Tuning the Activity and Stability of Platinum Nanoparticles Toward the Catalysis of the Formic Acid Electrooxidation

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The impact of tuning the electrodeposition potential (E_{Pt}) of platinum nanoparticles (PtNPs) on the catalytic activity and stability of PtNPs-modified glassy carbon (GC) (Pt/GC) catalysts toward the formic acid electro-oxidation (FAO) was electrochemically examined. Practically, different potentials ($E_{Pt} = -0.20, -0.10, 0.00, 0.10$ and 0.20 V) comprising the underpotential and overpotential deposition domains of PtNPs were employed while passing the same coulombic charge (10 mC) which ensured the deposition of the same loadings of PtNPs. The investigation disclosed the critical role of the deposition potential of PtNPs in the Pt/GC catalyst on justifying not only the catalyst's activity toward FAO which appeared boosted largely at the border potentials ($E_{Pt} = -0.20$ and 0.20 V) but also the catalyst's stability which owned the highest durability at 0 V. Several indices utilizing the current densities of the direct (favorable dehydrogenation) oxidation peak (I_p^d), the indirect (unfavorable dehydration – poisoning) oxidation peak (I_p^{ind}) and the backward oxidation peak (I_p^b) in the cyclic voltammetry of FAO were utilized to assess and compare the catalytic efficiencies of the catalysts. Interestingly, for the Pt/GC catalyst ($E_{Pt} = 0.2$ V), the I_p^d/I_p^{ind} ratio was 8 which reflected the preference of the FAO's mechanism to proceed via the favorable dehydrogenation pathway, while the I_p^d/I_p^b ratio was 0.77 which, moreover, highlighted the high tolerance of the catalyst for CO poisoning. While the catalytic enhancement of FAO was predominantly electronic at -0.20 V, it presumably originated geometrically at 0.20 V; as revealed from the electrochemical impedance spectroscopy.

Keywords: Formic acid electro-oxidation; Pt nanoparticles; Electrodeposition potential; Fuel cells.

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