

Ab-initio Investigation of the Pathway and Energetics of Electrocatalytic Methanol Oxidation over Platinum(111)

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The desire for portable, reliable and efficient power has prompted serious interest in further development of the direct methanol fuel cell and understanding the catalytic reactions that govern its performance. The coupling of methanol oxidation at the anode with oxygen reduction at the cathode controls the magnitude of the overpotential and overall cell performance. Our work presented here focuses on elucidating the pathways of methanol dehydrogenation and oxidation reactions occurring at the anode. This is especially important since spectroscopic identification of reaction intermediates has been plagued by complications due to the complex solution-phase environment, such as overlap of solvent vibrational bands, thus limiting the knowledge of the elementary pathway that controls methanol oxidation. Despite these difficulties, recent studies using infrared spectroscopy have revealed the presence of surface-bound formate in addition to carbon monoxide as stable surface intermediates, both subsequently reacting to form carbon dioxide.^{1,2} In addition to the two pathways which form carbon dioxide, experimental evidence supports other minor pathways which produce solution-phase formaldehyde and formic acid.³⁻⁵ The elementary steps as to how the various pathways proceed, however, are still unknown.

Ab-initio methods have developed to the point where they can begin to probe the reaction energies and pathways for complex metal/solution reaction environments and complement experimental efforts. Periodic density functional theory (DFT) calculations and ab initio molecular dynamics simulations are used to investigate the elementary steps of methanol dehydrogenation and oxidation over well-defined Pt surfaces in order to establish the electrocatalytic pathways. More specifically, the influence of solution as well as electrochemical potential on the activation of C–H and O–H bonds, oxygen addition reactions and the governing mechanism is systematically analyzed. We find that solvation and hydrogen bonding influence the stabilization of surface-bound intermediates and the ability to form protons, significantly affecting the reaction kinetics.

In addition, we have developed an approach to measure and tune the surface potential within the periodic DFT calculations, thereby enabling us to monitor the influence of potential on the reaction pathways and surface kinetics. Our results indicate that at potentials of relevance for fuel cell applications the major pathway for methanol (CH₃OH) activation proceeds via C–H activation to form the hydroxymethyl (CH₂OH*) intermediate. However, at these potentials, O–H activation is also thermodynamically favorable, leading to the formation of the methoxy (CH₃O*) intermediate which can go on to form formaldehyde (CH₂O) as a minor product. These results are consistent with the experimental studies by Iwasita⁴ which also suggest that formaldehyde is formed via the methoxy intermediate.

We describe the comparison of our first principle theoretical results with single-crystal chronoamperometric and cyclic voltammetric experiments from the Illinois group.

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