Affordable electrolyser technology based on transition metal catalysts for energy storage applications

Newton Agham Fund

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Background

The highly variable and intermittent nature of renewable enery sources necessitates the integration of efficient energy storage systems.The generation of hydrogen gas via **water electrolysis** proves to be a **promising energy storage technology** because of the highly efficient conversion of H_2 to electricity, and good energy density of H_2 relative to most batteries.

This project aims to build an **affordable anion exchange membrane (AEM) water electrolyser** This water electrolyser will be composed of anodes and cathodes based on **transition metal catalysts**, which are developed by the **University of the Philippines**, and of an **AEM** developed by the **Newcastle University**. The cost of this system can be reduced by 30% due to the non-usage of noble metal catalysts, more commonly used in polymer electrolyte membrane (PEM) electrolysers.

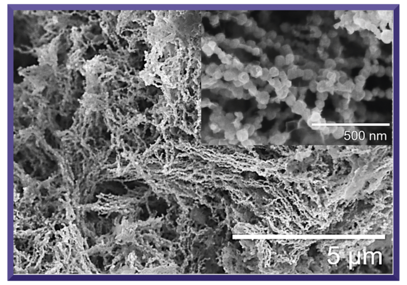
Methods

Herein, various electrocatalysts for hydrogen evolution reaction (**HER**) on the cathode and oxygen evolution reaction (**OER**) on the anode have been synthesized and characterized.

For HER, **loose powders** of **Ni**, **Co**, and **Ni-Co**, as well as **carbon fiber-supported** Ni, Co, and Ni-Co, catalysts were produced. For OER, **Co_3O_4-based catalysts** were prepared through **ethanol-assisted hydrothemal method**, and **solution combustion**. These electrocatalysts have been characterized both morphologically and structurally, and some have been tested for their electrochemical performance.

Electrocatalysts for HER

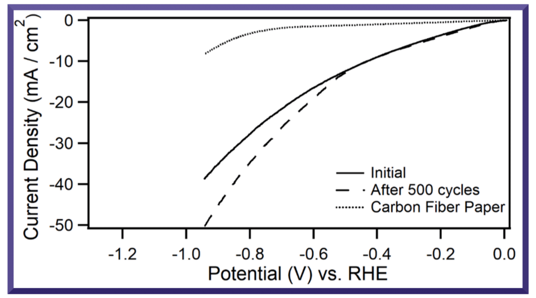
Bimetallic Ni-Co catalyst prepared through chemical reduction of Ni and Co salts in ethylene glycol using hydrazine



Material properties

Ni-Co nanoparticles with a mean diameter of 53.16 nm containing 49.47 wt % Ni and 50.53 wt% Co in two phases: fcc Ni and fcc Co

(SEM images of the Ni-Co NPs)



HER catalytic activity

Onset overpotential: **77 mV** (vs. RHE)

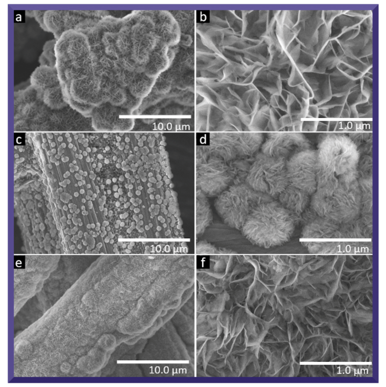
Overpotential at 10 mA cm^{-2}: **430 mV** (vs. RHE)

(LSV curve in 1 M KOH)

Carbon fiber paper-supported Ni, Co, and Ni-Co catalysts synthesized through hydrothermal method

Material properties

Interconnectted vertical sheets of Ni, Co, and Ni-Co on CFP with average thickness equal to 21,78,8.42, and 13.71, respectively. All are poorly crystalline to amorphous. The Ni-Co catalyst is composed of fcc Ni and fcc Co.

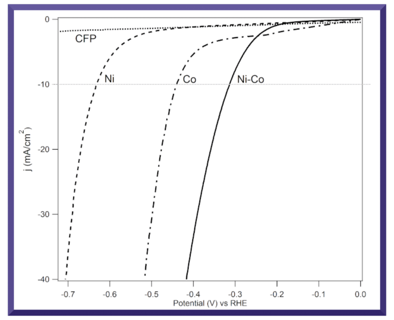


(SEM images of (a,b) Ni, (c,d) Co, and (e,f) Ni-Co on CFP)

HER catalytic activity

Overpotential at 10 mA cm^{-2}: 632 mV vs. RHE (Ni) > 441 mV (Co) > **313 mV** (Ni-Co)

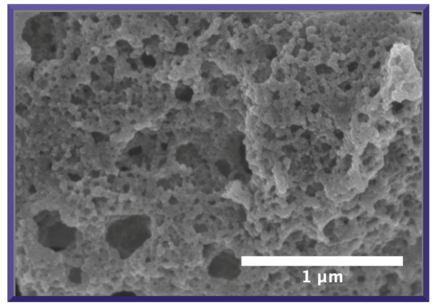
Ni-Co/CFP performed the **best** with also the **lowest Tafel slope** equal to **178 mV dec^{-1}**

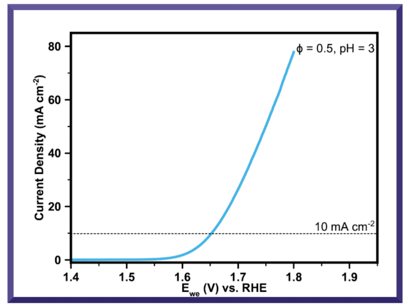


(LSV curves of Ni, Co, and Ni-Co/CFP in 1 M KOH)

Electrocatalysts for OER

Porous spinel Co_3O_4 catalyst synthesized through solution combustion



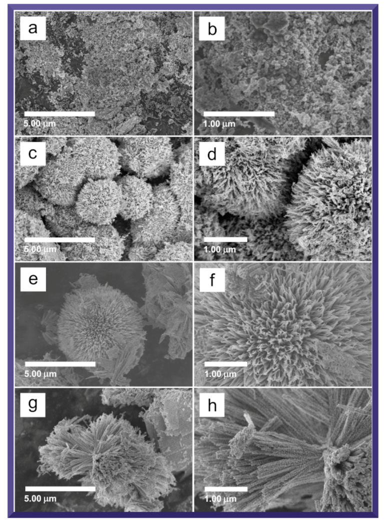


Poropus spinel Co_3O_4 produced using fuel-lean conditions (**ϕ = 0.5**) and unaltered precursor solution **pH = 3** exhibited the **best OER catalytic performance among the other solution combustion synthesized-products** due to its higher purity, lower crystallinity, and due to the absence of amorphous carbon.

Overpotential at 10 mA cm^{-2}: **409 mV (vs. RHE)**

Tafel slope: **62 mV dec^{-1}**

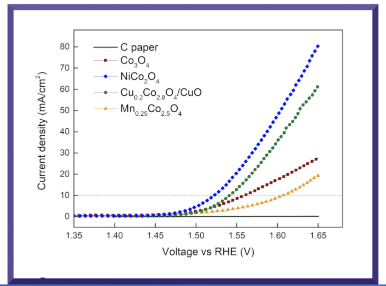
Transition metal-doped Co_3O_4 catalysts synthesized via ethanol-assisted hydrothermal route



Material properties

Undoped Co_3O_4 exhibited **spherical** morphology, whereas the transition metal **doped samples** had an **urchin-like morphology**. **$NiCo_2O_4$** had a **hollow interior** which exposes **more sites for OER** XRD results showed that the spinel structure was retained after doping.

(SEM images undoped (a,b), Ni (c,d), Cu (e,f), and Mn (g,h)-dopec Co_3O_4 electrocatalysts)



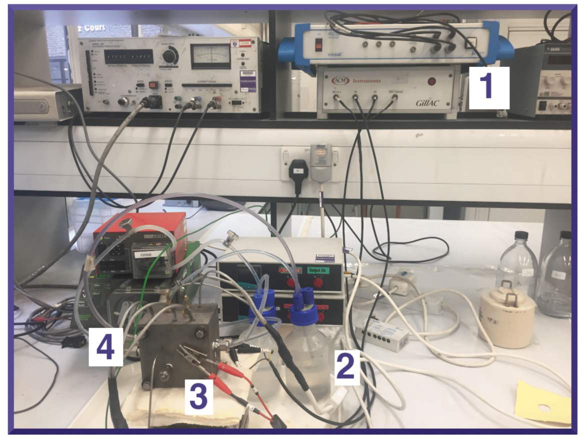
OER catalytic activity

Overpotential at 10 mA cm^{-2}: 370 mV ($MnCo_2O_4$) < **311 mV** (**$CuCo_2O_4$/CuO**) < 309 mV (**$NiCo_2O_4$**)

Ni- and Cu-doped Co_3O_4 also had **low Tafel slopes: 62** and **57 mV dec^{-1}**, respectively.

Anion exchange membrane water electrolyser assembly

Full cell testing setup in Fuell Cell Laboratorty, Newcastle University



1 Power source

2 NaOH/ KOH feed

3 Titanium cell containing the membrane electrode assembly

4 Thermostatically controlled cartridge heaters

Membrane electrode assembly

Anode

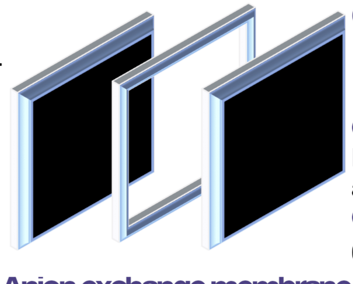
Ni or Cu-doped Co_3O_4 on Ti fiber gas diffusion layer (GDL)

Catalyst ink

catalyst in 12.5 wt% SEBS ionomer and NMP

Catalyst loading

2 mg cm^{-2}



Cathode

Pt/C on carbon GDL

Catalyst ink

Pt/C in 28 wt% SEBS ionomer and isopropanol

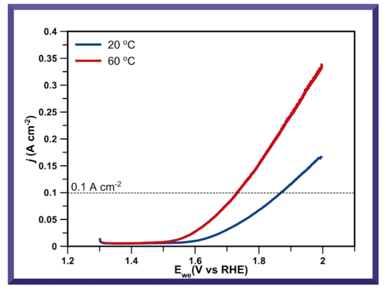
Catalyst loading

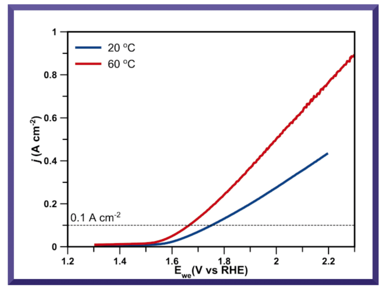
0.4 mg cm^{-2}

Anion exchange membrane

LDPE-VBC-TMA based membrane

Cell performance





Cell voltage required to reach 0.1 A cm^{-2} using $NiCo_2O_4$ on Ti GDL anode in 1 M NaOH:

1.87 V (vs. RHE) at 20 °C

1.73 V (vs. RHE) at 60 °C

using **$Cu_{0.75}Co_{2.25}O_4$** in 1 M KOH

1.74 V (vs. RHE) at **20 °C**

1.65 V (vs. RHE) at **60 °C**

The **Cu-doped Co_3O_4** catalyst performed better than $NiCo_2O_4$. Its performance also **compares favorably to those reported for other copper-doped cobalt oxide catalysts** and even to **some IrO_2-based anodes**..

(LSV curves of the assembled cell in 1 M NaOH using $NiCo_2O_4$ as the anode material (top), and in 1 M KOH with $Cu_{0.75}Co_{2.25}O_4$ (bottom) for OER)

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Capacity building for Philippine Researchers

Symposium on Materials Energy Applications

August 14 - 15, 2018

Balay Kalinaw, University of the Philippines Diliman

The two-day symposium served as a platform for research dissemination of established researchers from different universities to other researchers interested in pursuing a topic related to energy.

First day of the symposium involves the presentation of Dr. Mohamed Mamlouk and Dr. Gaurav Gupta of Newcastle University. Dr. Mamlouk and Dr. Gupta discussed the fundamentals of electrochemistry, water electrolysis and the recent progress of the project. Speakers from Ateneo De Manila University, University of Santo Tomas, Polytechnic University of the Philippines and University of the Philippines Diliman also presented their energy-related studies. Poster presentations with a theme on electrochemistry and energy applications made by participating students and researchers were also part of the symposium. Lastly, a workshop spearheaded by Dr. Mamlouk was conducted in the laboratory of Dr. Balela. This includes the use of water electrolyser and the basics of electrodeposition facilitated by Dr. Gaurav Gupta and Dr. Eden Dela Pena, respectively.

Dr. Mohamed Mamlouk and Dr. Gaurav Gupta during their presentations about the fundamentals of electrochemistry, electrolysis and water electrolyser technology, respectively.

(left) Attendees of the two-day symposium during a research presentation session
(right) Dr. Gupta facilitating the workshop on the use of water electrolysers

Research training

April 5 - May 5, 2019

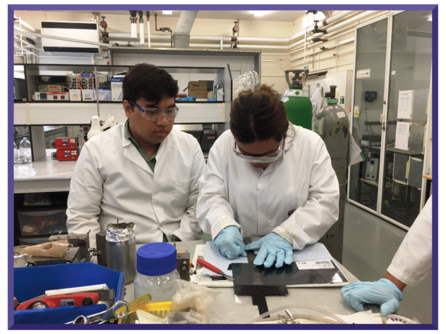
Fuel Cell Laboratory, Newcastle University

Dr. Mary Donnabelle Balela and the technical staff of went to Newcastle University last April to May, 2019. The purpose of this visit to benchmark the practices and eltrochemical procedures employed by the Newcastle University team in characterizing the catalysts produced.

This visit included a research meeting between the research teams to align, not only the techniques utilized in the experiments, but also the research flow and design to ensure the attainment of the deliverables of the project.

During this research training, the Filipino researchers employed in the project were able to do experiments in the Fuel Cell Laboratory of the School of Engineering of the University. They were under the direct supervision of Dr. Mamlouk and Dr. Gupta, and also worked alongside post-doctoral members and PhD students of the laboratory. They learned the standard electrochemical testing procedure employed by the Newcastle team to ensure that the results obtained in the Philippines can be compared more accurately with those obtained in the UK laboratory. Aside from the electrochemical testing stations, the PH researchers were also able to have the catalysts they produced in their home laboratory characterized in Newcastle.

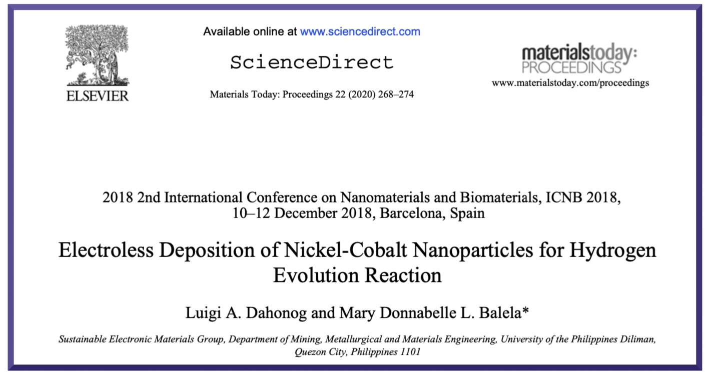
(left) Dr. Balela and the PH researchers with Dr. Mamlouk and Dr. Gupta after the research meeting
(right) PH researchers at the Newcastle University



PH researchers at the Fuel Cell laboratory

Research Publications

Conference Proceedings



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Materials Today: Proceedings 22 (2020) 268–274

2018 2nd International Conference on Nanomaterials and Biomaterials, ICNB 2018, 10–12 December 2018, Barcelona, Spain

Electroless Deposition of Nickel-Cobalt Nanoparticles for Hydrogen Evolution Reaction

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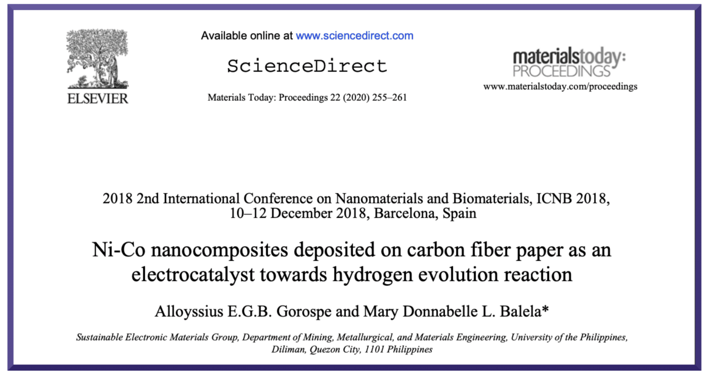

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Ni-Co nanocomposites deposited on carbon fiber paper as an electrocatalyst towards hydrogen evolution reaction

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2019 The 5th International Conference on Smart Materials Research — IOP Publishing

IOP Conf. Series: Materials Science and Engineering **856** (2020) 012008 doi:10.1088/1757-899X/856/1/012008

Micro/nanostructured MTMOs as Electrocatalysts for Oxygen Evolution Reaction in Alkaline Medium

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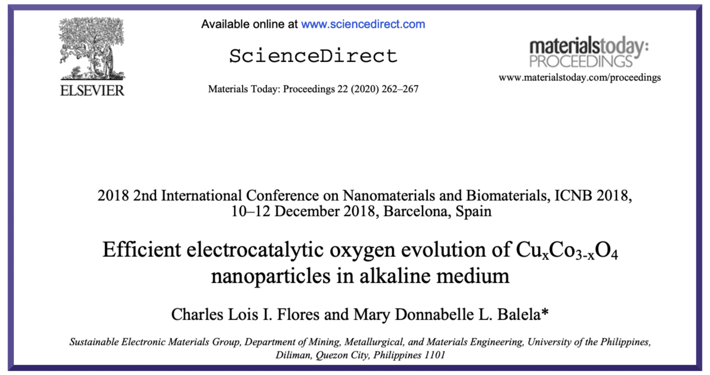

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Materials Today: Proceedings 22 (2020) 262–267

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Efficient electrocatalytic oxygen evolution of $Cu_xCo_{3-x}O_4$ nanoparticles in alkaline medium

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2019 5th International Conference on Chemical Materials and Process — IOP Publishing

IOP Conf. Series: Materials Science and Engineering **617** (2019) 012004 doi:10.1088/1757-899X/617/1/012004

Hierarchical Urchin-like Spinel $Cu_xCo_{3-x}O_4$ Particles as Oxygen Evolution Reaction Catalysts in Alkaline Medium

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L.A. Dahonog, M.D.L. Balela, Electroless Deposition of Nickel-Cobalt Nanoparticles for Hydrogen Evolution Reaction, Mater. Today Proc. 22 (2020) 268–274.

A.E.G.B. Gorospe, M.D.L. Balela, Ni-Co nanocomposites deposited on carbon fiber paper as an electrocatalyst towards hydrogen evolution reaction, Mater. Today Proc. 22 (2020) 255-261.

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Solution combustion synthesis of porous Co_3O_4 nanoparticles as oxygen evolution reaction (OER) electrocatalysts in alkaline medium

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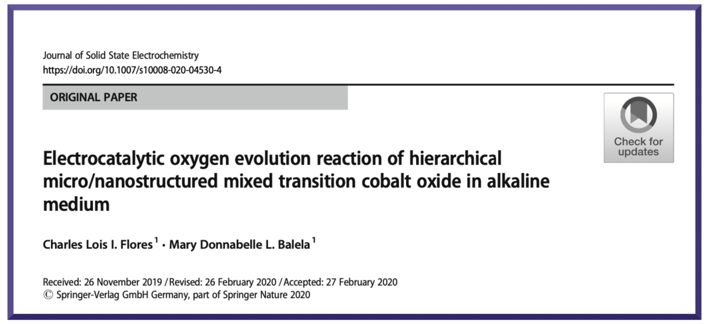

Journal of Solid State Electrochemistry

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ORIGINAL PAPER

Electrocatalytic oxygen evolution reaction of hierarchical micro/nanostructured mixed transition cobalt oxide in alkaline medium

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