

Platinum Electrochemistry and Electrocatalysis: Unraveling the Origins of Its Unique Behavior

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The emerging hydrogen economy that envisages water electrolyzers as hydrogen-generating devices (*electrical energy to chemical energy conversion*) and polymer electrolyte membrane fuel cells (PEMFCs) as hydrogen-consuming devices (*chemical energy to electrical energy conversion*) to generate electricity drives the interest in hydrogen electrochemistry and electrocatalysis. Platinum (Pt) is one of the most important and efficient electrode materials due to its excellent catalytic activity towards H₂ generation via water electrolysis or H₂ oxidation. Yet, the origin of its exceptional electrocatalytic activity towards these reactions and towards the oxidation of simple alcohols (*e.g. methanol and ethanol*) remains poorly understood and needs to be unraveled in order to develop guidelines for the design and manufacture of non-noble electrocatalysts. The contribution presents our recent results that shed new light on the understanding of the interfacial behavior of Pt under electrochemical conditions and focuses on the under-potential deposition of H (UPD H) on Pt and electro-oxidation of Pt.

Research on the thermodynamics of under-potential deposited H (H_{UPD}) on Pt allowed us to determine the values of $\Delta_{\text{ec-ads}}G^\circ(\text{H}_{\text{UPD}})$, $\Delta_{\text{ec-ads}}H^\circ(\text{H}_{\text{UPD}})$ and $\Delta_{\text{ec-ads}}S^\circ(\text{H}_{\text{UPD}})$, as well as the value of the Pt–H_{UPD} surface bond energy, $E_{\text{Pt-H}_{\text{UPD}}}$; the latter is in the 230–264 kJ mol⁻¹ range and slightly depends on the nature and concentration of aqueous electrolyte solution. The value of $E_{\text{Pt-H}_{\text{UPD}}}$ is almost identical to the value of $E_{\text{Pt-H}_{\text{chem}}}$ under low-pressure gas-phase conditions [1,2]. On a purely thermodynamic basis H_{UPD} resembles H_{chem} and one may conclude that alike H_{chem}, H_{UPD} is embedded in the surface lattice of the Pt electrode [3,4]. Because the electro-adsorption of H_{UPD} takes place at potentials higher than the onset potential of H₂ generation or H₂ electro-oxidation, it is reasonable to conclude that the electrolytic H₂ generation or H₂ electro-oxidation takes place not on a bare Pt but on Pt that is modified with a monolayer of H_{UPD}. Therefore, the incorporation of H_{UPD} in the surface lattice of Pt gives rise to unique interfacial electronic and wetting (*hydrophilic-hydrophobic*) properties. An in-situ electrochemical quartz-crystal nanobalance (EQCN) study of the behavior of Pt in aq. H₂SO₄, HClO₄ and NaOH electrolyte solutions reveals that the interfacial mass reaches a minimum at ca. 0.045 V_{SHE} as the applied potential is scanned from +1.50 V to -0.20 V_{SHE}, or vice versa. The minimum is referred to as the potential of minimum mass (E_{pmm}) and its value coincides with the completion of electro-adsorption of H_{UPD} and the commencement of H₂ generation. The value of E_{pmm} , that is different from the potential of zero charge ($E_{\text{pzc}} = 0.27$ V_{SHE}), and the structure of the Pt|electrolyte interphase in the vicinity of $E_{\text{pmm}} = 0.045$ V_{SHE} are discussed in terms of interactions of H_{UPD}, over-potential deposited H (H_{OPD}), anions, and H₂O molecules with Pt. The monolayer of H_{UPD} that develops prior to the onset of H₂ generation modifies platinum's wetting properties making the H_{UPD}-modified Pt surface hydrophobic-like, possibly facilitating the adsorption of H_{OPD}. The EQCN analysis also reveals an increase of interfacial mass in the potential region of HER that is assigned to hydrogen bonding-like interactions between H_{OPD} and H₂O molecules in the

double-layer. The EQCN results corroborate the outcome of our thermodynamic results and support the view that the embedded H_{UPD} defines the unique catalytic properties of Pt and Pt-group electrodes.

The electrochemical growth of surface oxides on Pt in acidic electrolytes is one of the model systems, whose mechanism and kinetics are thought to be well understood. Yet, our new results demonstrate that the comprehension of the Pt|Pt oxide system is far from complete and that some concepts widely accepted by the electrochemical community for ca. thirty years are inaccurate. Therefore, the understanding of some anodic electrode processes occurring at Pt (or oxidized Pt) might be incomplete and/or incorrect. This contribution presents the most comprehensive to-date analysis of the Pt|Pt oxide system; it comprises results obtained using cyclic voltammetry (CV), anodic polarization, Auger electron spectroscopy (AES), EQCN, and data modeling.

The electrochemical growth of surface oxides on Pt reveals a clear temporal and spatial behavior. Namely, an increase of the polarization time (t_p) and/or polarization potential (E_p) translates into a greater oxide's charge density (q_{ox}), thus its thickness (d). The growth behavior and stability of Pt oxides is also affected by the temperature (T) at which the process takes place (*thermal behavior*). The chemical composition of Pt oxides is examined using AES, whilst the molecular weight (M) using EQCN. The results prove that anhydrous PtO is the surface oxide species initially formed (the experimental $M = 15.8$ g mol⁻¹ is very close to the theoretical $M = 16$ g mol⁻¹) and that OH_{ads} does not participate in the process as a stable surface compound (for $E_p \leq 1.55$ V). A comprehensive analysis of the influence of E_p , t_p and T on the oxide growth provides 140 sets of data that are modeled using oxide growth theories. The very initial Pt oxide growth up to ~1 ML of PtO is limited by the interfacial place exchange of the Pt_{surf} and O_{ads} species that are associated with the presence of Pt^{δ+}–O^{δ-} surface dipole ($\mu_{\text{Pt-O}} = 1.30$ D). In the case of oxides thicker than ~1 ML of PtO, the process is limited by the escape of Pt²⁺ from the metal into the inner metal|oxide interface; the electric field (E) that establishes across the oxide and drives the process is in the 10⁸ – 10⁹ V m⁻¹ range.

The chemical composition, electronic properties, and thickness of Pt surface oxides determine their activity towards specific anodic electrochemical reactions, kinetics of electron transfer, and adsorption of reactants, products and intermediates. The absence of OH_{ads} as a stable surface compound participating in the Pt electro-oxidation puts in question the widely accepted mechanism of CO_{ads} oxidative desorption on Pt that implies a reaction between OH_{ads} and CO_{ads} with the formation of an activated complex. Since our results point to the absence of OH_{ads}, the mechanism of CO_{ads} oxidative desorption and the origin of O-containing species that participates in the process remains to be solved.

References

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