Design of oxide electrocatalysts for efficient conversion of CO2 into liquid fuels

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Electrochemical conversion of CO2 into high energy density liquid fuels utilizing renewable electricity can usher in a carbon neutral society without limiting the energy consumption. Lack of active and efficient electrocatalysts for this reaction remains a challenge. Research efforts towards catalyst development have obtained limited success due to adsorbate scaling relations on metallic surfaces. Preliminary experimental results indicate rutile oxide catalysts are active at very low overpotential, although the scientific understanding is missing. This thesis aims at delivering knowledge of atomic scale reaction thermodynamic needed to engineer efficient and active oxide electrocatalysts.

Rutile oxides are explored for CO2 reduction reaction (CO2RR) through density functional theory based simulation of reaction thermodynamics. Oxygen atom coordinated intermediates constitute the reaction mechanism active on such catalysts, annulling the scaling laws that limit metallic catalysts. Utilizing model rutile oxide surfaces, trends and limitations of CO2RR on oxide catalysts are analyzed. OH* binding energy is established as the descriptor for CO2RR activity on oxide surfaces. Scaling law based thermodynamic volcano relation for CO2RR is constructed. Guidelines for H* and OH* binding energy range for good activity and selectivity of oxide CO2RR catalysts is proposed. This provides guidance to future development of oxide CO2RR catalysts.

The key role of CO* spectators on reaction onset potential and product selectivity of RuO2 electrocatalyst is elucidated through simulations of CO2RR pathway with varying CO* coverage level. The effect of adsorbate-adsorbate interaction in CO2RR activity is significant. Steric effects from spectator coverage also play a role by altering binding geometry of adsorbates. It is concluded that under experimental condition, CO* coverage is necessary for methanol evolution from RuO2 electrocatalyst, but very high coverage lead to evolution of formic acid and hydrogen together.

Building on the understanding of descriptors for CO2RR activity and CO* spectator effects, a new method of further enhancing the oxide electrocatalyst activity is proposed utilizing ligand effects in mixed oxide systems. Such effects in CO2RR catalysts can produce striking behaviours for adsorbate binding and catalytic properties. Detailed study of such properties for Ru/Ir mixed oxide surfaces with varying metal atom composition as well as different CO* coverages is done. It is identified that monolayer or lesser amount of iridium oxide on RuO2 catalyst can have a methanol onset potential of -0.2 V below RHE. This is attributed to a combination of ligand effect and adsorbate interaction. Through thermodynamic and kinetic barrier calculations, the possibility of 2C products is explored.

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