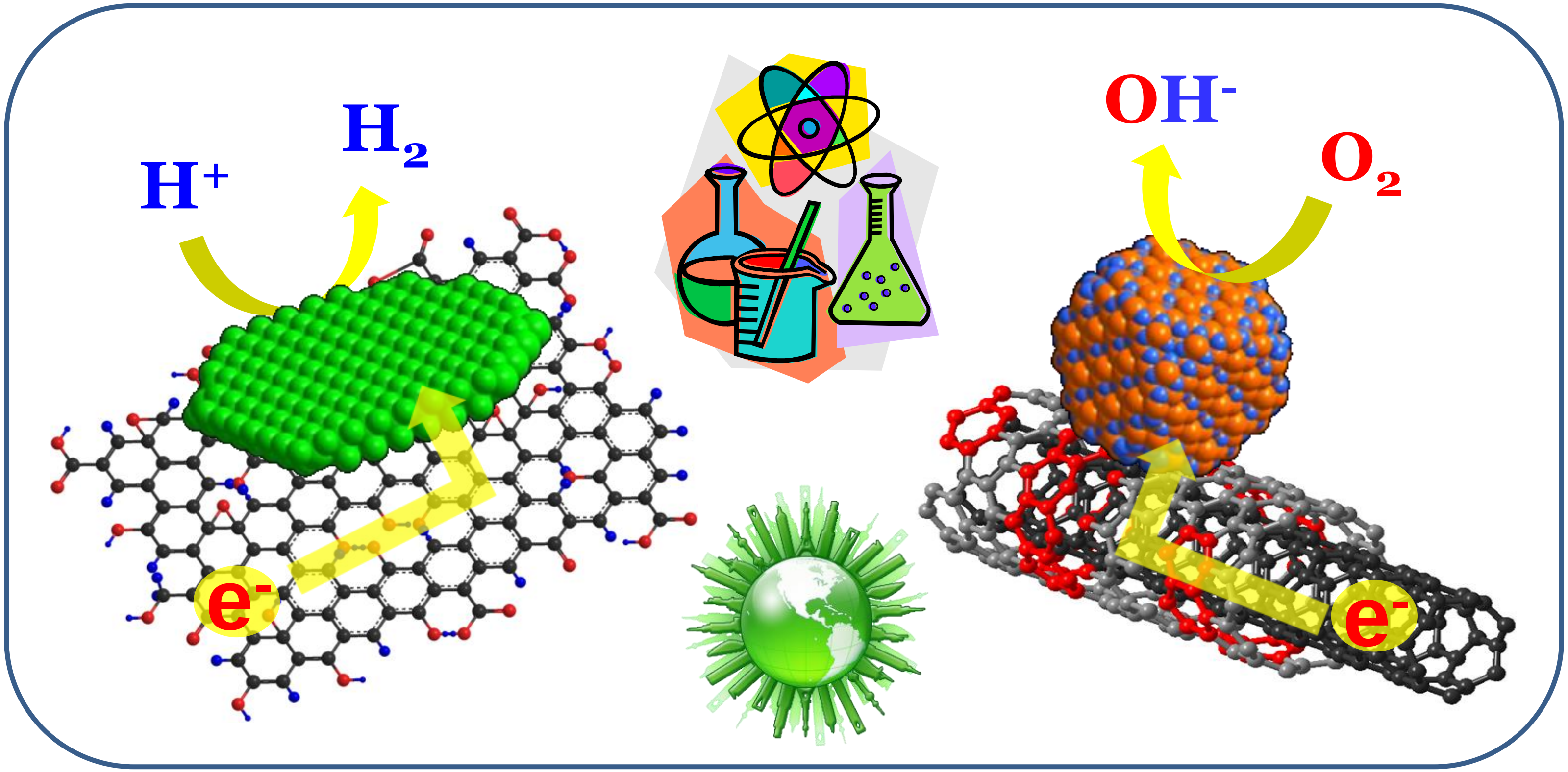


M. Lin et. al., **Nature,** 2015



- Low cost, active and stable electrocatalysts.
- Water to H_2 with high efficiency/low voltage.
- Develop new battery concepts.

Growth of Materials on NanoCarbon for Energy Storage and Electrocatalysis



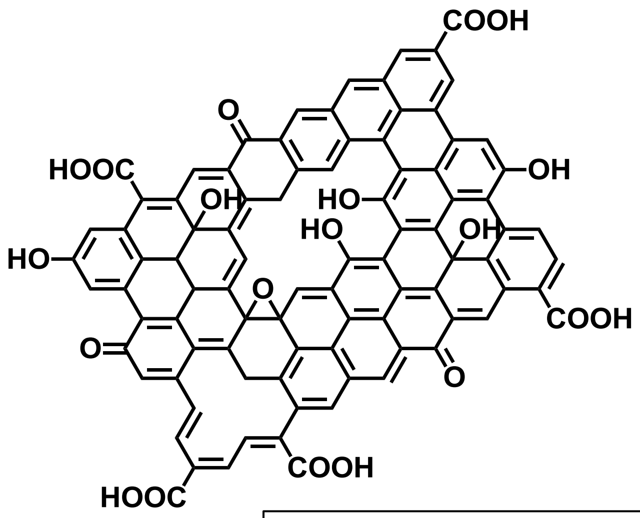
- High activity and fast speed.
- Durable.
- Low cost; non-precious metal based

(H. Wang et. al., **Chem. Rev.,** 2013)

[Y. Liang et. al., **JACS (perspective),** 2013]

Nucleation and Growth of Inorganic Materials on Oxidized Nano-Carbon

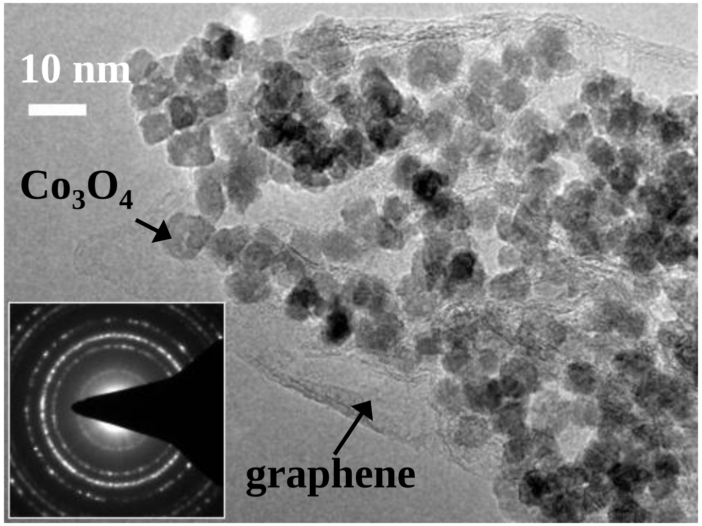
nucleation/growth on oxygen functional groups on nano-carbon

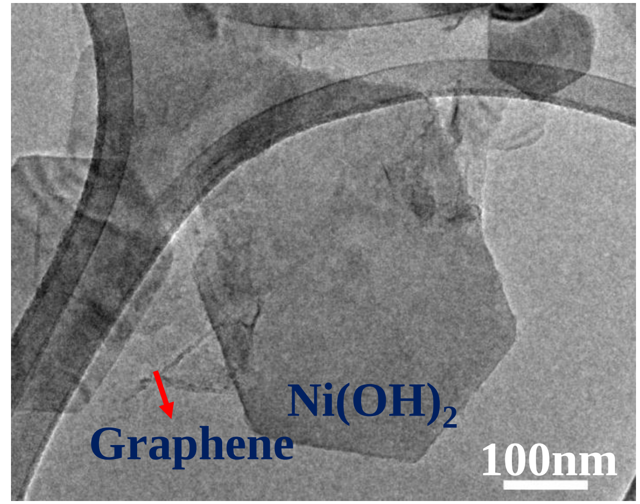


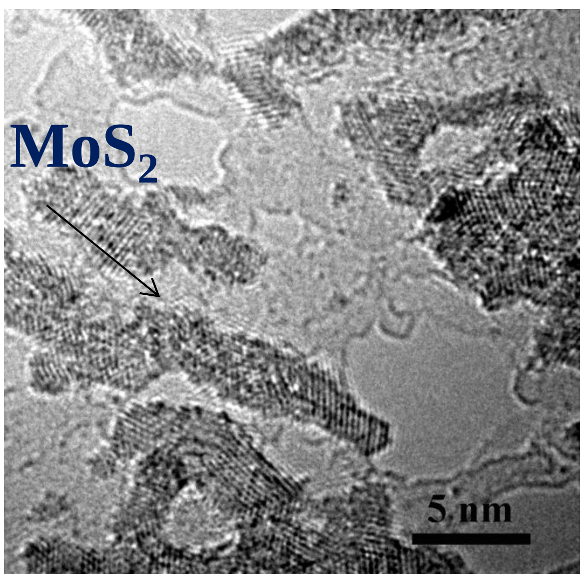
'Strongly coupled hybrid' Or 'covalent hybrid' of inorganic/nano-carbon

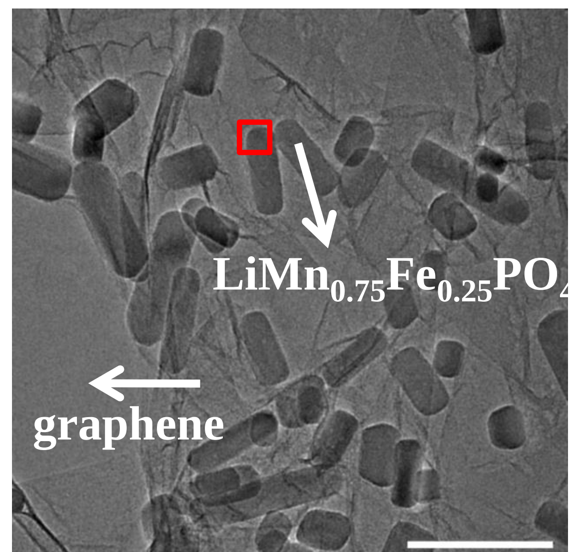
- **Excellent electronic coupling for high activity**
- **Excellent stability for high durability**

Growth of Oxides, Hydroxides, Phosphates, Sulfides… on Graphene & Nanotubes





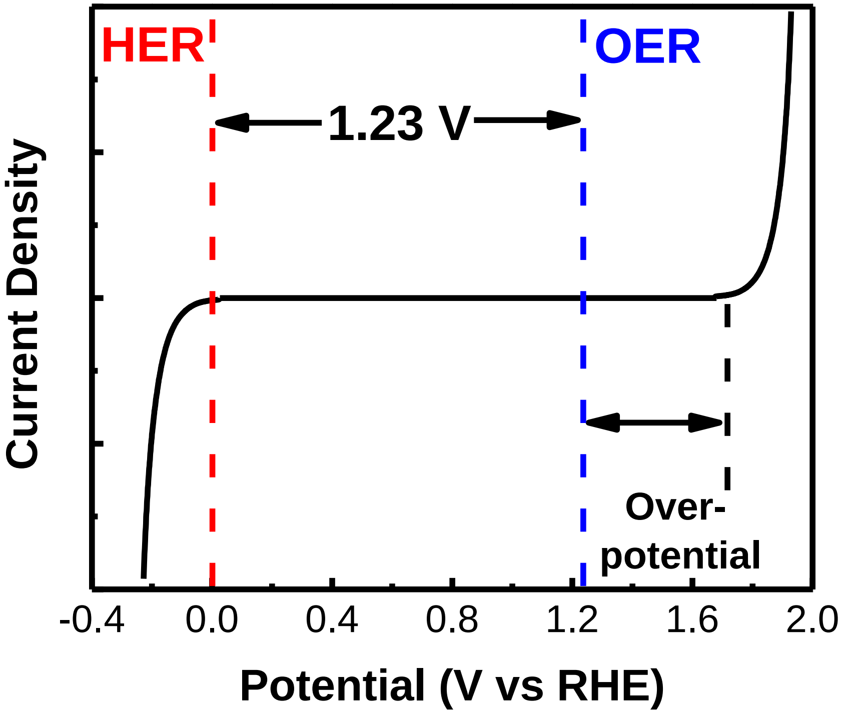




Electrocatalysts for High Efficiency Electrolysis

HER: $4H^+ + 4e \rightleftarrows 2H_2$

OER: $2H_2O \rightleftarrows O_2 + 4H^+ + 4e^-$



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)

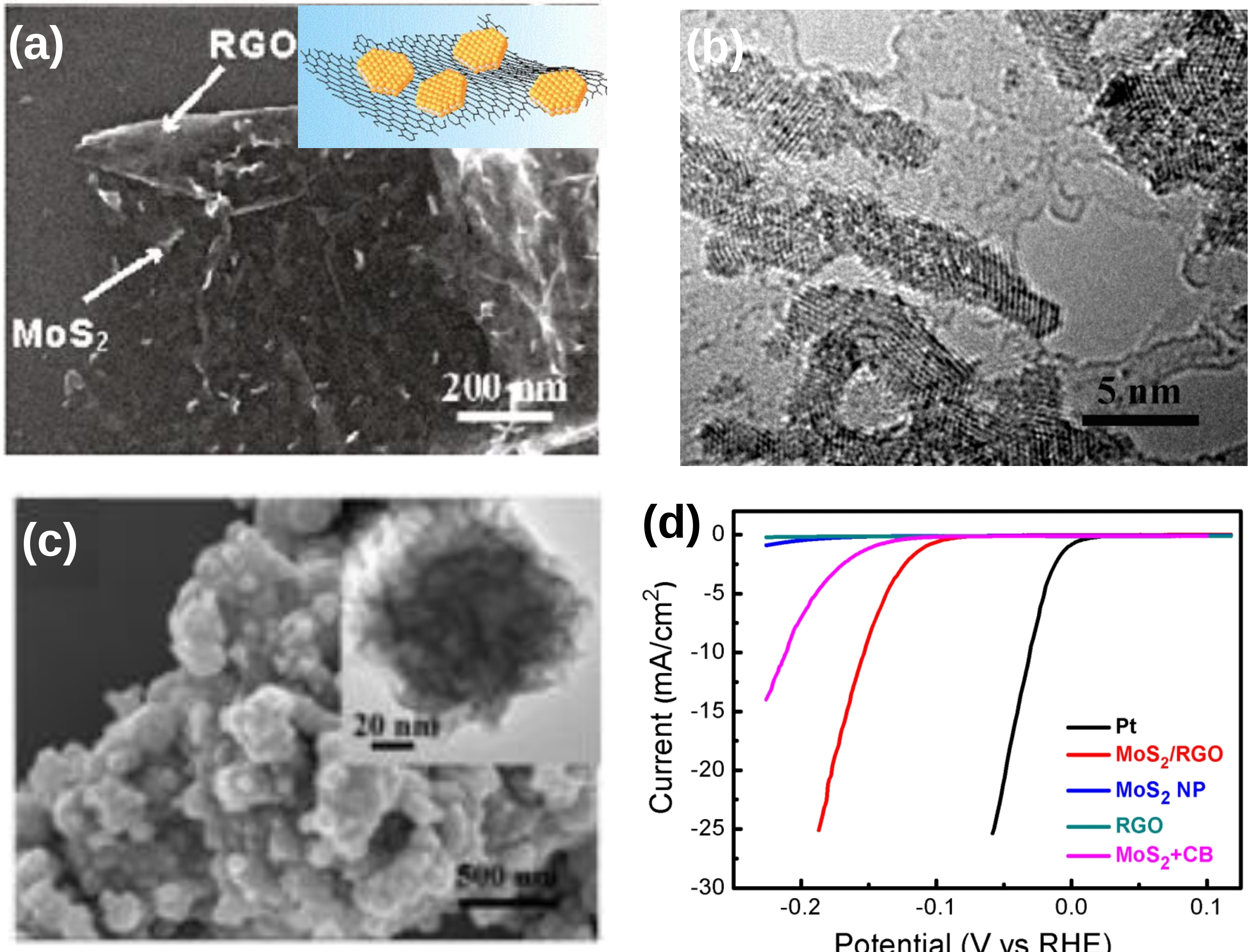
Industrial catalyst (> 1.8-2.0 V) (*Ni* for HER / *Stainless steel* for OER)

Need cheap and scalable electro-catalysts with high activity and durability

MoS_2 Grown on Graphene Oxide for Hydrogen Evolution Electrocatalyst (HER) in Acids

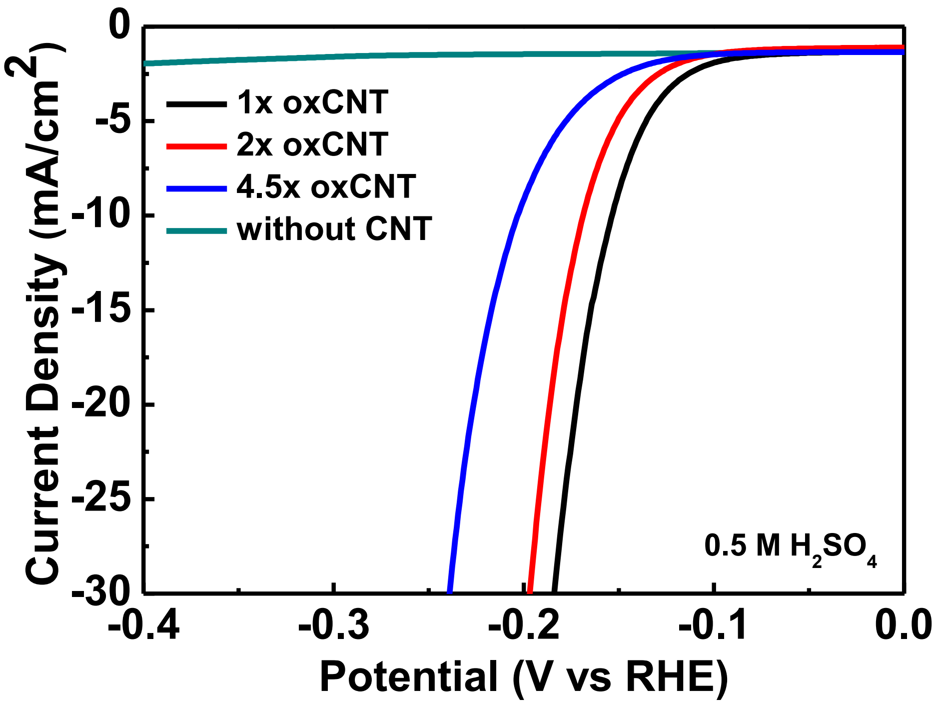
Growth on GO →

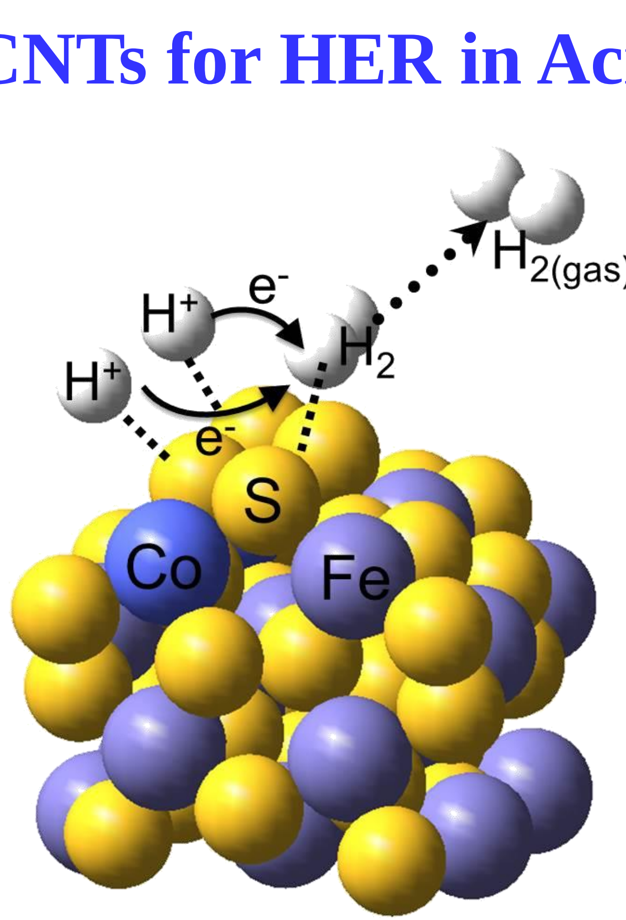
Free growth → Without GO



(Y. Li et al., **JACS**, 2011)

FeS_2 Doped with Co Grown on CNTs for HER in Acids



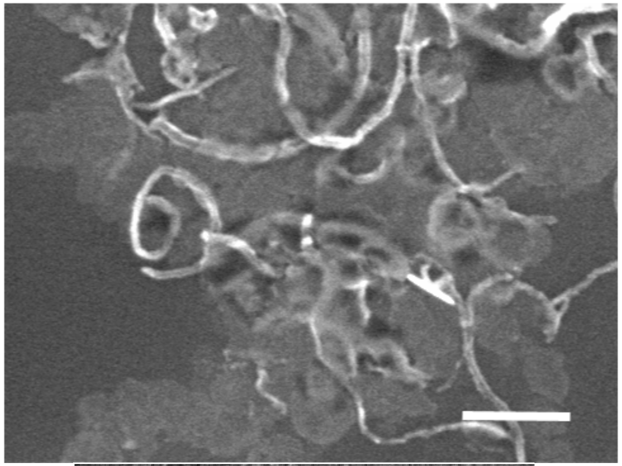


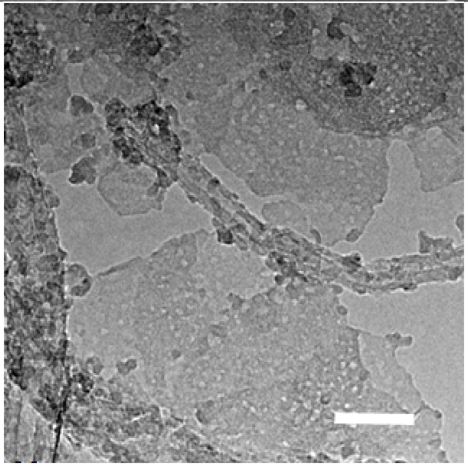
- Growth on CNT is critical
- FeS_2 affords suitable adsorption energy for H.
- Co doping lower the kinetic energy barrier by promoting H-H bond formation on two adjacently adsorbed H_{ads}.

(D. Y. Wang, et al, C. J. Chen, B. J. Hwang, H. Dai, **JACS**, 2015)

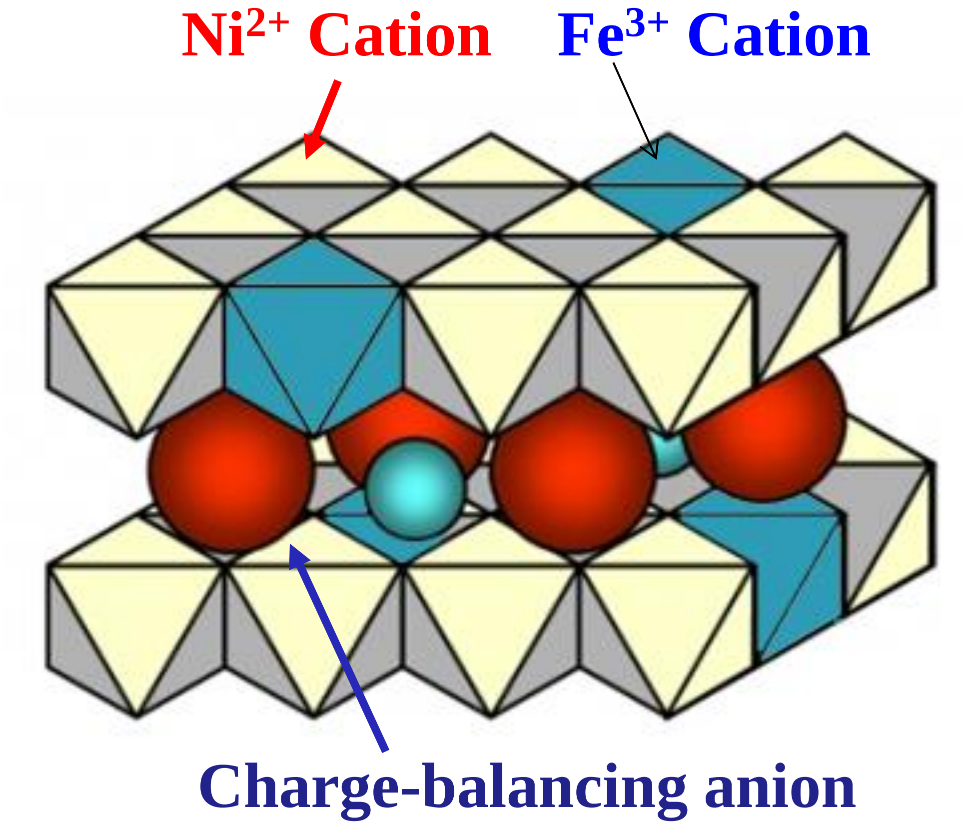
NiFe Layered Double Hydroxide (LDH) for OER in Base

OER: $4OH^- \rightleftharpoons 2H_2O + O_2 + 4e^-$





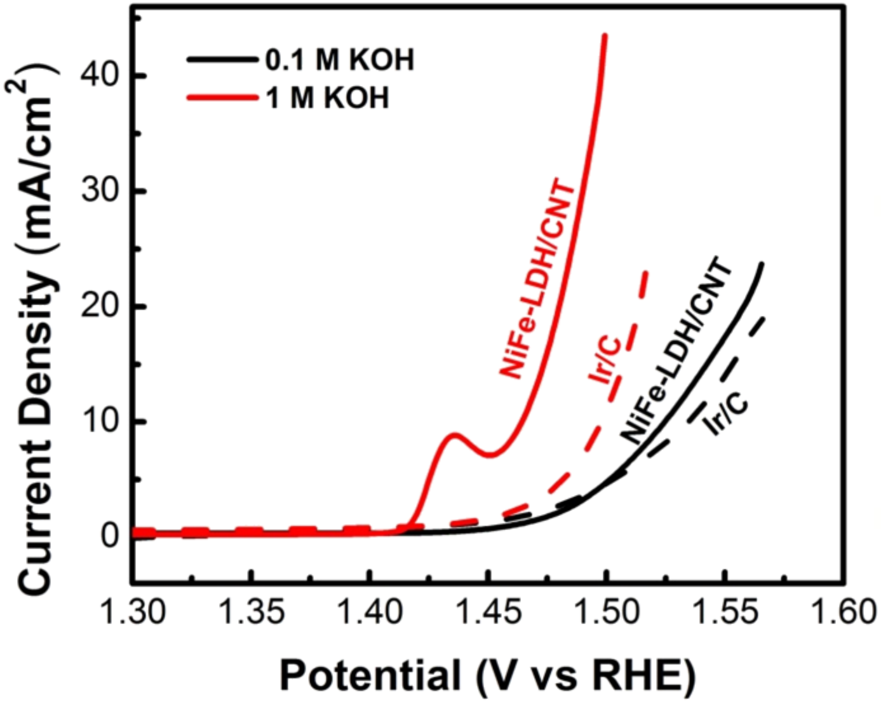
LDH structure

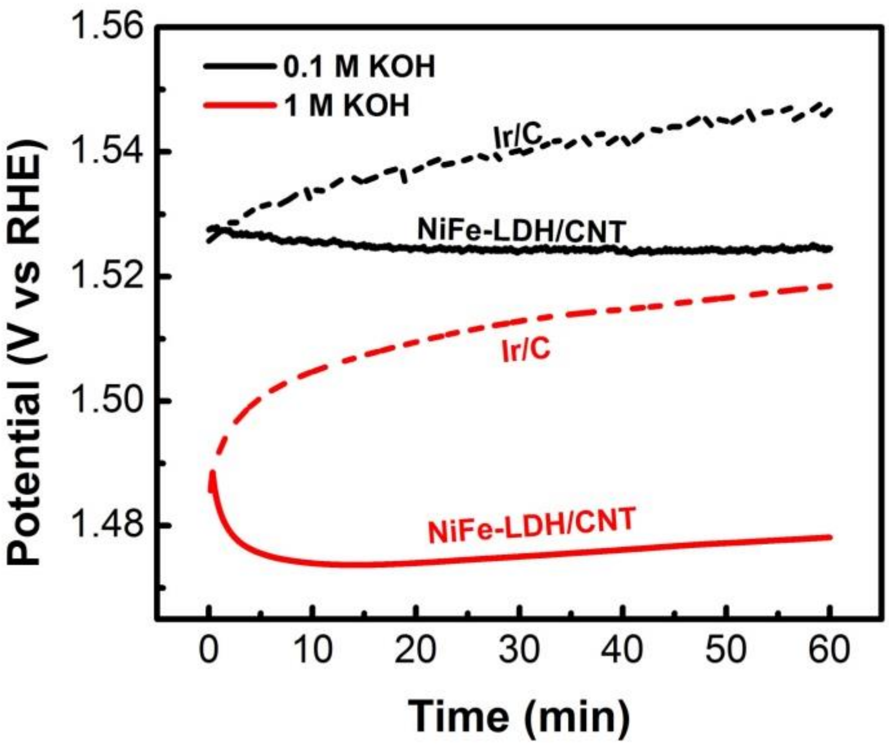


- **NiFe LDH grown on carbon nanotubes**

Gong, M. et al, ***J. Am. Chem. Soc.***, 2013, 135, 8452-8455

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





~ *240 mV* overpotential @ 10 mA /cm^2

Tafel slope of *31 mV/decade* in 1 M KOH

Gong, M. et al, ***J. Am. Chem. Soc***., 2013, 135, 8452-8455

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 Nazeeruddin,[1] Nam-Gyu Park,[3] S. David Tilley,[1] Hong Jin Fan,[2] Michael Grätzel[1]*

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.

rently 17.9% certified) in less than 5 years makes it highly promising for large-scale commercialization (*11*). Long-term stability, however, is currently a challenge with these solar cells.

The conversion of solar energy directly into fuels is a promising solution to the challenge of intermittency in renewable energy sources, addressing the issues of effective storage and transport. In nature, plants harvest solar energy and convert it into chemical fuel via photosynthesis. Inspired by nature, artificial photosynthesis has been proposed as a viable way to store the solar energy as fuel (*12*, *13*). Hydrogen, which is the simplest form of energy carrier, can be generated renewably with solar energy through photoelectrochemical water splitting or by photovoltaic (PV)–driven electrolysis. Intensive research has been conducted in the past several decades to develop efficient photoelectrodes, catalysts, and device architectures for solar hydrogen generation (*14*–*20*). However, it still remains a great challenge to develop solar water-splitting systems that are both low-cost and efficient enough to generate fuel at

Gratzel group:

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

[1]Laboratory of Photonics and Interfaces, Institute of Chemical Sciences and Engineering, School of Basic Sciences, Ecole Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland. [2]Division of Physics and Applied Physics, School of Physical and Mathematical Sciences, Nanyang Technological University (NTU), 637371 Singapore. [3]School of Chemical Engineering and Department of Energy Science, Sungkyunkwan University (SKKU), Suwon 440-746, Korea.
*Corresponding author. E-mail: michael.graetzel@epfl.ch

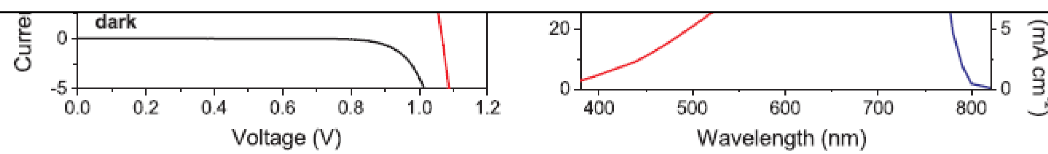
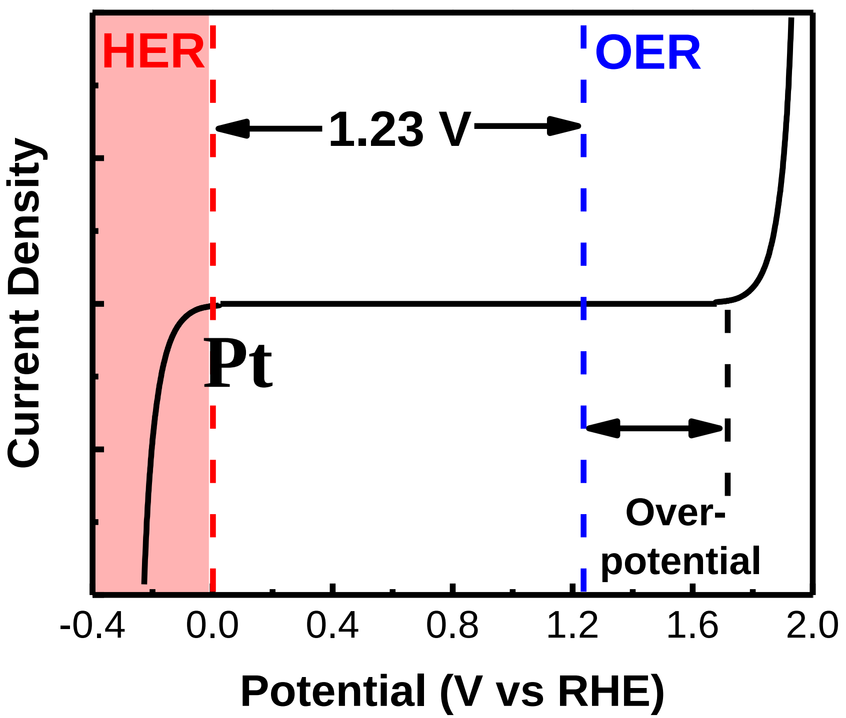


Fig. 1. Performance of perovskite solar cell. (**A**) Current density–potential curve (*J*–*V*) of the perovskite solar cell under dark and simulated AM 1.5G 100 mW cm^{-2} illumination. (**B**) IPCE spectrum of the perovskite solar cell and the integrated photocurrent with the AM 1.5G solar spectrum.

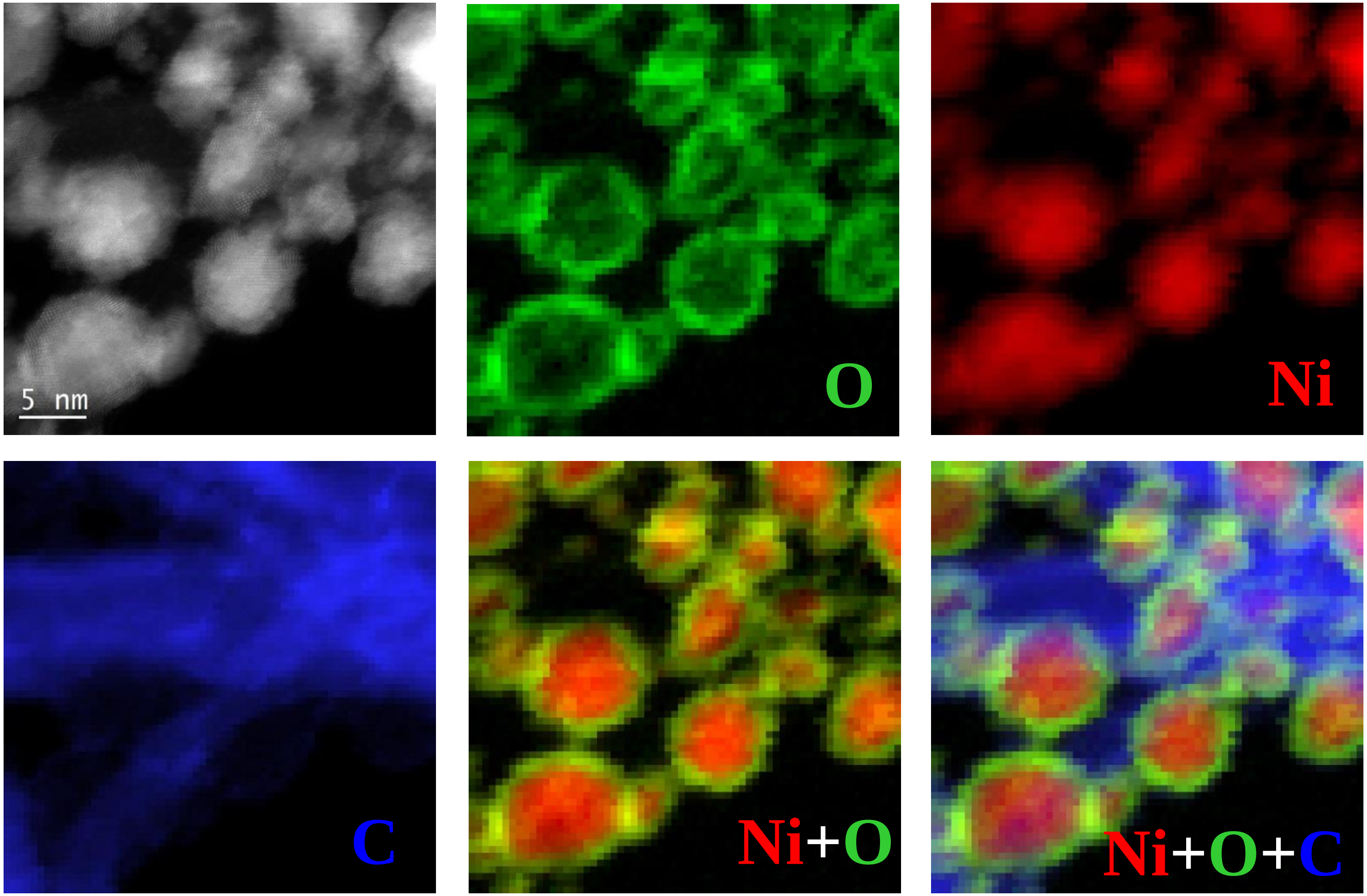
Hydrogen Evolution Reaction (HER) Electrocatalysis

***HER*:** $2H_2O \rightleftharpoons 2OH^- + H_2 + 2e^-$



- 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



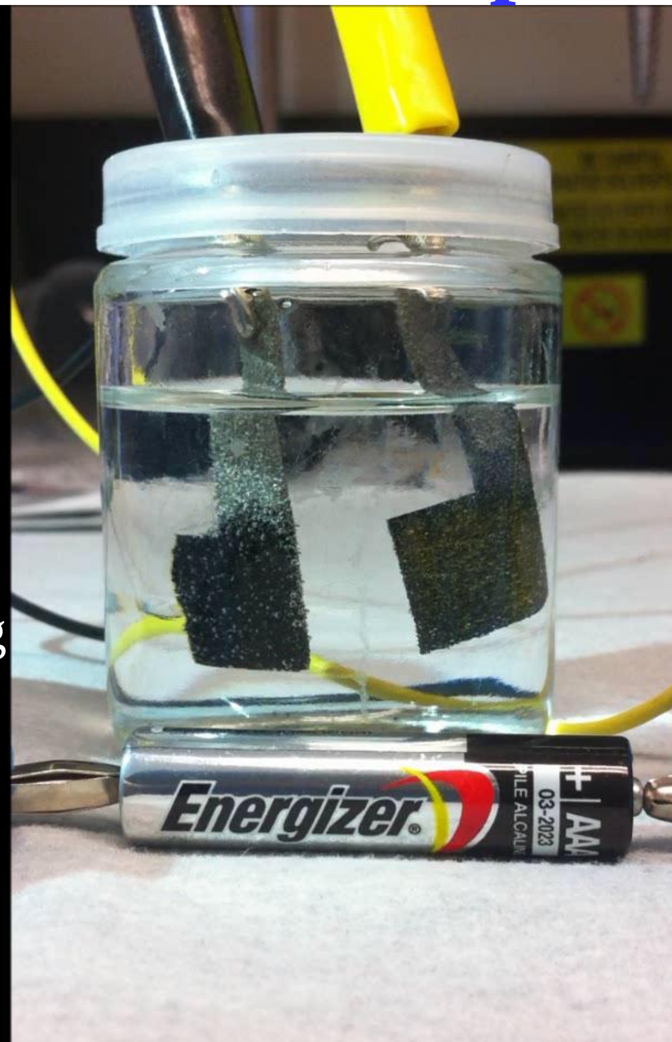
- Ni-NiO interfaces are highly active for HER
- Onset over-potential ~ 0 volt

Gong, M. et al. ***Nature Comm.,*** 2014, 5, 4695

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

Compared to 2V:

~ 25% energy saving



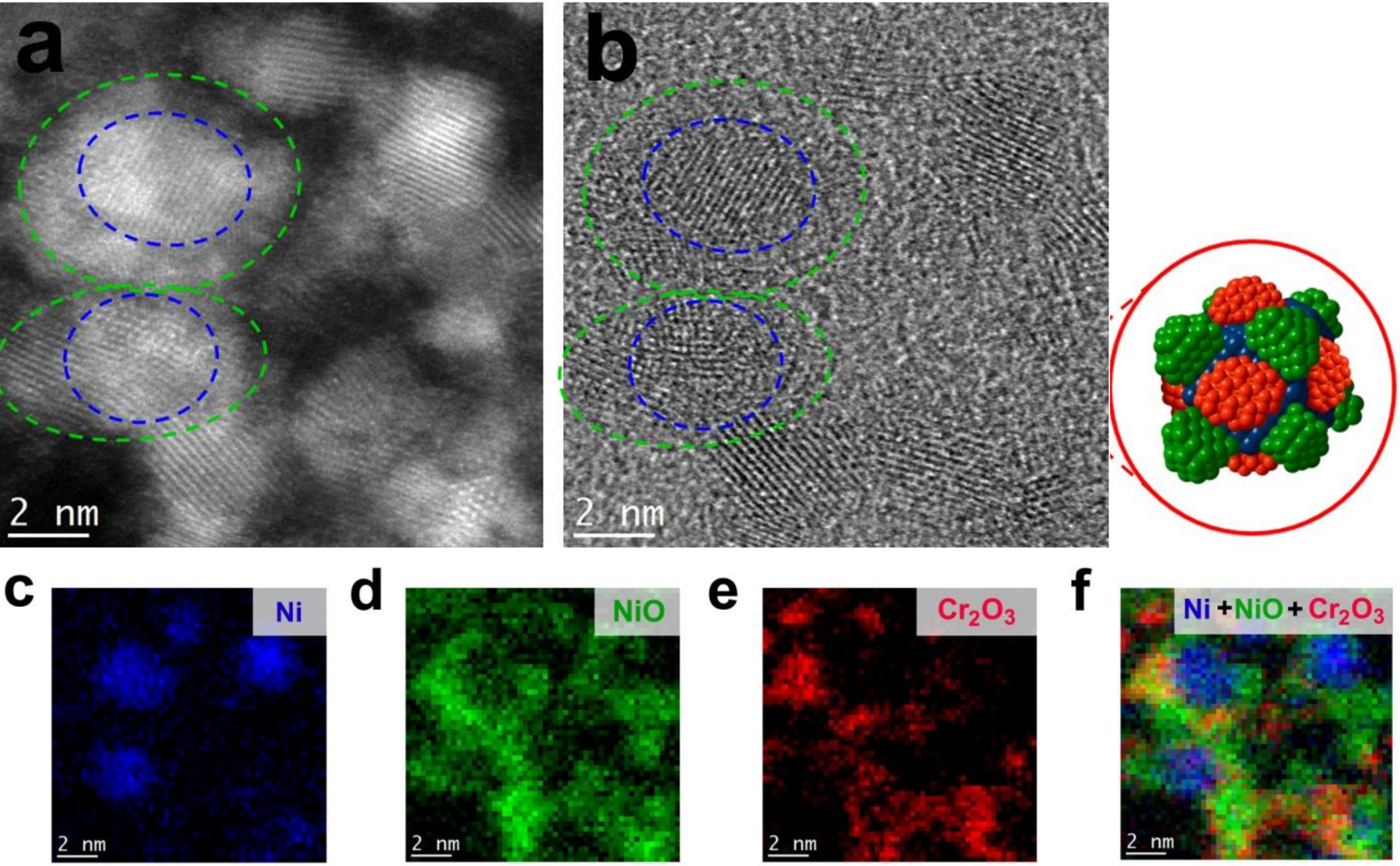
Thermodynamic limit = 1.23 V

Ming Gong, et al., **Nature Comm**.

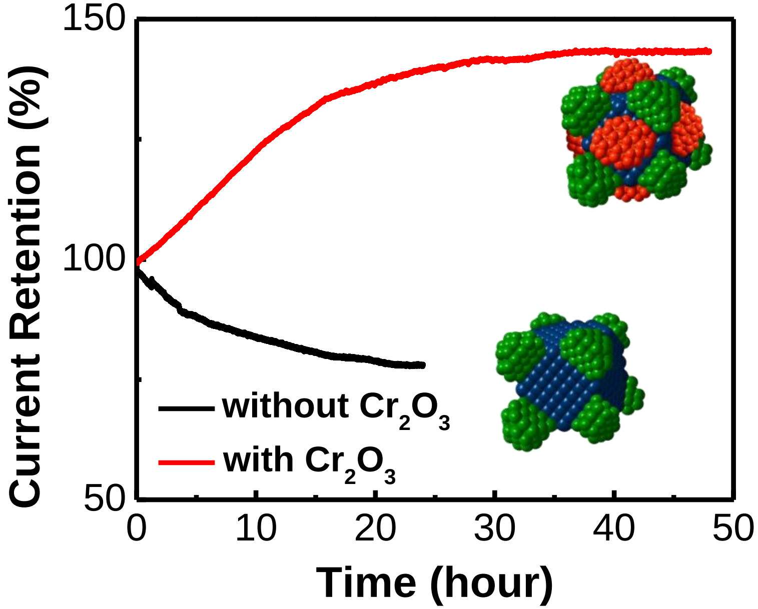
With Dr. Wu Zhou
S. Pennycook,
Oakridge

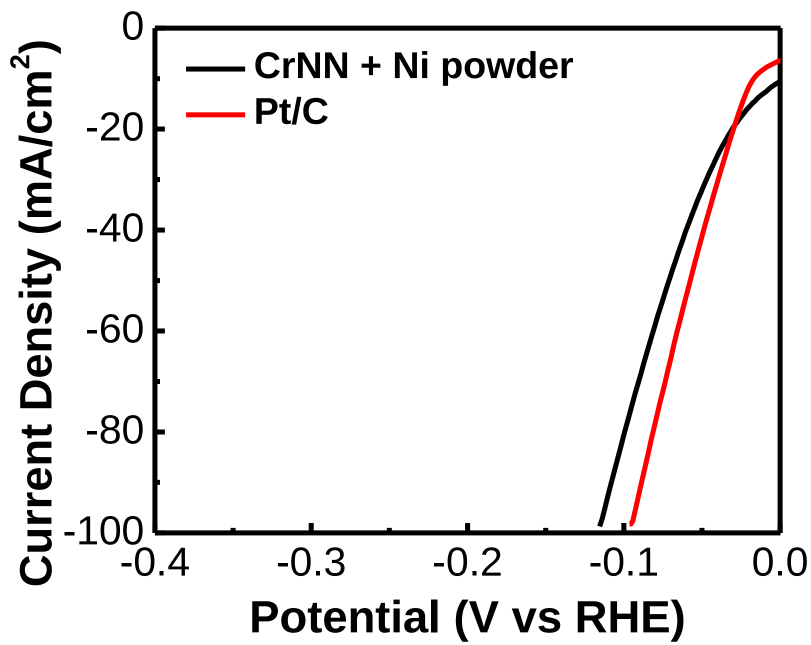
Latest: A Highly Stable Ni-NiO-Cr_2O_3 HER Catalyst

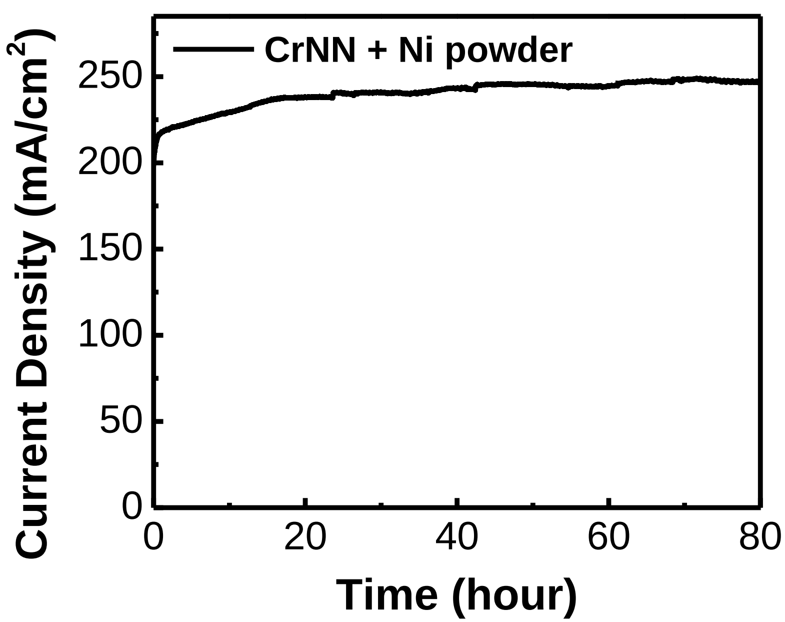
(Ming Gong, et al., **Angew Chemie**, 2015; with ITRI + Prof. BJH)



Ni-NiO-Cr_2O_3 HER Catalyst: Active and Stable



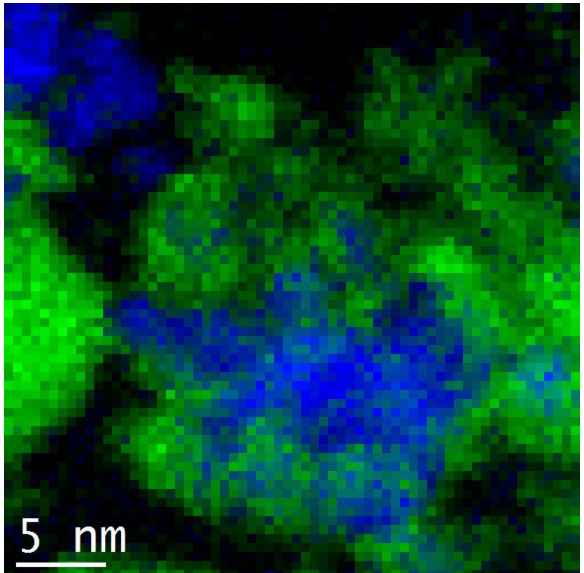




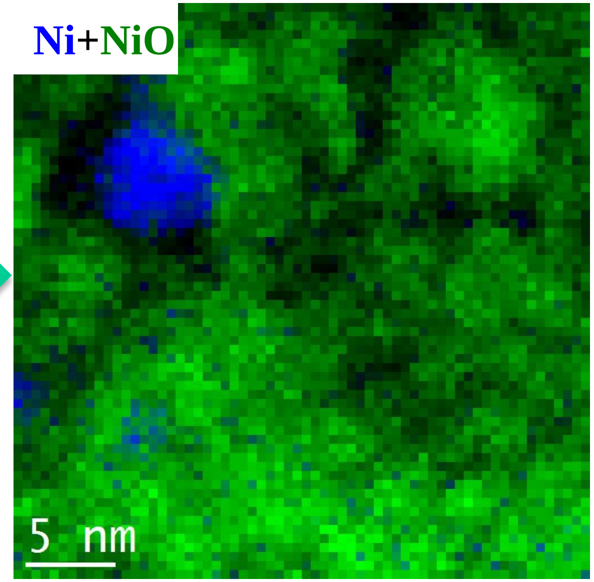
Ming Gong, et al., **Angew Chemie**, 2015.

With Dr. Wu Zhou &
S. Pennycook, Oakridge National Labs;
B. J. Hwang

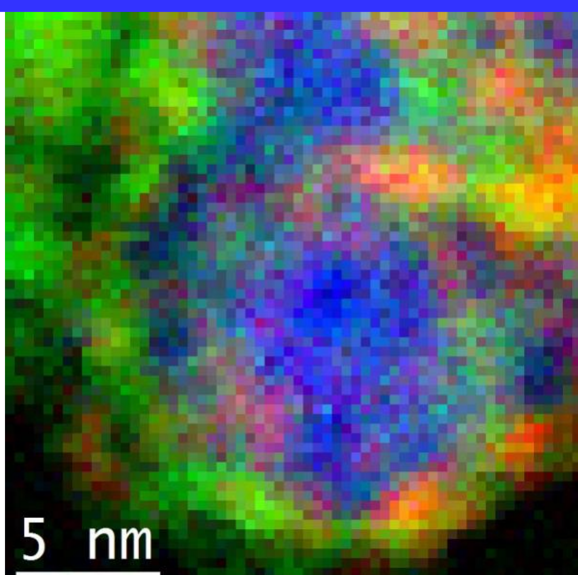
Why is Ni-NiO-Cr_2O_3 Stable for HER



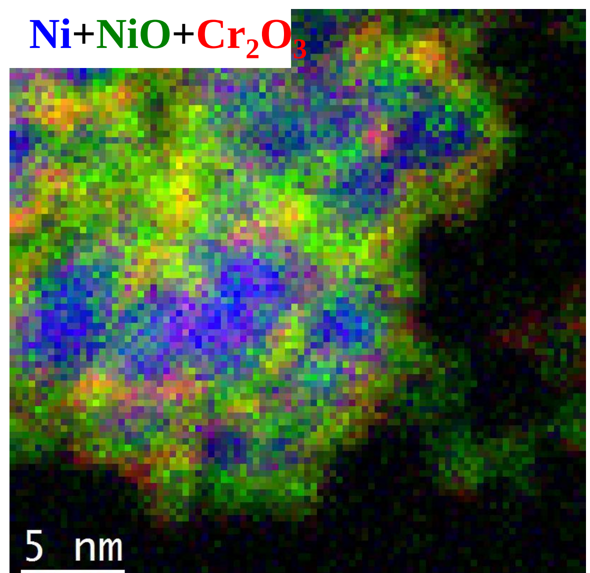
HER



No CrO_x

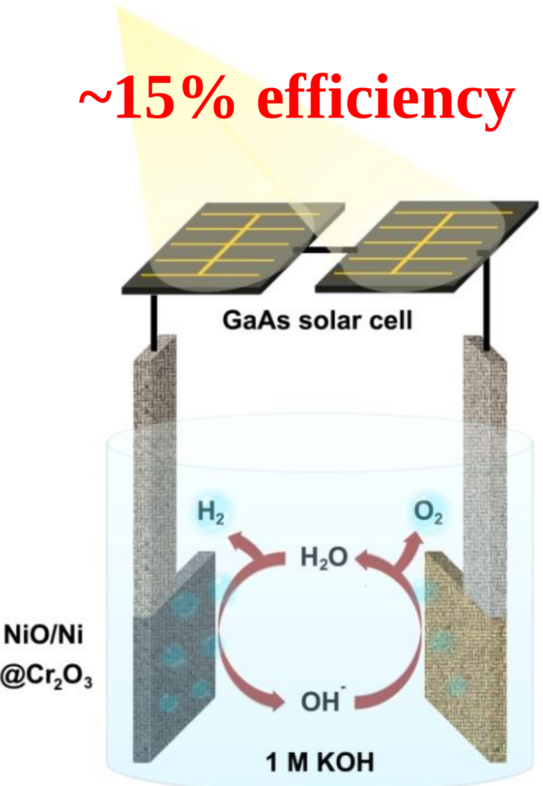


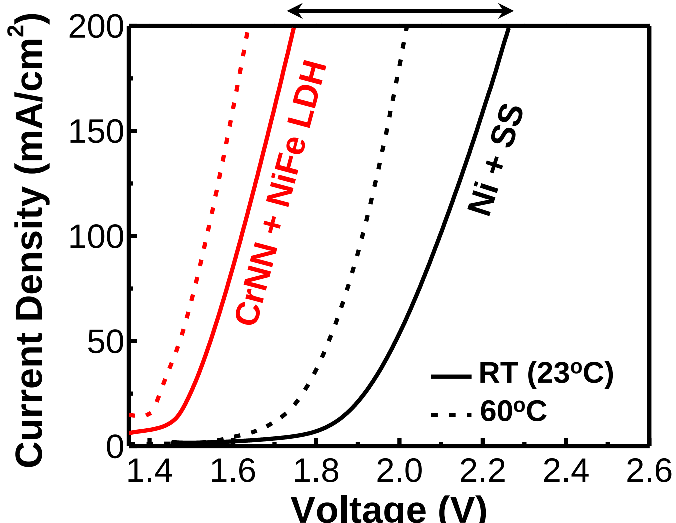
HER

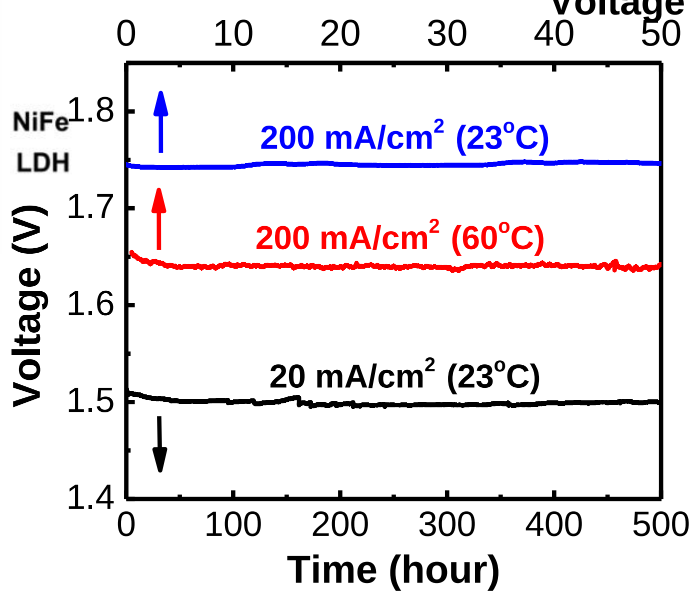


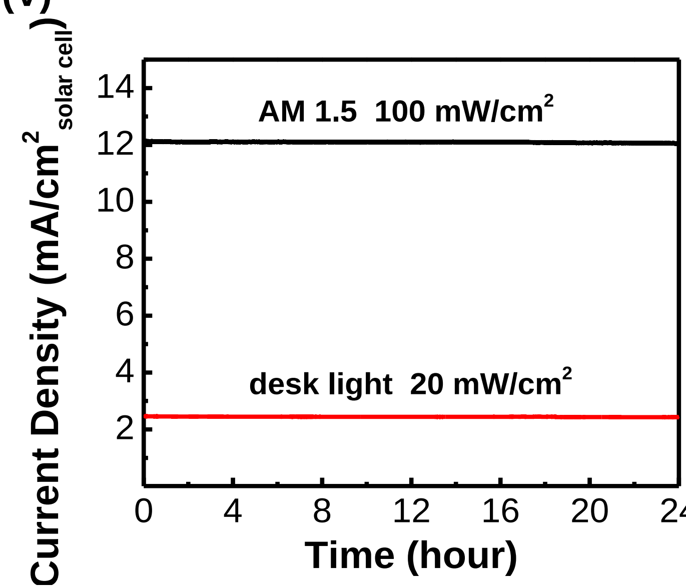
with CrO_x

Stable, Active Water Splitting Driven by GaAs Solar Cells







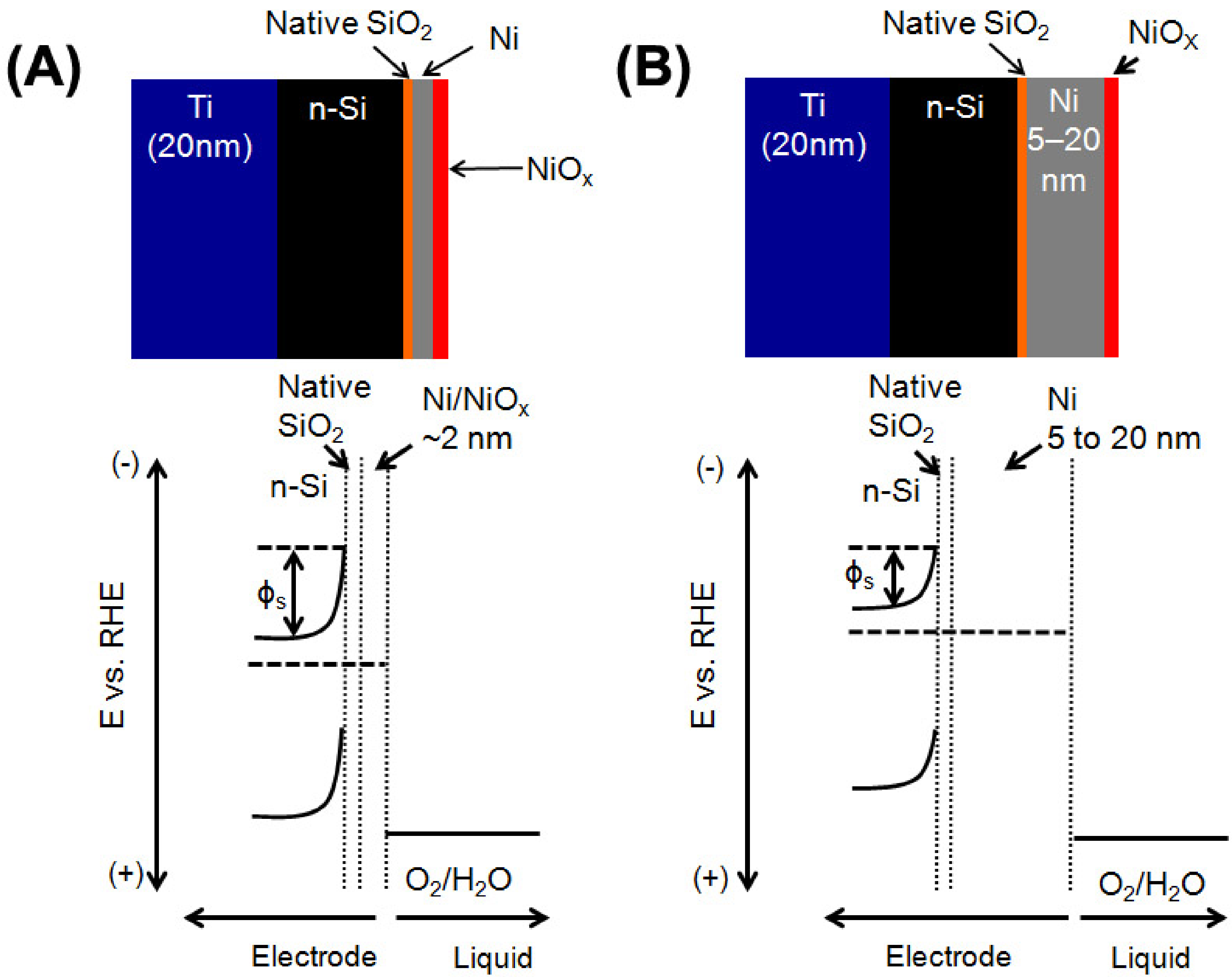


With R. Capusta, S. Cowley
Alta Devices, Sunnyvale
(Hanergy, 汉能)

Desk Lamp Driven Electrolysis

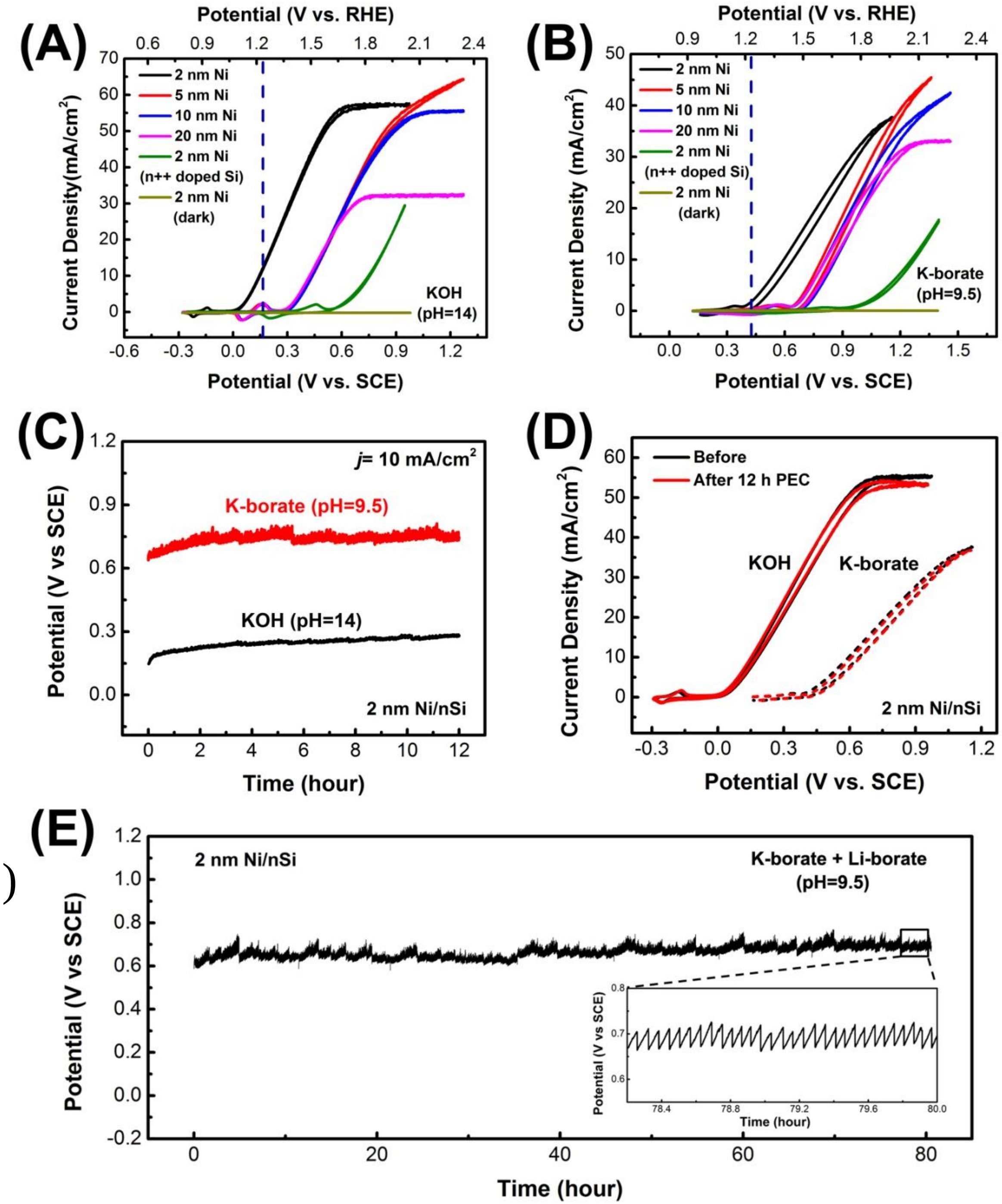
Split water using night light

Ultrathin Ni Metal Film Protection for Si Photoanode

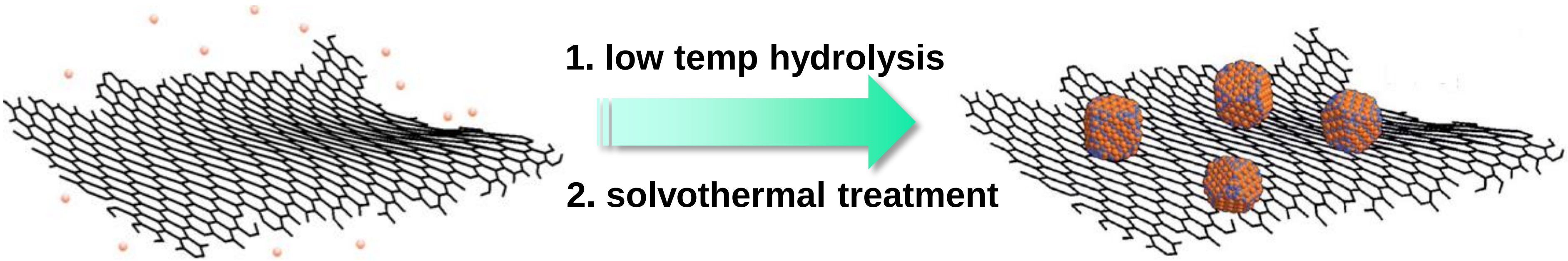


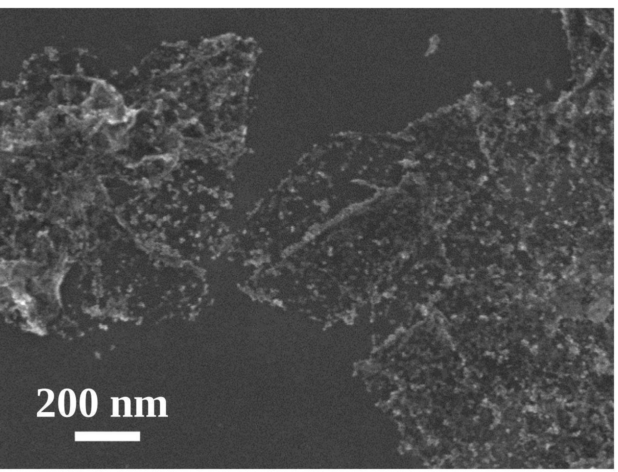
An Ultra-Stable Si Photoanode

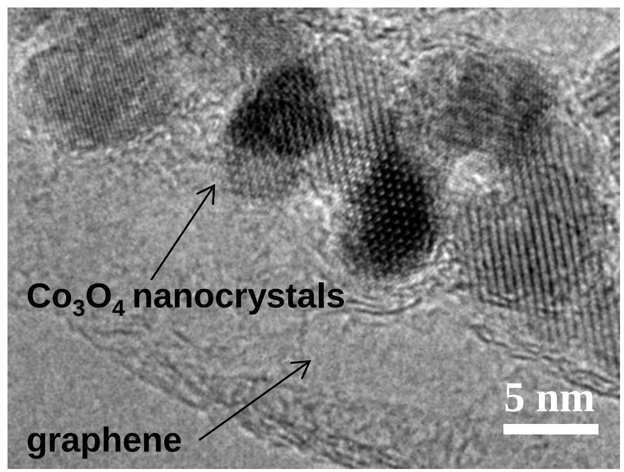
(M. Kenney, M. Gong, et al., **Science**, Nov. 15, 2013)

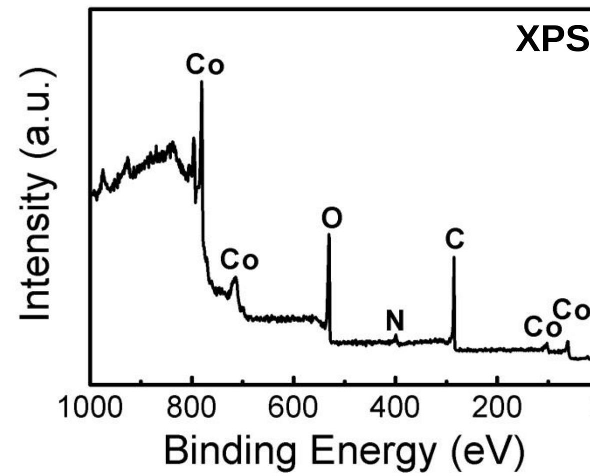


Cobalt Oxide–Graphene Hybrid Materials for Oxygen Reduction Reaction (ORR)





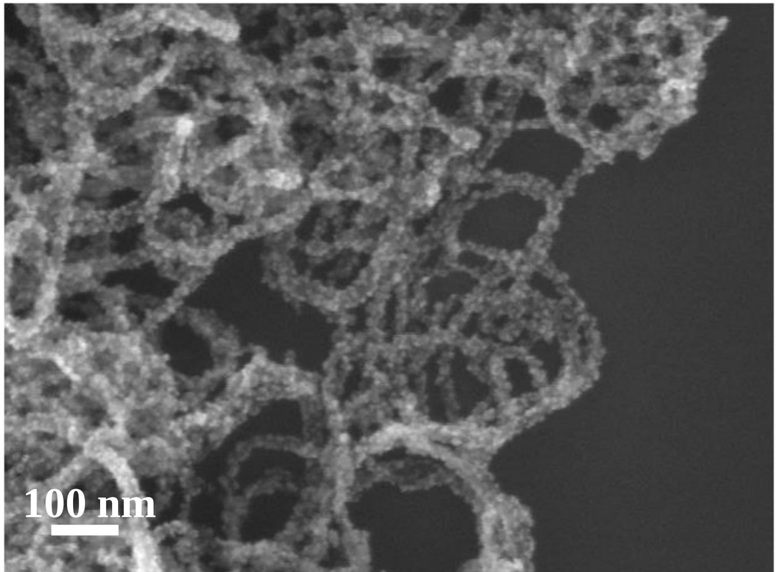


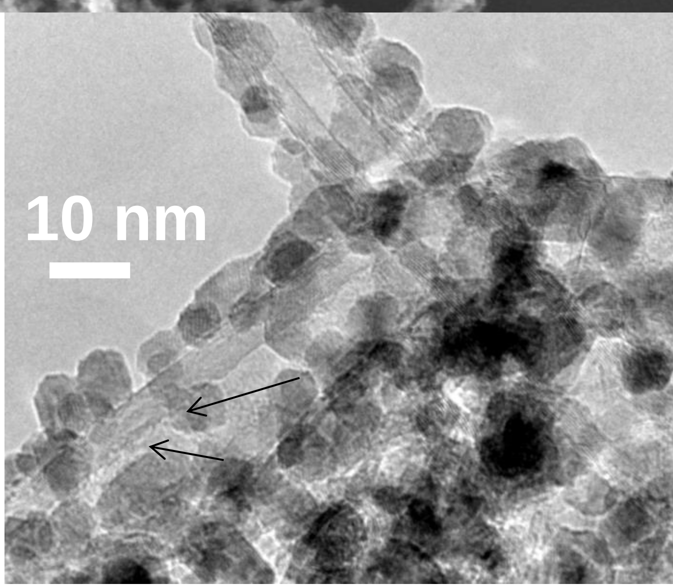


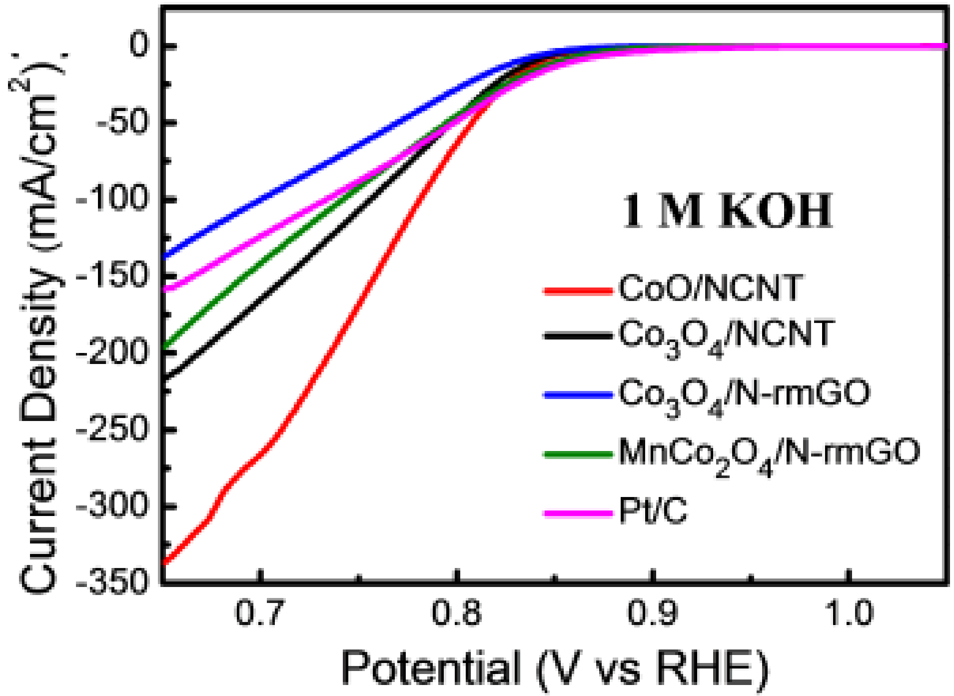
Y. Liang et al., **Nature Mater.** 2011, 10, 780.

CoO/Oxidized-Nanotube Electrocatalyst for ORR

(Y. Liang, Y. Li, H. Wang, et al., **J. Am. Chem. Soc.** 2012)





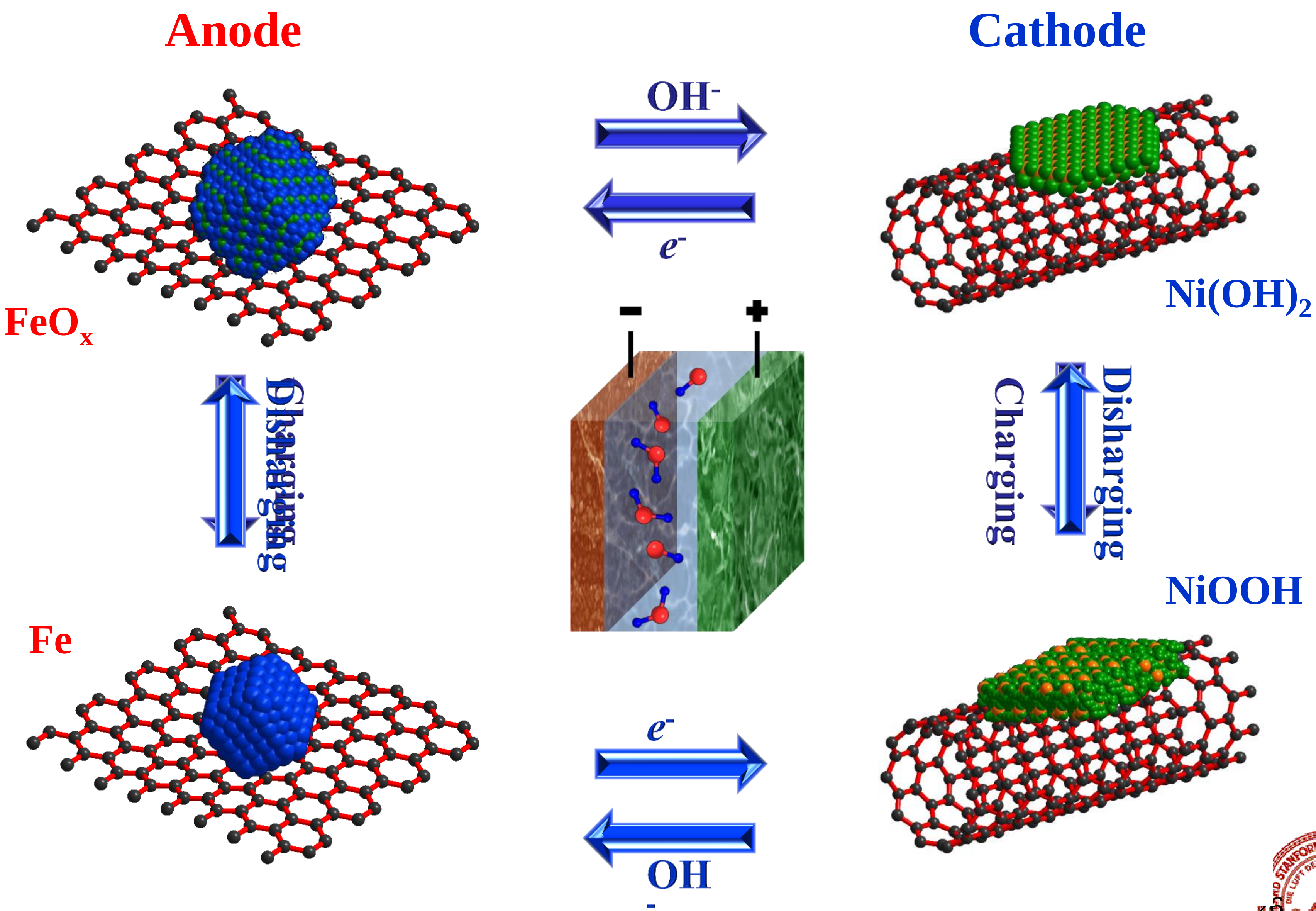


- Metal-oxide/Nanotube hybrid outperform metal-oxide/graphene
- Higher electrical conductivity of oxidized multi-walled nanotubes

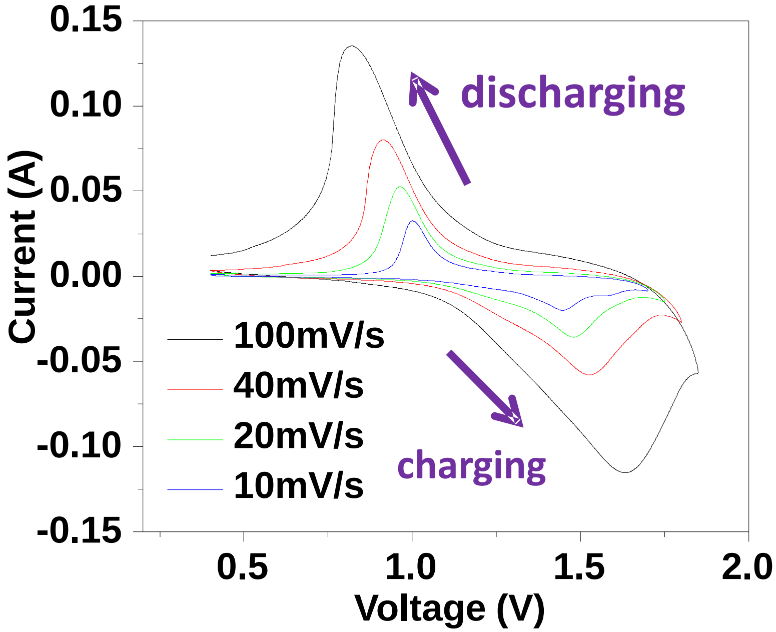
Battery Research
Ultrafast NiFe Alkaline Battery

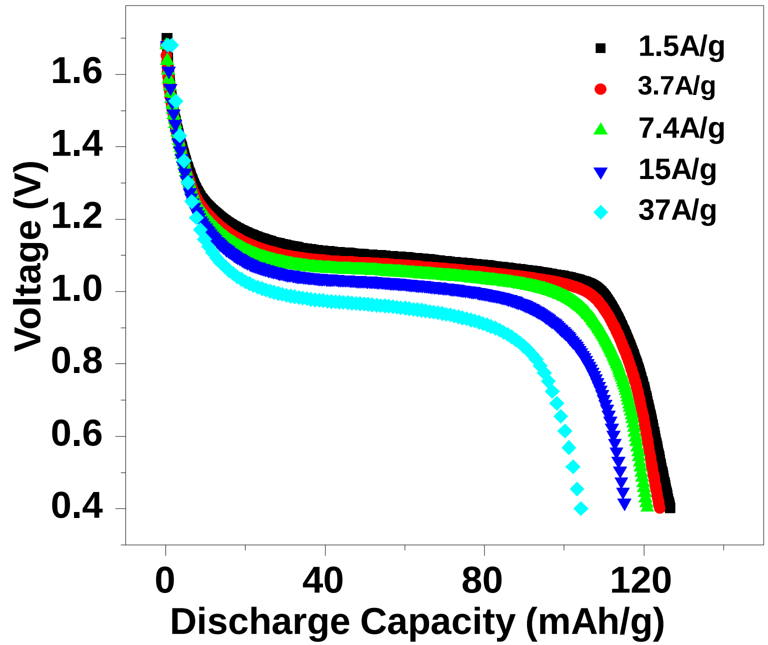
- Making the Ni-Fe Edison battery much faster

Ultrafast Ni-Fe Battery



Ultra-Fast Ni-Fe Battery





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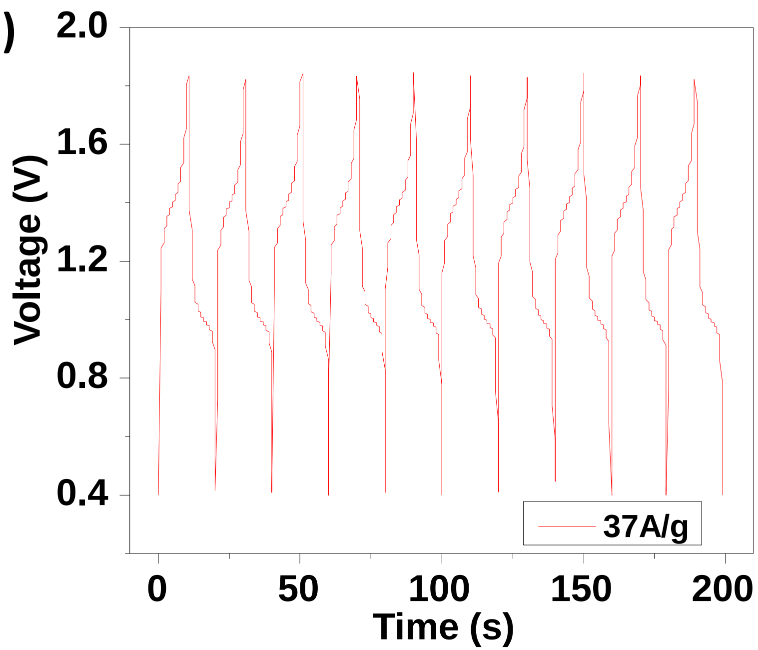


(H, Wang, et al., **Nature Comm., 2012**)

Los Angeles Times

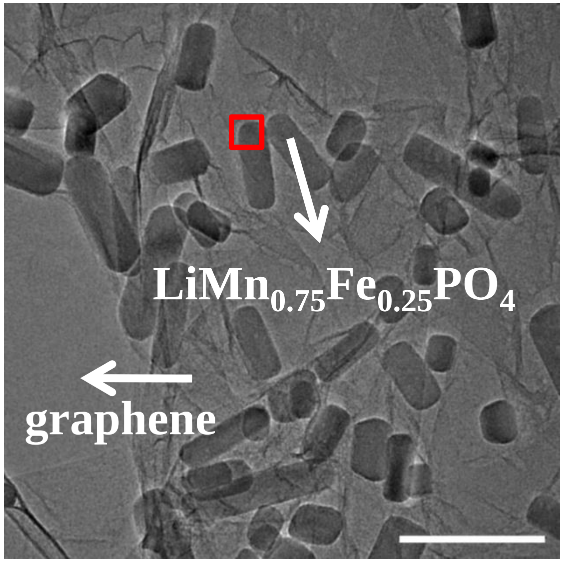
SCIENCE

Stanford researchers update safer, cheaper Edison battery

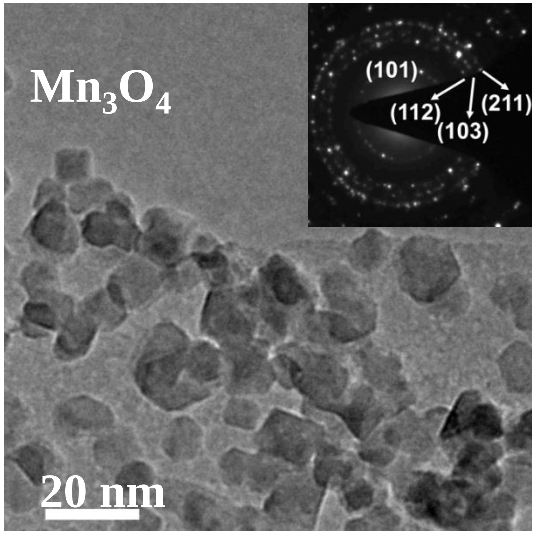
Towards recharging a car in minutes

To demonstrate the reliability of the Edison nickel-iron battery, a battery-powered Bailey was entered in a 1,000-mile endurance run in 1910. (National Park Service / June 26, 2012)

Lithium Ion Battery Materials Grown on Graphene



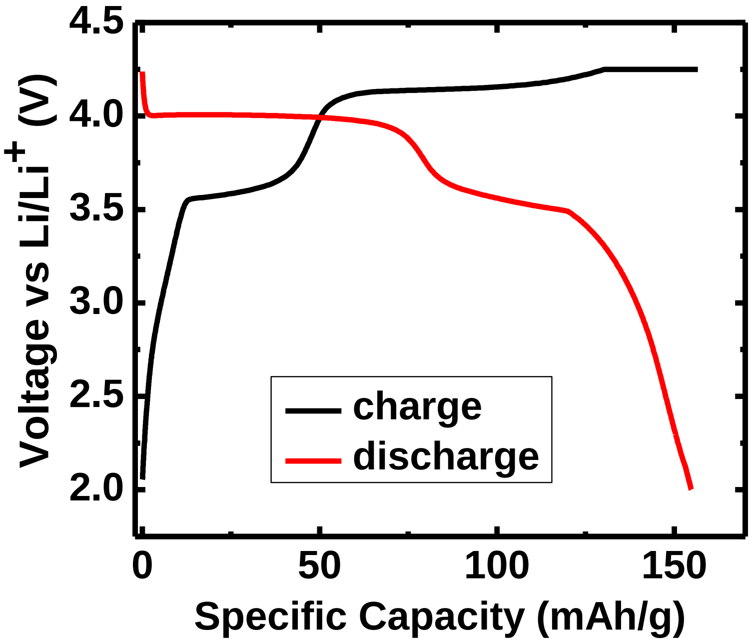
- Cathode Material

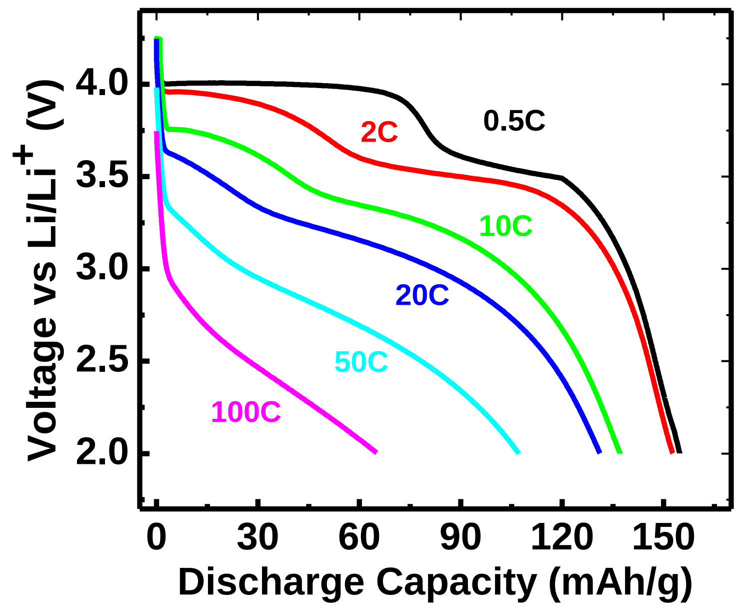


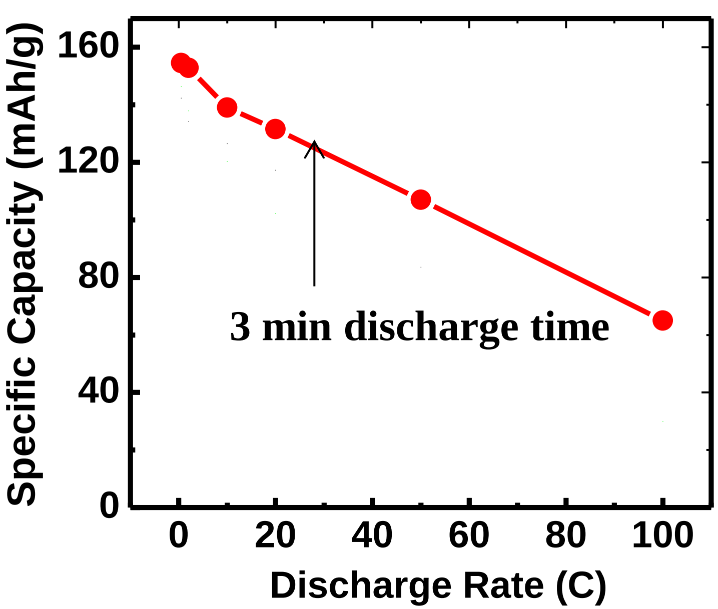
- Anode Material

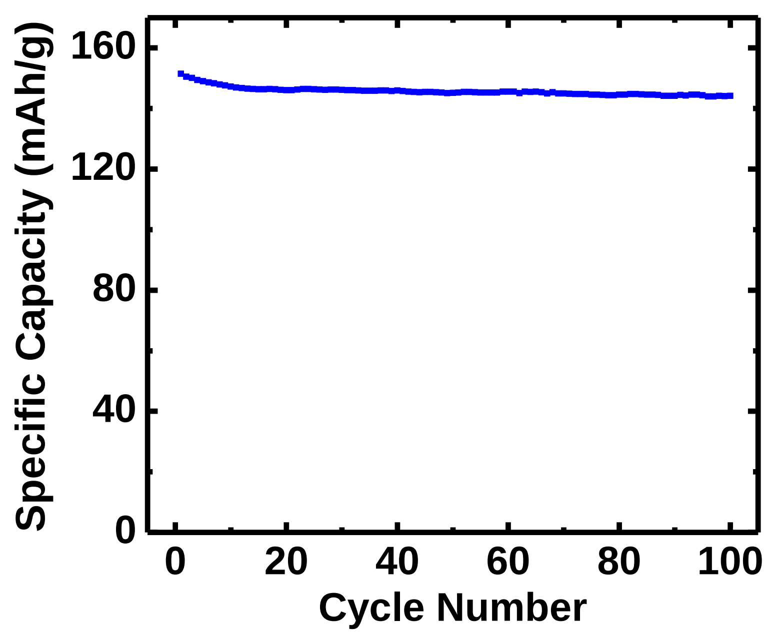
• High rate, high capacity

$LiMn_{0.75}Fe_{0.25}PO_4$ /GO as a Fast, High-Voltage, Stable Cathode Material for Li Ion Battery





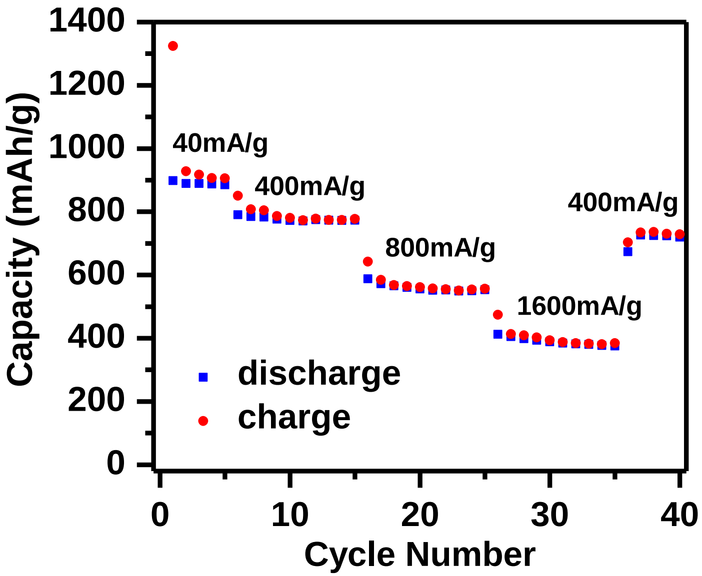


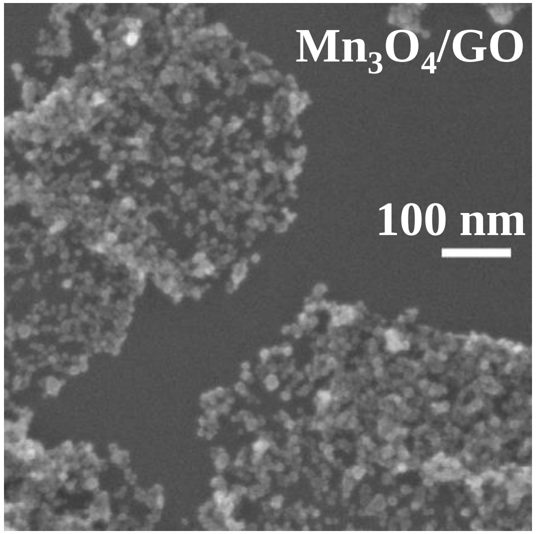


(H. Wang et al., with Yi Cui group, **Angew Chemie**, 2011)

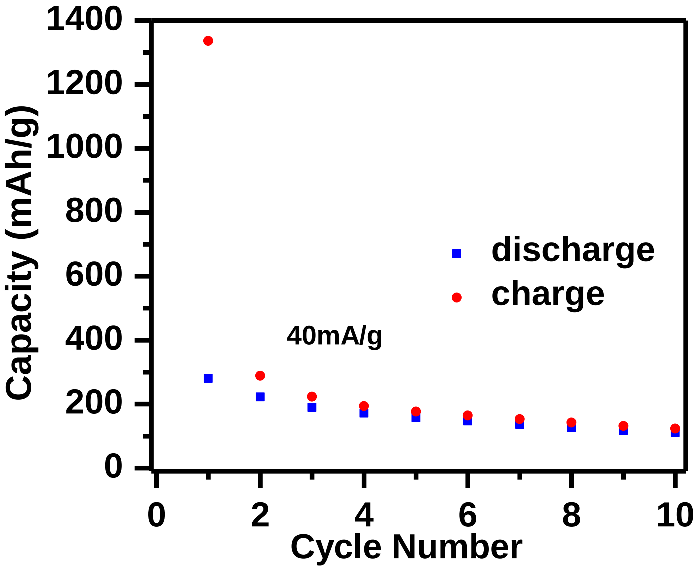
Mn_3O_4/Graphene Anode

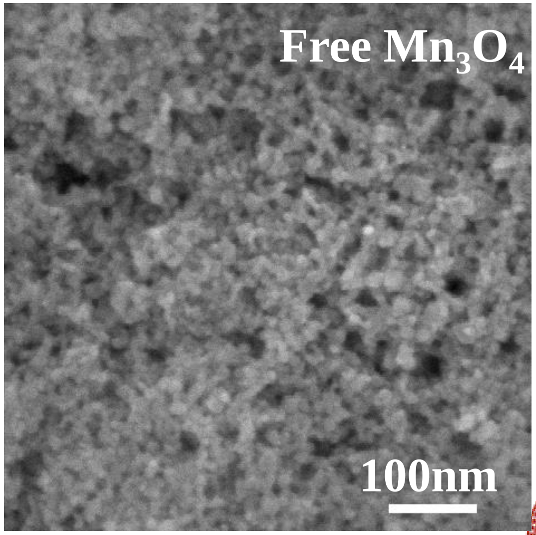
Graphene hybrid electrode:





Conventional mixture electrode:





Wang*, Cui* et al., ***J. Am. Chem. Soc***. 2010, *132*, 13978.

Electrocatalysts for Rechargeable Zn Air Batteries

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

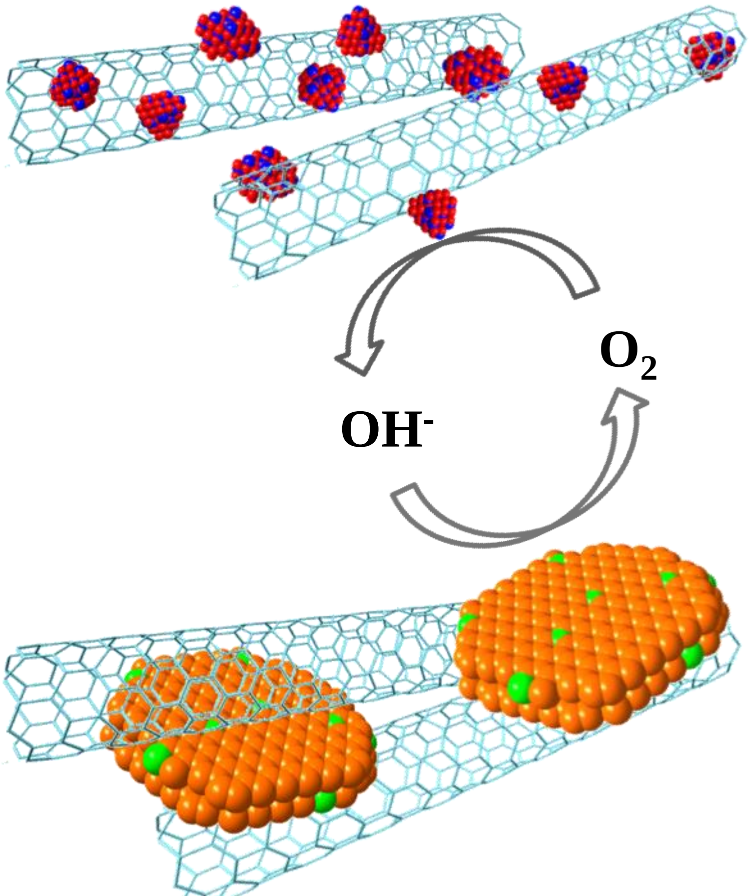
Cathode: $$O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^-$$ **(ORR/OER)**

ORR: oxygen reduction reaction
OER: oxygen evolution reaction

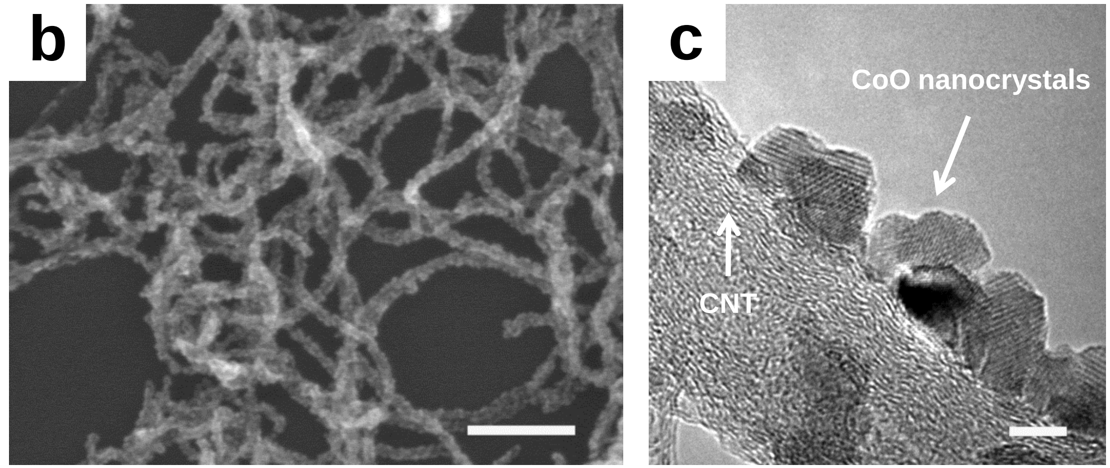
Need more active and stable electrocatalysts for ORR & OER to increase energy efficiency

Electrocatalysts for Zn-Air Oxygen Electrodes

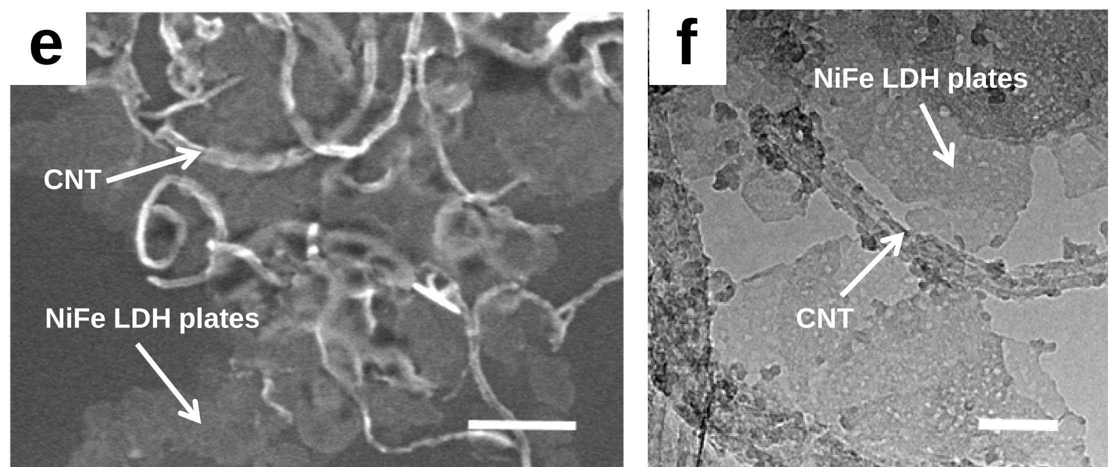
ORR: **CoO/N-CNT**



OER: **NiFe LDH/CNT**

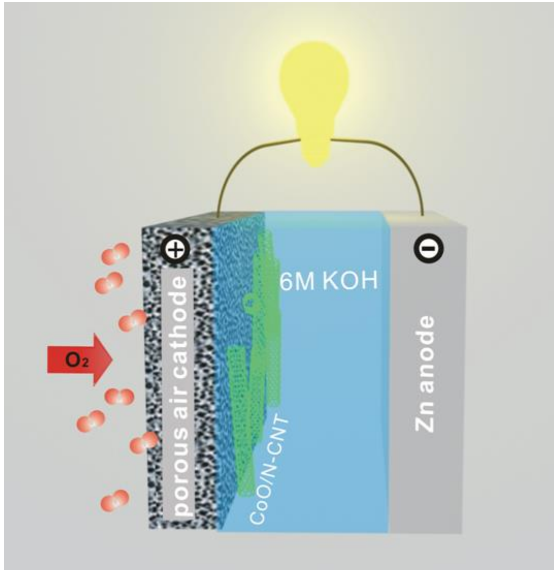


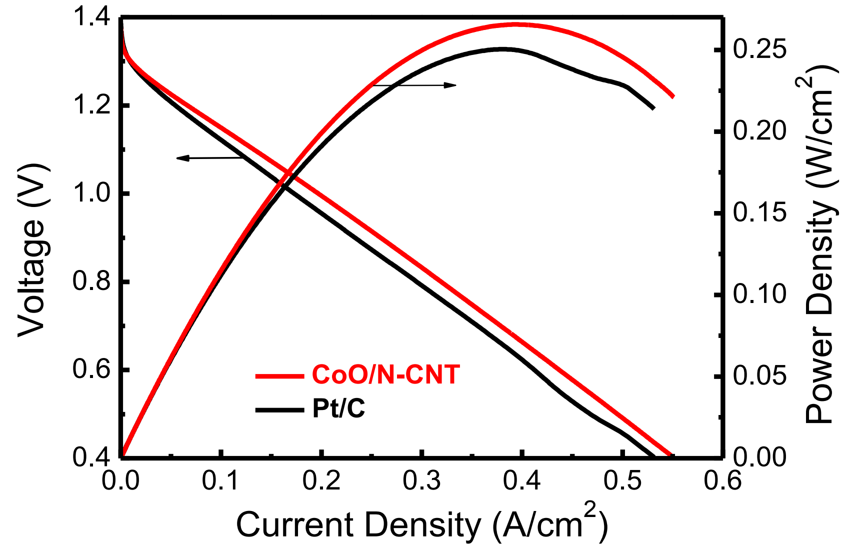
(Y. Liang, **Nature Mater.** 2011, **JACS**, 2012)

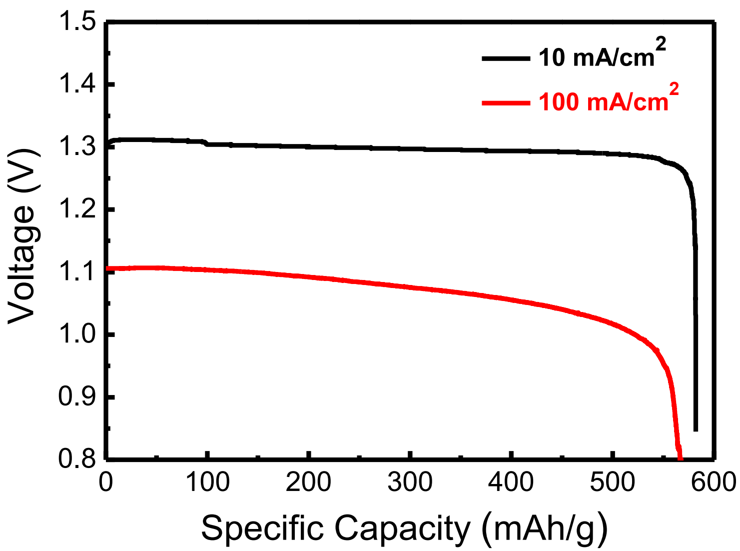


(M. Gong, **JACS**, 2013)

Primary Zn-Air Battery



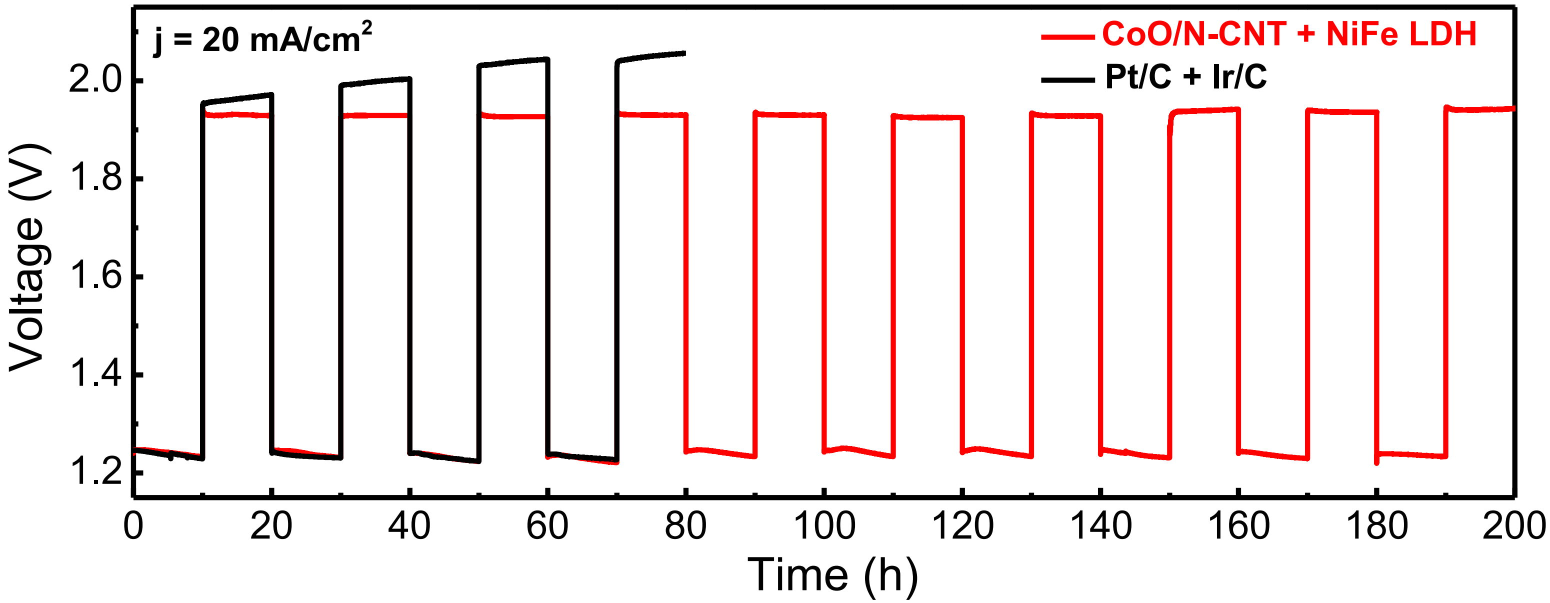




- High discharge peak power density ~265 mW/cm²
- Current density ~200 mA/cm² at 1 V
- Energy density > 700 Wh/kg.

Y Li et al., **Nature Comm.**, 2013

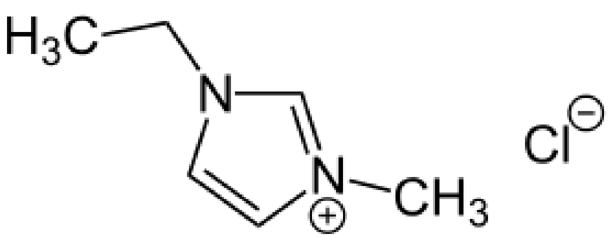
High Performance Rechargeable Zn-Air Battery



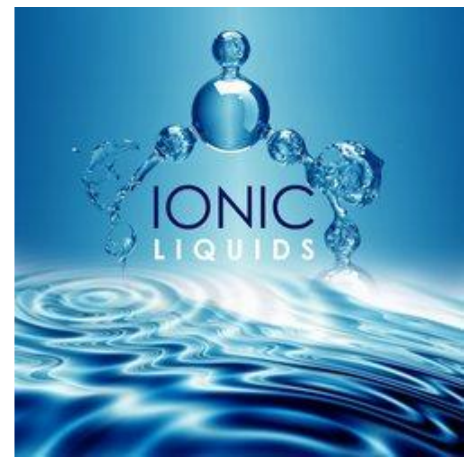
- Low charge-discharge voltage polarization of ~ 0.70 V at 20 mA/cm^2
- High reversibility and stability over long charge and discharge cycles (10 h discharge time)

Y Li et al., **Nature Comm.**, 2013

Aluminum + Graphite + Salts = Al Ion Battery



+ $AlCl_3$ =



1 : 1.3

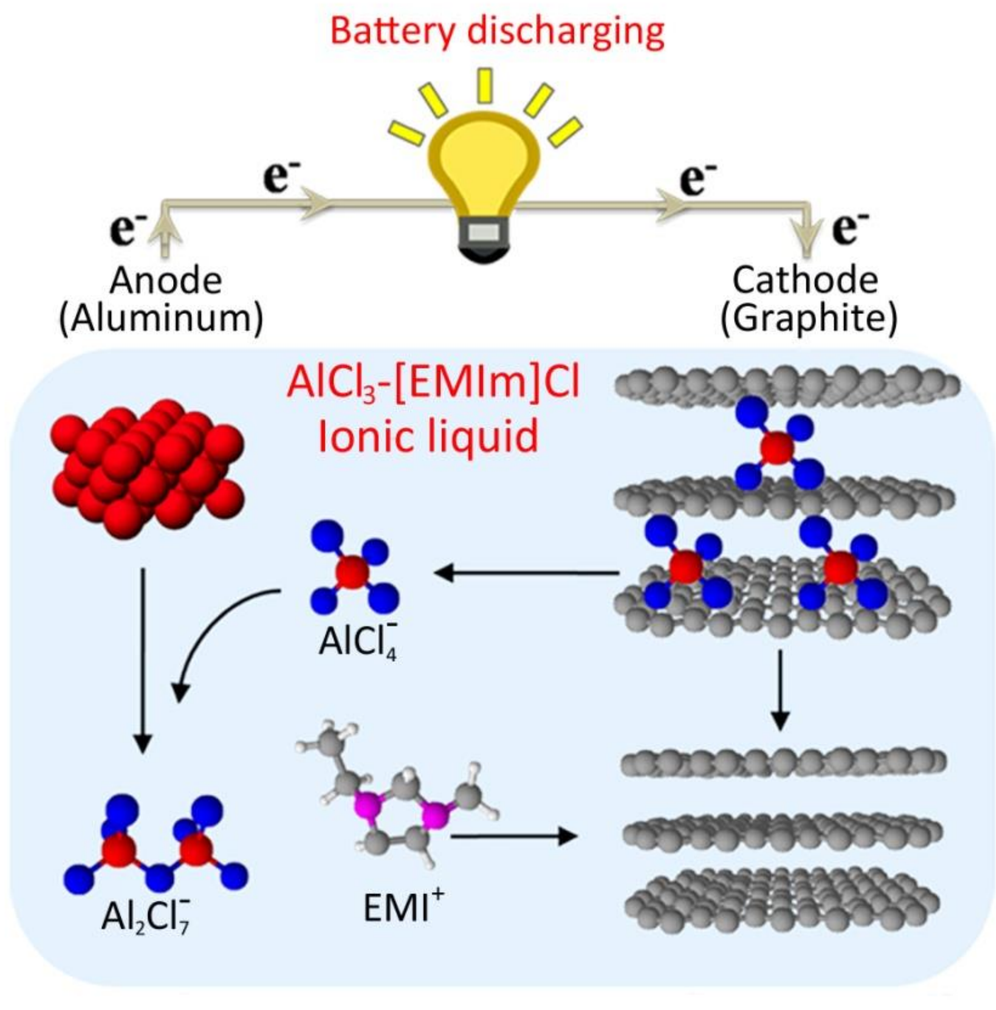
Abundant anions in ionic liquid solution:

$AlCl_4^-$ & $Al_2Cl_7^-$

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

Collaboration with ITRI Taiwan & Prof. B. J. Hwang.

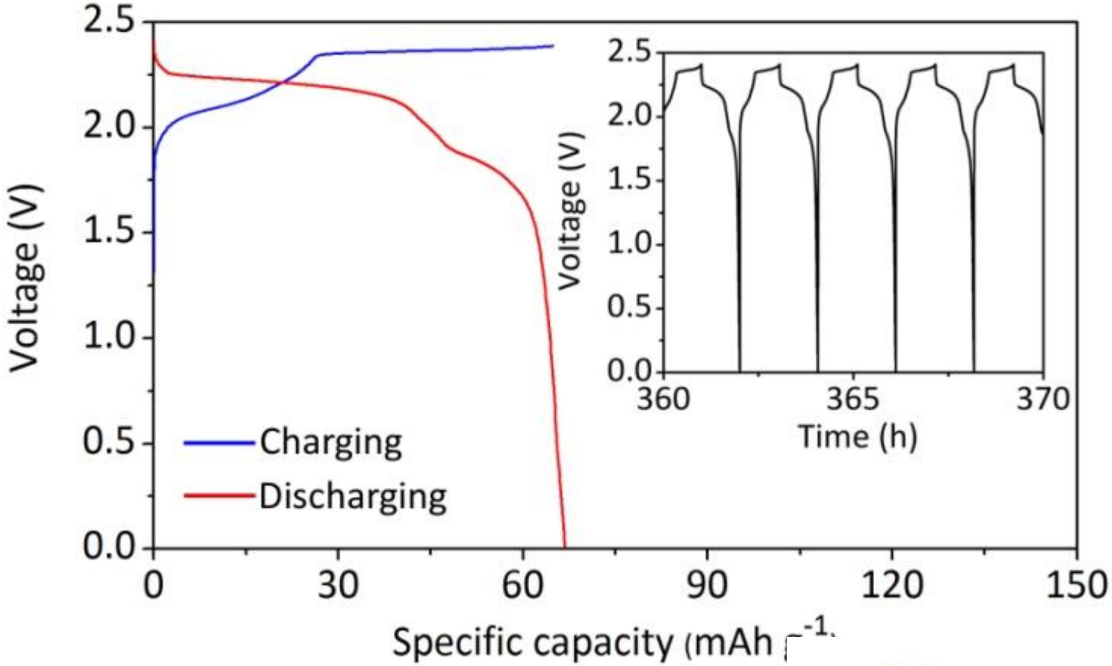
Al Redox + Graphite/Anion Redox Reactions

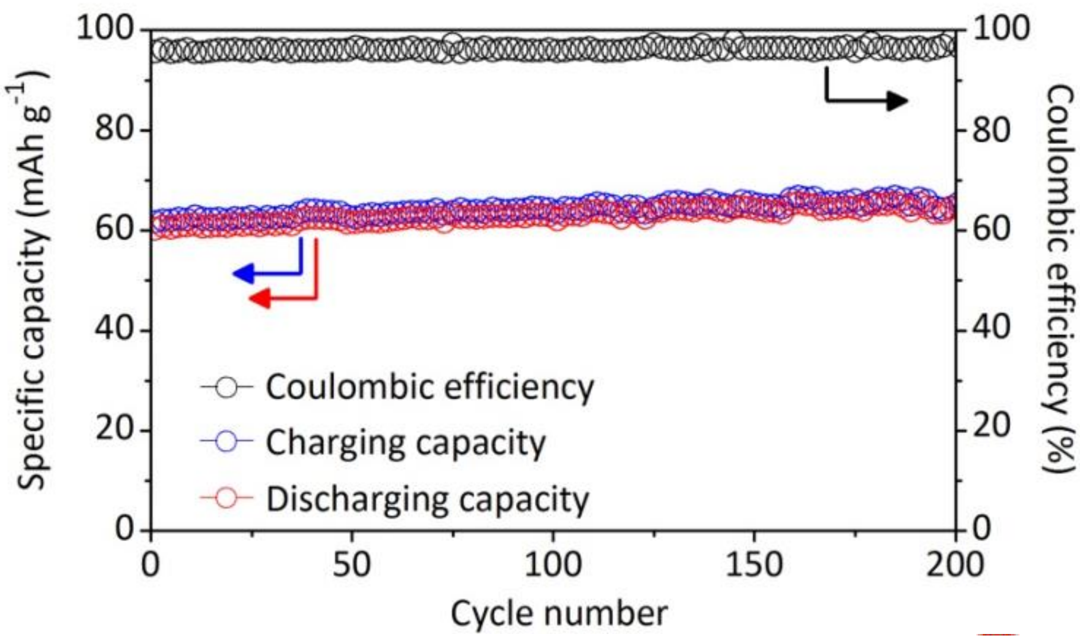


$4Al_2Cl_7^- + 3e^- \rightleftarrows Al + 7AlCl_4^-$ $\qquad$ $C_n + AlCl_4^- \rightleftarrows C_n[AlCl_4] + e^-$

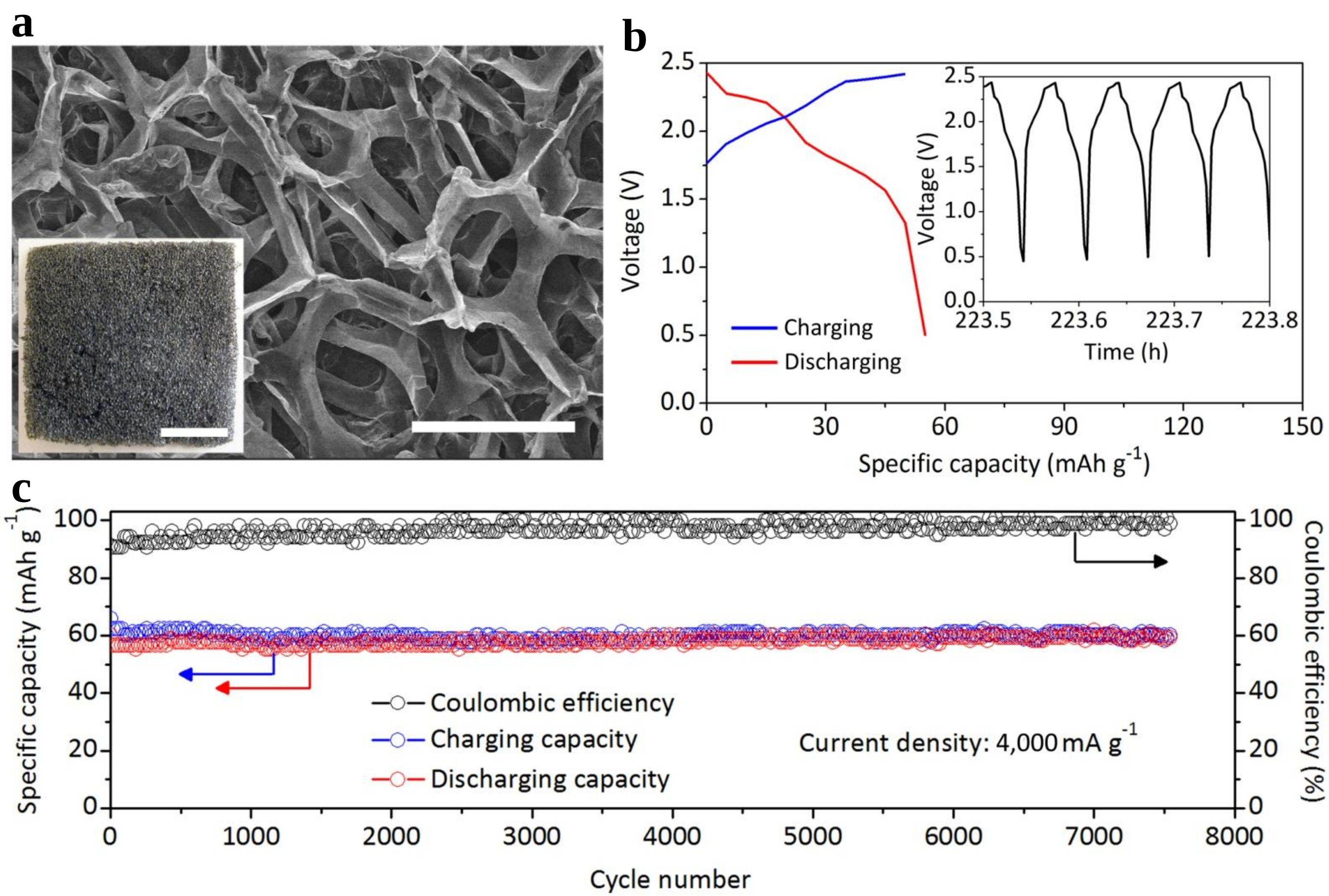
V ~ 2.0 volt

Al Ion Battery with Graphite Paper Cathode

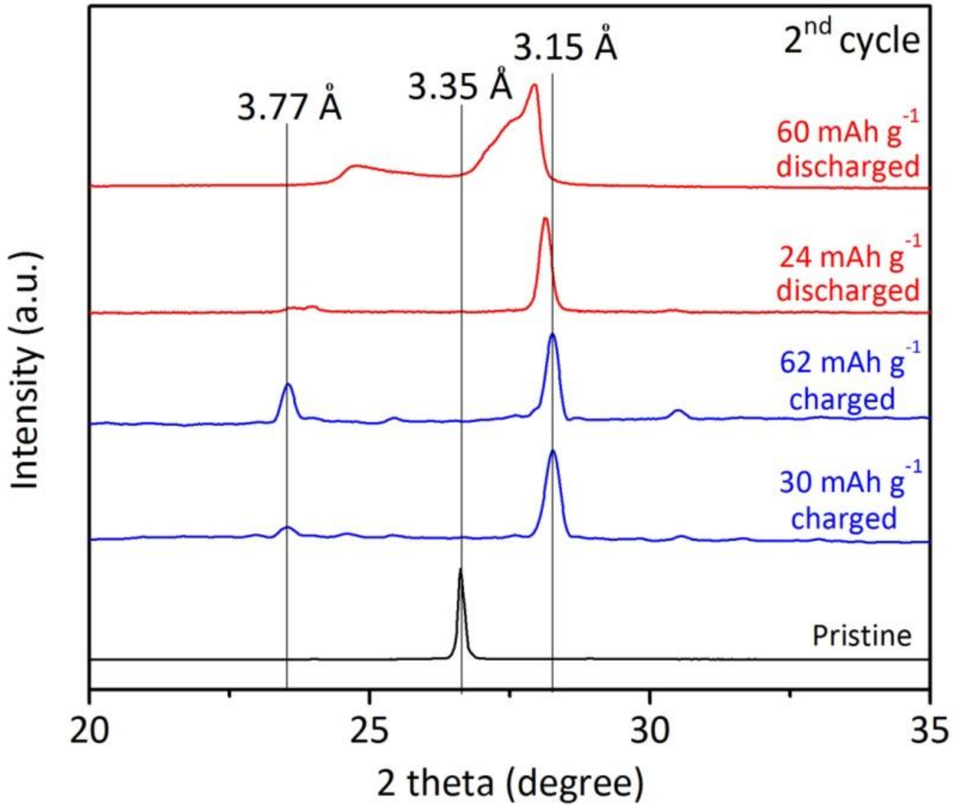


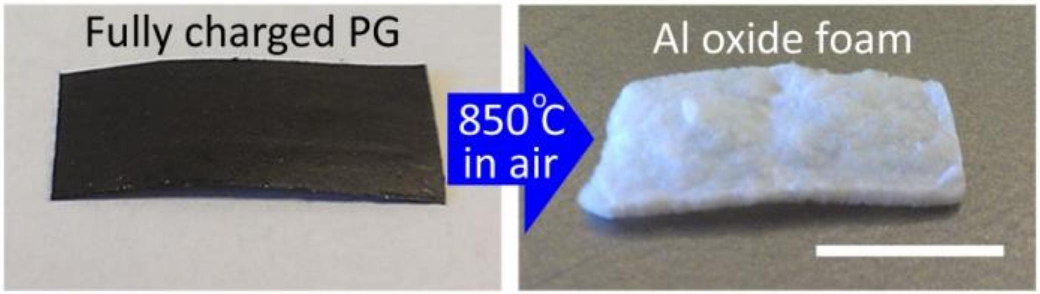


Fast Charging of Al Ion Battery with Graphite Foam Cathode

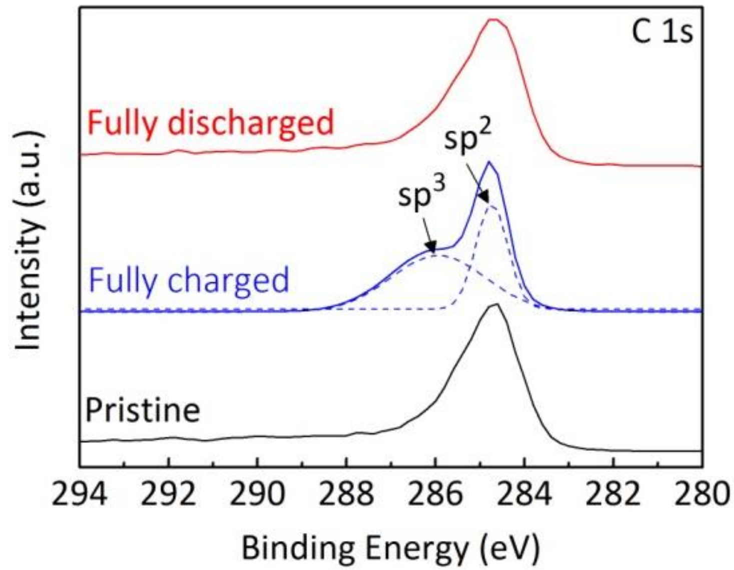


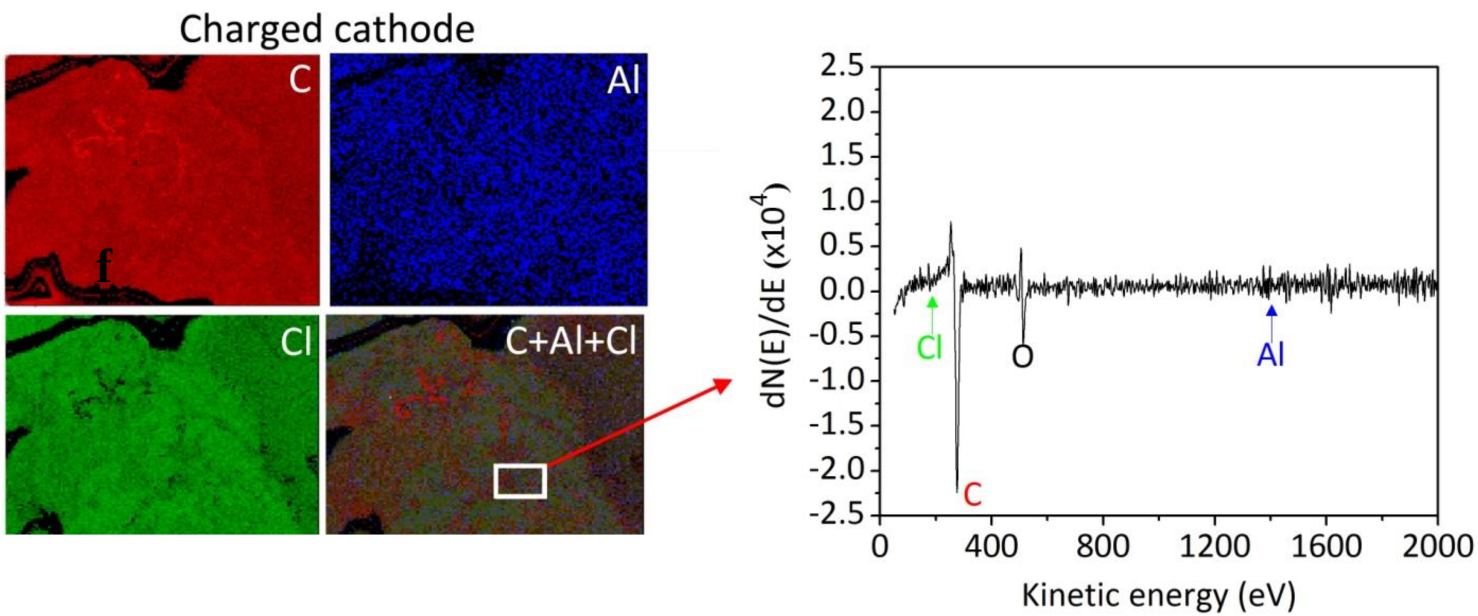
Al Anion/Graphite Paper Intercalation



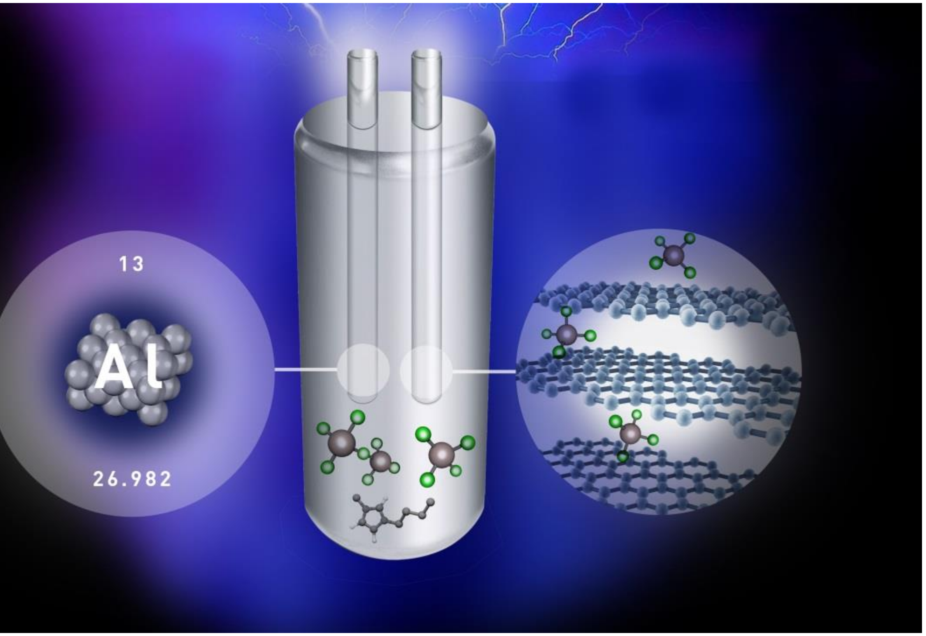


$AlCl_x^-$ Intercalation During Charging/Oxidation of Graphite





Potential of Al Battery



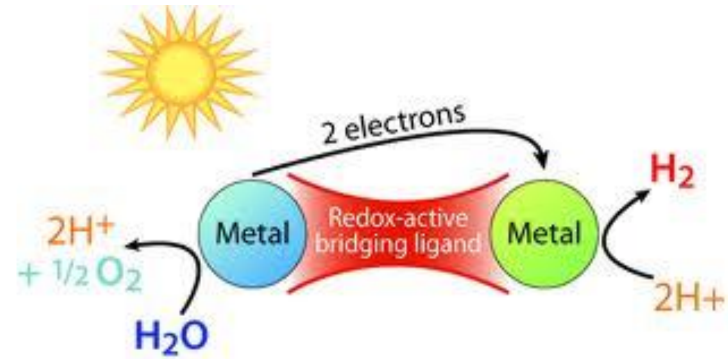
- Low cost:
- Uses earth abundant Al and C.
- Ionic liquid: 20$/kg at large scale quoted by a chemical company.
- Safe, non flammable
- Fast charging
- Long cycle life, > 10,000
- Energy density up to ~ 62.5 wh/kg with active materials, higher than supercapacitors;
- Pb acid replacement

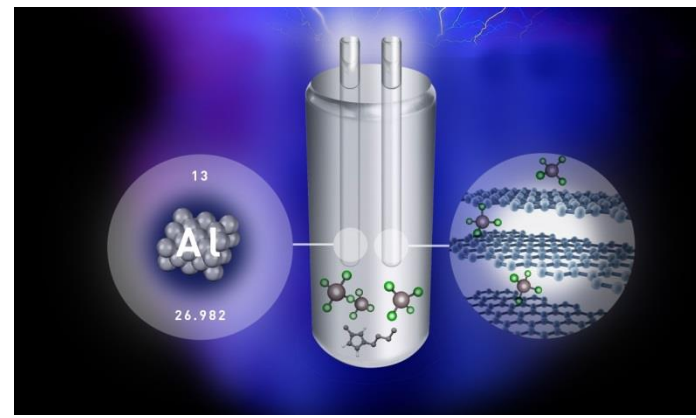
Applications:

- Grid storage
- Home use
- Mechanical tools

Clean Energy for a Sustainable Future

Hydrogen fuels





Convert wind- and solar-energy into:

- H_2 and methane fuels
- Energy stored in low cost, safe, high performance batteries

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