

NANOSTRUCTURED HYPO-HYPER-*d*-
INTERELECTRONIC ELECTROCATALYSTS
FOR PEMFC AND THEIR CHARACTERIZATION

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Two and three component intermetallic phases of transition elements, such as MoPt₃, MoPt₄, WPt₃, HfPd₃, MoPt₃Ni, MoPt₃Co, RuPt, were deposited either directly on Vulcan XC-72 carbon powder or grafted upon hypo-*d*-electronic oxide supports in accordance with the Strong Metal Support Interaction (SMSI), which contributes both to promote synergistically their catalytic activity and to improve their CO tolerance, or even to provide the bifunctional effect for simultaneous CO and M-H anodic oxidation in PEMFC. The grafting/deposition was done by the decomposition of mixed M₁M₂M₃-acac (acetylacetonates or 2,4-pentanedionates) upon anatase titania (TiO₂ anatase either sol-gel widespread as a monolayer upon Vulcan XC-72 powder or as particles of less than 10 nm in size, more than 250 m²·g⁻¹ in surface area) or titania with sol-gel impregnated tungstenia (WO₃ after calcinations).

So far the most thoroughly studied intermetallic type electrocatalysts are MoPt₄ and RuPt which exhibit high CO tolerance. In the case of Mo-Pt monophasic polycrystalline intermetallic phases along Mo-Pt phase diagram were considered as a reference system to characterize other nanostructured electrocatalysts. In this respect Fig. 1 shows remarkable changes in XPS binding peaks indicating strong interaction between the *d-d*-electrons of Mo and Pt which is considered as the main prerequisite in intermetallic electrocatalytic synergism.

The surface work function is one of the main surface properties which affects the chemisorptive bond and stability of CO on metal surfaces. It is known from literature that metal surfaces with high workfunction create a strong bonding with CO molecule (e.g. Pt) while low workfunction metal surfaces result in the dissociation of the CO molecules through the destabilization of the C=O bond (e.g. Fe). As shown in Fig. 2 the work function of the MoPt intermetallic compounds along Mo-Pt phase diagram exhibits minimum below the corresponding values measured for Mo and Pt thus providing a deeper insight for the higher CO tolerance observed for the various Mo-Pt combinations. Similarly the hydrogen evolution reaction was found to exhibit electrocatalytic volcano behaviour for both cathodic hydrogen evolution (HER) and its anodic oxidation (HOR), while Tafel slopes in broader current density range feature rather low slopes (30 mV·dec⁻¹)².

XPS analysis was also used for the investigation of the chemical state of nanostructured grafted electrocatalysts (e.g. Pt, Pd, Ni) on titania (Fig. 3) or tungstenia supports and their correlation with polarization characteristics or their electrocatalytic activity for CO/H₂ anodic oxidation.

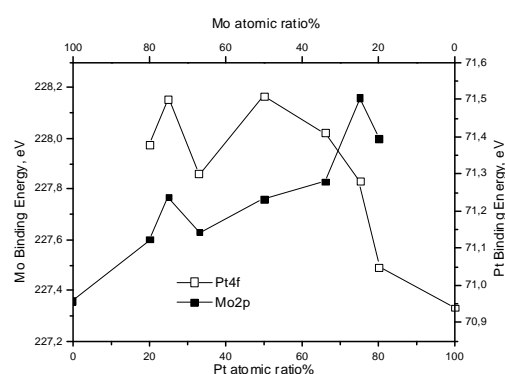


Fig. 1. XP binding energies of Pt4f and Mo2p along the phase diagram of Mo-Pt

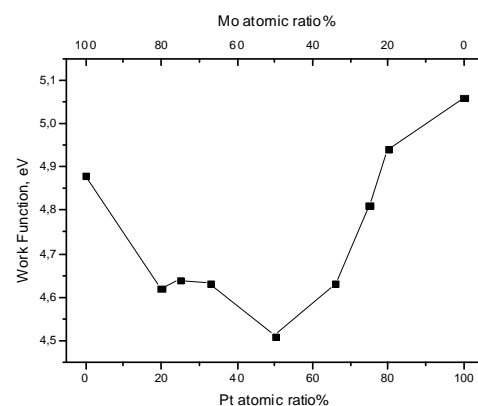


Fig. 2. Variation of Mo-Pt alloys work function along the phase diagram

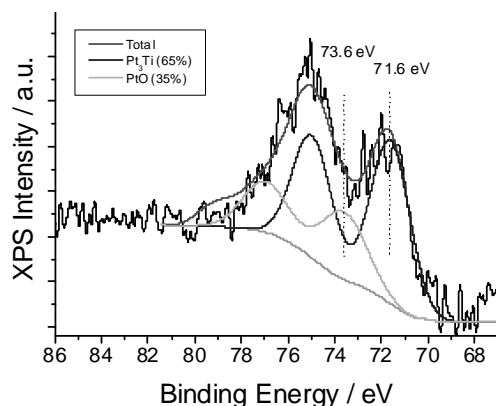


Fig. 3. The binding energy of Pt4f photoelectrons of Pt supported on TiO₂ show the formation of Pt₃Ti and PtO