Nanomaterials
Room Naupaka Salon 4 - Session NM-TuE1
NanoCatalysis

Moderator: Ellen Fisher, Colorado State University

5:40pm **NM-TuE1-1 Layered Iron Vanadate Electrocatalyst for Large Current Density Water Splitting***, **Fitri Nur Indah Sari**, J. Ting,* National Cheng Kung University (NCKU), Taiwan

Electrocatalysis water splitting is an attractive method to generate hydrogen from water. To date, the state-of-the-art catalysts to split water are based on noble metals, such as platinum for hydrogen evolution reaction (HER) and IrO_2 and RuO_2 for oxygen evolution reaction (OER). However, their scarcity and high cost limit the application. Therefore, great efforts have been devoted to exploring highly active and cost-effective catalyst materials. Recently, noble-metal-free Fe-based catalysts have been demonstrated to be highly efficient for OER. It would be a great advance if such Fe-based catalysts could become bifunctional for overall water splitting. This work investigates a unique layered iron vanadate Fe5V15O39(OH)9.9H2O (FVO) catalyst. The electrocatalytic activity of FVO is controlled by tuning the surface oxidation state and introducing anion and cation vacancies. This work provides a new avenue to design an efficient and stable electrocatalyst Fe-based material with a large current density.

Keywords: layered iron vanadate, surface oxidation state, anion and cation vacancies, water splitting.

6:00pm **NM-TuE1-2 Size Dependence of the N-Doped Graphene Nanocluster on the Oxygen Reduction Reaction Activity***, H. Matsuyama,* The University of Electro-Communications (UEC Tokyo), Japan*; L. Arellano Sartorius,* The University of Electro-Communications (UEC Tokyo) and Instituto Politécnico Nacional, Mexico*; **Jun Nakamura**,* The University of Electro-Communications (UEC Tokyo), Japan

N-doped graphene nanocluster (N-GNC) has been proposed as a promising candidate for catalysts of oxygen reduction reaction (ORR) in fuel cells, but its cluster size or concentration dependence has been unknown so far. In this study, the dependence of the ORR activity on the size of N-GNCs was investigated using first-principles calculations. With a radius of about 14 Å, the reaction step which determines the maximum electrode potentials U_ Max is switched from the H2O generation step to the OOH adsorption step. Thus, the volcano-shaped trend of U_ Max was predicted as a function of the cluster size [1,2]. Such a size-dependent ORR activity of the N-GNC is derived from the change in the confinement of a donor electron from the doped N atom. The adsorption energy of the reaction intermediates varies continuously because the spread of the supplied electrons from the doped nitrogen atoms to the surrounding atoms varies with the cluster size. This is due to the development of the so-called edge states as the cluster size increases, causing a decrease in the number of electrons contributing to the chemical bond of the reaction intermediate at the reaction site [3].

[1] H.Matsuyama, A.Akaishi, and J.Nakamura, ACS Omega 4, 3832 (2019).

[2] H.Matsuyama and J.Nakamura, ACS Omega 7, 3093 (2022).

[3] Y. Uchida, S. Gomi, H. Matsuyama, A. Akaishi, and J. Nakamura, J. Appl. Phys. 120, 214301 (2016).

6:20pm **NM-TuE1-3 a New High Entropy Glycerate for High Performance Oxygen Evolution Reaction***, **Thi Xuyen Nguyen**, Y. Su, C. Lin, J. Ruan, J. Ting,* National Cheng Kung University, Taiwan

Herein, we report a new high entropy material, i.e., a noble metal-free high entropy glycerate (HEG), synthesized via a simple solvothermal process.The HEG consists of 5 different metals of Fe, Ni, Co, Cr, and Mn.The unique glycerate structure exhibits an excellent OER activity with a low overpotential of 229 and 278 mV at current densities of 10 and 100 mA cm^{-2}, respectively, in 1M KOH electrolyte, outperforming its subsystems of binary-, ternary- and quaternary-metal glycerates.The HEG also shows outstanding stability and durability in the alkaline electrolyte.The result demonstrates the significance of synergistic effect that gives additional freedoms to modify the electronic structure and coordination environment.Moreover, HEG@HEG electrolyzer shows good overall water splitting performance and durability, requiring a cell voltage of 1.63 V to achieve a current density of 10 mA cm^{-2}.

6:40pm **NM-TuE1-4 Shape Matters, Nanostructured Materials with Unique Properties in Carbon Captureand Catalysis***, **Ryan Richards**,* Colorado School of Mines

The Richards' group is working on new synthetic methods to control the size, shape and composition of nanoscale materials and applying them in systems integral to alternative energy technologies and carbon capture. In particular, the ability to manipulate earth abundant metal oxides presents an important potential technology to develop sustainable materials with novel properties. These materials are of interest due to the coordination environments that can be achieved and to the high degree of control over properties that can result from tailoring the exposed facets and from mixing metal oxides including the formation of high entropy systems. The initial synthesis of MgO and NiO with (111) facets as the primary surface (Angew., Adv. Mater.) has been followed by recent work utilizing a multiscale characterization platform to discover the underlying phenomena associated with the electrolytic properties of NiO(111) for Li ion batteries (Nature Comm., Nano Letters) and electrochromics. In a joint experimental-theoretical work with international collaborators, we unravelled the potential of (111) polar surfaces for carbon capture (JACS). Most recently, in-situ microscopy studies have revealed insights into the NiO active sites for electrolysis (PNAS) and the underlying dynamics of doping with iron (JACS).

7:00pm **NM-TuE1-5 Molecular Single Iron and Cobalt Catalysts Over Carbon Nanotubes for Electrochemical CO_2 Reduction and H_2 Production***, **Paulina R. Martinez-Alanis**,* Institut de Recerca en Energia de Catalunya, Spain*; A. Berlanga ,* Universidad Nacional Autonoma de Mexico*; G. Montaña, K. Mejía,* Institut de Recerca en Energia de Catalunya, Spain*; F. Güell,* Universitat de Barcelona, Spain*; I. Castillo,* Universidad Nacional Autónoma de México*; A. Cabot,* Institut de Recerca en Energia de Catalunya, Spain*; T. Kallio,* Aalto University, Finland

Molecular single Iron or Cobalt p-terbutil-calix[8]arene compounds were bonded over carbon nanotubes (CNTs) or multiwall carbon nanotubes (MWCNTs) by π-π stacking. The obtained composites were deposited over a gas diffusion layer and proved in a flow cell in a $KHCO_3$ solution in a saturated atmosphere of CO_2. High Current densities around 80 mA/ cm^2, with faradaic efficiencies of 100 % for hydrogen production were achieved at pH near 7 in aqueous solutions in the flow cell. The selective production of acetate by the Fe and Co calixarene composites was obtained. The reaction conditions analysis, such as temperature, carbonate concentration, and salt, with the characterization of the samples' pre and post-catalysis by ultraviolet-visible, infrared, raman, x-ray photoelectron, and photoluminescence spectroscopy, scanning, and transmission electron microscopy were used to go further in the analysis of the mechanism around these catalytic systems. The understanding of these catalytic performances provides additional criteria for a new strategy for designing materials based on carbon composites as an option for the rational use of the transition metals, which is an environmentally friendly alternative to energy applications.

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