A combined first-principles molecular dynamics/density functional theory study of the electrooxidation of ammonia is conducted to gain an atomic-level understanding of the electrocatalytic processes at the Pt(1 0 0)/alkaline solution interface and to probe the mechanistic details of ammonia electrooxidation on the metal surface. A systematic study of adsorption and relative stability of ammonia and the intermediate species on the Pt(1 0 0) surface as a function of potential is carried out and activation energy profiles for the mechanistic steps in the ammonia oxidation are presented. The reaction mechanism is potential dependent: the modeling study supports the Oswin and Salomon's mechanism for moderate surface potentials (≥ +0.5 V vs. RHE), and the Gerischer and Maurer's mechanism for lower potentials (< +0.5 V vs. RHE). The high electrocatalytic activity of
Pt(1 0 0) is ascribed to the facile dimerization of bridging nitrogen atoms to form molecular nitrogen, whereas low activity of Pt(1 1 1) and Pt(1 1 0) is imputed to the nitrogen atoms that are strongly bound at hollow sites and poisoning the surface.

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