Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.
This journal is © The Royal Society of Chemistry 2020

Supplementary Information

A Cyclic Electrochemical Strategy to Produce Acetylene from CO_2, CH_4, or Alternative Carbon Sources

Joshua M. McEnaney,*[,a] Brian A. Rohr,*[,a] Adam C. Nielander,[a] Aayush R. Singh,[a]
Laurie A. King,[a] Jens K. Nørskov,[c] Thomas F. Jaramillo[a,b]

a SUNCAT Center for Interface Science and Catalysis, Department of Chemical Engineering Stanford University, Shriram Center, 443 Via Ortega, Stanford, CA 94305, USA. E-mail: jaramillo@stanford.edu

b SUNCAT Center for Interface Science and Catalysis, SLAC National Accelerator Laboratory, 2575 Sand Hill Road, Menlo Park, CA 94025, USA

c Department of Physics, Technical University of Denmark, DK-2800 Kongens Lyngby, Denmark

** These authors contributed equally to this manuscript*

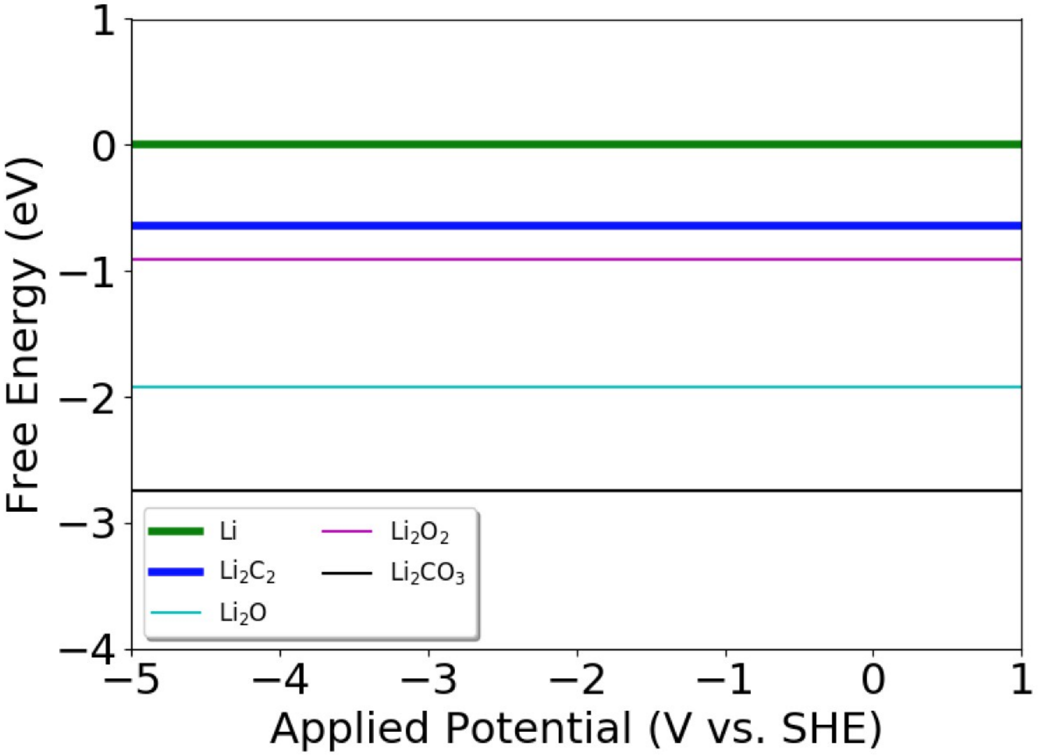

Fig S1. Pourbaix diagram that applies most directly to step 2 of the process: the reaction of $CO_{2(g)}$ with $Li_{(s)}$. Here, the oxygen reference is chosen to be ½($CO_{2(g)} - C_{(s)}$) since $CO_{2(g)}$ is the source of oxygen in this step. This diagram only includes species that are accessible during step 2, and there is no potential dependence on the Gibbs free energy of any of the species in this purely thermochemical reaction. This diagram more clearly shows that Li_2CO_3 is the most stable accessible species during this step.

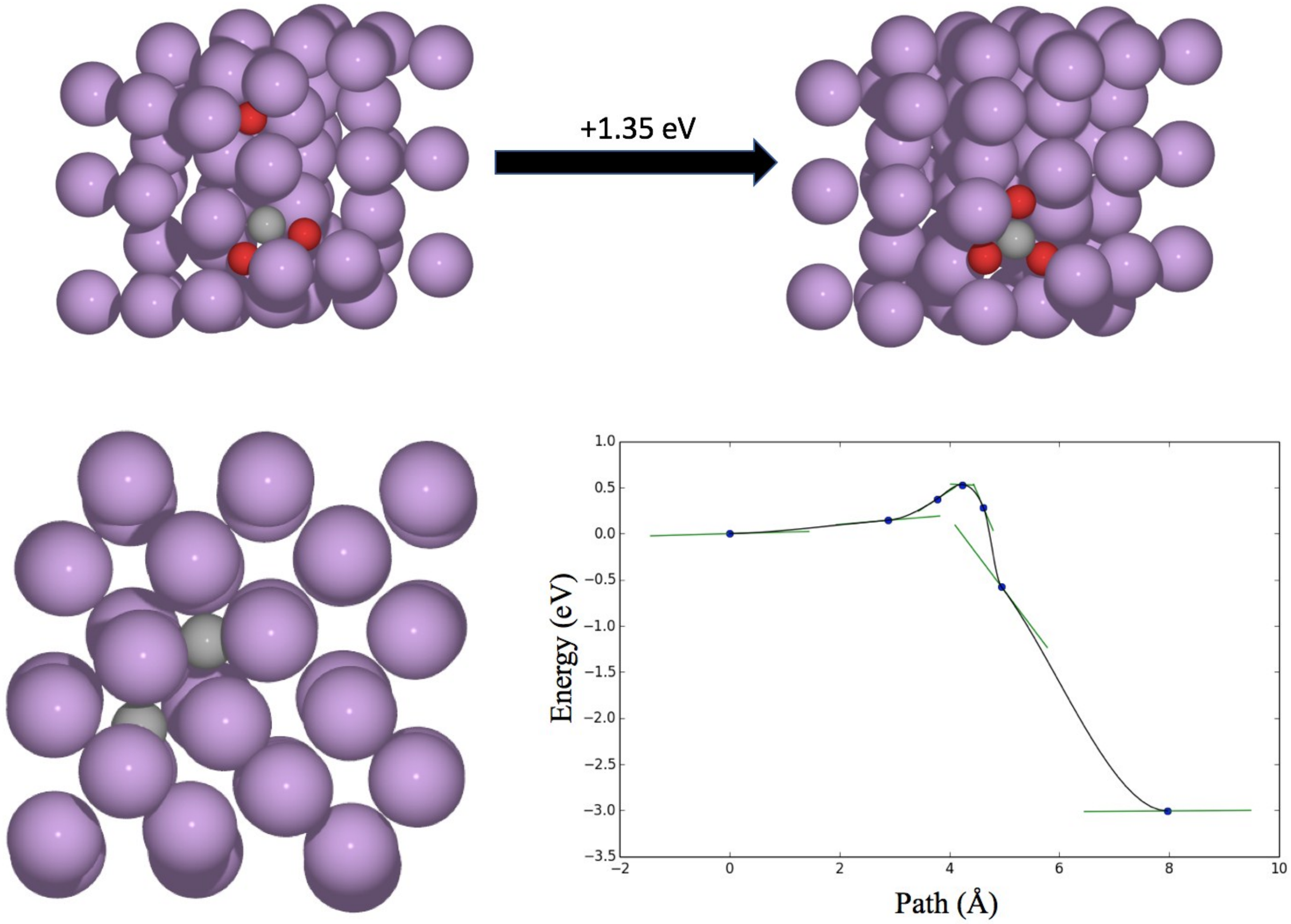

Fig. S2. Structure of the C-C coupling transition state (top left) and the energetics of the reaction pathway for the formation of a C-C bond from two separate carbon atoms in bulk Li (top right). The initial and final state structure for the formation of a carbonate anion in bulk Li is also shown (bottom). DFT shows that the formation of the first carbide anion in bulk Li is thermodynamically favorable and kinetically facile. However, the formation of the first carbonate anion in bulk Li is thermodynamically unfavorable, as the octahedral site must expand to accommodate this large anion. Even in the absence of an additional barrier beyond the thermodynamics (best case scenario for carbonate formation), the barrier for the formation of a carbonate anion in bulk Li is roughly 0.7 eV higher, or roughly twice as large, as the barrier for the formation of carbide in bulk Li.

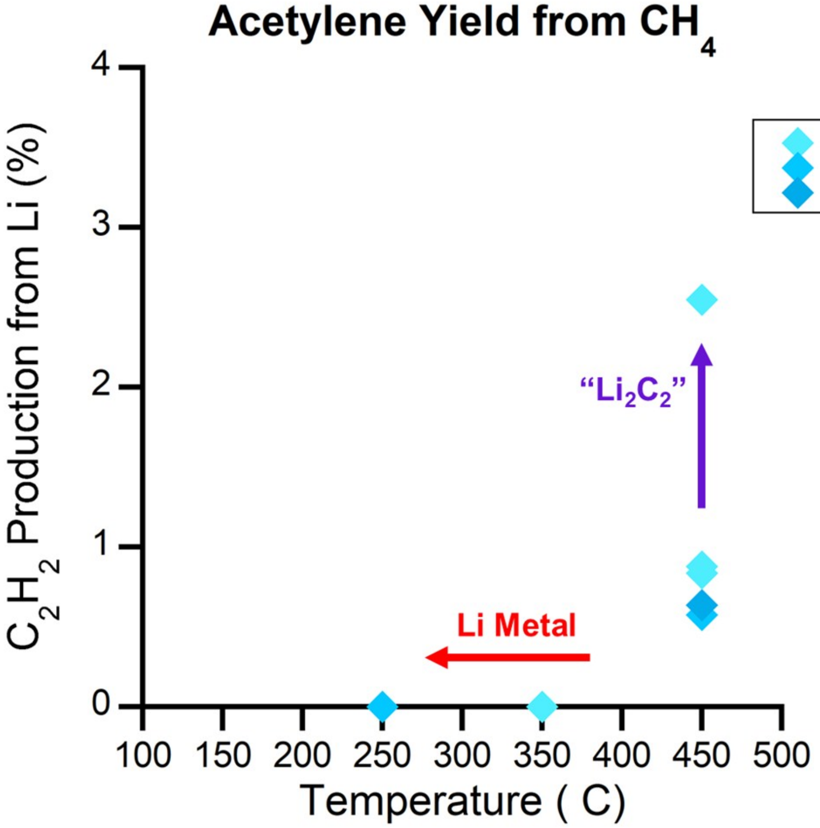

Fig. S3. Acetylene yield by flowing CH_4 over Li samples at variable temperatures and times. Carbon formation and surface coating currently inhibits product formation, however, these yields from hundreds of milliamps per cm^2 are high relative to aqueous electrochemical methane oxidation which operates at microamps per cm^2. For the peak 2 h point (vs the lower yield points), Li was placed directly on an alumina boat instead of a steel liner in the boat. This change increased the acetylene yield, likely due to some partial reaction or alloying process with the base material which may alter the surface and reaction dynamics of Li with CH_4.

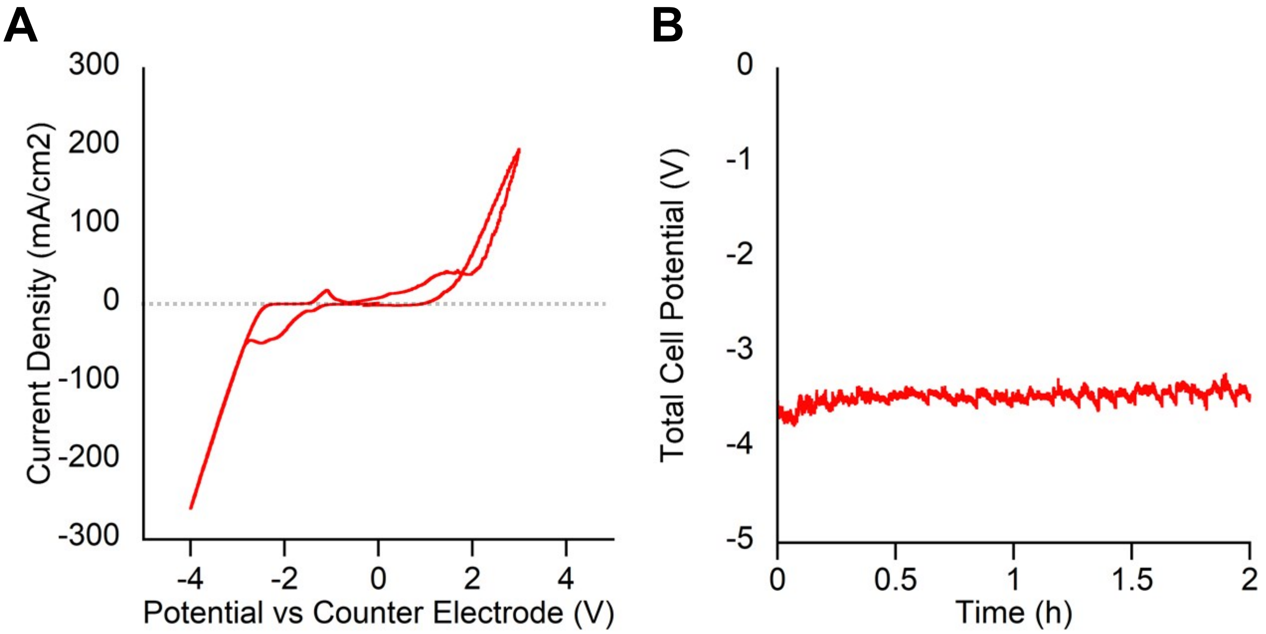

Fig. S4. Electrochemical characterization of the LiOH electrolysis cell equipped with a steel cathode, a graphite anode, a LiCl/KCl catholyte, and a LiOH/LiCl anolyte. A) Representative CV measuring working electrode (steel cathode) potential vs the counter electrode (graphite anode) and sweeping from 0 V to -4 V, up to 3 V, and back down to 0 V. B) Galvanostatic stability test, holding current density at -50 mA/cm^2 for 2 hours.