*Texas Center for Chlorine evolution selectivity in graphene Superconductivity at UH supported single atom catalysts [‡] William A. Brookshire Department of Chemical and Richard Tran^{**}, Najmeh Honari^{**}, Lars Grabow^{**} **Biomolecular Engineering**

Motivation

- 1. Chlorine evolution reaction (CER) is key to chlorine-mediated electrochemical synthesis of ethylene/propylene oxide and H_2 .
- 2. However OER is thermodynamically preferable w/lower equilibrium potential.
- 3. Studying CER/OER selectivity on isolated active sites of graphene supported TMN_4 ($TMN_4@G$) allows us to better understand the mechanism behind CER vs OER selectivity





Observe two different scaling relationships between ΔG_{O^*} vs ΔG_{OH^*} . SACs fitted to a larger intercept better select for CER. For ΔG_{OOH^*} vs ΔG_{OH^*} , intercept is 2.7 (close to ideal intercept of $2U_{OFR}$) \rightarrow SACs can be employed to exceed the Sabatier limit for OER. Inverse trend between ΔG_{O^*} and -ICOHP (covalency). Stronger covalent bonding between TM-O* \rightarrow stronger adsorption. Observe parabolic trend for ΔG_{O^*} and -ICOHP wrt periodic group. Adsorption gets stronger and peaks at Group 5, then weaker until Group 10, then stronger again for p-block metals. For O*, these trends are more exaggerated leading to two diverging scaling relationships, one for the TMs Group 4-12 and another for the p-block and Group 3.



Pt and Pd SAC by far exhibit the lowest ΔG_{RDS}^{CER} (overpotential) for CER followed by Mn, Ni, Tl, Cu, Ir and Fe. SAC with lowest to highest ΔG_{RDS}^{OER} is: Ir, Cu, Ni, Pt, Pd, Mn, and Fe.









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