510c Experimental and Theoretical Studies of Metal-Supported Pt Monolayer Catalysts for the Oxygen Reduction Reaction

Anand Nilekar, Ye Xu, J. Zhang, M. B. Vukmirovic, Radoslav R. Adzic, and Manos Mavrikakis

Electrochemical experiments show that the oxygen reduction reaction (ORR) on Pt monolayers supported on various transition metals exhibits a volcano-type behavior. Density functional theory (DFT) calculations reveal that, on these monolayers, O-O bond-breaking occurs more easily as O-H bond-making becomes more difficult, and explain why the Pd-supported Pt monolayer shows higher ORR activity than that of pure Pt. Furthermore, single crystal and supported nanoparticles experiments with mixed metal monolayers on top of Pd substrates, suggest that one can further enhance ORR kinetics, by taking advantage of favorable adsorbate-adsorbate interactions, as corroborated by DFT calculations and in-situ XANES studies. These results demonstrate the possibility of devising ORR catalysts both cheaper and more active, and with improved corrosion-resistance compared to pure Pt.