Center for Alkaline Based Energy Solutions (CABES)
EFRC Director: Héctor D. Abruña
Lead Institution: Cornell University
Class: 2018 – 2022

Mission Statement*: To achieve a detailed understanding of the nature, structure, and dynamics of electrocatalysis in alkaline media.*

CABES will integrate theory and computational methods for catalysis and interfacial structure/dynamics; the synthesis of model (electro)catalytic systems with atom-level control; ionically conducting/transporting polymers/membranes; catalyst support systems and architectures in contact with metal electrodes; computational materials science to guide the synthesis of next-generation materials; and the development of experimental tools that will provide *in situ/operando*, spatiotemporal characterization of systems under operation. The proposed studies are aimed at significantly advancing electrocatalysis in alkaline media through the rational design and development of new materials and architectures as well as experimental and computational tools necessary for, and critical to, a fundamental understanding of these processes. Results will, in turn, impact numerous technologies, including alkaline fuel cells, electrolyzers, and all metal/air batteries.

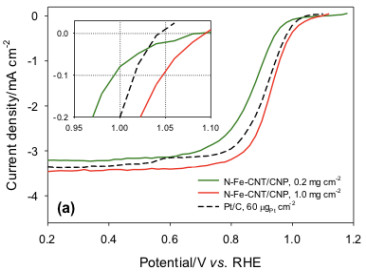

Fig. 1: ORR performance of N-Fe-CNT/CNP composite and Pt/C catalysts. Main Panel: RDE polarization plots in 0.1 M NaOH at 25°C and at 900 rpm. Inset: expanded view of the low overpotential region.

CABES will focus on: (1) <u>Electrocatalysts</u>: We will develop ORR electrocatalysts that exhibit high activity and long life in *alkaline* media with initial focus on ordered intermetallic structured cores and shape-controlled nanoparticles. We will explore the electrocatalytic activity of transition metal oxides and nitrides as well as PGM-free ORR electrocatalysts (Fig. 1). For the HOR, we will use, as a point of departure, recent findings on the HOR activity of IrRu/C, IrPd/C, and IrPdRu/C alloy nanoparticle catalysts. (Fig. 2).

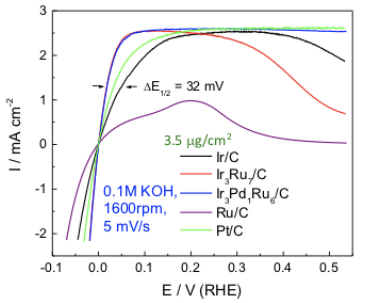

Fig. 2: RDE voltammograms of IrRu/C and IrPdRu/C in H_2 saturated 0.1 M KOH. Scan rate: 5 mV/s, rotation rate: 1600 rpm. The catalyst loading was 3.5 $\mu g_{metal}/cm^2$. Alloy catalyst compositions are indicated.

(2) <u>Support systems:</u> We will develop strategies for the design, synthesis and characterization of catalyst supports that are conductive and stable at high potentials under alkaline conditions. We will focus on the design, synthesis and characterization of hierarchical porous carbons as model catalyst supports in alkaline media. We will evaluate new hierarchical motifs to harness their complex functionality. We will take advantage of recent findings that Nb-doped rutile TiO_2 supports retain their electronic conductivity, even under the strongly oxidizing electrochemical conditions of a fuel cell or electrolyzer. We will also investigate mesoporous transition metal nitrides and oxy-nitrides. We will pursue a strategy for modeling the impedance of a supported catalyst by a transmission line model, using Kirchhoff's law current loops to model the serial-parallel flow of current (Fig. 3).

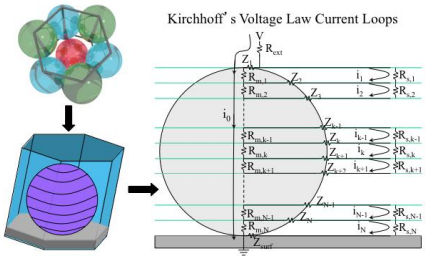

Fig. 3: Unit cell model of oxide support particles in a catalyst/ support/ electrolyte film, and Kirchhoff's law decomposition of the components of the film's impedance.

(3) Alkaline membranes: CABES will develop methods to synthesize phosphonium- and imidazolium functionalized norbornenes and *trans*-cyclooctenes. These monomers are unique because the ring strain of norbornenes and *trans*-cyclooctenes is higher than *cis*-cyclooctenes and consequently, these functionalized building blocks can be polymerized in a living fashion. We will also seek to understand the mechanism of membrane degradation and potential carbonate formation and precipitation, as they will guide the structural design and optimization of ionomers with improved stability and high intrinsic conductivity.

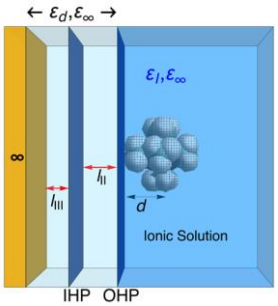

Fig.4 Dielectric continuum description of an electro-chemical interface. CABES will use first-principles simulations of the electrode-liquid interface to extract the information necessary to compute reorganization energies for complex systems.

(5) Theory: Our theory and computational efforts will involve the elucidation of intricate chemical-reaction and electron-transfer (ET) pathways as well as fundamental understanding of complex electrochemical environments (Fig. 4) that include externally applied voltages, solvent, mobile ions, the role of interfacial water and ions, mechanistic pathways such as proton-coupled electron transfer (PCET), and reactive intermediates.

(6) Analytical Methods: CABES will take advantage of its extensive expertise in the development and use of *in situ* and *operando* methods for establishing a synthesis/characterization feedback loop in engineering heterogeneity i.e., interfaces, defects, strains, confinement, charge-carrier distribution, and concentration of intermediate species for electrocatalytic reactions. We will carry out studies on multiple length scales from atomic-resolution maps of composition and bonding in catalyst nanoparticles, 1-2 nm resolution *operando* STEM and EELS, nanoscale 3-D microscopy with small (micro) X-ray beams (Fig. 5). We will employ a new EMPAD detector to map out strain on nanoparticle catalysts. The use of cryo-TEM will enable imaging of radiation-sensitive membranes.

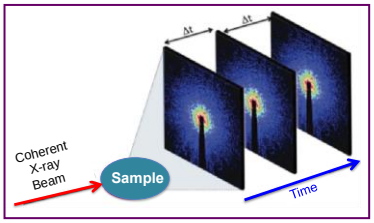

Fig. 5 Schemtaic of X-ray Photon Correlation Spectroscopy to study dynamics of catalytic surfaces.

Summary: Over the four-year period, we foresee the CABES effort as providing the basis for ushering in an Alkaline-Based Energy Technology Society.

Center for Alkaline Based Energy Solutions (CABES)	
Cornell University	Héctor Abruña (Director), Tomas Arias (Thrust Area Leader), Geoffrey Coates (Thrust Area Leader), David Muller (Thrust Area Leader), Joel Brock, Peng Chen, Francis DiSalvo, Robert DiStasio, Emmanuel Giannelis, Lena Kourkoutis, Andrej Singer, Jin Suntivich, Paul Mutolo (Executive Director)
University of Pennsylvania	Tom Mallouk (Thrust Area Leader)
University of Binghamton	Jiye Fang
University of Wisconsin	Manos Mavrikakis
Carnegie Melon University	Kevin Noonan
Los Alamos National Lab	Piotr Zelenay
National Renewable Energy Lab	Bryan Pivovar
Yale University	Sharon Hammes-Schiffer

Contact: Héctor D. Abruña, Director, hda1@cornell.edu
607-255-4928, https://cabes.cornell.edu/