Electrocatalysis is controlled by the elementary reactions that occur at the interface between the electrode and the solution phase along with the electrochemical potential that results across this interface. Elucidating the electrochemical behavior at this interface, however, presents a considerable challenge due to complexity of the surface chemistry, the explicit atomic and molecular structure of the solution phase at the interface, the presence and formation different ions and their specific location in solution or on the surface, and the surface potentials and electric fields that results as a function of the surface reactivity. First principles based simulations of electrocatalysis tend to be limited due the size of the systems required to appropriately model the interfacial structure, and by the fact that ab initio methods are typically constant charge rather than constant potential systems. We present an approach that can begin to simulate the elementary pathways and kinetics for constant potential systems and highlight the challenges of this approach. The results are used to construct first principles based kinetic Monte Carlo simulations to model different electrochemical systems. We discuss the application of the approach to simulate the electrocatalytic reduction of oxygen over transition metal surfaces as well as nitrogen doped carbon-based substrates.