THE OHIO STATE UNIVERSITY

# Ph.D. Thesis Defense

## The William G. Lowrie Department of Chemical and Biomolecular

**"Theoretical Studies of Nitrogen–Doped Carbon Electrocatalysts for Bromine Evolution in Oxygen–Depolarized Cathode Technology"**


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## Abstract

Bromine ($Br_2$) is a valuable chemical used in flame retardant, pharmaceutical manufacturing, energy storage, emission reduction, and water treatment applications. Traditional bromine production utilizes heated reaction towers to drive the oxidation of bromide ions in highly concentrated brine solutions with chlorine gas. However, bromine can also be more cheaply produced electrochemically via oxygen depolarized cathode (ODC) technologies, wherein the bromine evolution reaction (BER) takes place on the anode and the oxygen reduction reaction (ORR) takes place on the cathode. Recent experiments in the Ozkan group have shown promising BER activity for nitrogen-doped carbon nanostructures ($CN_x$), which have also been previously shown to be active for ORR as well. Thus, these materials serve as promising non-precious metal electrocatalysts for both reactions involved in the electrochemical production of bromine. However, $CN_x$ catalysts contain a range of possible local sites and clarifying the most active sites is critical for the optimal design of $CN_x$ catalysts for BER/ORR applications. To address this issue, density functional theory (DFT) calculations were used to evaluate the BER reaction mechanism and activity of ten candidate $CN_x$ sites. These studies suggest that the zigzag pyridinic and pyrrolic oxide sites are the most active for BER and that the Volmer-Heyrovsky reaction mechanism for BER can be promoted by surface bound Br and OH species on $CN_x$. DFT calculations were also combined with experimental electrokinetic and spectroscopic measurements to develop insightful tools and methodologies for exploring $CN_x$ active sites. Results gathered from these approaches suggest that the quaternary-type sites as well as the zigzag oxide site are the most active for ORR. The aim of this work is to guide future commercialization efforts to optimize $CN_x$ catalysts for more energy-efficient and cost-effective bromine production.