
The Extended Brewer Interactive Interionic Bonding Theory (EBIBT) has been developed to show the equivalence of interatomic and interionic bonding features, and for their mutual combinations, as well as its effect upon electrocatalytic properties for the hydrogen electrode reactions (HER). 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 been proved and inferred. TG (Thermal Gravimetry) analysis of TPR (Temperature Programmed Reduction) of mixed hypo-hyper-d-electronic oxides of transition elements was broadly employed to prove the EBIBT effect as reflected in dramatically decreased individual temperatures of their mutual reduction into intermetallic phases. The same interionic Brewer (and/or intermetallic) bonding effect has been confirmed both by UPD of hyper-d- upon hypo-d-electronic substrates and vice versa, and by the shift of bonding peaks in XPS analysis.

Basic Principles of Brewer Intermetallic Bonding Theory

The Brewer intermetallic bonding theory [1-5], as a generalized Lewis acid-base reaction model, thermodynamically predicts that whenever metals of the left half of the transition series or hypo-d-electronic elements, having empty or half-filled vacant d-orbitals (bonding d-band, d^1 to d^3), are alloyed with metals of the right half of the transition series or hyper-d-electronic elements (or anti-bonding d-band, d^3 to d^10), having interinarily paired d-electrons not available for bonding in the pure metal, there occur intermetallic phases and stoichiometric compounds usually of extraordinary stability, the letter increasing from 3d to 5d level (cf. [6-7]). The correlation between cohesive stability of hypo-hyper-d-interelectronic transition metal intermetallic phases and their electrocatalytic activity, for both cathodic hydrogen evolution (HER) and its anodic oxidation reactions (HOR), and primarily including rather profound synergism for the symmetric Laves phases, has long ago been pointed out [6-10].

Interionic Meaning of Interactive Brewer Theory

Since the whole Brewer intermetallic bonding theory is based upon the d-band and d-d-electron interactions, while the ions themselves, except for their solvation and some other effects of quite secondary significance, by the first principle do not differ neither in their metallic crystal lattice (example: electrode equilibria with the corresponding ions in solution, Appendix I), nor in crystal state of their compounds and mixtures, in aqueous media or other solvents, such state of evidence suggests the Extended Brewer interionic bonding theory. In other words, one of the main aims of the present paper would be to prove the equivalence of hypo-hyper-d-interelectronic bonding interaction besides within the transition metal intermetallic phases, but also in any other interactive states: (a) Mixture of ions in solutions; (b) Mixtures of their compounds or mutual composite stoichiometric states, primarily mixed oxides; and (c) Adsorbed ions mostly from aqueous or other solutions upon corresponding metallic surface. A classical interionic bonding state would be the thermodynamically stable and electrocatalytically active rutile crystal structure of mixed RuO2/TiO2 and IOx/TIO2.

There already exist lots of various indirect or straightforward hints for such rather broader meaning of the Brewer type of interionic interactive bonding, so that the Extended Brewer theory might seem as already implied within the existing intermetallic model statements [1-6], or that the interatomic and/or interionic bonding effects are either the congenial or at least of the equivalent effects [11-13].

The consequences of the equivalence in the interionic hypo-hyper-d-interelectronic interaction in both metallic and any other ionic state upon the effect of synergism in electrocatalytic properties for hydrogen electrode reaction (HER, both the HER and HOR) have already been proved and inferred [11-13]. In such a respect, as shown by Savačoglu [14-17], one of the most striking illustrative electrocatalytic issues represents rather long lasting and strong interactive bonding of polystyrene in its negligible amounts upon metallic Pt surface to catalyze both the cathodic oxygen reduction reaction (ORR) and the HER, and thereby advance the corresponding individual noble metal properties (cf. [11-13]).

One of the most typical interionic synergetic effects has been achieved by Trasatti [18-23] by mixed hypo-hyper-d-electronic inter-oxide electrocatalysts (TiO2/RuO2, TiO2/IrO2), which undergo partial reduction during cathodic hydrogen evolution to nonstoichiometric oxides (TiOx), otherwise being decisive for their catalytic...
behavior. In the same context one should mention a rather convincing volcano plot of Comninellis [24], (Fig. 17, ref. [12]), with pronounced synergic effect in the activity of the same mixed couple of oxides (TiO$_2$/TiO$_3$), as deposited on an indifferent (graphite) substrate for both open circuit and non-Faradaic (NEMCA) promotion of ethylene oxidation at elevated temperature. Although TiO$_2$ itself, like TiO$_3$, shows negligible catalytic activity as the effect of their $d$-$d$-bonding effectiveness, their equimolar mixture, provides a remarkable synergistic catalytic and induced NEMCA (Non-Faradaic Electrochemical Modification of Catalytic Activity) [25-27]) effect. Similar synergism in chemical and electrochemical catalytic activities of hypo-hyper-$d$-electronic pairs of sulfides (MoS$_2$-CoS$_2$, MoS$_2$-NiS$_2$) were already reviewed elsewhere [11,12]. Thus, mixed hypo-hyper-$d$-interelectronic oxide and/or sulfide deposits upon indifferent (Ti, graphite) substrate surfaces are typical external ionic interionic catalysts [11-13].

The striking starting point in the present theoretical approach represents the Brewer [4-6] intermetallic or interatomic bonding theory and therefrom resulting high temperature thermodynamics, which states that every hypo-$d$-electronic metal in interaction with the hyper-$d$-electronic half series of transition elements creates well defined and rather pronounced cohesive volcano plots in the corresponding free energy of interaction (Fig. 7, ref. [12]) [6-8]. The cohesive bonding maximum then arises distinctly shifted to non-symmetric position at about $d^2$-electrons, because of the prevailing amounts and thereby created a particular striking interactive effect of paired (anti-bonding) hyper-$d$-electrons of such an interionic constituent.

**SMSI as the Brewer Interactive Bonding Effect**

The second striking aspect in the light of the Brewer HDII effect has been the Strong Metal-Support Interaction (SMSI) of Tauster [28-37], as the initial and basic idea in contemporary catalysis (another starting or supporting point in the present theory), which has in the present paper been employed for the interactive grafting (or anchoring) of individual hyper-$d$-electronic and/or composite hypo-hyper-$d$-interelectronic metallic electrocatalysts with prevailing hyper-$d$-electronic component (AB$_3$ or AB$_5$ Laves type intermetallic phases), upon hypo-$d$-electronic transition metal (individual or composite) oxide substrates, that both together create bifunctional properties for simultaneous anodic hydrogen and CO as well as methanol oxidation [36]. In other words, the concept and entire effect of the SMSI already a priori implies and has implicitly been encompassed and substantially based upon the consequences of such an Extended Brewer interionic bonding theory, since always one uses hypo-$d$-electronic oxide support to bond strongly a nanosized hyper-$d$-electronic catalyst, and the stronger the bonding the higher catalytic activity for heterogeneous chemical reactions [28-37]. The point and result is that the same hyper-$d$-electronic metal under the same conditions, features different activities upon various hypo-$d$-electronic oxide substrates, and that both together they create a rather complex catalyst for heterogeneous chemical or electrode reactions. In the light of such an extended Brewer model, Pt/TiO$_2$ is by no means Pt itself, but something else in catalytic and interactive bonding sense, a composite and advanced electrocatalyst. While neither Au, nor titania by themselves are individually active for CO and O$_2$ adsorption, nanostructured Au/TiO$_2$ oxidizes CO even much below room temperature. In the light of the existing electrocatalytic theory [6-13], such an effect could a priori be expected, if the original Brewer interatomic bonding theory, with all accompanying consequences [1-5], holds for the interactive interionic bonding. Namely, after the heterogeneous catalysis has for several decades mostly been based upon rather developed, highly active, even pyrophoric reacting surface area of Raney-Ni [39,40] and similar composites, ever since Tauster [28-30] formulated the SMSI effect, the nanostructured and highly advanced active catalysts turned out to require much stronger bonding substrate supports, both for longer lasting and advanced activity, where titania in anatase crystal lattice, along with other hypo-$d$-electronic transition metal oxides and their mixtures, so far has been playing an unique role. In other words, Tauster [28-30] already spontaneously and intuitively indirectly introduced the Extended Brewer interionic interactive effect and its consequences in contemporary heterogeneous catalysis, while with nanostructured metallic part of catalysts keep their rather developed surface area. In the light of such statements, an hypo-$d$-electronic support clearly plays a rather pronounced interactive active role and together with the strong bonding of an individual or prevalingly hyper-$d$-electronic metallic part of such a composite (electro)catalyst, altogether enable to impose the selective grafting effect and form a well nano-distributed, uniformly dispersed, highly developed in surface area and rather advanced and complex catalytic body, so that even Au particles smaller than 4 nm upon titania behave as a quite another metal [41-63].

The substantial point and difference is that each individual nanoparticle in common catalyst takes the role of an independent micro-scale reactor and contributes to the overall integral catalytic effect, while in electrocatalysis all such individual centers have to be properly connected and integrated by the current collector.

The SMSI has been observed only on those metal systems that spontaneously adsorptively dissociate hydrogen or in systems where such dissociation is provided by another metal ingredient [28-30, 34-37]. The exception is Au at lower nanosizes and strongly
bonded (SMSI) upon titania. In such a respect, there is a strong indication for substantial similarity between the electronic interactions taking place within intermetallic phase and those at the strongly reduced TiO$_2$-supported metal catalysts, albeit chemical type of bonding so far has usually been ascribed them [37]. In other words, contemporary heterogeneous catalysis already implies that the electronic interactions in SMSI are similar to those in the Brewer type intermetallic phases [37]. Chemisorption IR (infra red) studies indeed show that otherwise irreversible adsorption of CO no longer occurs as such upon highly dispersed Pt particles interactively bonded over anatase titania (TiO$_2$) [35–37]. In addition, under CO hydrogenation reaction conditions, the IR-bands characteristic for CO irreversible chemisorptive bonds, could not longer be detected on Pt/TiO$_2$ catalysts, while they were still present upon non-hypo-$d$-electronic oxide supports (SiO$_2$, Al$_2$O$_3$) [35–37].

**Composite and Promoting SMSI Catalytic Effect**

The operational Tauster [28–30] definition of SMSI implies that the metal–oxide interaction (M/TiO$_2$) for heterogeneous catalysis in gas phase, in accordance with the bonding strength, results in substantial weakening and even suppression of both M–H and M–CO chemisorptive bonds. In fact, for metal atoms at the interface or directly contiguous with the TiO$_2$-support around the nanostructured circumference, and as the effect of H–adatom chemisorption, their intermetallics grow by the ease of titania reduction. According to such a hypothesis, the catalytic activity should increase with the interfacial perimeter, which, in its turn, arises roughly proportional to the second power of the metal dispersion. As a concluding catalytic remark, the ability of hypo-$d$-electronic oxide supports of transition metals (such as anatase titania, TiO$_2$), to undergo reduction and provide the intermetallic phase, Brewer type strong interactive bonding at such an interphase, mostly and substantially result by defined symmetric intermetallic phases, otherwise characterized by the maximal free enthalpy of formation (TiP$_3$, TiP$_6$, TiN$_2$), and this lies in the core of the SMSI and arises as an already naturally implied Extended Brewer interionic bonding theory.

**Chemisorptive and Bonding $d$-Band Properties**

Plentiful of papers [24, 31–34], books [35, 36] and chapters [37] in heterogeneous catalysis have been based on and following the original idea of Tauster [28–30] to define and use properties and consequences of SMSI, while there has so far been no theoretical explanation as concerns the driving force, causes and the nature of such an interaction. The core and quintessence of such a Strong Metal–Support Interaction, almost without any exception lies in the Brewer hypo-$d$-interionic interactive and substantially interionic bonding effect. This is the main aim and most significant theoretical statement and contribution for further consequences of the present paper.

The $d$-orbital is the prevailing bonding and chemisorptive band, and thereby, decisive catalytic and electrocatalytic band [6,7,11,12], while the $s,p$-band contributes a constant bonding term all along each transition series [1–4]. The higher the exposure of $d$-orbital in space, the higher individual catalytic activity, that thereby increases from $3d$-towards $5d$-level [6,8,12] and results in typical volcano plots for $d$-band energy, Fermi, cohesive and free surface energy [1–4,6,12]. Such a conclusion well agrees with the statement of Haruta [38–63] that Au with almost fulfilled $d$-orbital, at smaller particle size than 2 nm, due to its forced $d$-orbital exposure, behaves striking different catalytic behavior for many catalytic reactions, including superior CO oxidation. Goodman et al. [54], named such an effect – Quantum Size Effect (QSE). The same cause in $d$-band extension, as already pointed out [8], certainly arises in the hypo-$d$-interionic electronic interaction for synergetic advances in electrocatalysis of the HER [6,7,11,12].

In the same context, the hypo-$d$-electronic correlation between the bonding effectiveness amongst the Brewer type intermetallic phases [1–5] and electrocatalytic activity for the HER [6–13], along every hypo-$d$-interionic electronic phase diagram (Fig. 5, ref. [55], cf. ref. [11,12]), without exception shows, that the stronger the cohesive bonding (symmetric Laves phases, ZrNi$_2$, MoP$_8$, HfP$_2$, WP$_6$, CeP$_6$, TiN$_3$ [11,12]), the weaker the $H$–adatoms adsorption, and as the consequence Sabatier principle for interacting chemisorptive intermediate effect in the rate determining step (RDS) [6,7], the more pronounced synergetic electrocatalytic effect. The same certainly concerns CO adsorption and its abilities for anodic oxidation [37]. In such a context, there has already been inferred that every hypo-$d$-interionic electronic phase diagram behaves in all main physical properties, when plotted along, including electrocatalysis for the HER, as the part of Periodic Table between periods of two initial constituents [6,11,12].

There already exist lots of evidence for the hypo-$d$-interionic interactive bonding and therefrom resulting various versatile and remarkable consequences. First, majority of hypo-$d$-electronic metals, such as Mo and W, could by no means be cathodically deposited from aqueous media. However, as shown by Fukushima et al. [56], their codeposition with hyper-$d$-electronic transition metals (Fe, Co, Ni), proceeds both with rather high Faradic yields and surprisingly high percentage in electrodeposited alloys (Fig. 1). The cause for such facilitated electrodeposition doubtless arises in the nature of the Brewer type HHDII
of ionic species (an a priori prediction of the Extended Brewer theory) [1,2].

Brewer Type of Interactive UPD and Prediction of Catalyst Grafting Effects

Such state of evidence a priori imposes the expectancies, as a rule, that whenever some hypo-hyper-d-interelectronic bonding interaction exceeds individual cohesive energies of these two metals, there should appear the underpotential deposition (UPD) of one upon another element. Such UPD investigations are the subject of the present and forthcoming studies in our search for an approach towards the submonolayer catalysts and electrocatalysts for various applications. Meanwhile, the Brewer type of hypo-hyper-d-interelectronic bonding nature in the interactive interionic strength and effectiveness, as a further extended Brewer theory, afforded the basis for selective individual and composite (AB, AB₂, AB₃ and AB₅ type, with prevailing hyper-d-electronic constituent, B) intermetallic catalyst grafting upon individual and composite hypo-d-electronic oxide supports, that is the main subject of the present paper [36]. Further consequences of bifunctional interactive behavior in simultaneous anodic oxidation of hydrogen and CO are the subject of theoretical considerations and the resulting tenet of practical application and confirmation, too [57] (see further text downwards). In such a respect, the new rather complex nanostructured electrocatalysts rely on individual hyper-d-electronic elements and primarily even on their prevailing contents in hypo-hyper-d-interelectronic intermetallic phases (as the basic core metallic part of catalysts), being then grafted or anchored upon active sites of individual (titania, TiO₂) and/or rather composite hypo-d-electronic oxide substrates (titania, tungstenite, WO₃, hafnia, HfO₂, zirconia, ZrO₂, etc), in accordance with the SMIS effects and therewith further resulting mutually coordinated bifunctional catalytic contributions (see further text).

EXPERIMENTAL

The main hypo-d-electronic oxide catalytic carrier has been obtained by the sol-gel (co-precipitation and partially hydrolylation, Appendix II) procedure [58-60], as a submonolayer aerogel deposit of rather developed surface area (above 180 m² g⁻¹) and prevalently in the anatase TiO₂ crystal structure on Vulcan XC-72 (Cabot Corp., Boston, Mass.) carbon substrate (290 m² g⁻¹). In such a respect, Ti-isopropanoxide was hydrolyzed by 1.0 M HNO₃ in the ratio 10:1, respectively [61-63] in anhydrous ethanol solution and in an admixture of Vulcan XC-72 particles, and finally its percentage amounted between 20 and 40 wt.% TiO₂, depending on the desired nanoparticle size of the metallic catalysts. Namely, the ratio between the available active centers of TiO₂ and the amount of grafting metallic ingredients, as well as the initial concentration and total amount of the latter, provide nanized clusters to form a mutual composite electrocatalyst, and all together define the desired distribution and nanostructured metallic properties of the final catalyst. To keep a rather developed surface area of such an oxide carrier, proper supercritical drying at elevated pressure (90 bars) and at 37°C has been undertaken by liquid carbon dioxide, otherwise the exposed surface area is reduced at least three times (Appendix II). Various individual or composite mixtures of transition metal acetylacetonates (in short M–acac, or M-2,4-pentanediacacetates) were dissolved either in acetone, isopropanol or even ethanol and used for straight grafting upon such prepared Ti(OH)₄ non-calcinated substrates prior to hypercritical drying, to obtain up to 10 wt.% (preferably 5 wt.%) metallic part of the electrocatalyst at the end of the procedure. In such a sense the addition of composite M₁M₂–acac mixtures should properly occur between sol formation and the beginning of gelation (gel formation). Alternatively, calcination in an H₂ or Ar stream at preferably 300°C or not higher than 400°C precedes the grafting of the composite metal acetylacetonates, since some M–acac are soluble in liquid CO₂ and become removed from composed mixture. Decomposition accompanied by reduction and even calcination of the support under a hydrogen stream then occurs in a glass tube at programmed temperature in a hydrogen atmosphere at usually 250, and not more than 400°C for about 2 to 5 hours, with proper both heating and cooling procedures. Such a procedure guarantees the production and retention of a submonolayer polymeric network of TiO₂ in the anatase structure and homogeneously and uniformly distributed nanosized intermetallic catalyst deposits upon the latter.

The sol-gel process to obtain 10 nm-sized peroxopolytungstic acid (PTA) sol has been adapted following the Kudo [64,65], Livage [66-68] and Orel [69,70] procedures, which start with dissolving small fine particles of metallic W in 30 wt.% H₂O₂, followed by decomposition of the excess of the latter by the catalytic
effect of a piece of Pt. Water removal provides triple to four-times controlled evaporation of the initial aqueous volume in an admixture of five-fold higher amounts of anhydrous ethanol at carefully fixed temperature below 70°C, where mostly an azetropic mixture leaves the phase. Such an ethanol solution of homogeneous colloidal particle size (about 10 nm) of PTA has been used in admixture with Ti-isopropoxide to get mutual polymeric network of about 3 to 7 mol.% PTA, calculated on the basis of WO₃, that has been the main composite hypo-d-electronic oxide support for SMOI. After supercritical drying and in admixture of composite M₁,M₂-acac ingredients in desired proportion, the rest of the procedure is as displayed for individual issue of anatase TiO₂.

Along with such a synthetic polymeric TiO₂ anatase network, a similar particulate support has been employed for all investigated issues of composite and grafted electrocatalysts. This concerns basically Hombikat UV 100 (Sachtleben Chemie GmbH, Duisburg, Germany), which is essentially 100% anatase, of particle size bellow 10 nm, and with average surface area of above 250 m² g⁻¹, an ideal catalyst support. As in the above issues, its impregnation with about 3 to 5 mol.% of PTA has been considered as the main composite hypo-d-electronic oxide support.

The term electrocatalyst within the present concept, implies up to 10 wt.% individual or intermetallic nanosized catalyst on 20 to 40 wt.% hypo-d-oxide support, and the rest being mostly Vulcan XC-27 powder as the current collector. To improve conduction properties, some amount (up to 10 wt.%) of partially more graphitized Shawinigen carbon powder of much lower available surface (60 m² g⁻¹, Ketjen Black International, Chevront) was added to the admixture of Vulcan XC-72. In addition, in some issues, to improve conductivity, an amount of about 10 wt.% or more, even completely replacing Vulcan XC-72, of Ebonex®, the Magnell-phase titanium suboxide (Ti₀₂ₓ, 2.0 < x < 1.75) of general formula TiₓO₂₋ₓ, (10 ≥ n ≥ 4) (Table 1), with rather advanced electrical properties (300–1,000 S cm⁻¹, particle size bellow 10 microns, Areva Ltd., Mansfield, U.K.) has also been employed.

The XP spectra were collected in an UHV chamber (base pressure 8x10⁻¹⁰ mbar), equipped with a hemispherical electron energy analyzer and a twin anode X-ray gun. The unmonochromatized Al Kα line at 1486.6 eV and a constant pass energy mode for the analyzer were used in the experiments. Pass energies of 97 eV resulted in a half width at the half maximum (FWHM) of 1.8 eV for the Au 4f/2 peak of a reference foil. The energy scale of the spectrometer was calibrated with both the Au 4f/2 line at 84.0 eV, and the Ni 2p/2 line at 862.6 eV of carefully cleaned polycrystalline Au and Ni foils, respectively. The sample temperature was measured with a Ni-CrNi thermocouple which was mounted in the sample holder. Curve fitting was performed with a least-squares curve-fitting program based on a mixed Gaussian/Lorentzian function, which accounted for the band asymmetry to higher binding energies in the core level spectra of metallic species. The objective of the XPS measurements was to detect possible intermetallic bonding of hypo-hyper-d-electronic combinations of transition metals and their oxides.

TG TPR experiments (TA Instruments, New Castle, DE, USA) to define decomposition conditions of individual and admixtures of hypo-hyper-d-interionic combinations of transition metal acetylacetonates on oxide supports and/or mutual reduction of their oxides, have been employed and adopted to follow at the same time the homogeneity and its optimization for the resulting intermetallic phases and alloys with the aim to bring them to uniform status. The same measurements with and without hypo-d-electronic oxide support of transition elements enables one to obtain a measure of and an insight into the SMOI. The latter also concerns the crystallization agency effect and the effect of the third component upon the interionic bonding effectiveness and tailoring synergetic electrocatalysts. A mass spectrometer (Omnistar™, Pfeiffer) on line with TG has also been employed to follow the gaseous products of the various individual and composite metal-acac decomposition.

Potentiodynamic and polarization measurements have been carried out under typical conditions of three compartment cell. The same amount of catalyst was always homogeneously deposited on hydrophobicised porous carbon cloth or paper by a special mixer and gas flow provided three phase boundary contacts for reproducible measurements.

RESULTS AND DISCUSSION

Hypo-Hyper-d-Interionic Bonding of Transition Metal Oxides as the Basis for Catalyst Grafting

Hypo-hyper-d-interionic bonding with the aim to verify the extended Brewer interactive model has been tested by TG TPR of various oxide admixtures provided to be homogeneously mixed at their ionic level. In such a respect, various a priori defined ratios of Ni(NO₃)₂·6H₂O or Co(NO₃)₂·6H₂O salts were carefully mixed with corresponding amounts of (NH₄)₂MoO₄·4H₂O or WO₃·H₂O in aqueous media to obtain desired mixtures of their oxides after Temperature Programmed Oxidation (TPO) in a stream of air and by controlling their stoichiometry, followed in the next step by TPR in a hydrogen atmosphere. In parallel, the same ratios of MoO₂·acac in admixture with corresponding amounts of Ni-acac or Co-acac, were also decomposed in air and the resulting mixed oxides have been the subject of TPR in a hydrogen stream, for the sake of their mutual comparison. The ratios of selected initial mixtures were chosen so that the finally resulting
stoichiometric products correspond to their well proved intermetallic phases, stable and meta-stable, such as MoNi, MoNi2, MoNi3 and MoNi4. Individual components of all initial ingredients were also investigated for their oxides TPR in hydrogen stream to be able to cover the entire phase diagram of these various couples of hypo-hyper-δ-interelectronic combinations for four constituents.

While MoO3 reduction in hydrogen stream requires at about 730°C (Fig. 2a), and NiO reduces below 260°C (Fig. 2b), their intermetallic phases mostly appear between 300 and about 400°C, whereas reduction of the latter amounts of non-stoichiometric bonded Mo3 Nevertheless never approaches individual peak of the latter (Fig. 2c). Even the admixture of remarkably prevailing Mo content (MoO3: NiO2 = 3:1) mostly reduces below 500°C. Co, as a metal, which involves one δ-electron less than Ni, in such a HDII, produces the same type of TPR, but shifted about 100 degrees of centigrade towards higher temperatures, which perfectly well agrees with basic statements of the Brewer theory [4-6]. The differences are less pronounced in combinations of Ni and Co with W, since the oxide of the latter (WO3) reduces at about 600°C, but in all issues follow the Brewer theoretical intermetallic bonding prediction. More thorough and more illustrative presentation, including Differential Thermal Analysis and the entire isothermal or adiabatic reaction effect for more complete confirmation of the extended Brewer interionic bonding theory will be given in more detail elsewhere.

Such TPR experiments with hypo-hyper-δ-electronic combinations of corresponding oxides certainly represent the sound and convincing proof of the basic and generalized tenet for the Extended Brewer intermetallic bonding theory. At the same time such state of experimental evidence affords both theoretical and practical basis for grafting of nanostructured individual and intermetallic catalysts upon proper hypo-δ-electronic oxide substrates and thereby to create the SMSI effect and its further catalytic consequences. This is the main and leading subject of the present study, and in particular will be extended upon more critical issues, such as sol-gel prepared titania in admixture with Pt-acac homogenized at the molecular level and TPR in hydrogen stream, as well as other similar issues leading to the bulk crystallization of their most stable and most symmetric intermetallic phases (TiP3, HfP3, TiN5, CePt5, etc).

**XPS indication for the Existence of TiM3 Intermetallic Phases at M/TiO2 Interphase as the Effect of Reduction by H-Adatoms**

In such a context, XPS investigation of the two-phase boundary contacting interface between nanosized Pt upon developed anatase TiO2 surface (Hombikat UV 100) has shown some phenomena of far-reaching significance. In Fig. 3a and 3b, are presented the Pt 4f XPS spectra of 1% and 10% wt Pt/TiO2 catalyst. A careful line shape analysis of the Pt 4f peak for 1% Pt/TiO2 catalyst, taking into account the experimental resolution of the spectrometer, reveals the presence of three different Pt species. The more intense Pt 4f1/2 component centered at 71.6 ± 0.1 eV, is 0.5 eV shifted to higher binding energies compared with a clean Pt surface. Such an energy shift is consistent and reproducible in all measurements before, after and during annealing the sample at 570 K and corresponds
with distinctly different binding energies. The signal around 71.0±0.1 eV is assigned to metallic Pt\(^0\), whereas the smaller peak at 73.3±0.2 eV was present also in the 1wt % Pt/TiO\(_2\) sample and it is due to oxidized or hydroxidized Pt [71,74]. The presence of the TiP\(_3\) phase at 1 wt % Pt/TiO\(_2\), where Pt is more dispersed on the surface, testifies for rather strong ionic bonding between Pt and Ti (Δ = 1.0 eV). Even more so, there has been identified the appearance of TiP\(_3\) intermetallic phase, as the reduction effect of H–adatom adsorption upon grafted Pt particles under rather mild thermal conditions (250°C). Amongst all possible intermetallic phases along the Ti–Pt phase diagram, the affinity and thermodynamic properties predetermine the appearance of TiP\(_3\) as the most strong bonding species [4–8]. In fact, the latter (TiP\(_3\)) marks the main interbonding characteristics for SMSI being decisive for further electrochemical behavior and defines the main catalytic properties of such composite electrocatalysts. At the same time, such experimental insight affords the best illustrative picture and deeper physical sense of the hypo–hyper–d–interelectronic and interionic grafting, together with resulting physico–chemical consequences.

In the initial statements of the SMSI, Tauster [28–30] has predicted the existence of TiP\(_3\) intermetallic phase, and it has been the cause for previous thorough investigations of the latter both as a unit catalyst itself or upon defined Pt single crystal plates [76–79].

The more pronounced similar effect for creation of defined Brewer-type intermetallic phases has been found for both TiP\(_3\) and TiNi, since these metals feature hydrogen absorption beside its adsorption. In other words, while TiP\(_3\) arises along the Pt particle circumference, for Pd and Ni their intermetallic phases grow all over the interphase contact and provide rather strong SMSI.

**Reference Electrocat\'y\t\'ic System of Mo–Pt Intermetallic Phases**

Since various intermetallic phases of Mo–Pt, primarily stable MoP\(_3\), and metastable MoP\(_4\), so far represent the most promising composite electrocatalysts for low temperature PEM FC and provide some higher CO tolerance versus Pt itself (80–82), properly metallurgically prepared monophase polycrystalline specimens (Philips Research Center, Eindhoven, the Netherlands) have been thoroughly investigated as a reference electrocatalytic system. Kinetic measurements for both HER, cathodic hydrogen evolution and its anodic oxidation, upon the two most active catalysts (MoP\(_3\), MoP\(_4\)) display the appearance of super–activity and almost ideal polarization characteristics of about 30 mV/decade in Tafel slope for an unusually broad current density range investigated at rather high rotation speeds upon the RDE [83].

In such a context, in accordance with the Brewer intermetallic bonding theory, XPS analysis reveals (Fig.
4), the remarkable shift of the bonding peak of both Pt and Mo all along the phase diagram (Fig. 5). There is a strong indication of d–electron transfer from hyper-d–electronic Pt (antibonding band) to the deficient hypo-d–electronic Mo band, though at rather high Mo contents, there are signs of opposite way in the d–d–interElectronic transfer. Such XPS analysis affords reliable indications, besides Brewer high temperature thermodynamics [4–6], that hyper–hyper-d–intermetallic bonding is primarily based on the partial d–electron delocalization and interionic transfer. The equivalence in interionic d–d–bonding in metallic and any other ionic form seems now to be firmly proved.

In the same respect, there has also been of deeper fundamental interest and significance to scan the work function changes along the Mo–Pt phase diagram (Fig. 6). As theoretically predicted [7,8], the latter follows a characteristic volcano plot in close correlation with such typical changes of electrocatalytic activity for the HER [80–83]. It is also evident that the higher the CO tolerance, the lower the work function. In such a context, for example, Fe has a low work function and almost no CO adsorption at room temperature, in contrast to Pt, that features both a high work function and rather strong CO adsorptive bonding. Such state of evidence suggests the correlation between work function and CO adsorption. This is associated with the oxophilicity changes in various hypo–hyper-d–electronic combinations, and such a substantial decrease in work function enables the higher CO tolerance.

**Hypo–Hyper-d–InterElectronic Interaction and UPD**

The majority of hypo–hyper-d–electronic pairs feature submonolayer UPD one upon another in accordance with their cohesive affinity strength [38]. The
UPD effect is similar to the mutual hypo-hyper-β-interelectronic deposition (Fig. 1) and arises as the Brewer type of interionic interaction that facilitate such codeposition of alloys and intermetallic phases.

Such a typical and common issue gives UPD of Ni upon a V surface [38]. The coverage of Ni as derived from the area under the Ni 2p XPS peak, relative to that of V 2p, is plotted as a function of the applied potential (Fig. 7a), and expressed as equivalent monolayers (ML) with the assumption that 1 ML has a density of 1.8×10^20 atoms cm^-2. Such Ni submonolayer coverage, as derived by XPS measurements, shows first a gradual increase until -0.75 V scans (flat part), and then a sharp rise as the applied potential exceeds this value and creates multilayer growth. The limited thickness of the nickel film between -0.40 and -0.75 V, indicates that in this potential range Ni atoms are deposited only on available V substrate sites, which is a distinct UPD effect.

XP spectra were recorded for a Ni deposit before and after annealing the sample in UHV at 520 K. The Ni 2p$_{3/2}$ region is shown in Fig. 7b, for samples potentiodynamically scanned and afterwards annealed, respectively. The spectrum of a clean polycrystalline Ni foil is also shown as a reference. In the case of Ni obtained by cyclic voltammetry (curve a), the spectra indicate the presence of an oxidation layer, which according to the Ni 2p$_{3/2}$ binding energy, consists mostly of nickel hydroxide [Ni(OH)$_2$] [84]. Annealing the sample causes the appearance of a new Ni 2p$_{3/2}$ peak (curve b) at lower binding energies (853.1 eV), which appears at the expense of the peak initially present. The shift of the Ni 2p$_{3/2}$ peak at lower binding energies, as well as the attenuation of its satellite peak, can be safely assigned to decomposition of nickel hydroxides producing metallic nickel. However, the binding energy of the 2p$_{3/2}$ level for metallic reference foil (curve c) found at 852.6 eV, thus indicates that the Ni 2p$_{3/2}$ peak, after annealing is shifted about 0.5 V towards higher values. Such a 0.5 eV-shift for the nickel peak at the Ni/V interface can be explained by rather strong Ni–V–interelectronic Brewer type bonding, which leaves a slight positive charge on the Ni atoms (cf. [85]). This testifies for rather strong intermetallic bonding and has to be connected with the distinct UPD effect, evident in Fig. 7a. Hence, the mutual hypo-hyper-β-interelectronic UPD effect, as quantitatively confirmed by XPS measurements, is one more sound and systematic evidence for the Brewer type of β-β-electronic correlations in intermetallic and interionic bonding effectiveness. Even more so, after annealing, such a Ni
submonolayer shows much enhanced catalytic activity for the HER, than just the UPD effect itself.

Even rather convincing UPD peaks have been scanned by Cr deposition on Fe, Co, Ni electrodes (Fig. 8), with characteristic shift of their maximum in accordance with their position in Periodic Table and even as properly associated with their individual work functions. However, XPS analysis shows that such a charge capacities within these cathodic peaks have been spent for reduction of adhering CrO₃ within such a cathodic diffusion layer into the stable Cr₂O₃ oxide, as predicted by Pourbaix diagrams. Thus, in these and many other similar issues in the existing literature there remains the question whether these are the UPD peaks? They have all features of UPD peaks, but not for direct metal deposition. Such peaks are well shaped, behave all UPD properties and even become finished before the multilayer cathodic Cr growth. In fact, XPS analysis for majority of UPD deposits shows the prevailing existence of their oxides and/or hydroxides [38].

Such state of the UPD effect in intermetallic HDHi, as confirmed by XPS analysis, affords the basis for a new generation of much promising submonolayer or nano-layer catalysts with the Brewer type of intermetallic interaction. Namely, Rodriguez and Goodman [85] have already shown for majority of investigated issues of hypo-hyper-δ-interelectronic pairs a remarkable correlation between shifts in surface core-level binding energies and shifts in CO adsorption temperature.

**Theoretical Basis for Bifunctional Electrocatalytic Properties in Simultaneous Hydrogen and CO Anodic Oxidation**

The correlation between the hypo-δ-electronic oxide support reducibility and the extent of metal-support interaction upon the rate of heterogeneous catalytic reactions in the gas phase has been established long ago [28-30], with the conclusion that the SM5I feature only those metals that dissociatively adsorb H–atoms and enable its spillover interaction with the support [37]. The stronger the SM5I, the smaller the uptake of CO and the weaker the chemisorptive strength of both CO and hydrogen [37], and thereby, both effects together contribute to the heterogeneous catalytic reaction of CO oxidation, as well as the electrocatalytic HER. The reversible reducibility of such oxide supports is a prerequisite for reversible OH−–ionic transfer to metallic catalyst.

Haruta [41, and ref. 90 therein, 42,45] infers the substantial effect of moisture on the heterogeneous catalytic activity of Au/TiO₂ (anatase) for gas–phase CO oxidation at relatively low temperature, where the reaction rate increases by more than an and even two orders of magnitude. Apparently, titania provides such a dissociative transferring mechanism, the 'pumping effect', in which Au–OH imposes catalytic oxidation. Anatase TiO₂ of developed surface area is deficient in stoichiometric amount of Ti, which testifies that its crystalline structure contains hydrogen atoms and dissociatively formed transferable hydroxide ions [63]. In fact, metastable anatase does not exist in its stoichiometric TiO₂ status and always displays its transferable suboxide (TiO₃) properties, a large amount of water absorption and its interaction at the phase boundary, the a priori free OH− ion existence and its transfer [37]. In combination with higher valent WO₃, anatase enhances the entire 'pumping' process of dissolved water molecules as M–OH species at the catalyst surface, the latter featuring the spillover effect all over the metal surface. Meanwhile, there is even some evidence for an overlayer formation and thereby resulting spillover of TiOₓ upon the adjacent metal catalyst surface, too, named "decorration" and/or "encapsulation" [37,86-92]. This encapsulation effect is important and decisive for the overall catalytic reaction, for its further transfers into Magnéli phases, for the formation of intermetallic phases, as well as for the M–OH spillover and an overall altenvalent behavior of anatase titania.

In such a context, it is also important to note as a broader catalytic effect, that photochemical reactions on titania substantially depend on moisture content: the adsorption of water molecules usually causes structural changes in TiO₂ enhancing thereby the recombination of photogenerated electrons and holes [63,93-98].

In acid/base or donor/acceptor behavior of titania, mostly anatase, donors such as H₂O posses lone–pair electrons that can interact with acidic (cation) surface sites to give primarily dissociative chemisorption. The latter implies heterolytic cleavage, with transfer of H⁺–ions to a basic (TiO₂) oxide sites (O²⁻), so that normal dissociative interaction of water may be thereby written as [92],

\[
\text{H}_2\text{O} + \text{O}^{2-} = \text{OH}^-_{\text{bridge}} + \text{OH}^-_{\text{surface}}
\]

where the new OH⁻, as a basic species, coordinates to a surface metal ion and the other one to the bulk of titania.

Figure 8. UPD peaks for Cr deposition from its acidic sulphate solutions on Fe, Co, and Ni electrodes.
phase. This is the main and substantial chemical behavior of titania as a catalyst support enabling both its ion exchange and transferring membrane properties. The other is its strong interactive grafting bonding (SMi) with hyper-ε-electronic transition metals at the selective fivefold coordinate Ti atom positions \([56-92]\) and readiness for both (e) spontaneous reduction by H-atomics from metallic part of catalyst \([57]\), and ease for altervalent \(\text{Ti}^{4+} \rightleftharpoons \text{Ti}^{4+}\) changes.

The effect of moisture on the overall behavior of titania can be estimated and qualitatively assessed from the dependence of thermodynamic temperature of TiO reduction in hydrogen stream on extremely small amounts of water molecules. The variation of moisture from \(10^{-6}\) to \(10^{-10}\) (H\(_2\)O/H\(_2\)) enables to reduce temperature of TiO reduction from 2,020 to 1,250 K. The affinity of Ti versus water molecules is extremely high and the resulting overall behavior of titania substantially depends on and becomes determined by moisture content.

Amongst all so far investigated hyper-ε-electronic oxides for SMi and thereby imposed substantially advanced catalytic effects, titania, which appears in four crystal structures (Table I), plays a rather distinct and specific role \([26-37]\). After rather weak brookitite anatase features metastable properties and maximal degree of freedom \([63,99]\). The SMi decreases at rather more compact and stronger bonded rutile, where, thereby the interactive strength and OH-transfer substantially reduces \([37,99]\). Finally, the most compact layerlike and surface bonded Magneli phases show fascinating electron conductive properties and have been used as electrodes even for chlorate production and as substrates for metal deposition, as well as specific catalyst carriers. Unfortunately, as an almost ideal current collector with superior conductivity properties \((300\) to \(1,000\) S-cm\(^{-1}\)), such material requires improvement of its SMi for catalytic purposes, but then its compactness would be sacrificed for developed surface area. The common solution is in monolayer sol-gel deposited anatase as hyper-ε-electronic oxide carrier and its metallic catalyst thereby brought in direct contact with Magneli phases.

Gels (aero and xerogels) are biphasic systems in which solvent (water) molecules are trapped inside an oxide network, and such material can be considered as a water-oxide composite \([59]\). Water molecules are adsorbed at the surface of the oxide particles within such a supporting oxide network and consequently, such composite material exhibits specific properties arising from the intimate mixing of both phases. Depending on the pH value of hydrous oxide network, water molecules undergo ionization giving rise to hydronium or hydroxide ionic species (Appendix II). In fact, there is a strong first principle thermodynamic confirmation \([100]\) that water molecules undergo dissociative adsorption on anatase and even rutile TiO\(_2\) \([88-92]\). Transition metal ions usually feature several valence states giving rise to mixed valence compounds, so that such hydrous oxide networks, in particular of polyvalent hyper-ε-electronic transition elements, substantially behave as ion exchange membranes \([58,59]\). Thereby, electronic properties due to a hopping process within the solid phase have been observed and known (electrochromic properties) \([59,66-68]\).

Since as a general condition and property for semiconducting behavior of transition metal oxides, the latter appear capable of existing in several altervalent states, the conduction occurs by electron transfer from low to high valence state (Appendix II). Hyper-ε-electronic metals have lower work function and easily transfer electrons to the metallic catalyst of hyper-ε-electronic properties \([25-27]\). On the other side, water molecules are adsorbed at the surface of hyper-ε-electronic oxide and are the subject of easy ionization, ionic diffusion and transfer within the liquid phase \([59,100]\). Thus, both phases are involved in the interdependent electrochemical properties of transition metal oxide gels. Electron transfer occurs through the solid phase and ion diffusion through the liquid phase. It is well known that due to the very large interface between both phases, electron transfer at the oxide-water interface can be greatly enhanced, leading to specific photochemical properties \([63,93-98]\). In such a respect, Livage \([59,66]\) long ago pointed out that highly charged W\(^{2+}\)-cations favor the acidic dissociation of water molecules and electrochromic layers feature ion exchange properties. The altervalent tungsten effect in combination with anatase for the SMi catalytic effect has long ago been pointed out by loannides and Vyskics \([101]\). The strong interaction between unpaired electrons and the polar oxide network leads to a polarization of the lattice and causes a displacement of oxygen ions around the low-valence transition metal ions \([59]\). Such state of knowledge has recently stimulated endeavors even to synthesize ionic exchange membranes based on sol-gel basically produced of anatase network and in combination with WO\(_3\) or RuO\(_2\) \([62,102,103]\). The nature and behaviour of gel complex species depend on the initial charge (z), on the former coordination number (N), associated with covalently bonded water molecules, the electronegativity of the metal or the chemical potential of electrons \((\mu_e)\) and the pH value \([58,59]\) (Appendix II). The characteristic charge–pH diagrams show that only elements of higher altervalent charges \((z > 4)\), produce hydroxo and oxogels \([58,59]\), and in such a respect metastable anatase in combination with tungstic acid arises as highly favourable for water uptake and transfer of OH– ions \([101]\).

In such a context, the Livage \([66]\) issue of dissociative water uptake by WO\(_3\)-H\(_2\)O and resulting OH-transfer seems rather illustrative (Scheme I). The coordination expansion of neutral tungstic acid
architecture of metastable oxides (Scheme 1). In such a respect, an ideal composition of TiO$_2$ and WO$_3$ covers the charge range above critical $z = 4$ all along the charge–$p$H diagram and provides restrictively only hydroxo–oxo formation of aero and xerogels of unlimited ionic transfer [58,59].

The mechanism of M–OH formation and its spillover upon metallic catalyst surface are confirmed and known for various hypo-$d$-electronic oxide structures within their otherwise basically ionic exchange properties [58-60]. However, what is the cause or actual driving force for continuous dynamic proceeding and even spillover of such an ionic transfer?

**Potentiodynamic Evidence for Specific M–OH Effect**

There imposes a question of substantial significance for present considerations: Whether the reversible peak of oxide desorption on Pt, Au [106-109], otherwise associated with a rather fast electrode reaction,

$$M + 2H_2O \leftrightarrow M-OH + H_2O^+ + e^-$$

arises firmly fixed with certain defined individual potential values, or occurs along a broader potential range? Plentiful potentiodynamic experimental evidence testifies that whenever there exists enough supply of some species of rather fast oxidation ability, being much faster than the next step of M–OH transfer into the rather stable surface growing oxide (M=O) layer, such as are various aldehydes [110] and simple alcohols [111], their anodic reaction starts immediately after H-atom desorption, exactly at their reversible potentials (for H-CHO at 0.032 V vs. SHE),

$$R-CHO + M-OH + H_2O \rightarrow$$

$$\rightarrow R-COOH + M + H_2O^+ + e^-$$

proceeds all along the double layer range and even can extend at much more positive potentials than where oxygen evolution usually takes place in acidic or alkaline solutions. Such a rather broader charge capacity area (Fig. 9 and 10), features some very unusual properties of reversible anodic oxidation clearly limited by mass-transfer of reacting species. Namely, every potential hold within such an UPO peak leads to a sharp current drop to values typical for the steady-state of the same process or further to surface oxide growth. However, further continuation of anodic potential traversing, repeats in the first next cycle the former voltammogram typical for the given solution. Stepwise potential extension of positive potential limits towards oxygen evolution (OER), clearly reveals (Fig. 11), the absence of surface oxide growth almost until there starts evolving of oxygen. Thus, since during the reverse potential scan towards the HER, there arises oxide desorption much earlier than in the basic solution, the appearance of a characteristic sharp anodic current jump testifies for the repeated or hysteric aldehyde or alcohol oxidation even within the cathodic or former double layer charging range.
Figure 9. Cyclic voltammograms scanned on a polycrystalline Pt wire electrode in alkaline (0.1 M KOH) solution in admixture of formaldehyde (0.01 M (Fig. 9a) and 0.1 M (Fig. 9b) HCHO) at 200 mV/s sweep rate between hydrogen and oxygen potential evolving limits. Labels: (1) reversible hydrogen adsorption peak; (2) primary irreversible surface oxide desorption peak; (3 and 4) successive peaks of aldehyde oxidation; (5) sudden sharp current jump and reverse hysteresis peak of repeated aldehyde oxidation; (6) and (7) hydrogen oxidation and desorption peaks [110].

Figure 10. Cyclic voltammograms scanned on a polycrystalline spectroscopically pure Au wire electrode in alkaline (0.1 M KOH) solution in admixture of formaldehyde (0.1 M HCHO) at 100 mV/s in sweep rate between hydrogen and oxygen evolving potential limits. Labels: (a) the wave of cathodic formaldehyde reduction; (b) irreversible phase oxide desorption peak; (c and d) successive twin peaks of aldehyde oxidation; (e and f) sudden sharp current jump and successive hysteresis twin peaks for repeated aldehyde oxidation during the reversal scan traversing; and (g) the wave of surface oxidation of cathodically produced methanol. One minute hold in the potential range of partial oxygen evolution with consequent shift in repeated aldehyde oxidation [110].

Such state of plentiful (no exception) experimental potentialodynamic evidence [110,111] imposes several outstanding observations and conclusions:

There is no aldehyde or alcohol anodic oxidation upon surface oxide covered metal prior to the potential of molecular oxygen evolution, equally as the transfer of M-OH into the surface oxide layer (M=O) becomes prevented as long as the oxidation of rather more reactive species (aldehyde or alcohol) remarkably exceeds such a 'degradation' ('degeneration') of an active (M-OH) into rather passive (M=O) species. This implies that there is no anodic OER, as long as the (minimal) critical (M=O) surface oxide coverage is absent.

The generation and fast consumption of M-OH species, as a product of the rather fast reversible reaction, (Eq. 2)), in both directions occurs unrestricted within a broader potential interval covering the double layer charging range and even all along to the molecular oxygen evolution, as long as there is provided enough available supply of species of the higher reaction rate than for their oxidation and as long as the metal substrate is clean enough from any counteracting deposits.

Such final conclusion is of a far-reaching and outstanding significance for the present idea (concept) of bifunctional hypo–hyper-d-interelectronic combinations of composite and individual transition metal electrocatalysts based upon the SMI with hypo–d-electronic oxide substrates. 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, and thereby testify for almost unlimited reversible reaction rate (Eq. 2), as long as diffusional mass-transfer supply provides enough reacting species. Such behavior, though substantially different, resembles, at least by its intensity,
provided and enabled. In addition, one should imply that metallic part of electrocatalysts undergoes continuous polarization, in other words, experiences one more degree of freedom relative to classical heterogeneous catalysis, which imposes its consequences upon oxide support, and thereby the coordination with continuous spillover transfering of OH-adgroups to the reacting interface; this is the substance of the bifunctional effect.

In such a context, it would be worthwhile mentioning that the same and rather pronounced potentiodynamic results were obtained by Tseung et al. [112] with D-glucose aldehyde oxidation upon a specific electrode deposit cathodically produced by codeposition of Pt/WO3 from tungstic acid solution. In accordance with data obtained in the present paper, the latter probably was WP3 upon a WO3 support, also adjoined upon basic Pt/WO3 substrate, though the authors name it as the 'precious metal/hydrogen bronze anode catalyst', and label Pt/WO3 [113,114].

**First Principles Considerations of a SMSI System**

The main anodic reactions upon titania-supported transition metal catalysts in LT PEM FC are dissociative hydrogen adsorption

$$1/2H_2 + M \rightarrow M-H + e^-$$  \hspace{1cm} (4)  

followed by anodic oxidation of H-adatoms,

$$M-H + H_2O \rightarrow H_2O^+ + M + e^-$$  \hspace{1cm} (5)  

At little more positive potentials, there occurs the reversible and in both directions rather fast reaction of the first step oxide adsorption,

$$2H_2O + M \leftrightarrow M-OH + H_3O^+ + e^-$$  \hspace{1cm} (2)  

Accompanying reactions at anatase titania supporting interphase (same at tungsten, Scheme I), due to its ability of transferring OH− ions, are mutually dynamically combined and occur as follows:

$$Ti(OH)_3 + M \rightarrow Ti(OH)_3^+ + M-OH + e^-$$  \hspace{1cm} (6)  

$$Ti(OH)_3^+ + 2H_2O \rightarrow Ti(OH)_4 + H_3O^+$$  \hspace{1cm} (7)  

$$\Sigma \quad M + 2H_2O \rightarrow M-OH + H_2O^+ + e^-$$  \hspace{1cm} (2)  

In other words, their net overall summation (Σ) results in the basic reversible reaction of M−OH adsorption. This is the substance of Ti alternating features, the ion exchange properties of hydrated titania and the directional electric field effect from metal catalyst surface upon M−OH spillover, and this is the core of the theory displayed in the present paper. Such state of equilibria at catalytic surface enables simultaneous anodic CO oxidation (Scheme II),

$$M-OH + M-CO + H_2O \rightarrow$$  
$$\rightarrow CO_2 + 2M + H_2O^+ + e^-.$$  \hspace{1cm} (8)  

which certainly can occur as a chemical reaction, too,
The whole thermodynamic equilibria for a general issue of metal/oxidized electronic oxide support, such as M/TiO₂, is illustratively presented in Fig. 12. As a consequence, decreasing the M–OH chemical potential (Δµₘ–OH), causes the work function to decrease, and vice versa. In other words, any consumption of adsorbed M–OH upon metallic catalyst surface decreases its chemical potential, and imposes imbalance within established equilibria. The whole mechanism (Fig. 12) to keep constant both Δφ and cell voltage (ΔUWR), consists in the fact that titania phase automatically reacts and supplies hydroxyl ions (Scheme II) both from its structure and by reacting water molecules (Eq. (2) and (10)).

The main contribution to changes in work function comes from surface potential increment (Δφ), as the prevailing part of inner or Galvani potential changes (Δφ). Namely, Veseynas et al. [25,26,27] have proved on plentiful systems in solid state electrolyte and recently in aqueous media [116] the basic NEMCA relation,

\[ \Delta \Phi = e_\Delta U_{WR} \]  

that could also be considered as fundamental in electrode kinetics [117,118], where ΔUWR is the change in catalyst (working electrode, W) potential versus the reference electrode (R). Thus, as the conclusion associated with otherwise broad experience in NEMCA investigations and therewith resulting statements [25–27,115], in aqueous media for the equilibrium between metallic catalyst upon a hypo-d- electronic oxide support, OH– ions play the main promoting interactive role, while M–OH, as some dipole state, undertakes the spillover and substantially reacting role all over the metallic catalyst surface to keep established such thermodynamic equilibria [119–121]. In fact, there is no NEMCA effect for hydrogen oxidation in acidic media and apparently hydroxyl ions play such a substantial promoting role [119–121]. Therefore, any disturbance of such an equilibria, such as is the consumption of M–OH species as a disturbance of chemical equilibria (Δµₘ–OH), or imposition of an external polarization of electrocatalyst, reflects as a driving force (ΔUWR), and instantaneously tends to reestablish the former state (Fig. 12).

Since the adsorption of primary (M–OH) oxide [106–109] plays a decisive and critical role in the oxidative CO removal, the recent paper of Maricovic and Ross [122] might deserve higher attention. Namely, from the measured isosteric heat of adsorption of Pt–OH (ca 200 kJ/mol), the adsorptive Pt(111)–OH bond energy was estimated to be ca 136 kJ/mol, that is much less than the Pt=O chemisorptive bonding energy (ca 350 kJ/mol), and this is taken for the argument of higher catalytic activity of the OHads state in the surface electrochemistry of CO.

\[
e_\Delta \chi = \Delta \mu_{\text{M-OH}} = e_\Delta \phi
\]  

(Scheme II. Model presentation of M–OH transfer and spillover upon metallic part of electrocatalyst)

\[ 2\text{M–OH} + \text{M–CO} \rightarrow \text{CO}_2 + 3\text{M} + \text{H}_2\text{O} \]  

in particular at high temperatures and depending on catalyst activity.

At the interphases M/Ti(OH)₄ for such a simplified particular issue,

\[ \text{M + OH}^- \leftrightarrow \text{M–OH} + \text{e}^- \]  

the basic first principles thermodynamic relations are well known and are orderly listed with common symbols, as follows [25,27,115],

\[ \Pi = \mu_e - \phi = \mu_e - \varepsilon \chi - \psi \]  

\[ e\phi = -\mu_e + \varepsilon \chi \]  

\[ \Pi_e = -\phi = -\varepsilon \chi \]  

\[ \Pi_{\text{OH}^-} = \mu_{\text{M–OH}} + \Pi_e \]  

\[ \Pi_{\text{OH}^-} = \mu_{\text{OH}^-} - \phi_{\text{OH}^-} \]  

From Eq. (11), (14) and (15), there follows,

\[ \mu_{\text{OH}^-} = \mu_{\text{M–OH}} - \phi + \phi_{\text{OH}^-} + \mu_e \]  

\[ \phi = \phi_{\text{OH}^-} + \chi = \psi + \chi, \text{ or } \phi_{\text{OH}^-} = \psi \]  

From Eq. (14) and (17), there further follows,

\[ \Pi_{\text{OH}^-} = \mu_{\text{OH}^-} - \phi + \varepsilon \chi \]  

Further, from Eq. (11), (15) and (18), one also has,

\[ \Pi_{\text{OH}^-} = \mu_{\text{OH}^-} + \mu_e - \phi \]  

Replacing Eq. (19) in Eq. (18), and taking the derivative, since (Δµₑ = 0),

\[ \Delta \mu_{\text{OH}^-} + e\Delta \chi = \Delta \mu_{\text{M–OH}}. \]  

Finally, from Eq. (12), there follows,

\[ e\Delta \phi = e\Delta \chi \]  

and since ΔµOH⁻ ~ eΔχ [115], there definitely results

\[ e\Delta \chi = \Delta \mu_{\text{M-OH}} = e\Delta \phi \]  

(Scheme II. Model presentation of M–OH transfer and spillover upon metallic part of electrocatalyst)
that the interaction between Pt-acac precursor and the support surface initially occurs between its nucleophilic oxygen atoms and OH-groups of titania (cf. [50]). However, experiments in the present study testify that the main bonding effectiveness of such a molecular precursor arises from the d-d-interaction bonding of Pt straight with Ti atoms of the oxide support (Scheme III), and it imposes the substantial and decisive catalytic characteristics of the SMI. The size and distribution of final metallic phase depends on the ratio of available centers (nucleation sites) of titania (five-fold coordinated Ti on exposed anatase surface) versus the initial concentration of M-acac precursors. The latter results in hydrogen furnace by simple reductive decomposition of grafted composite M-acac precursors.

So far nanostructured colloidal particles of desired nano-size have been used as precursors to impregnate Vulcan XC-72 powder and then to create corresponding particulate metallic electrocatalysts after simple vacuum or thermal removal of organic stabilizing ligands [123–127] (Scheme III). The same procedure could certainly be also employed for grafting of such metallic nanoparticles upon hypo-d-electronic oxide supports and use the d-d-interaction bonding for SMI. The same conclusion definitely relates to so far the most successful Haruta catalytic approach, the so called precipitation-deposition method [41–53].

The closest to the present grafting idea has been the approach of Tseung et al. [112–114], embodied in codeposition of Pt together with tungsten oxide, named Pt/hydrogen bronze anode catalyst, with probable further WPtO creation at the interface by H-adatoms, and providing rather high (more than 500 ppm) CO tolerance and very promising polarization characteristics. Savadogo [128] similarly impregnated Vulcan XC-72 carrying Pt particles with polytungstenates and after thermal treatment recorded remarkable polarization improvements in PEM fuel cells. Finally, the impregnation of ion exchange membranes in LT PEM FC with anatase TiO₂ and internal Pt deposition by Watanabe [129–132], is rather close to the displayed idea of metal catalyst grafting upon titania supports. In the same context, such a rather increased anatase TiO₂ supporting amounts of LT PEM FC grafted catalysts, should substantially contribute to resolve the cross-over effect through Nafion membranes. However, the present method of electrocatalyst tailoring certainly requires rather improved conductivity properties to join all available metallic particles on the current collector. In such a respect, it might be significant to infer that XPS analysis shows the absence of any charge accumulation or separation upon Pt/TiO₂, which suggests that at least part of anatase in the presence of Pt metal undergoes partial thermal transfer into the conductive Magell phase. This is the main aim for the present concept: to keep ionic membrane transferring properties of anatase, and partially transfer the former into Magneli phases of metallic conductivity.

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**Scheme III.** 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 final hypo-hyper-d-d-bonding effect.
Since M-acac precursors decompose at very low temperature (mostly between 70 and 200°C), TG as a kinetic TPR analytic method has been adopted to follow and optimize such grafted electrocatalysts, and even to get some insight as concerns the intensity of interacting grafting bonding upon titania or composite (G-5 mol.% WO₃) oxide support, which is estimated as an optimal admixture [98,99]. TG-grams are almost identical in Ar and hydrogen streams, though the latter provides complete reduction of metal oxides and methane removal. Thus, the present TG-optimized method of catalyst formation is based on M₁M₂...Mₙ-acac decomposition at 200-400°C, in hydrogen atmosphere, within 2 to 5 hours, depending on degree and homogeneity of metallic part of catalyst crystallization primarily in face centered cubic structure (fcc), the amount of TiO₂, TiP₂ or TiN₂ intermetallic phase and Magneli phase one likes to create within the interphase, and proceeding further with cooling in the same reducible gas (H₂).

Some illustrative examples will show basic principles and conclusive remarks. While Ru- and Pt-acac, as grafted upon anatase, decompose between 100 and 230°C, their (1:1 molar) non-interactive mixture creates two distinct almost twin peaks (Fig. 13a), certainly first for Pt. The mass spectogram (Fig. 13b) on line scanned with time coinciding, clearly shows that the two other subsequent peaks correspond to the final methane release and catalyst arises free of carbon. However, in an air or oxygen stream their decomposition proceeds homogeneously and reflects as a distinct uniform peak of mixed oxides with no methane evolution [38].

Mo is usually used in its oxide MoO₂-acac form MoO₃(CH₃COCHCOCH₃)₂, and such state of facts, as well as rather high melting point, hinder the endeavor to provide favorable homogeneous intermetallic phase with Pt by a straightforward decomposition of their mixed acetylacetonates. Crystallization agencies help much in such a respect, and better results provide another form

![Figure 13. TG-grams of thermal decomposition of homogeneous equimolar (1:1) Pt-acac and Ru-acac mixture upon anatase (Hombikat UV 100) TiO₂ composed so to produce 10 wt.% of PtRu alloy: (a) TPR in hydrogen stream, ramp of 5 degrees of centgrade per minute, (b) Its synchronized on-line mass spectrometer scan indicating products of decomposition.](image1)

![Figure 14. TG-grams of thermal decomposition of a homogeneous mixture of MoO₂-acac, Pt-acac and Co-acac in a molar ratio (1:3:1) providing the appearance of nanostructured MoPtCo composite intermetallic phase on anatase (Hombikat UV 100) TiO₂ composed so to produce 10 wt.% metallic phase: (a) TPR in hydrogen stream, ramp of 5 degrees of centgrade per minute, and (b) Its synchronized on-line mass spectrometer scan indicating products of such a decomposition.](image2)
of such (oxygen and moisture sensitive) compound (Mo(CH$_3$COCHCOCH$_3$)$_3$), and the higher the atomic percentage of Pt, the more homogenous intermetallic phase arises, such as preferable MoPt$_4$. In such a respect, since usually steric factor arises as the most hindering homogeneous structure, the third proper component enables almost perfect resolving of such a problem and tunes in phase with an overall new trend towards three-component hypo-hyper-δ-intermetallic electrocatalysts.

So far the fastest and strongest bonding has been achieved in the combinations of MoPt$_4$Co (Fig. 14, a & b) and even more so for MoPtNi (Fig. 15, a & b). The reaction upon anatase occurs even at temperature lower than 100°C, and to be able to scan such a fast reaction and obtain a proper TG-gram, the ramp has had to be reduced from 5 to 1 K-minute$^{-1}$. This is the strong indication of the Brewer type HHDII effect, since individual M-acac decompose between 150 and 200°C.

Even more so, some hypo-hyper-δ-interelectronic combinations of M-acac (in particular Ru-acac, undergoing sublimation if not gasted), in admixture of anatase in ethanol, start vigorously interacting at rather low temperature, so that evaporation of solvent has to be carried out under vacuum. A rather close behaviour features CrPt$_4$Co, which might be so far the best electrocatalyst for cathodic oxygen reduction, though there arises the problem of Cr-acac desolution in liquid CO$_2$, that is critical for the phase of supercritical drying. From the same steric reasons Mo and Co (or Ni) produce at 150°C rather homogeneous and compact crystal structure of nanostructured catalysts upon titania (Fig. 16). The entire evidence so far testifies that the stronger the bonding, the higher the electrocatalytic activity for both the HER and ORR. These are, thereby, the most promising electrocatalysts for anodic oxygen oxidation. In that respect the TG-grams of TPR are a rather indicative measure to assess the Brewer type of bonding: the sharper the kinetic peak, the stronger the bonding and the more homogenous arises the intermetallic phase resulting from M$_1$M$_2$-acac (or M$_1$M$_2$M$_3$-acac) decomposition.

One of so far the best investigated electrocatalysts for the HER is one of the most stable Brewer intermetallic phase, HfPd$_3$ [9]; its melting point increases for more than 1,200 K [1-4]. Thus, their individual and composite Hf-acac and Pd-acac behavior has been of particular interest. While Hf-acac decomposes at about 160°C (Fig. 17a), and Pd-acac at 65°C (Fig. 17b), their homogeneous 1:3 molar mixture, due to the HHDII effect, produces HfPd$_3$ at about 80 degree of centigrade (Fig. 17c). However, the same mixture when gasted upon anatase titania, decomposes at 65°C, resulting with the same hypo-hyper-δ-intermetallic (HfPd$_3$) phase (Fig. 17d).

Intermetallic mixtures of acetylacetonates behave as colloidal particles of metal-organic compounds,
PtCl₂ + RuCl₃ + 5 N(oct)₄[Be₃H] → PtR[N(oct)₄Cl]₅ + 5 Be₃ ↑ + 2.5 H₂ ↑  \hspace{1cm} (1)

Pt(acac)₂ + Ru(acac)₃ + 8 Al( me )₃ →  \hspace{1cm} (2)

**Figure 17.** TG–grams of thermal decomposition of individual Hf-acac (a), Pd-acac (b), and their mixture in 1:3 molar ratio providing to produce homogeneous intermetallic phase HfPd₃ (c), and the same as nanostructured 10 wt. % deposit upon anatase (Hombikat UV 100) TiO₂: TPR in hydrogen stream, ramp of 5 degrees of centigrade per minute (d).

Scheme IV. Schematic illustration of nanostructured colloidal particle formation and stabilization by proper ligands (after Boenemmann et al. [123]). ((Noct₄[Be₃H]) is tetraoctyl-ammonium-triethyl-hydroborate).

similar as presented in Scheme IV, and when thermally decomposed become easily deprived from their ligands at rather low temperature, this way transferring straightforwardly into stable intermetallic phases that otherwise require rather high temperatures in classical metallurgical synthesis. Such stoichiometrically confirmed experimental evidence belongs to the most sound proofs of the Extended Brewer interionic interactive bonding theory. There has been a rather beneficial fact that Hf, though more electronegative element than Mo, produces directly bonded acetylacetonate of rather high stability and non-sensitive on moisture and oxygen, thereby enabling an unique TG experiment for TPR in hydrogen stream. At the same time this is one of most illustrative example of selective grafting of intermetallic phases as bifunctional

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electrocatalysts with prevailing hyper-δ-electronic component upon hypo-δ-electronic oxide (TiO$_2$) support (SMSI) and opens further prospects for three-component catalytic systems, such as IrPdCo.

Potentiodynamic Confirmation of Bifunctional Properties of Grafted Electrocatalysts for Simultaneous M-H and CO Anodic Oxidation

Cyclic voltammogram of nanostructured Pt electrocatalyst impregnated in Vulcan XC-72 (E-tek, Inc.) in 0.1 M H$_2$SO$_4$ features all typical peaks and overall shape characteristic for this metal (Fig. 18). In the presence of 2.0 Vol.% of CO in Ar, there arises its anodic oxidation peak at the ignition point and proceeds all along until oxygen evolution, while therefore charge capacity for the surface oxide desorption correspondingly decreases and hydrogen evolution becomes rather polarized.

A quite different potentiodynamic picture arises when scanned on Pt/TiO$_2$ grafted electrocatalyst under the same conditions. There arises a rather small peak for anodic CO oxidation even at its as high content as 20,000 ppm, which clearly further extends in surface oxide growth (Fig. 19), so that its charge capacity for desorption of the latter corresponds to amounts in CO-free gas. However, as the effect of SMSI upon TiO$_2$ carrier, the remarkable shift of oxide desorption peak deep in negative potential range testifies for the effect of such a passivation. A small polarization for the HER is visible from comparison of two voltammograms scanned in the presence and absence of CO. The main conclusion, when one compares Fig. 18 and 19, might be that majority of CO undergoes chemical oxidation by the spillover effect of primary Pt-OH oxide originating and transferring from titania, and that the small peak for anodic CO oxidation at its rather high concentration has reversible features. Such conclusions supports Fig. 20, which compares voltammograms of Pt/TiO$_2$ scanned in the absence of CO and at its various, but rather high concentrations (from 5,000 to 20,000 ppm). Dramatic decrease in charge capacity of otherwise rather small anodic oxidation peak testifies that only negligible amount of CO undergoes direct electrode reaction, while majority of these should be the subject of heterogeneous catalytic chemical reaction with Pt-OH. If so, this would be the main confirmation of the present interactive theoretical model for simultaneous Pt–H and CO oxidation at composite titania supported electrocatalysts.
The Extended Brewer Interactive Interionic Bonding Theory (EBIBT) has been developed to show the equivalance of interatomic and interionic bonding features, and for their mutual combinations, as well as its effect upon electrocatalytic properties for the hydrogen electrode reactions (HIER). The equivalance of interionic hyper-hyper-δ-interelectronic interaction in both metallic and any other ionic state and its effect upon electrocatalytic properties for hydrogen electrode reactions (HIER) has been proved and inferred. TG (Thermal Gravimetry) analysis of TPR (Temperature Programmed Reduction) of mixed hypo-hyper-δ-electronic oxides of transition elements was broadly employed to prove the EBIBT effect as reflected in dramatically decreased individual temperatures of their mutual reduction into intermetallic phases. The same interionic Brewer (and/or intermetallic) bonding effect has been confirmed both by UPD of hyper-δ- upon hypo-δ-electronic substrates and vice versa, and by the shift of bonding peaks in XPS analysis. The former affords the basis for new trends in submonolayer hypo-hyper-δ-interelectronic electro- catalysis of transition metals. SMSI (Strong Metal Support Interaction) of both individual and composite, prevalently hyper-δ-electronic metallic electrocatalysts upon individual and/or composite, usually hypo-δ-electronic oxide substrates, has been employed to create and graft (anchor) bifunctional electrocatalysts for simultaneous anodic hydrogen and CO oxidation in Low Temperature PEM (Polymer Exchange Membrane) Fuel Cells (LTPEMC). The selective interionic bonding method upon predestined active centers (five-fold-coordinated Ti atoms) of hypo-δ-electronic oxide supports has been adapted to avoid nanostructured colloidal precursors and directly graft (anchor) a priori defined nanosized intermetallic phases and synergetic bifunctional electrocatalysts from decomposition of corresponding stoichiometric mixtures of various individual or intermetallic acetylacetonates. An adapted TG method based on TPR has been properly used to define, control and/or stimulate the homogeneity of the intemetalllic crystal bonding and growth of nanostructured composite catalyts, mostly of rather extra strong bonding Brewer intermetallic phases upon proper SMSI oxide supports. In such a respect, XPS analysis strongly indicates that within the interphase of nanostructured Pt, Pd, and Ni upon anatase titania (TiO₂) support, under the effect of H₂-atoms, at relatively low temperature (250–400 °C), spontaneously grow the most stable stoichiometric TiPd₃, TiPd₂ and TiNi₃ intermetallic phases, that arise mostly responsible for such a SMSI and thereby resulting advanced catalytic activity. In other words, at M/TiO₂ interphases in hydrogen stream grow the same stable intermetallic phases as the ones that result from TPR of corresponding oxides mixed at their molecular level. Thus, it has been pointed out that the term SMSI has a broader hypo-hyper-δ-interelectronic interactive...
sense in both the bonding effectiveness and bifunctional catalytic meaning, and in fact stays in the core of such EBIIT.

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APPENDIX I

The hydration of transition metal ions leads to the formation of a partially covalent bond [59]. Such a partial charge transfer occurs from the filled 3δ* bonding orbital of oxygen in water molecule to the empty 3δ-orbital of transition metal ion, so that then positive partial charge of hydrogen atoms increases, and consequently water molecule, as a whole, becomes more acidic. The magnitude of electron transfer in the most simplified issue enables the following reactions and species to occur [59,66]:

\[ [M-OH_2]^+ \rightleftharpoons [M-OH]^{(2-1)+} + H^+ \rightleftharpoons [M-O]^{(2-2)+} + 2H^+ \]  
(A1)

In otherwise noncomplexing aqueous media such species are named aquo (-OH2), hydroxo (-OH) and oxo (=O) ligands. In general, with coordination number (N) of covalently bound water molecules, the initial rough formula for any inorganic precursor can then look as \([\text{MO}_N\text{H}_{2N-N}]^{(2-N)+}\), where h is defined as the molar ratio of hydrolysis. Apparently now, when h=0, the gel precursor arises as an 'aque-ion' \([\text{M(OH)}_n]^{(2-N)+}\), while for h=2N, the resulting ligand is an 'oxo-ion' \([\text{MO}_N]^{(2-2N)+}\). If the molar ratio of hydrolysis arises somewhere in between, 0 < h < 2N, the precursor can be an hydroxo complex, \([\text{M(OH)}_n]^n\), an hydroxo–oxo complex, \([\text{M(OH)}_n\text{OH}_2]_n^{(2-N)}\) for h>N, and oxo–hydroxo ligand, \([\text{MO}_N\text{OH}_2]_n^{(2-N)}\), for h>N [59,66].

This is the theoretical basis of Livage [59] so called partial charge model (PCM) to quantify and establish charge (z) – pH relationship and therefrom resulting such a diagram, which shows that aquo ligands can not exist for higher ionic charges (z > 4) [59,66]. The theoretical basis of the PCM-model is that when two atoms combine, charge transfer occurs causing each atom to acquire a partial positive or negative charge, \(\delta^+\) or \(\delta^-\). The electronegativity equalization principle, which is equivalent to the thermodynamic principle of chemical potential equalization, requires that electron transfer stops when electronegativity of all atoms involved equals the mean electronegativity, \(\chi (\chi(\text{OH})=2.71)\) [59].

The PCM affords insight into inorganic sol-gel polymerisation pathways, since in nucleophilic substitution (SN) and nucleophilic addition reactions (A), common to hydrolysis and condensation chemistry, the substituent with the largest partial negative charge, \(\delta^+\), is the nucleophile, and vice versa for the largest partial positive charge, \(\delta^-\). Nucleophilic reactions cease when the strongest nucleophile acquires a partial charge \(\delta > 0\).

According to the PCM, charge transfer in acidic media implies spontaneous hydrolysis,

\[ [\text{MO}_N\text{H}_2^+] + \text{H}_2\text{O} \rightleftharpoons [\text{MO}_N\text{H}_{2(N-N)}]^{(2-N)+} + \text{H}_3\text{O}^+ \]  
(A2)

and arises by the cleavage of the O–H bond due to the high polarizing power of metal ion M, so that such reaction proceeds as long as \(\delta(\text{OH}) > 0\). The number of protons, p, removed through spontaneous hydrolysis \(p = 1.80547\), in accordance with the PCM, is given by the relation [59],

\[ p = 1.452 - 0.45N - 1.07 (2.71 - \chi(\text{OH}) / \sqrt{\chi M}) \]  
(A3)

Under alkaline media, the limiting reaction is the cleavage of the M–OH bond arising from the low polarization of metal atom M,

\[ [\text{MO}_N\text{H}_2^+] \rightleftharpoons [\text{MO}_N\text{H}_{2(N-N)}]^{(2-N)+} + \text{QOH}^- \]  
(A4)

and occurs as long as hydroxo ions can be formed and thereby proceeds until \(\delta(\text{OH}) = -1n [\text{MO}_N\text{H}_{2(N-N)}]^{(2-N)+}\), where 2N-q corresponds to the number of protons that cannot be removed even at very high pH. The corresponding relation for transfer of hydroxido ions, according to the PCM is as follows [59,66],

\[ q = 1 + 1.25z - 0.92 (2.49 - \chi(\text{OH}) / \sqrt{\chi M}) \]  
(A5)

Both relations (Eq.(A3) and Eq.(A5)) show that the number of protons (p) and hydroxido ions (q) depend on the formal charge (z) of metal ion \(\text{M}^{(z)+}\), the coordination number (N), and the electronegativity \(\chi(M)\) or chemical potential of the metal (M).

Such consideration and involved relations afford some insight in the OH– ions transfer by reducible transition metal oxides and their gels.

The entire sol-gel procedure to obtain proper hypo–electric support imposes some facts to be obeyed: Drying of so formed gel by simple evaporation under normal conditions gives rise to capillary pressure that causes shrinkage of the gel network! The resulting dried gel, called aerogel (zero means dry) is often reduced in volume by a factor of 5 to 10 as compared to the original wet gel. However, if the wet gel is placed in an autoclave and dried under supercritical conditions, there is substantially no interface between liquid and vapor, so that there is no capillary pressure and relatively, if any, shrinkage, and the product is named aerogel. During super– or hyper-critical drying, there may be indeed mostly air, having volume fraction as low as \(\approx 1\%).
IZVOD

NOVI TRENDOVI U ELEKTROKATALIZI: PROŠIRENA BRUEROVA INTERAKTIVNA I INTERJONSKA VEZUJUĆA TEORIJA I SELEKTIVNO INTERAKTIVNO KALEMLJAVANJE KOMPOZITNIH BIFUNKCIJALNIH ELEKTROKATALIZATORA ZA SIMULTANU ANODNU OXIDACIJU VODONIKA I UGLJEN MONOKSIDA

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