d-Band Catalysis in Electrochemistry

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We have developed the first theory for electrochemical electron transfer reaction that can account for specific catalytic effects. By abandoning the wide-band approximation, we have been able to introduce specific interactions with d-bands, which lower the activation energy. We have applied this model to the breaking of a bond in a diatomic molecule; this is a particularly important case, since generally bond breaking requires a strong catalytic effect of the electrode. When this molecule is far from the electrode, its bonding orbital is filled and its antibonding orbital is empty; during the reaction the antibonding orbital is filled and the bond is broken. The final states consist of two ions, which strongly interact with the polar molecules of the solvent. As is well-known from the theory of Marcus for simple electron transfer, this interaction stabilizes the ions, and the electron transfer generally involves a reorganization, or fluctuation, of the solvent.

Our theory permits the calculation of potential energy surfaces $V(q,r)$ as a function of the solvent coordinate $q$ and the bond distance $r$. An example is shown below.

In order to explore the consequences of our model, we have performed calculations based on a simple, semi-elliptic form of the d-band. In this way, we were able to demonstrate and understand a number of qualitative effects: the change in the density of states as the reaction proceeds and the system passes the saddle point; the importance of a high density of d-band states near the Fermi level, which interact with the anti-bonding orbital as it passes the Fermi level; the loss of symmetry between the anodic and cathodic direction, which implies transfer coefficients different from 0.5; the decrease in the energy of activation with increasing interaction, which in extreme cases can result in dissociative adsorption without barrier. A strong catalytic effect can be expected, when the antibonding orbital is split by a strong interaction with a d-band as it passes the Fermi level.

The model gives some justification to recent suggestions that the center of the d-band is a key factor for the electrocatalysis, and it offers a route for calculating reactions rates using results from ab initio calculations as input.

Density functional modeling of redox properties using ab initio molecular dynamics simulation
The redox (thermochemical) and electron transfer (kinetic) properties of a large class of transition metal coordination complexes in solution can be understood and analyzed using Marcus theory. The central quantities in Marcus theory are the reaction free energy change and the reorganization free energy. Computer simulation has contributed by relating these properties to the microscopic characteristics of a given model system. As shown by Warshel, the key quantity making this link is the vertical energy gap (ionization potential and electron affinity of the condensed phase system). We have recently developed a density functional theory (DFT) based ab initio molecular dynamics (MD) implementation of this approach[1,2].

The special feature of ab initio MD is that it treats solute and solvent at the same level of theory. In this talk, using aqueous coordination complexes of group VIII cations (Fe$^{2+/3+}$, Ru$^{2+/3+}$) with simple ligands (H$_2$O$^{2-}$, NH$_3$ pyridine, CN$^-$, Cl$^-$[3]) as illustration, we show that this fundamental perspective has certain advantages for the computation of the redox properties and the understanding in terms of the electronic structure of one-electron states. We then continue with a brief discussion of the application to a small iron-sulfur protein, rubredoxin, using a quantum/classical hybrid approach.[4]

[4] Collaboration with P. Carloni (Sissa, Italy) and U. Rothlisberger (EPFL, Switzerland).

First-Principles Insight into Electrocatalysis: Electooxidation of Methanol

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Electrocatalysis is controlled by the elementary reactions that occur at the interface between the electrode and the solution phase and require an accurate accounting of the electrochemical potential that results across this interface. Elucidating the electrochemical behavior at this interface, however, presents a considerable challenge due to complexity of the surface chemistry, the explicit atomic and molecular structure of the solution phase at the interface, the presence and formation different ions and their positions, and the applied surface potentials that results as a function of the surface reactivity. First principles simulation of electrocatalysis tends to be limited by the fact that ab initio methods simulate constant charge systems rather than constant potential systems. We have developed a new methodology by which we can begin to model constant potential systems. The approach is used here to probe the elementary pathways involved in methanol oxidation and to screen different bimetallic and ternary alloys in an attempt to identify potential catalysts for the electrocatalytic oxidation of methanol for use in direct methanol fuel cells. In addition, we present a multiscale approach by which to connect the ab initio results to electrocatalytic kinetics.

Realistic, quantitative descriptions of electron-transfer reactions: diabatic free-energy surfaces from first-principles molecular dynamics

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A general approach to calculate the diabatic surfaces for electron-transfer reactions is presented, based on first-principles molecular dynamics of the active centers and their surrounding medium. The excitation energy corresponding to the transfer of an electron at any given ionic configuration (the Marcus energy gap) is accurately assessed within ground-state density-functional theory via a novel penalty functional for oxidation-reduction reactions that appropriately acts on the electronic degrees of freedom alone. The self-interaction error intrinsic to common exchange-correlation functionals is also corrected by the same penalty functional. The diabatic free-energy surfaces are then constructed from umbrella sampling on large ensembles of configurations. As a paradigmatic case study, the self-exchange reaction between ferrous and ferric ions in water is studied in detail.

**Bimetallic and Ternary Alloys for Improved ORR**

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Periodic self-consistent Density Functional Theory (DFT-GGA) calculations have emerged as a valuable partner to experiment in explaining reactivity of transition metal surfaces. These methods provide detailed *atomic level* mechanistic information on individual elementary reaction steps, in terms of reaction thermochemistry, reaction paths, pre-exponential factors and activation energy barriers. In this presentation, we will attempt to demonstrate how first-principles methods can help with guiding catalyst synthesis to reach the ambitious goal of “catalysts by design”. We will discuss opportunities to design bimetallic and ternary alloy catalysts, which are cheaper and more active than pure Pt for the oxygen reduction reaction. The role of strain, electronic coupling, and surface poisoning by reactive intermediates will be highlighted. Finally, the strong and fruitful interaction between theory and experiment in advancing transition metal catalysts and electrocatalysts design will be emphasized.

More information on the work to be presented can be found at:


**Surface chalcogenide catalyst for the polymer electrolyte fuel cell cathode**

Piotr Zelenay

In a three-way collaboration with the University of Illinois at Urbana-Champaign, Université de Poitiers and Los Alamos National Laboratory, we have recently demonstrated chalcogenide catalyst for the polymer electrolyte fuel cell (PEFC) cathode obtained by surface modification of metal black particles (ruthenium in particular) rather than on the synthesis of a bulk metal-chalcogen compound. The catalyst can be obtained by depositing controlled quantities of selenium onto the surface ruthenium from either organic phase (xylenes) or directly from aqueous media. Electrochemical, non-electrochemical and fuel cell testing reveal high activity of and good methanol tolerance of such catalysts obtained by either synthesis approach. Uniquely
for Pt-free cathode catalysts, surface chalcogenides also exhibit very good performance durability under fuel cell operating conditions at 70°C. In this presentation, we will focus on hydrogen-air and direct methanol fuel cell (DMFC) performance of selenium-modified Ru blacks as well as on the mechanism of oxygen reduction reaction (ORR) on Se/Ru catalysts, as determined in rotating ring disk-electrode (RRDE) and PEFC studies. We will introduce methods for potentially reducing ruthenium content (loading) in surface chalcogenide catalysts, required for making these catalysts practically viable not only in DMFCs for predominantly portable use but also for higher-power applications, in which catalyst cost is a major cause for concern and a potential commercialization barrier. Finally, we will discuss an enabling role of methanol-tolerant ORR catalysts in the development of alternative fuel cell systems that use mixed reactants, methanol and oxygen (air), in the anode and cathode feed streams.

Metal oxide photo-catalysts for hydrogen production

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One of the main requirements for a future hydrogen economy is a clean and efficient method for producing hydrogen. The production of hydrogen from water and sunlight (photo-electrolysis) is one of the few methods that are both renewable and sustainable. While this can be achieved with conventional coupled solar cell-electrolyzer systems, direct photo-electrolysis with a semiconductor photo-electrode is a more elegant and potentially more efficient and cheaper approach. Promising strategies for this approach will be outlined. On the materials side, most research efforts have been focused on titanium dioxide due to its excellent photo-chemical stability and high activity in the UV. However, its poor sensitivity to visible light continues to be a major drawback. In the search for visible-light active photocatalysts, many efforts have been undertaken to modify TiO₂ (e.g. by doping), or by exploring alternative materials such as Fe₂O₃, WO₃, or more complex metal oxides. We will discuss some results obtained for anion- and cation-doped TiO₂. Special attention will be given to metal-doped TiO₂ with a fractal morphology made by chemical vapor deposition. Anomalously high photocurrents in the visible part of the spectrum are observed for this material. The origin and stability of these photocurrents can be traced to the presence of ionic point defects, and will be discussed. In addition, some recent results on a ternary metal oxide, InVO₄, will be shown. The thin film catalyst form of this material is much less photo-active than the particle form, which can be explained in terms of charge carrier mobility and defect density.

Size dependent properties of supported Pt nanoparticles

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In order to understand the size dependent-electrocatalytic properties of metal particles industrial catalysts consisting of carbon supported platinum nanoparticles ranging in size from 1 to 30 nm are characterized and their catalytic activity for CO electrooxidation as well as oxygen reduction is evaluated. The order of activity for the oxidation of a saturated CO adlayer is 1 nm ≤ 2 nm < 5 nm < 30 nm [1]. This is the same order of activity with size found for the oxygen reduction reaction [2, 3]. TEM analysis revealed that the Pt crystallites are not perfect cubo-octahedrons and that the large particles have “rouger” surfaces than the small particles. By varying the
experimental procedure it is found that defects play a significant role for the catalytic activity for CO electro-oxidation.


Single crystal approach to the surface characterization of platinum nanoparticles.

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Some electrocatalytic reactions would require the presence of wide surface domains. A route to characterize the presence of (111) and (100) domains on platinum nanoparticles through irreversibly adsorbed adatoms has been recently proposed [1]. Calibration curves from series of well-defined stepped surfaces have been used to achieve this purpose. The technique enables the classification of the different nanoparticles and predicts its reactivity towards ammonia oxidation, which is extremely sensitive to the presence of Pt(100) sites. Recent results on the application of irreversible adsorbed Te [2] and Tl as probes for characterization purposes will be discussed. On the other hand, specific site reactions, such as the reduction of acetaldehyde oxime on Pt(111) domains, have been studied in an attempt to improve the surface characterization of the reactivity of platinum nanoparticles. Adsorbed CO stripping has also been studied on platinum nanoparticles with well-characterized surfaces. Single crystal work has shown that the reaction is a complex structure sensitive process. In particular, the reaction enables the detection of wide domains, either with (111) or (100) symmetry on the surface of platinum nanoparticles [3].

References.

Particle-size effect of nanoscale platinum catalysts in oxygen reduction reaction

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Oxygen reduction reaction (ORR) was investigated at a series of carbon-supported platinum nanoparticle electrocatalysts (Pt/CB) with average diameters in the range of roughly 1-5 nm in comparison with bulk Pt in 0.1 M HClO₄ solution at 30 to 110 °C by using a channel flow double electrode method. ORR rate constants and H₂O₂ yields evaluated from hydrodynamic voltammograms did not show any particle size dependency. We have found that the apparent rate constants \( k_{app} \) (per real Pt active surface area) for the ORR at bulk-Pt (with and without Nafion-coating) and Nafion-coated Pt/CB (19.3 wt % and 46.7 wt % Pt, \( d_{Pt} = 2.6 \) to 2.7 nm) thin-film electrodes were in beautiful agreement with each other in the operation conditions of polymer electrolyte cells (PEFCs), i.e., 30 – 110 °C and ca. 0.7 to 0.8 V vs. RHE. The H₂O₂ yield was 0.6% to 1.0% at 0.7 V to 0.8 V on all of Nafion-coated Pt/CB and bulk-Pt and irrespective of Pt-loading level and temperature. Nafion-coating was pointed out to be a major factor for the H₂O₂ formation on Pt catalysts modifying the surface property, because H₂O₂ production was not detected at the bulk-Pt electrode without Nafion coating. We conclude that there is a negligible difference in the surface electronic properties of these Pt/CB catalysts due to size
variations and therefore, the ORR activities are not affected by the differences in the particle size.

**Electrocatalytic Pathways on Supported Electrocatalyst at a Polymer Electrolyte Interface: Some Insights Using XANES Spectroscopy**

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There is a need for a substantial jump in the ability to design, characterize, and test new catalysts, particularly nanostructured catalysts with specifically tailored properties. In the endeavor for a widespread hydrogen economy, the ability to better characterize electrocatalysts in situ under actual cell operating conditions with element specificity and surface sensitivity is crucial. There are very few techniques however that lend themselves to such rigorous requirements, where the individual role of different transition metal components of nano-phasic materials (typical cluster dimensions in the range of 1.5 to 10 nm) can be investigated in both amorphous and crystalline forms. We have recently reported a new analytical technique along with theoretical calculations, which enables the amount and specific adsorption site of H, OH, O, CO, other C1 moieties and even anions such as bisulfate to be determined in situ on a metal surfaces using synchrotron XANES data1-3. This technique called the ‘Delta µ Technique’ can be taken in situ in both electrochemical cells and operating fuel cells, and can be obtained from a wide variety of transition metal surfaces and alloys3, including non-noble metal electrocatalysts such as pseudo-binary and ternary chalcogenide complexes4 with element specificity. EXAFS data taken concurrently provide information on the changes in short range atomic order around the absorber atom thereby providing structural information such as bond distances and coordination numbers (thereby information on average cluster size, homogeneity and surface segregation etc.). This in situ information, now available for the first time, provides a unique opportunity to gain new understanding of reaction pathways, corrosion and durability (surface segregation and sintering for e.g) of transition metal reaction centers.

The unique capabilities of this new in situ technique for determining adsorbate coverage can be better realized by comparison with other techniques. X-ray photoelectron spectroscopy (XPS), an ex situ technique, shows that most of the alloying elements; e.g. Ru, Sn, Mo, are oxidized even under the UHV although they are not in the electrochemical cell; indeed recent in situ XANES results prove this5. In situ FTIR diffuse reflection spectroscopy (FTIR-DRS) has been routinely used to track such adsorbates as CO, CO2, and HCOOH, etc. but the adsorption sites (e.g. on the Pt or Ru site) cannot be determined with this technique6,7. Further it cannot be used to track OH and H adsorption. To our knowledge adsorbed OH has not yet been directly observed on any Pt anodes except via the XANES technique herein described; thus the evidence for its formation to this point must come from the coincidence of the potential for the onset of water oxidation with the peak for CO oxidation. The related technique, SNIFTIRS (subtractively normalized interference FTIR), although providing detailed site information on CO compact adlayers on Pt and PtM8-10 requires mirror surface finishes on the electrodes, and thus are not yet able to be used on porous carbon based electrodes11. Electrochemical thermal desorption mass spectroscopy (ECTDMS), is a very powerful technique for the identification of reaction intermediates, but it is an ex situ technique with limited value for detecting surface adsorbates12.

The unique direct spectroscopic information obtainable from XANES data with the new analysis technique is highlighted here. Prior reports have extensively dealt with the nature of water activation and H adsorption on Pt electrocatalysts2,13 in addition to the influences of alloyed transition metals (e.g. the bifunctional mechanism) on the water activation pathway.3 A recent study has sought to tie together our expertise with this technique, and observe and explain the different effects of the cluster size and morphology of PtRu electrocatalysts in respect to CO, O(H), and H adsorption simultaneously. This study is important in the context of
understanding the mechanisms by which PtRu anodes out-perform unalloyed Pt electrocatalysts especially when functioning in reformate (methanol and CO-saturated) feeds.

Data was collected with two separate PtRu electrocatalysts (from E-TEK and those prepared using the Watanabe method) in 1.0M HClO₄ + 0.3M methanol at both the Pt L₂,₃ and Ru K edges. Δμ analysis of the XANES signals in respect to potential as previously reported allowed for the isolation of O(H), CO, and H adsorbates on both Pt, Ru, and Pt-Ru sites. Figure 1 expresses the relative Δμ amplitudes of these adsorbed species (in respect to potential) at various geometric positions on PtRu electrocatalysts. This has allowed not only for observation of the concentrations of adsorbed species relative to each other, but also permits us to show the effects of both particle sizes and morphologies on these reactions. The E-TEK electrocatalyst is predominantly alloyed with Ru atoms whereas the Watanabe material is much closer to a true mixed oxide system of Pt and Ru oxides. The results of the differing amounts of reactive Pt-Pt, Pt-Ru, and Ru-Ru edges in these catalysts plainly leads to the different adsorption profiles. This study expectedly carries important consequences for the design and synthesis of next generation PtM electrocatalysts for DMFC anodes.

Pt-based electrocatalysts have proven to be ideally suited to the dmu analysis primarily because of the extensive morphological characterizations (X-ray diffraction, single crystal electrochemical evaluations, UHV spectroscopy, etc.) performed over the past decades. In light of these considerations, we have recently applied the Δμ technique to a novel mixed-phase chalcogenide electrocatalyst (RhₓSᵧ, commercially available from E-TEK, Inc).Because this material exists as a balanced phase of three distinct Rh:S stoichiometries (orthorhombic Rh₂S₃, monoclinic Rh₃S₄, and cubic Rh₁₇S₁₅), where each phase exhibits different degrees of metallic character.

The RhₓSᵧ electrocatalyst was probed in an inert 1M TFMSA electrochemical cell at the Rh K edge over a wide set of potentials. Application of the dmu technique p (for RhₓSᵧ: Δμ = μ(V) – μ(0.40 V)) allowed for the isolation of the O(H) adsorbate signals (Figure 2). The theory curves were generated from a model of the RhₓSᵧ phase with the FEFF 8.0 code (Rehr, Univ. Washington). This phase exhibits both the RhS₆ insulating backbone that is the predominant constituent of Rh₂S₃, and maintains some of the metallic character of the superconductor Rh₁₇S₁₅ in the form of repeating Rh₆ octahedra. Our results show that RhₓSᵧ, akin to Pt, adsorbs O(H) in an atop (1-fold) coordination at low potentials. As the potential increases, the O moves to both a 2 and 3-fold coordination via exchange with a sulphur atom. These results not only represent the first time that water activation has been observed on a chalcogenide electrocatalyst, but also the first elucidation of the structure/property relationship of a chalcogenide.

References:
Electrooxidation of small organic molecules on single crystal and bi-metallic electrodes

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One of the major problems in the development of efficient and reliable low temperature fuel cells (such as a direct methanol fuel cell, DMFC) and hydrogen fuel cells is poisoning of the catalytically active anode, usually platinum by virtue of its catalytic activity, by decomposition products of the oxidized fuel or by contaminants in the gas feed. Carbon monoxide (CO) has been identified in many studies as primary poisoning species. It is present as a trace species in most commercially available hydrogen gasses, but can also be formed during incomplete catalytic oxidation of organic fuels (C1-C3) at low temperatures. CO binds strongly and irreversibly to the Pt surface, thus, occupying reaction sites otherwise used for the reaction, which results in a decrease in the activity of the catalyst. Oxidative removal from the catalyst greatly reduced the efficiency of the fuel cell and is, therefore, undesirable.

From the fuel cell technology perspective, it is interesting to investigate the mechanism and kinetics of the CO formation from small organic molecules and the CO electrooxidation on platinum and other catalytically active electrode materials. The ultimate goal, of course, is to develop a more CO tolerate catalyst, or to find a catalyst which circumvents its formation entirely. To this end we will address the following topics in the presentation.

One of the most effective ways for obtaining molecular-level knowledge of the mechanism and kinetics of these reactions is to use atomically well-defined surfaces, i.e. single crystal electrodes. Using these surfaces, the decomposition and oxidation reaction of methanol to CO and intermediates was investigated. The results show that steps of monoatomic height and crystalline surface defects catalyze the decomposition of methanol.[1] If an ensemble of both step and terrace sites is available, CO formation is preferred.[2] Moreover, the formation of soluble intermediates like formic acid and formaldehyde, formed in a reaction parallel to the formation of CO, was also found to occur preferably at these step sites.[2]

As industrial and commercially available catalysts consist primarily of nano-scale particles, a study on the effects of particle size and shape of Pt-nanoparticles on the electrooxidation of methanol, formic acid (an intermediate in the methanol oxidation reaction) and CO was also performed. In light of the much debated particle size effect, our results favor the theory that the shape of the particles rather than their actual size primarily dictates the characteristics of the catalyst.[3]

In order to find a more CO tolerant catalyst we have tried to verify experimentally Density Functional Theory calculations which suggested that platinum monolayer systems on noble metal substrates may have good CO oxidation characteristics, in particular Pt monolayers on Rhodium surfaces. After a detailed study of the CO electrooxidation reaction on bare rhodium surface,[4-7] the catalytic properties of this bi-metallic surface were investigated.[8] In agreement with what was suggested by the theoretical calculations, we found that modifying a
rhodium substrate with a platinum monolayer results in a more CO tolerant surface. The potential at which CO oxidizes was lowered by ca. 200 mV due to modification of the electronic structure of the platinum monolayer.


Oxidation mechanisms of small organic molecules at nanostructured dispersed electrocatalysts.

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The anodic reactions, which occur in Low Temperature Fuel Cell need active and specific catalysts, mainly when hydrogen is not this fuel or when traces of CO, coming from the reforming step, are present. A fuel such as alcohols or more generally small organic molecules requires catalyst able to perform complex electrocatalytic reactions with different steps. Fundamental studies of these mechanisms are still a key point to design optimized electrocatalysts. However, the other important point is the conception of real catalysts for Low Temperature Fuel Cell. These catalysts should be highly dispersed on conducting support. The synthesis of nanoparticles, mainly bimetallic ones, is crucial.

The aim of this communication is to discuss some recent results with the examples of methanol, ethanol but also some other possible alternative fuels (DME or DMM). The problem of the C-C bond cleavage in the case of C2 molecules will be also discussed from these examples.

The influence the structure and the size of nanoparticles dispersed on a carbon powder support will be considered. Results obtained from different kinds of nanoparticles preparation procedures, and the effect of the different treatments (chemical or thermal) following these preparations will be also discussed.

Strategies in the study of electrocatalytic reactions based on reaction pathway mapping and the use of single crystals

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One topic discussed will be the formation of formaldehyde during the oxidation of 1.0 M methanol in 0.1 M H2SO4 over bulk, arc melted PtRu alloy electrodes. Electrodes with Ru mole fractions (X_Ru) of 0.1, 0.3 and 0.9 were employed. Reactions were carried out under conditions that kept the methanol depletion in the cell below 1%. For potentials ≥ 0.7 V_{RHE}, the formaldehyde yields tended to become lower as the Ru content of the alloy electrode increased. However, at low (0.5 V_{RHE}) potentials the formaldehyde yields were at a minimum in reactions over the X_Ru = 0.3 material. The results are considered in terms of atomic level models for methanol-electrode interactions. The use of single crystal Pt electrodes as standards in the study of small molecule electrocatalytic reactions will also be described. The oxidation of CO on Pt(111) and Pt(100) electrodes probed through cyclic voltammetry and potential step
measurements is being used to attain benchmark responses in parallel with measurements involving other electrode materials.

Catalytic reactivity for CO electro-oxidation on Pt-and Pd-modified quasi single crystal Au thin film electrodes

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The electrocatalytic behavior of metals of the platinum group has been one of the most interesting topics for a long time because of their wide use in various applications, in particular, in the development of low temperature fuel cells. Understanding of the electro-oxidation of CO on platinum metals is critical for the improvement of CO tolerant fuel cell catalyst. The CO electro-oxidation on platinum-group metals was explored in many investigations. Studies on relationships between the electrocatalytic behavior of single crystal electrodes and that of metal particles-modified electrode such as gold substrates, which are stable in a large potential region, have been carried out because of fundamental aspects as well as of applied reasons to improve the performance of low temperature fuel cell catalysts.

The aim of the present study is to characterize Pt-and Pd-modified quasi-single crystalline film electrodes and to investigate the effect of these tailored surface structures on the the electro-oxidation of CO by electrochemical and spectroscopic methods. The properties of the Pt-and Pd-modified Au film electrodes will be compared with data employing single crystal electrodes.

The preparation of Pt modified Au(111-25nm) thin film and Au(hkl) massive electrodes was carried out using two approaches: The first one involves the spontaneous deposition of tetrachloroplatinate from 100 µM acidic solution onto Au electrodes, contact time 1 ~ 10 min, and the subsequent electro-reduction in a separate electrochemical cell in K2PtCl4 - free electrolyte [1]. As a second method we applied the potential-controlled electrochemical deposition from 100 µM K2PtCl4 acidic electrolyte [2]. Pd-modified Au electrodes were also prepared by the second method [3]. Pd single crystal electrodes were fabricated according to a modified Clavilier-type technique, and subsequent annealing under argon by inductive heating [4].

The Pt-and Pd-modified Au electrodes were characterized in sulfuric and perchloric acid solution in the absence and in the presence of CO employing cyclic voltammetry (CV), chronocapmery and surface enhanced infrared spectroscopy (SEIRAS). The recorded current – potential curves illustrated that this reaction depends on the structure of the gold substrates and on the coverage of the Pt – particles respective Pd films. Furthermore, the potentials of zero total charge (PZTC) of the Pt-modified Au(hkl) and thin film electrodes were investigated by CO displacement measurements. The values of the PZTC for the Pt-particle modified Au(hkl) electrodes were consistent with results reported for Pt(hkl) electrodes. These results imply that the structures of the Pt - particles are strongly affected by the substrate morphology.

Two CO oxidation peaks were observed on the Pd-Au electrodes and high index Pd single crystal electrodes. The CO stripping experiments on Pd[111]x(110) electrodes showed a strong influence of the step density on the CO electro-oxidation reaction. This result suggests that the oxidation of CO on the (110) step sites proceeds at more negative potentials than that on terrace site. The single crystal experiments for CO oxidation will be compared with SEIRA studies employing Pt- and Pd-Au electrodes.

Sum-Frequency Generation Spectroscopy (SFG) is based upon the second-order nonlinear optical process, is inherently interface specific and is emerging as a powerful in situ vibrational spectroscopy for investigating electrochemical interfaces. The focus in our groups (1,2) is on use of a femtosecond broad-band multiplex SFG (BB-SFG) apparatus to study electrochemical solid/liquid interfaces, including single crystal interfaces. The method (1,2) permits rapid spectral acquisition (5 s⁻¹) synchronized with the potential sweep at a rate of up to 5 mV/s. The electrochemical cell has an ideal configuration where the thickness of the supporting electrolyte (25 µm) is controlled by a spacer. Measurements of acetic acid adsorption and adsorption/oxidation of carbon monoxide on Pt and Pt/Ru electrodes will be reported. The work will include the most recent results obtained with Pt nanoparticles physically deposited on gold. With the CO-free electrolyte and Pt surface covered by CO, the loss of SFG signal from CO upon its oxidation quantitatively tracks the CO surface coverage, as determined by the integrated current (or charge). The CO peak shift undergoes the Stark tuning at a rate of ca. 28 ± 2 cm⁻¹V⁻¹ until the electrode potential slightly shifts below the onset of the CO oxidation. As CO is oxidized, the peak frequency dips and then recovers, while the peak linewidth broadens and then narrows. CO BB-SFG amplitudes and the Stark tuning values with Pt(111)-CO and Pt(100)-CO will be reported showing interesting and different features, e.g., a clear 2D CO phase transition on Pt(111) but not on Pt(100), neither on Pt(poly). On Pt(111)/Ru, two distinctive CO species were resolved: Pt(111)/Ru-CO, with CO chemisorbed on Ru sites; and Ru/Pt(111)-CO with CO chemisorbed on Pt sites (3). The SFG assignment of these species (measured at 0.1 V vs. RHE) is that the 1970 cm⁻¹ peak corresponds to the linear-bonded CO on Ru and 2070 cm⁻¹ to the linear-bonded CO on Pt. These spectral features are clearly associated with two current-potential voltammetric peaks at ca. 0.55 V and 0.67, respectively.

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Probing Ultrafast Electrode Dynamics by Picosecond Time-Resolved Surface-Enhanced Infrared Spectroscopy

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Kinetic studies by conventional electrochemical methods are limited to reactions having rate constants less than 10⁴ s⁻¹ due to the time constant of the double-layer charging (typically 0.1-1 ms). A possible way to circumvent this limitation is the use of the so-called laser induced temperature jump method. Irradiation with a short pulse suddenly raises the temperature of the
electrode and the interface, which spontaneously change the rest potential of the electrode. In this presentation, we will report the first picosecond IR monitoring of the interface after visible laser irradiation [1]. The laser-induced potential jump was monitored through the shift of the C-O vibration of CO adsorbed on a Pt electrode.

With the aid of surface-enhanced IR absorption (SEIRA)[2,3], the CO vibrational mode was observed clearly in the picosecond time scale and a 6 cm\(^{-1}\) red-shift of the C-O vibration was observed after the visible pump pulse irradiation with a delay about 200 ps as shown in Fig. 1 (circles). The red-shift is ascribed to the heating of the in-plane frustrated translational mode of CO and the negative shift of potential. These two contributions can be separated with the aid of the transient of the background reflectivity of the electrode (triangles), which is a good measure of the surface temperature. The laser induced potential jump estimated from the Stark tuning shift of 30 cm\(^{-1}\) V\(^{-1}\) was about –150 mV. The heating of water layers near the surface is mainly responsible for the potential jump through the orientation change of water molecules. This method is promising as a tool to examine ultrafast electrode dynamics.

References

Trends in Electrocatalysis: From Extended to Nanoscale Surfaces

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In order to make hydrogen viable as a renewable energy source, many fundamental problems still need to be solved. In the case of fuel cell technology, in which chemical energy is converted directly into electrical energy, the key issue is to improve or replace Pt as the anode/cathode catalyst. In this presentation we demonstrate that a fundamental approach to understanding the catalytic behavior, in which trends in electrocatalytic activity are established across the Periodic Table, can lead to the future design of a new generation of catalyst materials. We discuss how the calculational methods in close connection with experiments can be used to develop advanced concepts in the quest for the search for surfaces with desired activity or selectivity.

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Activity Trends of Electrode Materials
We calculate adsorption energies of the intermediates along the reaction paths at different metal electrode surfaces using ab initio density functional theory. On top of the calculated energies, we have developed a simple method for including the electrochemical potential. By applying the Sabatier principle we can calculate trends in activity for different electrode materials and determine a necessary, but not sufficient “descriptor” of the reaction activity. The descriptor is essential for doing knowledge based electrode material design.

The effects of CO coverage and Pt alloy cluster composition on the stretching frequencies of linear bound CO

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Stretching frequencies of atop CO adsorbed on Pt clusters as a function of CO coverage, and the stretching frequencies of a single atop CO on compositionally tuned alloy clusters are calculated using X3LYP and B3LYP functionals respectively. The LACVP*** basis set is used throughout. Coverage effects are studied on a three layer 26 atom Pt cluster (1)(12)(13) and compositional effects are studied on clusters ranging in size from 9 atoms to 26 atoms. The effects of site specific dipole-dipole coupling on Pt clusters are discussed. FEFF8 Local Density of States, DFT Density of States and Crystal Orbital Overlap populations (COOP) of the CO adsorbed orbitals with the d-band of Pt_{26}(CO)_n cluster will also be discussed.

Electrochemical Reduction of oxygen to hydrogen peroxoide – an electron density functional theory study

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Hydrogen peroxide is a widely spread and powerful oxidizing and bleaching agent with many industrial and domestic applications. Electrochemical reduction of oxygen to hydrogen peroxide is one of the best candidates for the on-site or in-situ production of the chemical. Experimentally it has been established that gold single crystal electrodes could be used for this purpose. It was also found that Au(111) are most active towards production of peroxide, while Au(100) in alkaline solutions results in the full four-electron reduction of molecular oxygen to water.

In this work we investigate this difference comparing computational models for the two surfaces and the reaction intermediates. Different reaction paths, including an active role of the solvating water molecules, are investigated providing a description of the (electro-)chemical processes and the reaction pathways on a molecular level.

Electrochemical behaviour of metallic monolayers on noble metal surfaces

L.A. Kibler*
It is well-established that the physical and chemical properties of thin metallic overlayers deposited onto foreign substrates can be significantly altered compared to the bulk material. Especially the first monolayer often reveals unique properties, which demonstrate that the nature of the support is crucial for both geometric and electronic variations of the surface monolayer. This is reflected, e.g., in pseudomorphism and in work function changes for many systems. The consequences for the electrochemical behaviour may involve substantial shifts in the potential of zero charge, one of the most fundamental parameters in characterising metal electrode surfaces. In addition, variations in the electronic structure for metallic monolayers on different substrates may lead to stronger or weaker interaction with molecular species, which in turn is reflected in significant potential shifts for the respective adsorption peaks. In many cases, energies of activation for bond breaking and formation are linearly related with adsorption energies. For this reason, kinetics of electrocatalytic reactions involving adsorbed intermediates can be tuned by tailoring chemical composition and surface structure of an electrode. An overview on exemplary model monolayer systems shall be given.

**Combinatorial First-Principles Screening of Alloys for Electrocatalysis**

Jeff Greeley

Density Functional Theory-based techniques have the potential to efficiently screen large numbers of transition metal alloys for desirable catalytic properties at relatively low cost. However, the triple challenges of identifying suitable descriptors for reactions of interest, of finding methods to efficiently determine the values of these descriptors on different metals and alloys, and of reliably estimating the stability of promising catalytic candidates in reactive environments, have generally limited the application of computational screening techniques to electrocatalytic systems. In this talk, I describe a general methodology for electrocatalyst screening using atomic-scale simulation methods. The method employs DFT calculations to estimate important features of catalytic performance, including catalyst activity, structure, and stability, and it is applied to the analysis of hundreds of transition metal alloys for use in two reactions of interest in electrochemistry, the hydrogen evolution and oxygen reduction reactions.

**On the electrocatalytic activity of gold nanoparticles on basic media**

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Oxygen reduction is a very important reaction in fuel cells, since it is the only practical cathodic reaction on these cells. On gold electrodes, oxygen reduction in basic media yields mainly hydrogen peroxide [1]. This reaction is very sensitive to the gold surface structure. In this way, Au(100) shows the highest catalytic activity and yields water as a final product in a limited region. On the other hand, Au(111) electrodes shows the lowest catalytic activity, with hydrogen peroxide as final product. Practical electrodes should be made from nanoparticles of a electrocatalytic material dispersed on the appropriate matrix. A question that arises is whether it
would be possible to induce the best surface structure for the desired reaction on the nanoparticles. Gold nanoparticles were synthesized using different methods in order to change their shape and surface structure. These nanoparticles were characterized using TEM and surface sensitive reactions, such as lead UPD. The catalytic activity for oxygen reduction will be compared to their shape in order to better understand their reactivity.

Another important reaction that has been studied on the gold nanoparticles is methanol oxidation. Methanol oxidation has been studied in different NaOH solutions. Two different oxidation regions can be observed: between 0.2 and 0.9 V (RHE) and above 0.9 V (RHE). In the first region, the onset for the oxidation is at ca. 0.2 V and reaches a maximum current, which is partially controlled by the diffusion at 0.7 V. The current rises again at potentials above 0.9 V. When compared to smooth single crystal electrodes, methanol oxidation in this media only takes place above 1 V [2]. Therefore, the low potential region has to be associated to the unusual properties of the nanoparticles, probably to the presence of a high ratio of low coordinate gold surface atoms. Moreover, the catalytic activity is pH dependent and significant oxidation currents have been measured at potentials as low as 0.3 V in 1 M NaOH. From the obtained results, an oxidation mechanism will be proposed.

CO and NO on a stepped platinum surface

Ellen Backus, Andreas Eichler, Aart W. Kleyn and Mischa Bonn

‘Coordinatively unsaturated’ surface atoms are responsible for most of the catalytic activity of metal surfaces. Although these catalytically highly active sites are clearly a minority species, they are essential to understanding catalysis on metal surfaces. Femtosecond studies of surface processes have provided important information on the rates and pathways of energy flow into the system’s different degrees of freedom. However, these studies have remained limited to atomically flat (i.e. defect-free) surfaces.

We have investigated the role of controlled defects (atomic steps) on the femtosecond desorption and dynamics of nitrogenmonoxide (NO) adsorbed on a Pt surface. We use the stepped Pt(533) surface, which consists four-atom wide (111) terraces and single-atom (100) steps. Desorption of NO, from both the terrace and step sites, is induced by femtosecond laser pulses. Our results demonstrate that coupling of the NO to the laser-heated electrons is more efficient for molecules adsorbed to the step sites, as compared to those on the terraces, although NO is clearly more strongly bound on the steps.

Another important step in surface (catalytic) reactions is the diffusion of molecules on surfaces. Whereas in conventional catalysis diffusion is governed by thermal processes, non-thermal control of surface diffusion has received much attention, e.g. for the potential growth of novel materials. Recent Scanning Tunneling Microscope (STM) experiments have demonstrated controlled diffusion of molecules on a surface, induced by electrons, provided by either the STM tip or a femtosecond laser pulse. Although this STM detection scheme provides excellent spatial resolution, information on the timescales of the hopping process is lacking.

Here, we report the real-time observation of the motion of carbonmonoxide (CO) molecules, initiated by a femtosecond laser pulse, on a single crystal platinum (Pt(533)) surface. Sub-200 fs temporal resolution is obtained by using femtosecond time-resolved vibrational sum-frequency generation, monitoring the internal C—O stretch vibration. Sub-nm spatial resolution is obtained indirectly, through the morphology of the surface. The differently bound CO molecules on the steps and terraces exhibit distinct vibrational frequencies, allowing us to quantitatively follow the time-dependent population of CO molecules on the terraces and the steps. Hopping of CO molecules from steps to terraces is induced by 800 nm pulsed excitation of the surface, with depopulation of step sites occurring on sub-picosecond timescales.

In-Situ Video STM and SXRD of Catalytic Surfaces

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We employ scanning tunneling microscopy (STM) and surface X-ray diffraction (SXRD) to obtain direct information on the structure and the atomic and molecular processes that occur on the surface of a catalyst while it is active in a chemical reaction under the high-temperatures and high-pressure conditions typical in catalysis. STM-movies obtained during the oxidation of CO on Pt and Pd surfaces, demonstrate that at high O₂ pressures the surface oxidizes and the reaction changes from a Langmuir-Hinshelwood to a Mars-Van-Krevelen mechanism [1,2]. We resolve various ultrathin oxide structures, which only appear under high partial pressures of oxygen [3]. Finally, we introduce a new explanation for self-sustained oscillations in the reaction rate [2], which involves a novel role for atomic steps in catalysis [4].

[4] B.L.M. Hendriksen et al., to be published.

Billion-year old oxygen cathode that actually works: respiratory O₂ reduction and its biomimetic implementations.

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I will review (i) the mechanism and the energetics of the 4 electron, 4 proton (4e'/4H⁺) reduction of dioxygen to H₂O by terminal oxidases, a class of enzymes responsible for the final step of aerobic respiration; (ii) O₂ reduction catalysis by iron porphyrins with various degree of stereoelectronic resemblance to the catalytic site of terminal oxidases; and (iii) lessons learned from such biomimetic work for the design of molecular catalysts for O₂ reduction. Topics I will emphasize include (i) the effects of the second metal and the axial ligand to the heme on the selectivity and rate of O₂ reduction; (ii) the strategies that terminal oxidases utilize to capture ≥80% of the free energy of O₂ reduction despite relying on fairly reducing electrons (≤250 mV vs. NHE).

Respiration satisfies the vast majority of energy needs of an aerobic organism, reducing >90% of O₂ consumed by the organism. This 4e'/4H⁺ reduction to H₂O occurs at a bimetallic catalytic site of terminal oxidases. The catalytic site, particularly that of the heme/Cu superfamily of enzymes, has been a major focus of biomimetic studies for the past 30 years. Objectives of these studies included both understanding the structure/activity relationship at the site and attempts to develop efficient O₂ reduction catalysts for fuel cell applications. The use of molecular catalysts, that can be studied both as adsorbants on an electrode and free in solution has helped enormously our understanding of the O₂ reduction mechanism at an Fe porphyrin site. Until now the fairly low stability of known Fe porphyrins under O₂-reducing conditions and the limited selectivity of the cheapest Fe porphyrins have precluded their application as O₂ reduction catalysts in fuel cells. However, recent advances in our understanding of the mechanisms of O₂ reduction by such molecules potentially permits rational design of new Fe porphyrins tailored for use as cathode catalysts.

A selective and sensitive fluorescence based method to follow the activity of the O₂ reducing enzyme laccase in bionanotechnological applications

In biology, the ‘clean’ reduction of molecular oxygen to water is chiefly catalyzed by copper and/or iron containing proteins. One of these proteins, the copper enzyme laccase, is currently under investigation by several groups to function as the O₂ reducing component in biofuel cells. It couples the four electron reduction of dioxygen with the oxidation of small organic substrates. Laccase contains two chromophores: a blue ‘type-1’ copper site, which accepts electrons from reducing substrate, as well as the green trinuclear ‘type-4’ copper cluster, which is the site of O₂ reduction. The optical absorption of these centres depends on their oxidation state. Thus, the color of the protein reports on the redox-state of the enzyme and, therefore, its catalytic activity. This feature can be exploited to provide information on the enzymatic mechanism or may be used as an activity probe in laccase based applications, such as in biofuel cells. Yet, measuring the absorption of small quantities of (immobilised) protein in complex systems is often impossible. We have developed a fluorescence based method to translate absorption into fluorescence, which is sensitive and selective enough to allow studies down to the level of single molecules. The methodology allows to monitor the redox state of the type-1 and type-4 centres individually. Several examples illustrating the technique will be discussed.