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Primary oxide (Pt-OH) latent storage induced spillover and reversible electrocatalysts for oxygen electrode reactions

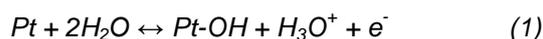
ABSTRACT

Primary oxide (Pt-OH) latent storage and electrocatalytic spillover properties for the reversible oxygen electrode (ROE) behavior have been identified and substantiated, back and forth, all along the potential axis between hydrogen and oxygen evolving limits. Such advanced electrocatalytic properties imply interactive (SMSI – Strong Metal-Support Interaction) nanostructured Pt (Au, RuPt) clusters grafting upon composite mixed valence hypo-d-(f)-oxide supports, the latter featuring extra high stability and pronounced electronic conductivity, along with spontaneous dissociative water molecules adsorption, and resulting renewable primary oxide latent storage by continuous vapor supply and membrane type hydroxide ions surface migration. The latter as individual species, under imposed polarization transfer their prevailing part of electrons to the metallic electrocatalyst, thence resulting as Pt-OH (Au-OH) dipoles, and by their surface repulsion obey reversible spillover distribution and impose the electrocatalytic ROE properties all over the catalyst surface and DL pseudo-capacitance charging and discharging.

Keywords: Primary oxide (Pt-OH, Au-OH, M-OH); surface oxide (Pt=O, Au=O); spillover (effusion); SMSI (Strong Metal-Support Interaction); d-(f)-metallic properties, UPD (OPD) double layer (DL) charging/discharging pseudo-capacitance; nanostructured bronze type electrocatalyst; alterpolar revertible cell.

1. INTRODUCTION

Ever since Sir William Grove [1] invented fuel cells (FCs), reversible oxygen electrocatalysis has been the main imperative target, challenge and dream of the entire electrochemical science, primarily focused on noble (Pt,Au) metals, while the reversible primary (Pt-OH, Au-OH) and polarizable surface (Pt=O, Au=O) oxides, along with H-adatoms (Pt-H, Au-H) represent interactive species defining the overall electrode behavior and properties. In such a respect potentiodynamic spectra usually reveal within a narrow potential range the highly reversible peaks of primary oxide adsorptive growth and desorptive removal [2,3],



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as a typical double layer (DL) charging and discharging pseudo-capacitance [4-7], which soon later disproportionates into the strongly polarizable, more adsorptive and more stable surface oxide (Pt=O) monolayer [2,3],

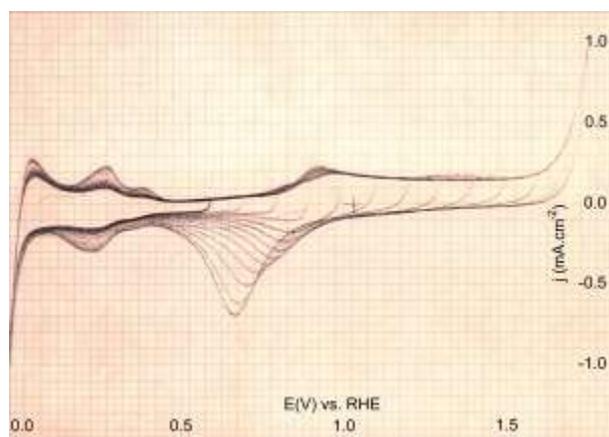
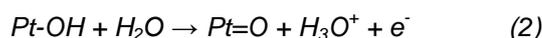
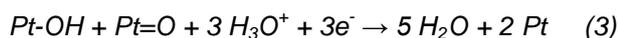


Figure 1 - Cyclic voltammograms of polycrystalline Pt scanned in 0.1 M NaOH at sweep rate 100 mV.s⁻¹

The latter imposes such a critical and typical, very pronounced **reaction polarization** range (Fig. 1) all along until oxygen evolving potential limits, and in both scan directions [4-7].

Such highly reversible (Eq. 1), relative to the subsequent strongly irreversible and substantially polarizable (Eq. 2) transient, has been decisive as concerns the overall electrocatalytic oxygen (ORR and OER) properties of both Pt and Au electrode. Since the equimolar ratio of the primary and surface oxide concentration defines the optimal interfering self-catalytic spillover reaction step in cathodic oxygen reduction reaction (ORR) [8],

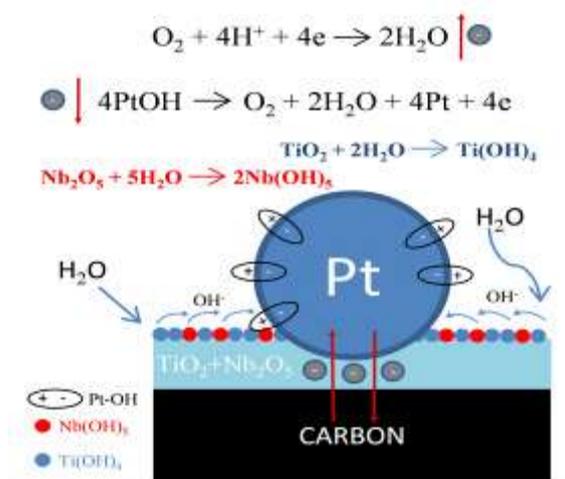


the irreversible disproportionation (Eq. 2) imposes an extremely high **reaction polarization** barrier (see later downwards) that amounts for even more than 600 mVs and then, in absence of the Pt-OH, makes plain Pt (and Au) and non-interactive supported both (Pt/C or Au/C) platinum and gold irreversible for the oxygen electrode reactions. In other words, plain and non-interactive (Pt/C and/or Au/C) supported Pt(Au) electrodes themselves by no means can behave electrocatalytic features of the reversible oxygen electrode (ROE) all along the potential axis between hydrogen and oxygen evolving limits. The strongly adsorptive and thence highly polarizable Pt=O (Au=O), deprived from any local and/or the external Pt-OH (Au-OH) supply, defines one of the most pronounced issues of the **reaction polarization** in the entire electrochemical science: No Pt-OH, means that there is no reversible reaction (Eq. 3).

2. ELECTROCATALYSIS AND SPILLOVER ELECTROCATALYSTS FOR THE ROE

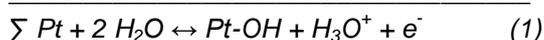
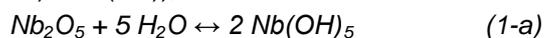
Whereas hydrogen molecules undergo spontaneous adsorptive dissociation on plain Pt (Pt/C) yielding H-adatoms (Pt-H) to establish thermodynamic equilibrium of the RHE (Reversible Hydrogen Electrode, (Pt(H₂)/Pt-H/H₃O⁺)), within the above identified critical potential range Pt (Au) is deprived (Eq. 2), from the Pt-OH (Au-OH) to provide reversible properties for the ROE ((Pt(O₂)/Pt-OH,Pt=O)/OH⁻), and both together from the reversible hydrogen fueled L&MT PEMFCs. In other words, the Pt-OH (Au-OH) plays the same thermodynamic constitutional role for establishing the equilibrium ROE, as Pt-H does for the RHE, and thence, unavoidably imposes continuous need and requires a permanent source of the former to overcome the reaction polarization and enables the reversible electrocatalytic properties of the ROE [4-7]. In such a respect, the first main step in the present concept towards the ROE implies that catalytic hyper-d-metals (Pt,Au,Ru) establish with hypo-d-(f)-oxides (or their mixed valence compo-

unds, like Nb₂O₅,TiO₂,CeO₂ or Ta₂O₅,TiO₂,CeO₂) the interactive Brewer type (d-d or d-f) bonding effect [9,10], otherwise well known in heterogeneous catalysis as Tauster [11] SMSI (Strong Metal-Support Interaction), one of the strongest in the entire chemistry (Scheme 1,[4]). Consequently, this way interactive inter-bonded composite electrocatalysts (example, Pt/Nb₂O₅,TiO₂) impose remarkably stretched d-orbitals, and thereby exhibit much weaker adsorptive interbonding strengths of intermediates (Pt-H, Pt-OH) in the RDSs (Rate Determining Steps), thence correspondingly facilitated cleavage of the latter, and thereby, increased the catalytic activity both for hydrogen and oxygen electrode reactions. Meanwhile, some other accompanying effects, in particular the ones associated with the Pt-OH spillover, play more significant role for the latter. First, hypo-d-oxides and their mixed valence compounds exhibit extra high stability in both acidic and alkaline media, and many of them pronounced (above 300 S/cm) electron conductivity (ending with 1,000 S/cm for Magneli phases).



Scheme 1 - Visual presentation of novel spillover latent storage Pt-OH type interactive supported electrocatalyst for oxygen electrode reactions, exemplified for Pt/Nb₂O₅,TiO₂/Nb(OH)₅,Ti(OH)₄ issue

Furthermore, majority of hypo-d-(f)-oxides and in particular of higher multivalent numbers, feature prevalently high percentage of dissociative water molecules adsorption [12,13], (Eq. (1-a)), and thence, the mostly enhanced surface membrane type of hydroxyl ions migration mass transfer [14], (Eq. (1-b) and (1-c)),



ending up with the prevailing electron transfer to the interactive supported metallic catalyst, so that the Pt-OH behaves as a pronounced dipole species [15], and thus, exhibits the strong spillover surface transfer and distribution. At the same time, the highly pronounced reversible potentiodynamic peaks testify for the extremely fast overall spillover reaction (Eq. 1), in both directions [2,3], primarily used for DL charging and discharging, and being ready and available for fast heterogeneous electrocatalytic reactions. In the same context, it would be significant inferring that whenever anodic oxidation reactions of the Pt-OH (Au-OH), exceed at least for an order of magnitude the disproportionation rate (Eq. 2), such as the ones with HCHO [4-7], and other aldehydes, simple alcohols and their acids, then this way these succeed highly to suppress and remarkably postpone the Pt=O growth all along the potential axis till the close proximity of oxygen evolving limits, and consequently show enormous broad extension growth of the Pt-OH (Au-OH) adsorption peak (Fig. 2, [4]).

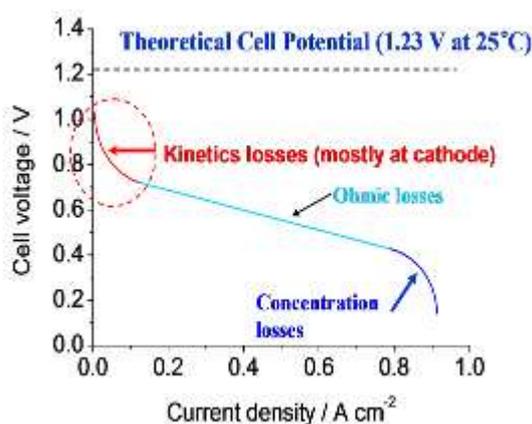


Figure 2 - Classical and characteristic energy chart diagram for nanostructured Pt/C electrocatalyst in LT PEMFCs (constructed and courtesy by R. Adzic).

In such an overall constellation, individual hypo-d(f)-oxides, and even more so their mixed valence composite compounds, when in expanded (sol-gel synthesis with thorough liquid CO₂ supercritical drying) hydrated surface state, behave as unlimited latent storage and spillover sources of the primary oxide [4,6,16,17], continuously being renewed and recovered simply by water vapor supply and instantaneously proceeding spontaneous dissociative adsorption of water molecules. In such a respect, it is certainly worth mentioning the auto-catalytic Ertel [18] effect of water molecules for the Pt-OH growth that mostly occurs in all heterogeneous oxidation processes, particularly when these appear as dipoles polarized within double layers (Eq. 1). Haruta [19] in the same sense has pointed out the lowest threshold moisture content below which there is no CO oxidation upon

interactive supported catalysts (nanostructured Au/TiO₂). Meanwhile, Boudart [20, 21] inferred on the continuous minimal monolayered vapor condensation as precondition for fast spillover of H-adatoms upon hydrated (Pt/Nb(OH)₅) state, and *vice versa*, the same for the Pt-OH [2,3], even at ambient temperature, while in dried oxide state, it needs 400 °C. In fact, there establishes an entirely thermodynamic equilibrium (Pt/H_xNb₂O₅ ↔ Pt/Nb(OH)₅), which enables the reversible alterpolar interchanges and therefrom the substantiation of superior revertible cells altering between PEMFCs and WE (Water Electrolysis), otherwise of substantial significance for the hydrogen energy balance and performances (overnight energy sufficiencies, and daily deficiencies). In other words, no spillover of primary oxides (Pt-OH, Au-OH), means that there are no reversible alterpolar changes and no advanced revertible cells!

In general, nanostructured Pt (Au) electrocatalysts selectively interactive grafted upon hypo-d(f)-oxide supports, when the latter exists in the hydrated external surface state (Scheme), and thence consequently exhibits enriched Pt-OH (Au-OH) latent storage, as the feedback oxophilicity effect and property, so that the corresponding primary oxide continuously features renewable spillover, simply by water vapor supply (surface phenomena, no concentration polarization), and further continuously resulting spontaneous dissociative adsorption of aqueous species, then the reversible anodic oxygen evolution (Eq. 4) takes place straight from pronouncedly exaggerated and also the highly reversible Pt-OH (Au-OH) adsorptive peak capacities (Fig. 3 and 4) [5,16]



and, thence, at the thermodynamic equilibrium (ROE) potential value.

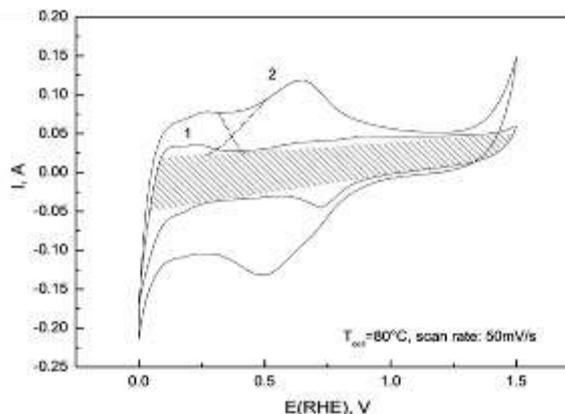
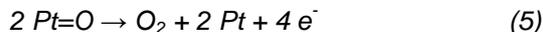


Figure 3 - Cyclic voltammograms of interactive (SMSI) supported nanostructured Pt electrode (Pt/TiO₂, WO₃/C), on mixed valence hypo-d-oxides, scanned in He stream, ones at negligible moisture content (curve 1) and at 80 °C water vapor saturation (curve 2) (scanned by D. Labou).

Quite on the contrary, in classical issues (Fig. 1), the latter occurs from the strong irreversibly deposited and highly polarizable monolayer of the Pt=O, (Eq. 2), and thereby, while being deprived from primary oxides, at rather high anodic overpotentials,



and *vice versa*, the same occurs both in these reversible and/or irreversible states, as concerns the ORR, all along the reverse cathodic scan and polarization (Figs. 1, 3 and 4) [4].

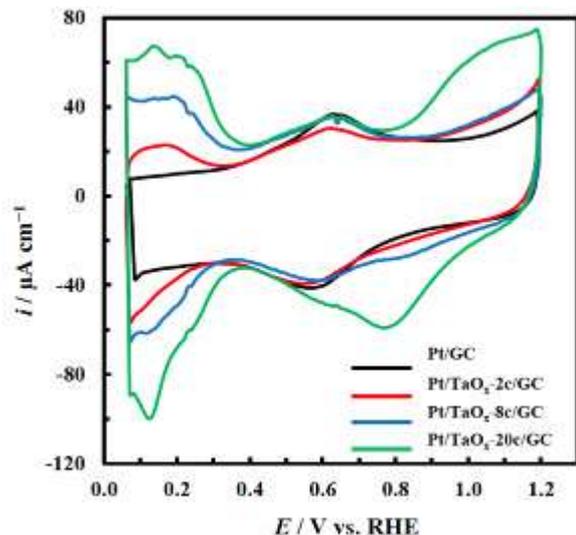


Figure 4 - Cyclic voltammograms scanned at the Pt/GC and Pt/Ta₂O₅/GC catalytic electrodes with 2c, 8c, and 20c (cycles) in Ar-saturated 0.5 M H₂SO₄ solution at scan rate of 50 mV·s⁻¹, revealing the effect of proportional increasing of interactive Pt supporting Ta₂O₅ deposit on the Pt-OH spillover effect and growth for the ORR (courtesy by T. Ohsaka [16])

The transient between the reversible and irreversible status features some sharp thresholds both as a function of hypo-d(f)-oxide unit content and/or wetness percentage (Figs. 3 and 4, [4]), and substantially reflects the Pt-OH (Au-OH) properties (present or absent) for the oxygen electrode reactions [4-6]. In such a context, plain and non-interactive supported Pt (Pt/C), in the absence of primary oxides, and thereby established *a priori* existing the broad reaction polarization range, by no means can feature the overall reversible oxygen electrode properties within the whole potential axis, in between of the hydrogen and oxygen evolving limits. Thus, there exists either the reversible behavior in the presence or continuous external supply of primary oxides, or highly irreversible properties in the absence of the Pt-OH (Au-OH), and this is the substance for Pt and Au electrocatalytic properties! In such a context, the

simple stoichiometric combination of Eq.1 and Eq. 4, reveals that the overall reversible anodic oxygen evolution initiates from water molecules and obeys the auto- or self-catalytic Ertel framework [18], with the general oxidation mechanism based on and catalyzed by M-OH species, or the primary oxides as the main interfering electrocatalytic species, and substantially takes place at the reversible oxygen potential value; the same in the reverse cathodic ORR scans. However, when oxygen evolving initiates from Pt(Au) monolayer covered by the strongly adsorptive and polarizable surface oxide (Pt=O, Au=O), the anodic, and reverse cathodic reaction have both to overcome remarkable overpotentials (Eq. 5, adjoined with Eq. 2). This is the substance and difference as concerns the irreversible plain (Pt,Au) and non-interactive supported (Pt/C,Au/C), and/or the enriched latent storage and continuous external spillover feeding of the primary oxide for interactive hypo-d(f)-oxides supported Pt) electrode.

3. ELECTROCATALYTIC CONSEQUENCES

Since Pt(Au) electrocatalyst becomes interactive d-d(f)-bonded with and grafting fixed upon hypo-d(f)-oxide type catalytic supports in new composite nano-structure, there is no more its metallic surface diffusion and agglomeration, nor any Nafion membrane cross-over of hydrogen. Even more so, from the same reasons, the life-time of Pt(Au) is at least twice longer and can be guaranteed. Alterpolar changes in the revertible PEMFC versus WE proceed reversibly and instantaneous smoothly and enable their superior unique operation and interchanges. There is a great number of parametric and structural variability for the voltage/current optimization and stability, such as hypo-d-oxide radius of small, medium and large d(f)-metals (Y,Ti,Nb,Ta,W,Ce,Ho,La, etc.), to keep low Tafel slope within 0 – 1.0 A cm⁻². Since some of hypo-d(f)-oxide supports of composite electrocatalysts (NbO, TaO, TiO) feature advanced electron conductivity, nano-particulate carbon carriers and current collectors can be completely avoided that is substantially significant for WE and mostly for anodic oxygen evolution. In such a respect, the present paper defines the main substantial and advantageous frameworks in electrocatalysis of reversible electrocatalysts for oxygen electrode reactions (mostly ORR and OER), primarily for L&MT PEMFCs, WE, and revertible combinations, and as the overall main conclusion, hopefully means the most important contribution all after Sir William Grove. All stated herein for Pt, means even more for Au when oxygen electrode reactions are in consideration (ORR, OER) [22-27]. The actual target: Tafel

slopes 60 mV/dec, or $\eta = 180$ mV at $1,000 \text{ mA/cm}^2$, or ideal 30 mV/dec, or 90 mV at 1.0 A/cm^2 .

4. STEP BY STEP THEORY DEVELOPMENT AND CONFIRMATION

Although Pt best satisfies electrocatalytic requirements of PEMFCs for hydrogen electrode reactions (HER), both common energy chart diagrams (Fig. 2), and interconnected cyclic voltammograms (Fig. 1) heuristically show that the reversible behavior for cathodic oxygen reduction (ORR), like a broad plateau in the energy conversion, starts within the potential range of reversible peak of the Pt-OH desorption and consequently, overall loses within the preceding critical potential range amount for more than half of thermodynamic available value; or about 600 mVs. The main obstacle arises as the reaction polarization between the reversible adsorption/desorption peaks of the primary oxide growth and removal (Eq. 1), and anodic oxygen evolution, in both potential scan directions, as the result of irreversible disproportionation (Eq. 2) of Pt-OH (Au-OH) into highly polarizable and strongly adsorbing surface oxide (Pt=O, Au=O). Thus, ever since Sir William Grove [1] invented fuel cells (FCs), the electrocatalytic search for the reversible oxygen electrode (ROE), and most particularly the ORR, became the main challenge and imperative target in electrochemistry of aqueous and PEM media, while its substantiation is the subject matter of the present paper. The substance is to replace the potential range of the reaction polarization of the monolayered surface oxide by the reversible electrocatalysis and make Pt(Au) catalytically active all over the potential axis between hydrogen and oxygen evolving limits, back and forth.

5. GENERAL THEORY AND ITS SUBSTANTIATION

Whereas hydrogen molecules undergo spontaneous adsorptive dissociation on plain Pt and non-interactive supported (Pt/C) and H-adatoms (Pt-H) establish thermodynamic equilibrium of the RHE (Reversible Hydrogen Electrode, (Pt(H₂)/Pt-H/H₃O⁺)), within the above identified critical reaction polarization range Pt (Au) is deprived from the Pt-OH to provide reversible properties for the ROE ((Pt(O₂)/Pt-OH,Pt=O)/OH⁻), and both together the reversible hydrogen fueled L&MT PEMFCs. In other words, the substantial and decisive point is that even within the highly reversible peak of the anodic Pt-OH growth, (Eq. 1), there immediately proceeds the strongly adsorptive and highly polarizable electrode process of its irreversible Pt-OH (Au-OH) disproportionation into the stable surface oxide (Pt=O), (Eq. 2), and imposes such a critical polarization range (Fig. 1 and 2) all along until

anodic oxygen evolution, and equally so in the reverse scan direction.

In such a respect, polarization properties of some typical and characteristic novel interactive hypo-d-oxides supported nanostructured Pt electrocatalysts for both the ORR and OER [4,22], enable to select some diagnostic kinetic criterions on the way towards the ROE, revealing from their Tafel plots: (i) Nano-dispersed Pt/C clusters (10 wt.% Pt) adhering upon sol-gel developed indifferent nano-particulate E-tek, Inc., Vulcan-XC-72 carbon (240 sq.m/g) carrier and current collecting species, considered for the classical issue of such an electrocatalytic activity comparison; (ii) The interactive supported nanostructured Pt particles upon both the extra stable and electron conductive (300 – 1,000 S/cm), ceramic Magneli phases (Ebonex[®]), Ti_nO_(2n-1), in average Ti₄O₇, usually defined as a shared rutile structure, accommodating the oxygen suboxide deficiency in the structure by the formation of crystal shared planes along the nth layerlike plane of octahedron, so that Ti₄O₇, has one TiO for every three TiO₂ layers; (iii) Advanced interactive selective grafted and homogeneously distributed nanostructured Pt clusters down to the prevailing (2.2 ± 0.2 nm) nano-size, upon the optimized structure of mixed valence hypo-d-oxide compounds (Pt/Nb₂O₅,TiO₂/C), and even further extended (iv) composites with hypo-f-oxides (Pt/Nb₂O₅,CeO₂,TiO₂/C, including doped GdO₂, HoO₂, and LaO₂ itself), and their relative combinations of extra high stability and remarkable electron conductivity, too.

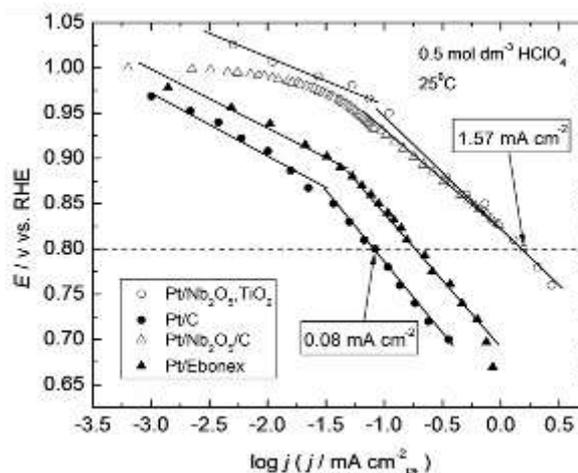


Figure 5 - Tafel plots for the cathodic ORR scanned on RDE in 0.5 M HClO₄ solution at 25 °C for E-tek, Inc., Pt/C (Vulcan XP-72, closed circles); Pt/Ebonex (Magneli phases, closed triangles); Pt/Nb₂O₅ (20 wt.%)/C (70 wt.%) (open triangles); and Pt/Nb₂O₅ (5 mol.%), TiO₂ (95 mol.%) (open circles) (Pt 10 wt.% in all issues), (scans and search N.V.Krstajic)

Such comparable diagnostic Tafel polarization interdependences distinctly display Fig.5, with differences of more than an order of magnitude in the electrocatalytic activity for the ORR that arise **only as** the result of different hypo-d-f-oxide type of interactive catalyst supports, relative ratios of their amounts *versus* metallic part of the catalyst (Pt), and their corresponding SMSI [11].

6. LEADING IDEA FOR THE ROE ELECTROCATALYSTS

Some subtle potentiodynamic survey of fundamental significance has then been focused on the actual mixed interfering Pt-OH/Pt=O coverages at selected points (Fig. 6, a&b) within the characteristic potentials close to the open circuit value and all along the reversible potential range of low Tafel slopes (mostly 30 mV/dec).

The main conclusions then have been that Pt electrodes, both plain and interactive supported upon hypo-d-oxides, have been covered by mixed Pt oxides, while at higher irreversible polarization (120 mV/dec), they were completely deprived from such adsorptive layers. In other words, while within the reversible range, the ORR is associated with and **proceeds upon mixed oxide covered Pt surface**, as the interfering self-catalytic spillover electrode process, (Eq. 3), otherwise known as the fastest reaction step [8], the oxide-free Pt surface imposes much higher polarization for the direct electron transfer reaction to occur. Thus, the conclusive observation has now been that **Pt oxides (in particular the Pt-OH), play the same self-catalytic role to establish the ROE properties**, as the spontaneous hydrogen (Pt-H) adsorption does and means for the RHE. In fact, the leading idea consists now from the extension of the reversible Tafel plot for the ORR all along the potential axis down from or up to the thermodynamic value (1.29 V vs. RHE) that implies enriched external latent Pt-OH storage and continuous spillover supply all along in both scan directions, and particularly within the critical potential range (Fig. 1 and 2). Namely, so far the problem and obstacle were the initial highly reaction polarizable potential range of strongly adsorbed monolayered Pt=O and missing the Pt-OH, which cannot be supplied from aqueous solution, but only as the adsorptive species. These rather specific potentiodynamic measurements even more clearly show that the ORR upon Pt/Ebonex starts and finishes at remarkably more positive potential values (1.05 down to 0.86 V, *versus* 0.95 down to 0.8 V, all *versus* the RHE), relative to polycrystalline Pt metal and/or nanostructured Pt/C [4,22]; whereas the other two congenial issues (iii & iv) initiate with 1.29 V as the completed reversible property of the ROE (Fig. 3

and 4). These have been decisive observations of substantial significance for reversible electrocatalysis in oxygen electrode reactions.

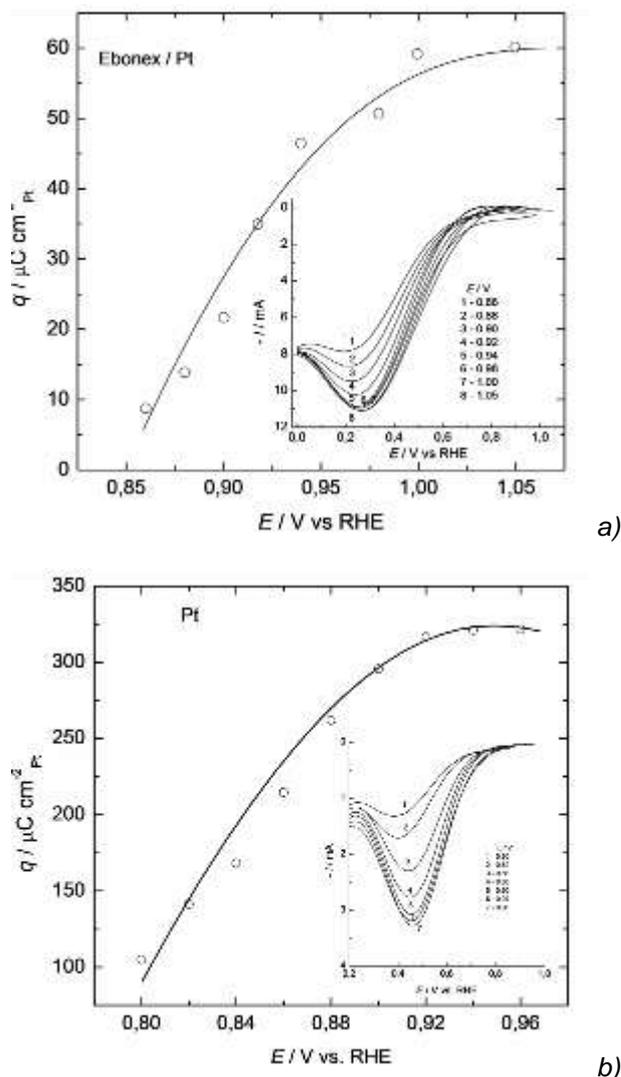


Figura 6 - (a) Charge density (q) that required adsorbed oxygen species (Pt-OH/Pt=O) for their reduction, presented as a function of potential for Pt/(Magneli phases) (5 mg) electrode, same as in Fig. 5. The inset shows potentiodynamic I vs. E relations scanned from indicated different initial potentials (hold) with sweep rate of $5 \text{ V} \cdot \text{s}^{-1}$. (idea, scans and consideration by N. V. Krstajic). (b) The same as in (a), but for polycrystalline Pt metal

In such a respect, the guiding concept implies homogeneous nanostructured distribution and selective grafting while interactive hypo-hyper-d-d-interelectronic bonding of Pt(Au) nano-clusters upon various individual and preferably mixed valence hypo-d-oxide supports, taken for the reversible external interconnected latent storage and spillover Pt-OH (Au-OH) sources, primarily $\text{Nb}_2\text{O}_5, \text{TiO}_2$ (or $\text{Ta}_2\text{O}_5, \text{TiO}_2$), because of their much

advanced both stability and electronic conductivity. In such a constellation, nano-particles of solid oxides and Pt establish the SMSIs, the ones of strongest in the whole chemistry (Scheme 1, [4]), together with the electron conductive transfer, while external surface of hypo-d-oxide deposit undergoes spontaneous dissociative adsorption of water molecules and thereby becomes, along with continuous further water vapor supply (Scheme), the renewable and dynamically almost unlimited latent storage and spillover source of the Pt-OH.

7. SPILLOVER PHENOMENA IN ELECTROCATALYSIS OF THE ORR

Spillover phenomena in general impose strong repulsion forces, when RDS intermediates (Pt-OH, Pt-H) partially transfer their charge to the metallic catalyst surface and become dipoles [15]. The driving force for such effusion effects imposes the gradient of electrochemical potential, which implies chemical potential for heterogeneous catalytic processes. Namely, the fundamental Guldberg-Waage law of mass action predicts that the faster the spillover effect of the reacting intermediate species in the RDS, the faster the corresponding electrode reaction becomes.

8. ADSORPTIVE DISSOCIATION OF WATER MOLECULES AND MEMBRANE TYPE SURFACE MIGRATION

The first decisive step towards rather fast spillover widespreading phenomena of the Pt-OH is the consequence of a strong first principle thermodynamic confirmed evidence (Density Functional Calculations, DFC) by Vittadini *et al.* [12], that water molecules undergo prevailing spontaneous dissociative adsorption on anatase and even rutile titania, and more so on the higher altermultivalent oxides [13] of tungsten, molybdenum, tantalum, niobium and/or cerium, etc., (Fig. 7), as the general oxophilicity properties of hypo-d-metals.

In addition, the first-principles molecular-dynamic simulations showed the existence of a mechanism for thermodynamically favored spontaneous dissociation of water molecules even at low coverage of oxygen vacancies of the anatase (101) surface [13], and consequently at the Magneli phases, as substantially suboxide structure significant both as highly bulk electronic conductive, membrane type surface transferring hydroxide species and interactive catalyst support [5,6]. In fact, this is the status of reversible open circuit dissociative adsorption of water molecules at the equilibrium state, something like capillary phenomena in adsorption after some critical

coverage extents. Meanwhile, in the presence of the nano-sized metallic part of the catalyst, and continuous enough moisture supply, directional electric field (or, electrode polarization), further disturbs such an established equilibrium and dynamically imposes further continuous forced dissociation of water molecules, and as the consequence, their membrane transport properties[14], (Eqs. (1-a), (1-b), (1-c)) summation (Σ) yields Eq. (1), see the main part of this paper), definitely resulting with spillover features.

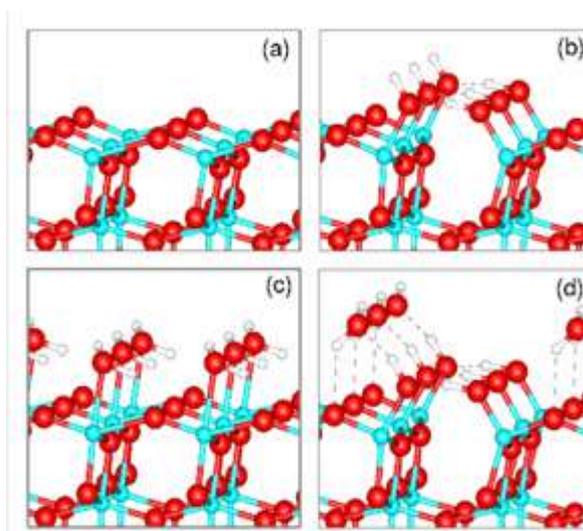
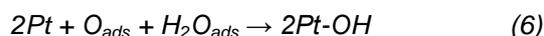


Figure 7 - The perspective views of DFT-optimized atomic structures for: (a) the clean anatase (ADM) ad-molecule model of unreconstructed (001) surface; (b) the dissociated state of water (0.5 monolayer) on (001); (c) the relaxed geometries of molecular state of adsorbed water (1.0 monolayer) of hydroxylated anatase on (001); and (d) the mixed state of water on (001) with a half-dissociated coverage of adsorbed monolayer water molecules (courtesy by A. Vittadini, cf. 12).

Such an oxide network, in particular of polyvalent (high altermultivalent numbers) hypo-d-elements, when in hydrous state, distinctly behaves as an ion exchange membrane even for the surface hydroxide migration. In fact, gels (aero and xerogels) are biphasic systems in which solvent molecules are trapped inside an oxide network, and such a material can be considered as a water-oxide membrane composite [14]. At the same time, the highly pronounced reversible potentiodynamic peaks testify for the extremely fast and *independent* overall spillover reaction (Eq. 1), in both directions [2,3], primarily used for DL charging and discharging pseudo-capacitance [4-6] and being always available for heterogeneous electrode reactions (see further downwards).

9. ELECTROCATALYTIC SPILLOVER PHENOMENA

The first spillover phenomenon in heterogeneous catalysis was observed and defined by Boudart [20,21] for the interactive supported bronze type (Pt/WO₃) catalyst, initially at high temperature (above 400 °C) for pure solid oxide system. Meanwhile, after the dissociative adsorption of water molecules on hypo-d-oxide supports of Pt, the fast interactive effusion of H-adatoms over its hydrated (W(OH)₆) surface becomes dramatically sped up even at ambient conditions in the ultimate presence of condensed at least monolayer aqueous precipitate, and *vice versa*, establishing capillary phenomena of speeding up effusion of the main catalytic reaction intermediates (Pt-OH). Such a striking sharp wetness impact upon the overall spillover phenomena associated with hydrated hypo-d-oxides in aqueous media, implies Ertel [18] autocatalytic molecular water effect, too, which states that the catalytic reaction of hydrogen oxidation upon Pt surface, even at deep low temperatures (140 °K), proceeds with remarkable amounts of the Pt-OH, as the decisive and accumulated intermediate, including the self-catalytic step with adsorbed water molecules,



In fact, Ertel has pointed out the substantial overall significance of water molecules in heterogeneous catalysis for oxidation processes that in general proceed over the Pt-OH generation and spillover.

This is significant both for the evidence of the extremely fast spillover widespreading and thereby resulting with imposed the reversible hydrated substrate reduction. The latter finally leads to the corresponding form of electrocatalytically active bronze (Pt/H_{0.35}WO₃) for cathodic processes, in which non-stoichiometric incorporated hydrogen obeys the same free reactive properties like adsorptive (Pt-H), and is the main source for the electrode or heterogeneous catalytic reactions. In other words, the point is that spontaneous dissociative adsorption of water molecules [4,5,12,13] imposes much smaller activation energy for transformation of the resulting hydrated W(OH)₆, into corresponding bronze state, and occurs even at ambient temperature, then behaving remarkably different than the initial solid oxide WO₃, and thereby, dramatically facilitates the overall spillover effect under pronounced wet status (the activation energies thence being in the ratio of 2.2, one with another). The alterpolar interchanges between the bronze type electrocatalyst and its hydrated state are correspondingly approved

occurring instantaneously and reversibly fast, exactly because of the substantially facilitated Boudart [20,21] spillover effect and behave as a thermodynamic equilibrium (Pt/H_{0.35}WO₃ ↔ Pt/W(OH)₆ or, Pt/H_xNbO₅ ↔ Pt/Nb(OH)₅).

Hypo-d-electronic transition metal oxides usually feature several altervalent states giving rise even to interactive mixed valence compounds, such as, for example, TiO₂/WO₃, TiO₂/Nb₂O₅, TiO₂/Ta₂O₅, or TiO₂/Nb₂O₅/CeO₂, and then correspondingly increase the overall latent storage and spillover effect of both H-adatoms and primary oxides (M-OH). The whole spillover and SMSI effect behave typical synergistic electrocatalytic properties and never any individual hypo-d-oxide enables that much as mixed altervalent composites.

The problem so far was in unattainable nanostructured Pt-bronze, the catalytic activity of which exponentially increases with decreased Pt nano-size approaching maximum at monoatomic dispersion [22,23]. This requirement has now been fulfilled by the grafting implementation of Pt-acetylacetonate within colloidal particles of peroxopolytungstic acid, niobia (Nb₂O₅), tantalum (Ta₂O₅) and ceria (CeO₂).

10. ANODIC HCHO OXIDATION AND PRIMARY OXIDE SPILLOVER

Since the heterogeneous reaction of formaldehyde oxidation with Pt-OH, and in particular Au-OH, proceeds as a fast reversible anodic process mass transfer limited, and since HCHO is soluble in all ratios in aqueous media, the primary oxide generation rate and its yielding spillover, have primarily been investigated by potentiodynamic spectra within the broader concentration range and between hydrogen and oxygen potential evolving limits (Fig. 8 a&b). Such for an order faster anodic reaction is able to postpone within unusually long potential range the recombination of the primary (Pt-OH), into the more polarizable, more adsorptive and more stable surface oxide (Pt=O), (Eq. 2).

Formaldehyde oxidation starts at its reversible potential (0.32 V vs. RHE), merges with the second UPD desorption peak of H-adatoms, and extends as an exaggerated broad twins peak all along the anodic scan, nearly until the beginning of OER (Fig. 8a). In the same sense anodic Pt-OH striping CO oxidation on composite hypo-d-oxides supported Pt or Pt,Ru catalysts takes place even within the usual interval of UPD H-adatoms desorption (Fig. 7, [22]). In other words, Pt-OH arises available for reaction not only within its nominal reversible adsorption/desorption peak limits in regular mineral acid or alkaline aqueous

solutions, but depending on the reactant (HCHO, HCOOH, CO, etc.) concentration, affinity and its actual reaction rate, along a broad and extendable potential range. Meanwhile, as the link of DL charging/discharging, it actually extends and appears available all along the whole potential axis

of cyclic voltammograms. Such an unusually broader charge capacity area (Fig. 8, a&b), usually features all the properties of typical under- and over-potential oxidation (UPO,OPO) peaks, in particular when compared with cathodic UPD properties of H-adatoms on various metals.

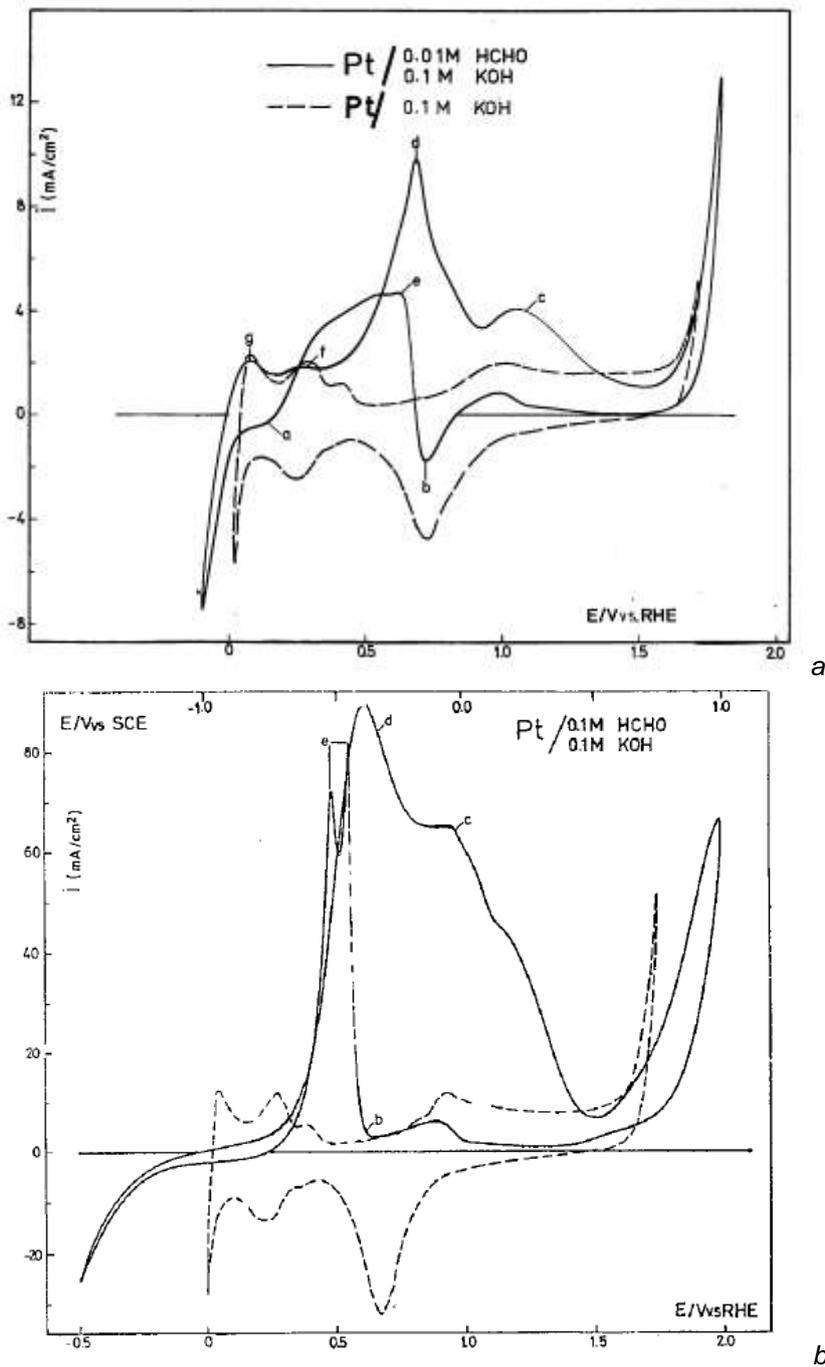


Figure 8 - Cyclic voltammograms scanned on a polycrystalline Pt wire electrode in alkaline (0.1 M KOH, dashed lines) solution and in admixture of formaldehyde (0.01 M (Fig. 8a) and 0.1 M HCHO (Fig. 8b), full lines) at 200 mV s^{-1} sweep rate between hydrogen and oxygen potential evolving limits. Labels: (a) reversible hydrogen adsorption peak; (b) irreversible Pt surface oxide (Pt=O) desorption peak; (c and d) successive peaks of anodic aldehyde oxidation; (e) sudden sharp current jump and reverse peak of repeated HCHO oxidation in the course of successive cathodic scan; (g and f) reversible H-adatoms oxidation and desorption peaks, respectively. (scans and discussion by C.M.Lacnjevac).

Stepwise potential extension of positive potential limits toward the oxygen evolution reaction (OER), clearly shows (Fig. 8, a&b) the absence of Pt=O growth almost until oxygen starts evolving. Then, since during the reverse potential scan toward the HER, as the result of the former, there arises the Pt=O desorption much earlier and of dramatically reduced charge capacity than in the simple acidic or alkaline solutions, the appearance of a characteristic sharp anodic current jump testifies for the hysteretic (cathodic sweep, anodic peak) aldehyde oxidation within the former DL charging/discharging range, and this way reflects the specific and highly reactive properties of the Pt-OH. In other words, as a corollary, there is no anodic aldehyde, alcohol, their simple acids, and even CO oxidation, nor the ORR, upon any M=O (Pt=O, Au=O) covered metal surface prior to the potential of molecular oxygen evolution, when the latter becomes broken, but only upon prevailing Pt-OH spillover deposits.

Namely, since aldehydes are often soluble in aqueous media almost in all ratios, their voltammograms at high contents feature imprinted extremely high both charge capacities and limiting currents at their peaks (Fig. 8b), and thereby testify for almost unlimited reversible reaction rates (Eq. 1), as long as diffusional mass-transfer supply provides enough reacting species. Even more so, for interactive supported Pt and Au upon higher altermultivalent hypo-d-oxides and their mixed valence compounds, since these behave as highly enriched latent storage capacities of primary oxide spillover sources [16,17,28,29].

This is the cause and reason why within the reversible part of Tafel plots electrocatalytic metal (Pt,Au) surface is always covered by the interacting Pt-OH/Pt=O species, and naturally tends to impose the reversible oxygen electrode properties, and these are experimental evidence that the optimal catalytic rate implies their optimal ratio.

Meanwhile, in such a context, one of the most outstanding observations has been that cyclic voltammograms of both formaldehyde (Fig. 4,[28]) and formic (muriatic) acid (Fig. 4, [29]) anodic oxidation distinctly differ upon plain (Pt/C) and the same, but more or less enriched supports in specific amounts of interactive hypo-d-oxide (Pt/Ta₂O₅/C). In other words, the all parameters and conditions being the same, the reaction rate becomes dramatically different upon various supported electrocatalysts in their hypo-d-oxide amounts, as the result of distinctly different the additional Pt-OH spillover feeding and spreading effects, and as the only distinctly imposed difference. Such a conclusive observation belongs to the main experimental arguments to prove the

theory of the M-OH interfering self-catalytic spillover contributions in electrocatalysis of aqueous media, (Eq.3), [4-7], finally providing the ROE behavior and properties, and traced the way and entire approach for its substantiation. In such a respect, cyclic voltammograms deeper enlightened and more revealed the spillover reaction impact properties of the Pt-OH.

11. POTENTIODYNAMIC SCANS OF PRIMARY OXIDE LATENT STORAGE AND ELECTROCATALYTIC SPILLOVER SPREADING

Some intermolecular compatible hypo-d-oxide mixed valence architecture (Pt/WO₃,TiO₂/C, Pt/Nb₂O₅,TiO₂/C), as the interactive catalytic submonolayer supports of high altermultivalent number or capacity, have been investigated by potentiodynamic scans to reveal both the primary oxide latent storage and resulting spillover yielding properties, along with same for H-adatoms. In this respect, cyclic voltammograms scanned at low moisture content of He stream (just enough to enable basic electrode processes to proceed), insufficient for WO₃ (or TiO₂) hydration, repeatedly reveal similar potentiodynamic spectra characteristic for indifferent carbon supported (Pt/C), or plain Pt itself (Fig. 3), but with high double layer charging capacity, because of the accompanying parallel charging of Vulcan carbon particles beside the metal (with correspondingly large charge value, Q_{DL}= 1.07 C).

In contrast to such fairly common occurrences, a continuous supply of saturated water vapor in the He stream at higher temperature (80 °C), imposing condensation (Boudart spillover precondition [20, 21]), and leading to the appearance of wet titania-tungstenia mixed valence oxide composite, along with spontaneous dissociative adsorption of water molecules all over its exposed surface, as the interactive catalytic support, has been accompanied by the unusual phenomenon of a dramatic expansion of two reversible pairs of peaks of both the primary oxide high striking reversible values (Q_{Pt-OH(a)} = Q_{Pt-OH(c)} = 1.453 C), and H-adatoms (247 versus 47 mC cm⁻², or in the ratio of about 5.3:1.) chemisorptive deposition and desorption (Fig. 3), like a DC capacitance of extremely developed electrode surface. Since these are highly reversible and evidently behave pronounced exaggerated high the latent Pt-OH storage (cf. [4,5,12]), they keep the same their extents even after multiple and repeating number of cycles at any other time. The latter have both been of unusually high spillover charge and discharge capacity values and for Pt-OH (UPD and OPD) shifted towards both much more negative and far positive potential limits, in common with Fig. 6a&b, and discussion thereon. In fact, two distinctly

different cyclic voltammogram shapes and charge capacities (Fig. 3), appear only as the result of the difference in water vapor supply, all other parameters being unaltered the same, and as the effect of the equivalent dipole (Pt-OH) charging and discharging of the double layer, since nothing else takes place in between. Every cessation in the steam supply instantaneously imposes the sudden reversible shrinkage of both such rather exaggerated pairs of peaks down to the same initial potentiodynamic shape similar to the nanostructured Pt/C voltammogram spectra themselves. *Vice versa*, the renewed saturate water vapor feeding immediately leads to their former Pt-OH peaks and the same former charge capacities; namely, the effect already noticed and scanned for formaldehyde [28] and formic acid [29] oxidation. Such an appearance without exception behaves as a typical reversible transient phenomenon by its endless altering repetition, and never appears upon the plain Pt/C electrocatalyst, both wet and/or dry, nor with small and insufficient amounts of catalytic hypo-d-oxide supports.

The complementary interactive Ta₂O₅-based electrocatalytic support strongly reinforces just displayed potentiodynamic features of Pt/WO₃,TiO₂/C by their coinciding and congenial spectral behavior: The distinct growth of Pt-OH and H-adatoms adsorption and desorption peaks, reflecting their different accumulated latent charge capacities, as a function of the amount (charge density) of interactive composite hypo-d-oxide deposits per unit electrode surface (Fig. 4) [16]. In fact, such Pt-OH latent storage growth (including the corresponding spillover effect) does not extend endlessly and usually passes over remarkably pronounced maximum in the ORR catalytic rate and activity.

What is now the substantial difference between voltammograms in Fig. 3, wet state, and Fig. 8,a&b (or Fig. 4)? Even when mostly suppressed in the surface oxide (Pt=O) adsorptive growth (Fig. 8,a&b), the reversal backward cathodic scans on plain Pt proceed still highly polarized for about 600 mV with negligible or zero current, exactly corresponding to Fig. 1. In other words, there is still no stored Pt-OH on plain Pt to start the self-catalytic interfering reaction (Eq. 3) of the ORR, or HCHO oxidation. However, on the hypo-d-oxide interactive supported Pt catalyst, the *a priori* latently accumulated initial storage of the primary oxide from the beginning is ready and available, and thence, continuously provides and spillover enhances the latter to proceed as the uninterrupted and extra fast reversible electrode reaction, as long as there is continuous water vapor supply. However, for the plain Pt (or Pt/C), the sudden hysteretic sharp anodic current jump in the course

of reversal cathodic sweep (Fig. 8, a&b) rearises at and coincides with the classical position of the reversible peak for the Pt-OH growth, reflects the local interfering self-catalytic effects at such potential range, provided by the repeated Pt-OH spillover growth (Scheme). This is the striking point and the core substance of the present study, while Fig. 3, supported by Fig. 4, are the best illustrative issues of the substantiated reversible electrocatalyst for the oxygen electrode reactions (ORR, OER), (Eq. 3 and 4).

12. CONCLUSION

Classical potentiodynamic spectra in aqueous media, (Fig. 1), straight after adsorptive Pt-OH peak, reveal unusual, anomalous, longer and stronger anodic polarization even within the thermodynamic equilibrium potential values ($\Delta E = \Delta E_o + \eta_r + \eta_a$), and from the same cause and reasons, along the reverse cathodic sweep, too. Since the entire amount of reversibly adsorptive Pt-OH sooner, out of the same reversible peak, undergoes complete disproportionation into highly polarizable and irreversibly deposited Pt=O monolayer, (Eq. 2), and thereby becomes unavailable for further reaction within such a longer (about 600 mVs) potential range, as the result, there imposes the typical pronounced **reaction polarization**, (η_r), which suppresses further proceeding of the interfering Pt-OH/Pt=O reversible reaction (Eq. 3), within both scan directions. The latter extends further by the **activation polarization** (η_a), and all together they impose very strong and broad polarizable properties, (Fig. 1). On the contrary, interactive (SMSI) supports of mixed valence hypo-d-(f)-oxides, *a priori* behave as continuously renewable and recoverable enormous (Pt-OH) latent storage capacities and spillover sources (Scheme) all along the potential range between oxygen and hydrogen evolving limits. Thus, there is now, under continuous Pt-OH spillover supply, no reaction polarization, ($\eta_r = 0$), and since the OER occurs straight from the enormous broad Pt-OH peak, and thereby exactly at the thermodynamic ROE value, ($\Delta E_o = 1.29 \text{ V}$, $\eta_r = \eta_a = 0$), the reversible electrocatalysts of various interactive hypo-d-(f)-oxide support compositions for oxygen electrode reactions (ORR, OER) have finally been substantiated and tested on Pt and Au. The present conclusive discussion strongly asserts, implies and reveals why plain, non-modified Pt by no means can ever become reversible electrocatalyst for the oxygen electrode reactions, or at least not within the whole potential range between hydrogen and oxygen evolving limits (Fig. 1 and 2).

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IZVOD

LATENTNO SKLADIŠTENJE PRIMARNOG OKSIDA (Pt-OH) KAO PODSTAKNUTOG IZVORA PRELIVANJA REVERZIBILNIH ELEKTROKATALIZATORA ZA ELEKTRODNO REAGOVANJE KISEONIKA

Latentno skladištenje primarnih oksida (Pt-OH, Au-OH) za podsticaj svojstava elektrokatalitičkog prelivanja i sticanje osobina reverzibilne kiseonične elektrode (ROE), bilo je ustanovljeno i ostvareno u oba smera duž čitave potencijalne ose između granica katodnog razvijanja vodonika i anodnog izdvajanja kiseonika. Tako poboljšana elektrokatalitička svojstva podrazumevaju snažno interaktivno (SMSI – Snažna Interakcija Metal-Nosilac) usađujuće vezivanje nanostrukturisanih čestica (klastera) Pt (Au, RuPt) na kompozitnim alervalentnim hipo-d-(f)-oksidnim nosačima mešane strukture, koji ispoljavaju ekstra visoku stabilnost i naglašeno povećanu elektronsku provodljivost, naporedo sa disocijativnom adsorpcijom molekula vode, a samim tim rezultujuće obnovljivo latentno skladištenje primarnog oksida, neprekidnim napajanjem vodenom parom i membranskim tipom površinske migracije hidroksilnih jona. Ovi potonji, kao individualna vrsta, pod dejstvom polarizacije prenose pretežni deo elektrona na metalni deo elektrokatalizatora, odakle rezultuje Pt-OH (Au-OH) kao dipolna struktura i svojim površinskim odbijnim silama sledi reverzibilnu prelivajuću raspodelu i nameće elektrokatalitička ROE svojstva preko čitave izložene katalitičke površine, odnosno dvojnosljednog punjenja i pražnjenja pseudo-kondenzatora.

Ključne reči: Primarni oksid (Pt-OH, Au-OH, M-OH); površinski oksid (Pt=O, Au=O); prelivanje; SMSI (Snažna Metal-Nosac Interakcija); d-(f)-metalna svojstva, UPD(OPD) (podpotencijalno i nadpotencijalno dvojnosljno (DL) punjenje/pražnjenje pseudokapacitora; nanostrukturisan elektrokatalizator tipa bronz; reverzibilna ćelija izmenjivog polariteta.

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