356h Theoretical Studies of Oxygen Reduction Intermediates on Pt - Co Alloys

Eduardo J. Lamas and Perla B. Balbuena

Oxygen reduction on surfaces has attracted a great deal of attention in the last few years because of its use on fuel cells, which are environmentally friendly candidates for fossil fuels replacement. The major technological challenges that remain to be solved in the cathode side, where the oxygen reduction occurs, are the cost of the catalyst and the oxygen reduction slow kinetics. This reaction in acidic media is believed to progress through two different pathways, the first does not involve the formation of hydrogen peroxide on the surface, while in the second one this component is present as one of the intermediates. The aim of this work is to study the interaction of oxygen reduction intermediates with a Pt0.75Co0.25 (111) surface, and to use this to get insights about the catalytic activity of the alloy compared with Pt (111). We characterize this system with a set of Ab Initio studies in plane wave pseudopotential formalism, which is the technique that arises as a natural candidate for studying reactions in extended periodic surfaces. The unit cell is modeled as a three layer - 4 atoms per layer Pt0.75Co0.25 (111) surface, where different Co distributions are tested on the system, including one with a Pt skin. Periodic boundary conditions are applied in the three spatial directions and 10 Å of vacuum space is left between periodic images in the z-direction, perpendicular to the surface. We adopted the PBE functional and Vanderbilt ultrasoft pseudopotentials to decrease the computational requirements associated with the description of inert core electrons. The plane wave cut off was set to 50Ry and the first Brillouin zone was sampled with a uniform mesh with 7x7x1 k-points. In order to facilitate convergence fractional occupancies were allowed, we applied Mazzari-Vanderbilt smearing with sigma = 0.1 eV. All simulations were performed using the quantum ESPRESSO package.