

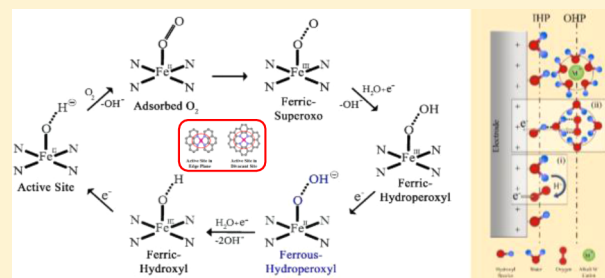
# Activity Descriptor Identification for Oxygen Reduction on Nonprecious Electrocatalysts: Linking Surface Science to Coordination Chemistry

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## Supporting Information

**ABSTRACT:** Developing nonprecious group metal based electrocatalysts for oxygen reduction is crucial for the commercial success of environmentally friendly energy conversion devices such as fuel cells and metal–air batteries. Despite recent progress, elegant bottom-up synthesis of nonprecious electrocatalysts (typically Fe–N<sub>x</sub>/C) is unavailable due to lack of fundamental understanding of molecular governing factors. Here, we elucidate the mechanistic origin of oxygen reduction on pyrolyzed nonprecious catalysts and identify an activity descriptor based on principles of surface science and coordination chemistry. A linear relationship, depicting the ascending portion of a volcano curve, is established between oxygen-reduction turnover number and the Lewis basicity of graphitic carbon support (accessed via C 1s photoemission spectroscopy). Tuning electron donating/withdrawing capability of the carbon basal plane, conferred upon it by the delocalized  $\pi$ -electrons, (i) causes a downshift of  $e_g$ -orbitals ( $d_z^2$ ) thereby anodically shifting the metal ion's redox potential and (ii) optimizes the bond strength between the metal ion and adsorbed reaction intermediates thereby maximizing oxygen-reduction activity.



## INTRODUCTION

Parallel forces aiming to achieve climate stabilization and energy independence have accelerated the pursuit of clean and efficient electrochemical energy conversion devices such as fuel cells and metal–air batteries.<sup>1,2</sup> These devices are expected to play definitive roles in the widespread utilization of renewable energy sources.<sup>3</sup> At the crux of these devices lies the grand challenge of developing highly active, inexpensive, and stable electrocatalysts for the kinetically sluggish oxygen reduction reaction (ORR).<sup>4–6</sup> In accordance to Sabatier's principle of catalysis, designing bottom-up approaches for catalyst synthesis involves identification and optimization of various material properties that govern reaction rates on active surfaces.<sup>7</sup> For instance, d-band vacancy/center,<sup>8,9</sup> surface lattice strain<sup>10</sup> (in platinum-based systems), and  $e_g$ -orbital filling of transition metals<sup>11</sup> (in perovskite-based systems) have been identified as fundamental material properties that act as ORR activity descriptors. In essence, to maximize surface catalytic activity, tuning such electronic and structural material properties optimizes the d-orbital occupancy near the Fermi level; thereby achieving a fine balance between the chemisorption energy of ORR intermediates and the number of surface sites available for initial O<sub>2</sub> adsorption.<sup>4,12</sup>

The drive to replace expensive precious-metal-group (PGM) systems for ORR has led to a class of catalysts comprising transition metal ions stabilized by nitrogen functional groups on carbonaceous surfaces (Fe–N<sub>x</sub>/C).<sup>13–16</sup> These active sites are adventitiously synthesized via pyrolysis of precursors

containing transition metals, nitrogen, and carbon, all of them present in either the same source or different sources.<sup>17</sup> Potential multiplicity of active sites for initial O<sub>2</sub> adsorption and the lack of suitable analytical techniques complicates a lucid understanding of the nature of active sites and the reaction mechanisms in these composite catalysts.<sup>14</sup> Despite high activity and durability of pyrolyzed Fe–N<sub>x</sub>/C catalysts shown recently,<sup>18–20</sup> current progress primarily involves an experimental approach of trial-and-error combination of precursors and pyrolysis conditions to maximize performance. Lack of fundamental understanding of the mechanistic origin of ORR and the underlying surface material properties that govern catalytic activity clearly limits further progress. Here, for the first time we present a direct structure–activity relationship between the intrinsic ORR turnover number (i.e., kinetic current-density normalized by electrochemically active site-density quantified via square-wave voltammetry) and a surface material property of pyrolyzed Fe–N<sub>x</sub>/C catalyst, thus providing deep insight into the fundamental mechanistic origin of ORR and potentially opening the door to elegant bottom-up catalyst synthesis strategies.

Electrocatalysis on *nonpyrolyzed* metal macrocycles is governed by the nature of the (i) central metal ion and (ii) the surrounding macrocyclic ligand.<sup>21</sup> While d-electron density on the metal ion determines the progress of ORR via adsorbed

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