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OXYGEN TOLERANT HYDROGEN EVOLUTION AND CO₂ REDUCTION

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Salle D2

Biographie

Abhishek Dey has a background in electronic structure and synthetic inorganic chemistry. His research aims at emulating the reactivity of enzyme active sites in synthetic analogues using the geometric and electronic structure function relationships present in natural systems. His current area of interest includes multi-proton and multi-electron transformations that are key for clean energy and environment and development of new analytical techniques to spectroscopically investigate heterogeneous electrocatalysts.

Abstract :

Hydrogen generation via proton reduction and reduction of CO₂ are two very important reactions for attaining a sustainable clean energy cycle. Both processes are catalyzed by low valent transition metals which are highly susceptible to oxidation by molecular oxygen. The sensitivity to molecular oxygen presents a genuine challenge towards practical implementation of these technologies. For example, the instability of [FeFe]-H₂ases and their biomimetics towards O₂ renders them inefficient to implement in practical H₂ generation (HER). Previous investigations on synthetic models as well as natural enzymes proved that reactive oxygen species (ROS) generated on O₂ exposure oxidatively degrades the 2Fe sub-cluster within the H-cluster, active site. Recent electrochemical studies, coupled with theoretical investigations on [FeFe]-H₂ase suggested that selective O₂ reduction to H₂O could eliminate the ROS and hence tolerance against oxidic degradation could be achieved (Nat. Chem., 2017, 9, 88-95). We have prepared a series of 2Fe subsite mimics with substituted arenes attached to bridgehead N-atoms in the S to S linker, (μ-S(CH₂)₂NAr)Fe(CO)₃]₂. Structural analyses find the nature of the substituent on the arene offers steric control of the orientation of bridgehead N-atoms, and their proton uptake and translocation ability. These complexes show HER at near neutral pH and at low overpotentials (~180 mV). In addition, bridgehead N-protonation, and subsequent H-bonding capability, is established to be effective to facilitate the O-O bond cleavage resulting in selective O₂ reduction to H₂O. This allows a synthetic [FeFe]-H₂ase model to reduce protons to H₂ unabated in the presence of dissolved O₂ in water at nearly neutral pH; i.e., O₂ tolerant, stable HER activity is achieved. Using a new approach of utilizing spin crossing barrier, oxygen tolerant hydrogen evolution and CO₂ reduction is demonstrated.