

An Overview of Electrochemical Hydrogen Adsorption and Absorption

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The need for renewable and carbon-free energy sources drives interest in hydrogen as an energy source and carrier, which is the most important element of the emerging hydrogen economy. This overview presentation focuses on the atomic-level understanding of the fundamental steps of the electro-adsorption (electrochemical adsorption) of hydrogen (H) on transition-metal electrodes. It presents basic events of the physisorption and chemisorption of H under gas-phase, as well as the electro-adsorption of H under electrochemical conditions, with the objective of identifying characteristics that are unique to the gas-phase and the electrochemical environments. The electrochemical environment, which typically comprises a solid transition-metal electrode, an aqueous electrolyte solution, and an electrostatic field, creates favourable conditions for the electro-adsorption of two different H species, namely the under-potential and over-potential deposited H (H_{UPD} and H_{OPD}). The electro-adsorptions of H_{UPD} and H_{OPD} occur within two distinctive potential ranges and, consequently, the associated thermodynamic state functions of the processes ($\Delta_{ec-ads}G^\circ$, $\Delta_{ec-ads}H^\circ$, $(\Delta_{ec-ads}S^\circ)$) as well as the surface bond energies ($E_{M-Hec-ads}$) and surface adsorption sites are different. While the electro-adsorption of H_{OPD} takes place on all metallic and non-metallic materials on which molecular hydrogen gas, $H_2(g)$, can be generated electrochemically, the electro-adsorption of H_{UPD} is observed only in the case of the platinum (Pt) group metals (PGM, *e.g.*, Pt, Rh, Pd) and the species does not take part in the $H_2(g)$ generation. Consequently, it is a unique property of PGM's. The existing spectroscopy results, although limited and inconclusive, support the concept of two distinct electro-adsorbed H species (H_{UPD} and H_{OPD}). However, they also call for additional and dedicated research. The processes can also be studied and elucidated using the electrochemical quartz crystal nano-balance (EQCN) technique, and our recent investigations led to the discovery of the potential of minimum mass (E_{pmm}) for Pt electrodes. The H_{UPD} species modifies the interfacial hydrophilic-hydrophobic properties of Pt making it hydrophobic-like and, consequently, minimizes the interactions between the Pt surface and the electrolyte components. The E_{pmm} property together with other physical and chemical properties of Pt (noble character, chemical stability, electronic structure) further confirm why Pt is the best transition metal for electrochemical reactions involving H, such as the hydrogen evolution reaction (HER), the hydrogen oxidation reaction (HOR), and the electrocatalytic hydrogenation (ECH). This presentation discusses the elementary steps involved in the electro-absorption of H (electrochemical absorption) and the roles of the H_{UPD} and H_{OPD} species play in the process. It also explains that in the case of palladium (Pd) both H_{UPD} and H_{OPD} become absorbed, while in the case of metals that do not reveal the under-potential deposition of H phenomenon, it is only the H_{OPD} species that participates in the process.

Selected References

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