
V.G.6 Room Temperature Electrochemical Upgrading of Methane to Oxygenate Fuels

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Program Scope

This program supports the Office of Basic Energy Sciences mission to control energy-relevant molecular transformations. Specifically, this program focuses on the design and understanding of the reaction pathways involved in the near room temperature electrochemical activation of methane and synthesis of small molecule organic molecules such as methanol. Aqueous, low temperature (25°C–220°C) methane electrochemistry has been studied extensively since the 1960s. Acid reactions typically result in either no reaction or complete oxidation to CO₂, and alkaline transformations have been ineffective because OH⁻ anions tend to oxidize species by accepting protons rather than donating oxygen – giving OH⁻ anions a limited ability to attack methane. The lack of an efficient alkaline oxygen donor has severely handicapped the low temperature electrochemical conversion of methane to syngas.

Unlike previous low temperature electrochemical cells, this program leverages our group's recent discovery that carbonate (CO₃²⁻) anions can act as an efficient oxygen donor at room temperature. The fact that carbonate oxidizes incoming species by oxygen donation is very important and provides an opportunity to form new C-O bonds through oxygen insertion and not C-H bond breakage, which is a key reason why this project has succeeded where previous attempts have failed. The early work done during this program shows that near room temperature, carbonate-enabled natural gas, and biogas conversion has significant promise, but there is considerable fundamental work remaining.

One of the most important aspects of this program is to better understand the electrochemistry and electrocatalysis behind the formation and reaction of carbonate anions, uncovering the key catalytic properties to allow for the rational design of high efficiency, room temperature methane electrocatalysts.

FY 2016 Highlights

- Elucidated the dynamics of CO₃²⁻, HCO₃⁻ and OH⁻ formation, transport and consumption in the presence of various oxygen acceptors.
- Investigated (bi)carbonate decomposition and the possibility of using this chemistry for electrochemical CO₂ separation from flue gas effluent and utilization.
- Investigated methane activation dynamics using OH⁻ anions coupled with transition metal hydroxide-oxyhydroxide transformations.
- Developed electrode structures and processes to increase turnover number and improved spectroscopic sensitivity to products.
- Explored reaction pathways on multi-functional oxide-oxide and metal alloy nanocage catalysts.