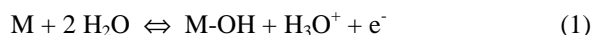


**SMSI GRAFTING OF SYNERGETIC  
ELECTROCATALYSTS FOR SIMULTANEOUS  
ANODIC OXIDATION OF CO & M-H IN PEM FC**

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The equivalence of interionic hypo-hyper-*d*-interelectronic interaction in both metallic and any other ionic state and its effect upon electrocatalytic properties for hydrogen electrode reactions (*HER*) has already been proved and inferred<sup>1,2</sup>. Strong *Metal Support Interaction (SMSI)*<sup>3</sup> has been the initial and basic idea for interactive grafting (or anchoring) of individual hyper-*d*-electronic and/or composite hypo-hyper-*d*-interelectronic metallic electrocatalysts upon hypo-*d*-electronic transition metal(s) oxide substrate(s), that both together create bifunctional properties for simultaneous hydrogen (M-H) and CO, as well as methanol anodic oxidation. The stronger the *SMSI*, the smaller uptake of CO and the weaker the chemisorptive strength of both M-CO and M-H, and thereby, both effects together contribute to the heterogeneous catalytic oxidation of CO and the electrocatalytic *HER*. The stronger the *SMSI* bonding effectiveness, as it is otherwise well known in contemporary heterogeneous catalysis, the higher the catalytic activity, while moisture plays decisive role in the overall catalytic effect. Titania (anatase, TiO<sub>2</sub>, tungstenia, WO<sub>3</sub>), as aero- and xerogels, are basically *biphasic systems* in which solvent molecules are trapped inside their oxide network, and such material can be considered as water-oxide composite. Transition metal ions usually feature several valence states giving rise to mixed valence compounds, so that such a hydrous oxide networks in particular of polyvalent hypo-*d*-electronic transition elements, substantially behave as *ion exchange membranes*. Thereby, electronic properties due to a hopping process within the solid phase have been observed in both directions, the charge and OH-adgroup transferring,



as well as reduction of oxide support by H-adatoms, therefrom creating hypo-hyper-*d*-intermetallic phases, such as TiPt<sub>3</sub>, that, in fact contribute to the *SMSI* and all wherefrom resulting bifunctional catalytic consequences, such as anodic CO oxidation,



The first principle thermodynamic analysis has shown that the spillover effect of M-OH reestablishes any disturbance in equilibria, while OH<sup>-</sup> ions of the support play the main promoting interactive role based on the 'water pumping' (Scheme I).

The Brewer<sup>4</sup> intermetallic bonding theory has been extended on the overall *interionic interactive bonding effect* and proved by plentiful *TG-TPR* measurements with various molecular level mixed hypo-hyper-*d*-interelectronic oxides in hydrogen stream. Such a theoretical model and experimental evidence has been the basis for the *selective interactive grafting* (or anchoring)

of individual hyper-*d*-electronic metals (Pt, Ru, Pd, Ni), and/or composite, usually the Brewer<sup>3</sup> type hypo-hyper-*d*-intermetallic phases (MoPt<sub>3</sub>, MoPt<sub>4</sub>, WPt<sub>3</sub>, HfPd<sub>3</sub>, MoPt<sub>3</sub>Ni, MoPt<sub>3</sub>Co, or PtRu) upon simple (TiO<sub>2</sub>), or mixed (3 – 5 mol.% WO<sub>3</sub> with TiO<sub>2</sub>, or 32 mol.% RuO<sub>2</sub>) in the sol-gel produced polymeric composition with TiO<sub>2</sub>-WO<sub>3</sub>.

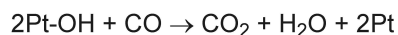
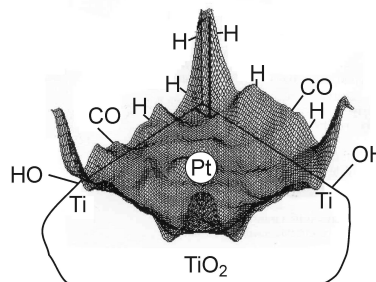
The selective grafting of such intermetallic hypo-hyper-*d*-intermetallic phases upon hypo-*d*-electronic transition metal oxide supports in nanostructured and predestined in their nano-size composite electrocatalysts were obtained by a rather mild thermal decomposition of anchored precursors (Scheme II), originating from proper mixtures of various acetylacetonates (or M-2,4-pentandionates). The ratio of active centers of oxide support, the initial concentration and total amount of such composite precursors per unit support mass, define the final average size of nanostructured electrocatalysts, resulting from hydrogen furnace at low temperature treatment (250 °C for about two hours). The *TG-TPR* method has been adapted for optimization of catalyst composition as the result of the interactive bonding of intermetallic phases upon hypo-*d*-electronic supports in the light of the *SMSI*.

**Acknowledgements**

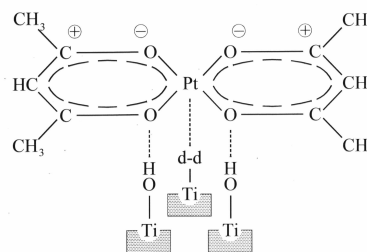
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*Scheme I.* Model presentation of M-OH transfer and spillover upon metallic part of electrocatalyst.



*Scheme II.* Schematic diagram presentation of the initial grafting (anchoring) of Pt-acac upon titania, indicating charge density distribution within the molecule and its effect upon the interactive bonding on such a support, as well as the hypo-hyper-*d-d*-interelectronic bonding.