Communication

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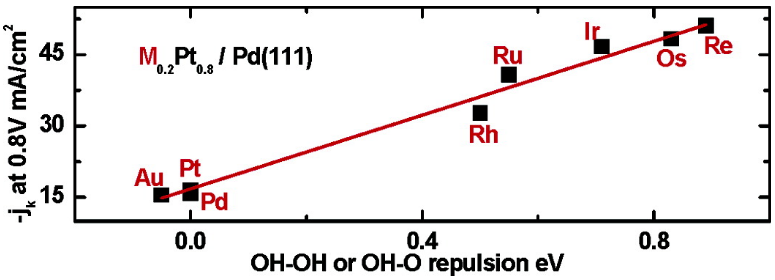

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Mixed-Metal Pt Monolayer Electrocatalysts for Enhanced Oxygen Reduction Kinetics

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Electrocatalytic oxygen reduction reaction (ORR) has been the focus of considerable attention because of its slow kinetics and the need for better electrocatalysts with decreased Pt content for fuel cell cathodes.[1−5] One promising way to make progress on these major difficulties is by using electrocatalysts made with a Pt monolayer supported on suitable metal nanoparticles.[6−8] In this communication, we report on a new class of ORR electrocatalysts, consisting of Pt and another late transition metal (M, where M = Ir, Ru, Rh, Pd, Au, Re, or Os) deposited as a monolayer on the surfaces of Pd(111) single crystals or carbon-supported Pd nanoparticles, that can greatly ameliorate both of the above problems. These new electrocatalysts have a very high activity compared to that of pure Pt ORR catalysts and a considerably lower Pt content. A gain in current density up to a factor of 400%, compared to all-Pt, has been realized by replacing part of the Pd-supported Pt monolayer with another transition metal, M, where M = Ir, Ru, Re, or Os.

The high OH coverage on Pt has been shown to inhibit ORR.[2,4] The very high catalytic activity measured for the Pd-supported Pt−M mixed monolayers, with M adsorbing OH or O strongly, reflects the decreased OH coverage on Pt, caused by lateral repulsion between the OH adsorbed on Pt and the OH or O adsorbed on a neighboring surface metal atom, M. Hence, the role of the second metal is to lower the OH coverage on Pt.

Figure 1a illustrates that effect schematically. The initial OH coverage on Pt, which is about $^1/_2$ monolayer on pure Pt at potentials of 0.80 V, where the fuel cell cathode operates, declines due to lateral repulsion by the OH or O adsorbed on the second metal, M. The electrodeposition of Pt−M monolayers was accomplished by galvanic displacement of a Cu monolayer deposited at underpotentials on Pd(111) or Pd nanoparticles, while the electrode was immersed in a stoichiometric mixture of Pt and M chlorides.[7]

Our hypothesis, as sketched in Figure 1a, was verified by the enhanced ORR activity measured when Pt is mixed with Ir or Ru. Both Ir and Ru are known to have a high coverage of OH at considerably lower potentials than Pt. Figure 1b shows the kinetic current densities obtained from the Koutecky−Levich plots for ORR at 0.80 V for mixed Pt−Ir and Pt−Ru monolayers as a function of the M/Pt ratio. The maximum activity in both cases is obtained with the monolayers consisting of 80% Pt and 20% Ir or Ru. The kinetic current density is more than 3 times larger than that for the pure Pt monolayer, whose activity is already considerably higher than that of pure Pt(111).[7] Moreover, the $Pt_{(1-x)}Ir_x$ mixed monolayer on carbon-supported Pd nanoparticles has higher activity than a pure Pt monolayer or a state-of-the-art commercial electrocatalyst Pt(10%)/C. This remarkably enhanced Pt mass-specific activity of the $(Pt_{80}Ir_{20})_{ML}$/Pd/C catalyst, which was 21 times greater than that of the Pt(10%)/C catalyst, shows that this new class of mixed-metal monolayer electrocatalysts is very promising.

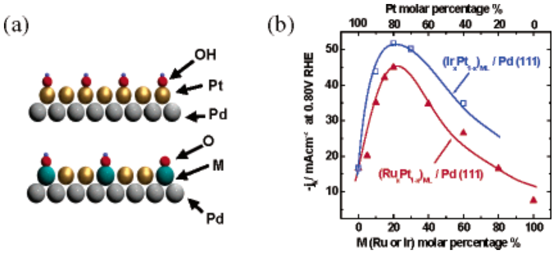

Figure 1. (a) Model for the decrease of the OH coverage on Pt, caused by a high OH or O coverage on a second metal M. (b) ORR activity of two mixed-metal monolayer electrocatalysts supported on Pd(111), expressed as the kinetic current density at 0.80 V as a function of the M/Pt ratio.

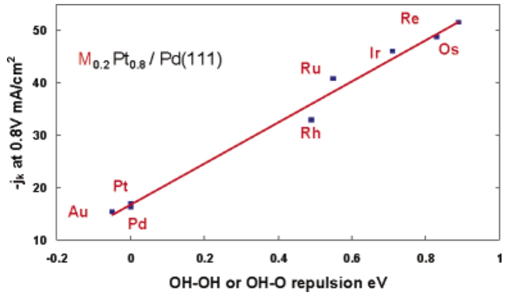

Figure 2. Kinetic current at 0.80 V as a function of the calculated interaction energy between two OHs, or OH and O in a (2 × 2) unit cell (see Figure 3 for details). Positive energies indicate more repulsive interaction compared to Pt_{ML}/Pd(111).

According to the general view that OH on Pt inhibits the ORR, a decrease in Pt−OH coverage would enhance the ORR kinetics, in agreement with our results shown in Figure 1b. Evidence that Ir decreases the oxidation of Pt (Pt−OH formation) was obtained for Pt supported both on Pd(111) and on Pd nanoparticles. Data collected with in situ X-ray absorption near edge structure spectroscopy (XANES) on carbon-supported $(Pt_{80}Ir_{20})$/Pd/C nanoparticles clearly suggest that the oxidation of Ir occurs readily in the mixed $Pt_{80}Ir_{20}$ monolayer, whereas the oxidation of Pt in the same monolayer is highly suppressed, occurring only at significantly higher potentials (1.17 V).

To further verify the concept of adsorbate−adsorbate repulsion, we performed similar experiments with Au, Pd, Rh, Os, or Re as the alternative M component in the Pt−M mixed monolayer supported on Pd(111). Figure 2 shows the results for all mixed monolayers at the 80:20 Pt:M ratio, wherein the measured kinetic current densities are plotted against the effective repulsion energy between two OH(a)s or an O(a) and an OH(a) for the case of M = Re or Os, as calculated from first-principles (vide infra). A very good linear correlation is observed, indicating that the primary effect in enhancing the ORR kinetics on Pt can be attributed to the reduced OH coverage on Pt, which, in turn, reflects the repulsion experienced by Pt−OH in the presence of M−OH or M−O formed at

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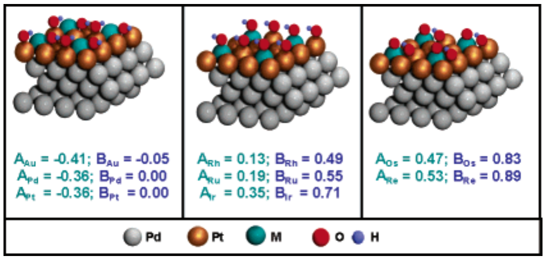

Figure 3. Calculated most stable configurations for OH or OH + O ($^1/_2$ ML total coverage) on seven different $(Pt_3M)_{ML}$/Pd(111) surfaces and on a Pt_{ML}/Pd(111), which is used for reference for the data in Figure 2. Energies are in eV. First two panels: A provides the attractive (when negative) or repulsive (when positive) interaction between two OHs in the unit cell, referenced to the BE of OH at the $^1/_4$ ML coverage. B gives the same quantity, but referenced to the corresponding value on Pt_{ML}/Pd(111). Last panel: A provides the repulsion between adsorbed O and OH, whereas B reflects the same quantity referenced to the interaction between two OHs on the Pt_{ML}/Pd(111) surface.

lower potentials. The second metal (M) used is important; Au binds OH weakly, and consequently, Au atoms in the mixed Pt−Au monolayer decrease the ORR kinetics in comparison with a pure Pt monolayer. Pt−Rh showed an intermediate behavior since Rh binds OH less strongly than Ru or Ir. Higher activity was observed for Pt−Ir and Pt−Ru, in accord with the strong adsorption of OH on Ir and Ru at low potentials.

The highest activity of all the Pt−M monolayers tested was recorded for M being Os or Re, both of which, as we discuss below, tend to adsorb O rather than OH. The repulsion on OH adsorbed on Pt, caused by adsorbed O on M, is even greater than that caused by OH, thereby enhancing ORR the most.

To investigate the structural details of the origin of the ORR-enhanced kinetics observed experimentally and to establish its molecular foundations quantitatively, we have performed periodic, self-consistent, density functional theory (DFT) calculations. The calculations were done in the generalized gradient approximation (GGA-PW91) using ultrasoft pseudopotentials[9] as implemented in DACAPO,[10−13] with a kinetic energy cutoff of 25 Ry and 18 k-points in the first Brillouin zone.[14,15] To study the effect of metal M on the surface chemistry, one of the four Pt atoms of the Pt_{ML}/Pd(111) slab was replaced by a metal atom M ($\theta_M = 1/4$ ML). The binding energies ($E_b = E_{total} - E_{substrate} - E_{gas-phase\ adsorbate}$) and geometries of adsorbed species were studied on the relaxed surfaces. The interaction energy between two OHs in the unit cell was calculated by comparing the binding energy of OH on the Pt_3M/Pd(111) slab at $^1/_4$ and $^1/_2$ ML coverages for M = Au, Pd, Pt, Ru, Rh, and Ir (Figure 3). A XANES surface analysis indicates that the monolayer consists of ca. $^1/_4$ Ir (the other metal) and $^3/_4$ Pt in the actual experiment (cf. Supporting Information). For Au, Pd, and Pt, that interaction is *attractive*, but for Ru, Rh, and Ir, the interaction is *repulsive*. For $\theta_{OH} = {}^1/_2$ ML (Figure 3) and for Au, Pd, and Pt, one OH is bridge-bonded to two Pt atoms, with the second OH on top of the third Pt atom of the unit cell. For Ru, Rh, and Ir, one OH is on top of these second metal atoms, with the second OH on top of a Pt atom. Coadsorption of two OHs in the same unit cell, where M is Os or Re, resulted in a spontaneous reaction toward H_2O and adsorbed O or (O(a)). Apparently, these two metals are significantly more reactive than the others considered in this study and break the O−H bond in one of the two coadsorbed OHs to yield atomic O plus H_2O. This last finding led us to extend our comparisons of adsorbate-induced destabilization of OH(a) for the Pt_3Os/Pd(111) and Pt_3Re/Pd(111) surfaces.

As shown in Figure 3, atomic O preferentially binds on top of Os or Re atoms on these surfaces, with OH binding to the bridge between two Pt atoms. The most stabilizing interaction of all metals M resulted for Au, whereas the most destabilizing interaction resulted for Re. Adopting the magnitude of this interaction on Pt_{ML}/Pd(111) as the reference zero, we derived an effective repulsion energy (denoted by B in Figure 3) between two OH(a)s or an O(a) and an OH(a) for M = Re or Os, both adsorbed in the same unit cell; this quantity was plotted against the measured kinetic current density in Figure 2. As described above, the very good linear correlation shown in that figure suggests that the destabilization of OH on Pt, due to adsorbed OH or O on M, is responsible for enhancing the ORR kinetics.

In conclusion, our studies open a new way of synthesizing improved ORR catalysts through the modification and control of the surface reactivity of Pt-based mixed monolayers supported on transition metals other than Pt. Besides their decreased Pt-loading, this new class of catalysts can be tailored to show significantly enhanced ORR kinetics, and at the same time possess increased stability of Pt under typical fuel cell operating conditions. Furthermore, our studies demonstrate that less costly and, at the same time, significantly improved ORR electrocatalysts can be designed by developing a fundamental understanding of their atomic-scale phenomena, using a combination of state-of-the-art experimental techniques and modern computational chemistry methods.

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Supporting Information Available: XANES and single-crystal data on Pt and Ir oxidation (OH adsorption) and the Pt:Ir ratio determination. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) Convergence of the results with respect to various calculation parameters was verified in all cases. The Pt−M monolayer surfaces were modeled by a single layer of Pt−M placed on top of Pd(111). The calculated equilibrium PW91 lattice constants for bulk Pt and Pd were 4.00 and 3.99 Å, respectively, in good agreement with the corresponding experimental values (3.92, 3.89 Å) (ref 15). Each surface was constructed from a (2 × 2) unit cell and modeled by a slab consisting of four layers of metal atoms. The top two layers were allowed to relax.
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