The fuel cell is a promising alternative to environmentally unfriendly devices that are currently powered by fossil fuels. In the polymer electrolyte membrane fuel cell (PEMFC), the main fuel is hydrogen, which through its reaction with oxygen produces electricity with water as the only by-product. To make PEMFCs economically viable, there are several problems that should be solved; the main one is to find more effective catalysts than Pt for the oxygen reduction reaction (ORR), \( \frac{1}{2} \text{O}_2 + 2\text{H}^+ + 2\text{e}^- = \text{H}_2\text{O} \). The design of inexpensive, stable, and catalytically active materials for the ORR will require fundamental breakthroughs, and to this end it is important to develop a fundamental understanding of the catalytic process on different materials. Herein, we describe how variations in the electronic structure determine trends in the catalytic activity of the ORR across the periodic table. We show that Pt alloys involving 3d metals are better catalysts than Pt because the electronic structure of the Pt atoms in the surface of these alloys has been modified slightly. With this understanding, we hope that electrocatalysts can begin to be designed on the basis of fundamental insight.
We studied polycrystalline alloy films of the type Pt_3M (M = Ni, Co, Fe, and Ti). Although such alloys have already been considered[1–4] the role of the 3d metals in electrocatalytic activity of Pt for the ORR remains elusive. In previous work,[1,3] one of the difficulties in illuminating the effect of alloying components was that the kinetics of the ORR was determined on poorly characterized Pt_3M electrodes. However, we have recently studied Pt_3M alloys that were then annealed to 1000 K under ultrahigh-vacuum (UHV) conditions and subsequently characterized in detail.[5] From the analysis of low-energy ion-scattering spectra, we found that the first surface layer of these alloys consists of pure Pt. The surface enrichment of Pt atoms occurs as a result of a surface segregation phenomenon, whereby one of the alloy components (in this case Pt) enriches the surface region.[6] UHV experimental and theoretical analysis revealed that a strong enrichment of Pt in Pt_3M alloy systems is counterbalanced by the depletion of Pt in the first two or three layers, resulting in a concentration profile that oscillates around the bulk value.[7–11]

Subsequent testing of these Pt overlayers in electrochemical environments showed significant differences in the activity for the ORR. For the purpose of demonstrating catalytic enhancement by alloying Pt with the 3d elements, two representative sets of polarization curves for the ORR on Pt and Pt_3Co, along with data on the corresponding production of peroxide, are summarized in Figure 1. Note that after these samples were removed from the electrochemical cell they were again characterized in the UHV chamber, and the Pt overlayer structure was found to be essentially unchanged. Although the rate of the ORR is significantly enhanced on Pt_3Co (Figure 1 a,b), equally small amounts of peroxide are detected on the ring electrode on both surfaces, in agreement with previous studies.[5] The rate of the ORR on Pt alloyed by the 3d metals is dependent on the nature of the alloying component (see Figure 1 c). While the Ni, Co, and Fe alloys show a large improvement in activity compared to pure Pt, the enhancement is smaller for the earlier 3d metals. We thus have a series of well-characterized alloys showing an interesting volcano-shaped variation in the electrocatalytic activity. As such, this result is an excellent basis for developing an understanding of the factors that control the kinetics of the ORR.

A model of the ORR developed previously[12] was used as the starting point for the analysis of the experimentally observed volcano-shaped dependence as the 3d metal changes from Ni to Ti. By using density functional theory (DFT) calculations, the free energies of all intermediates of the ORR were calculated as a function of the cell potential (see Experimental Section). On this basis, a kinetic model was developed that gives the rate of the ORR at a given potential as a function of a single parameter characterizing the catalyst surface—the oxygen chemisorption energy, \( \Delta E_O \). Figure 2 shows how this model leads to a volcano-shaped dependence of the rate on \( \Delta E_O \). For metals that bind oxygen too strongly (to the left of the maximum), the rate is limited by the removal of adsorbed O and OH species; that is, the surface is oxidized and thus unreactive, as also suggested by Ross and co-workers.[13,14] For metal surfaces that bind oxygen too weakly, the rate is limited by the dissociation of O_2, or more likely, the transfer of electrons and protons to adsorbed O_2. These different rate-limiting steps are associated with different oxygen reduction mechanisms. Two such mechanisms, involving either O_2 dissociation or proton and electron transfer to molecular O_2, were considered in our analysis. The mechanisms are both characterized by \( \Delta E_O \), but they give rise to different slopes on the right side of the volcano-shaped plot (Figure 2). The volcano shape thus illustrates very well the Sabatier principle,[15] with the important new viewpoint that it is quantitative; thus, we know which bond energy gives the maximum of the “volcano”.

Figure 1. a) Production of peroxide from the oxygen reduction reaction (ORR) detected on a ring electrode and b) polarization curves (kinetic current density vs potential) for the ORR on Pt and Pt_3Co alloy surfaces on the disc electrode in 0.1 M HClO_4 recorded at 50 mVs\(^{-1}\) at 333 K (1600 rpm; RHE = reversible hydrogen electrode). Arrows indicate the values of the half-wave potential, which on Pt_3Co is shifted positively by about 50 mV. c) Specific activity of Pt and Pt_3M electrodes expressed as a kinetic current density for the ORR at 0.9 V (0.1 M HClO_4, 333 K).
The predictions of the model for Pt3M (MD shown relative to the predictions for Pt at the DFT-calculated values of Angew. Chem. Int. Ed. 2006, 45, 2897–2901)

Model of the activity (A = kT ln(i) / i) as a function of the adsorption energy of oxygen, ΔE₀. On the left side of the plot, the rate is limited by removal of adsorbed O and OH species; immediately to the right of the maximum, the rate is limited by O₂ dissociation; and on the extreme right, the limiting step is protonation of adsorbed O₂. Also shown in red are the measured activities relative to that of Pt. The activity of the experiment is A = k_T ln(i) / i₀, where i₀ is the current density relative to Pt, and Aₚt is the theoretical value for the activity of Pt. It is assumed that the number of active sites per surface area is the same for Pt and all the alloys. A factor of two in the preexponential factor would give rise to a difference of only ±0.02 eV (k_T ln2) in the activity. Changes in coverage for the different alloys are not considered. See text for details.

The predictions for Pt3M (M = Ni, Co, Fe, Ti) alloys are shown relative to the predictions for Pt at the DFT-calculated values of ΔE₀.

A one prediction of the model is that Pt binds oxygen a little too strongly, and finding a better electrocatalyst for the ORR thus amounts to finding a surface that binds oxygen more weakly than Pt does by about 0.2 eV. To test this prediction, we calculated ΔE₀ for the (111) surfaces of a series of Pt₃M alloys with pure Pt in the first layer and only 50% Pt in the second layer to model the enrichment of Pt in the surface layer and the depletion of Pt in the next layer (the slabs thus retain bulk Pt₃M stoichiometry). The composition of the second layer can vary modestly from one alloy to the next for the different metals (see Reference [16] for a discussion of Pt–Fe, Pt–Co, and Pt–Ni alloy segregation). However, the calculated binding energies are not highly sensitive to such changes; changing the composition of M in the second layer from 50% to 25%, for example, changes binding energies by only approximately 0.05 eV for M = Fe, Co, and Ni. Thus, our simple stoichiometric model should be accurate for determining the trends in activities. These data, plus the corresponding activity predictions of the model, are shown in Figure 2. Clearly, the alloy surfaces form weaker bonds to oxygen than pure Pt, and the predicted activities (relative to pure Pt) are compatible with the experimental measurements that are also included in the figure. Experiment and theory agree almost quantitatively, but this excellent agreement in the relative rates is not the most significant point. Rather, we stress that we have a model of the ORR that accurately predicts trends in the catalytic activity; when appropriate models are employed, DFT calculations are known to be capable of reproducing such trends quite well.[17]

As ΔE₀ is a good descriptor of the ORR activity of a given surface, the question arises as to which property of the catalyst determines it. It is well-established in the literature of surface science and heterogeneous catalysis that surface bond energies correlate with the average energy of the d states on the surface atoms to which the adsorbate binds (the d-band center).[18–25] This conclusion also holds for bonding of oxygen to the Pt₃M alloys, as illustrated in Figure 3. Similar effects have been observed for Pt(111) with a 3d transition metal in the second layer, or for Pt(111) overlayers on 3d metals.[26–27]

The origin of this relationship is as follows: The variation in the oxygen–metal bond from one transition-metal surface to the next depends to a large extent on the strength of the coupling between the oxygen 2p states and the metal d states. This coupling forms bonding and antibonding states as illustrated in Figure 3 b–d. The bonding states are filled, and the filling of the antibonding states, and thus the strength of the interaction, varies from surface to surface. In a metallic environment the filling depends on the position of the states relative to the Fermi level. An upward shift of the d states relative to the Fermi level must therefore result in an upward shift of the antibonding states, leading to less filling and thus to a stronger bond. For Pt overlayers or other structures involving bonding of oxygen to Pt, in which other factors that determine the coupling strength are approximately the same, this effect leads to the relationship shown in Figure 3.

Unlike the oxygen bond energy, which is hard to measure, the d-band center is accessible experimentally. We measured it for all of the alloys by using synchrotron-based high-resolution photoemission spectroscopy, a methodology pre-

Figure 2. Model of the activity (A = k_T ln(i) / i) as a function of the adsorption energy of oxygen, ΔE₀. On the left side of the plot, the rate is limited by removal of adsorbed O and OH species; immediately to the right of the maximum, the rate is limited by O₂ dissociation; and on the extreme right, the limiting step is protonation of adsorbed O₂. Also shown in red are the measured activities relative to that of Pt. The activity of the experiment is A = k_T ln(i) / i₀, where i₀ is the current density relative to Pt, and Aₚt is the theoretical value for the activity of Pt. It is assumed that the number of active sites per surface area is the same for Pt and all the alloys. A factor of two in the preexponential factor would give rise to a difference of only ±0.02 eV (k_T ln2) in the activity. Changes in coverage for the different alloys are not considered. See text for details.

The predictions for Pt₃M (M = Ni, Co, Fe, Ti) alloys are shown relative to the predictions for Pt at the DFT-calculated values of ΔE₀.

Figure 3. a) The correlation between the d-band center and the oxygen adsorption energy. The d-band center was calculated (DFT) as the average for the Pt atoms in the two top layers. b) sp-broadened 2p orbital for O(g), c) projected p density of states of oxygen atoms on Pt(111), and d) projected d density of states of Pt(111).
viously described. Measurement of the d-band centers allows us to directly correlate the variations in the catalytic activity for the ORR with the variations in the surface electronic structure. As summarized in Figure 4, the activity (A) versus d-band center position at 0.9 V exhibits a classical volcano-shaped dependence, which agrees very well with the activity predicted from DFT calculations. For catalysts that bind oxygen too strongly, the rate is limited by the removal of surface oxide, while for catalysts that bind oxygen too weakly, the rate is limited by the transfer of electrons and protons to adsorbed O₂.

Note that a shift in the d states can also often be measured as a core-level shift, as the d states and the core levels shift together. This effect can explain the correlations between ORR activity and the surface core-level shifts observed by Watanabe and co-workers.

In summary, we have established how alloying Pt with 3d transition metals tunes the electronic structure to change the performance of an alloy for the ORR, and we have thus developed a model for the electrocatalytic activity of a metal surface for this process. The activity is given by the strength of the oxygen–metal bond interaction, which in turn depends on the position of the metal d states relative to the Fermi level. In this way we have established a new approach for the screening of new catalysts for the ORR, by looking for surfaces that bind oxygen a little weaker than Pt or, specifically for Pt skins, by looking for surfaces with a down shift of the Pt d states relative to the Fermi level.

Experimental Section
DACAPO, the total energy calculation code, was used in this study. For all calculations, a four-layer slab, periodically repeated in a supercell geometry with six equivalent layers of vacuum between any two successive metal slabs, was used. A 2 x 2 unit-cell was employed, and the top two layers of the slab were allowed to relax. Adsorption was allowed on only one of the two surfaces exposed, and the associated dipole was corrected for electrostatically. Ionic cores were described by ultrasoft pseudopotentials and the Kohn–Sham one-electron valence states were expanded in a basis of plane waves with kinetic energy below 340 eV; a density cutoff of 500 eV was used. The surface Brillouin zone of close-packed metal surfaces was sampled at 18 special Chadi–Cohen k points. In all cases, convergence of the total energy was confirmed with respect to the k point set and with respect to the number of metal layers included. The exchange-correlation energy and potential were described self-consistently within the generalized gradient approximation (GGA-RPBE). The self-consistent RPBE density was determined by iterative diagonalization of the Kohn–Sham Hamiltonian, Fermi population of the Kohn–Sham states (kᵦ T = 0.1 eV), and Pulay mixing of the resulting electronic density. All total energies were extrapolated to kᵦ T = 0 eV. The d-band centers were calculated with an infinite cutoff radius.

On all metals and alloys (composition Pt:M) investigated in this study, oxygen was found to adsorb at face-centered cubic (fcc) sites. Owing to the limited size of the unit cell, only two different fcc sites were present, one of which is close to one of the M atoms in the second layer, while the other is close to two M atoms. The latter was the most stable for all the considered alloys.

Solvent and potential effects were treated with the same model as used in our previous study. In that work, it was confirmed that a bilayer of water has no effect on the binding energy of atomic oxygen. For the other species in the full model (not explicitly involved in the present calculations), the binding energies were corrected by the interaction of a water bilayer with the appropriate species on Pt(111). Potential effects were included by adjusting the free energies of adsorption (per transferred electron) by –eU. Electric-field effects were not explicitly included, but these effects were found to change the adsorption energies by less than 0.05 eV, and the effect was essentially constant from one metal to the next.

Keywords: alloys · density functional calculations · electrochemistry · oxygen · platinum

Received: December 9, 2005
Revised: February 6, 2006
Published online: April 5, 2006