

Systematic Theoretical Study of Alloys of Platinum for Enhanced Methanol Fuel Cell Performance

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Systematic Theoretical Study of Alloys of Platinum for Enhanced Methanol Fuel Cell Performance

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ABSTRACT

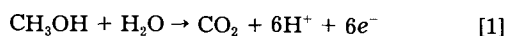
The ability of substitutional atoms in the (111)Pt surface to attract a water molecule and activate the formation of OH_{ads} on them is calculated using the ASED-MO theory. OH_{ads} is believed to be the oxidant that removes the CO poison from Pt anode surfaces in organic fuel cells. A total of 42 alloying atoms is treated, Sc through Se from period 4, Y through Te from period 5, and La through Po from period 6. As surface substitutional atoms, no elements to the right of the Pt group are found to attract H₂O strongly enough to activate OH dissociation. Some of these elements, including Sn, are known to be active in the electrocatalytic oxidation of CO_{ads} but are believed to be atoms or complexes on or near the Pt surface. Of the elements to the left of the Pt group, a number from the first and second transition series attract and activate H₂O with comparable or greater effectiveness than Ru, a known activator when present on Pt electrode surfaces. Whether these can be made stable alloy surfaces for organic fuel cell operation is an experimental issue. Past experimental work in the literature suggests promise for some of them.

Introduction

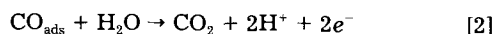
Pt anodes.—The most significant issue in the development of useful low-cost high-efficiency methanol fuel cells for generating electric current is the poisoning of the platinum anode by carbon monoxide that is generated during the oxidation. So far, platinum remains the material of choice for the anode application because in the potential region where methanol oxidation commences in acid electrolyte,¹ ~0.2 V compared to the standard hydrogen electrode (SHE), its surface remains unpassivated by hydrogen or oxy-hydroxy adsorbates. Carbon monoxide molecules formed from the early steps of methanol oxidation adsorb on and block polycrystalline platinum electrode surfaces and are not oxidized away by reaction with water to make carbon dioxide unless the anode potential is increased to about 0.6 V (SHE). The net result of doing this is an unacceptable loss of cell voltage and efficiency. It has been found that by adding oxygen to the system the carbon monoxide can be oxidized at a lower potential, but the gain in the cell voltage is not large.²⁻⁴

Furthermore, there is a loss of power because no current is generated when carbon monoxide is oxidized by oxygen on the anode surface whereas, on the other hand, oxidation of carbon monoxide by water yields two electrons and two protons.

The overall methanol oxidation reaction is



and the CO_{ads} poison that forms is oxidized by water



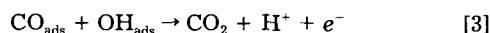
Three decades ago⁵ it was proposed that reaction 2 proceeds by direct attack by a H₂O molecule on the adsorbed CO. A recent molecular orbital study on (111)Pt⁶ suggested that for this to occur the H₂O molecule would not need to be adsorbed on the surface. Results of a kinetic isotope study were consistent with the formation of an activated complex of H₂O and CO_{ads} for which deprotonation was not rate limiting.⁷

The involvement of OH_{ads}, formed from H₂O decomposition on electrode surfaces in oxidizing organic fuels was proposed three decades ago.⁸ Its formation was advanced as the rate-determining step for the electro-oxidation process.

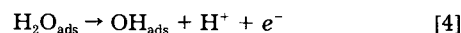
Initially, the identity of the poisoning species was not certain. In addition to CO_{ads}, adsorbed HCO⁹ and COH¹⁰ were advocated as the poisoning species. Now, HCO is thought to be a short-lived reaction intermediate,¹¹ and

there is no definitive evidence for COH. Evidence has accumulated that CO_{ads} is the rate-controlling poison.¹²⁻¹⁸ In current work, such as Ref. 1, it is taken for granted that the poison is CO_{ads}.

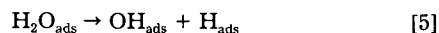
The oxidation of CO_{ads} by OH_{ads} proceeds as follows



The hydroxyl group is formed by oxidation of H₂O on the anode



The OH_{ads} oxidant has not yet been directly observed on Pt anodes. Evidence for its formation comes from the coincidence of the potential for the onset of H₂O oxidation with the peak for CO oxidation.^{18,19} A molecular orbital²⁰ study of the potential dependence of water decomposition on a (111)Pt anode by the reaction



showed the proper potential dependence. In this study the activation energy for forming adsorbed OH and H decreased as the potential increased. The increase in electrode potential was modeled by shifting the surface cluster band energy, and along with it, the Fermi level, down in several steps. It was proposed that reaction 5 is the rate-limiting step in CO oxidation. The adsorbed H atoms are assumed to discharge spontaneously into solution



Further calculations yielded, in the low-coverage limit, a disconcertingly high activation energy for CO oxidation by reaction 3 and, furthermore, this activation energy increased slightly as the potential increased. However, the crowding effect of high CO coverage overcame the problem by reducing the calculated activation energy to a value low enough to suggest that reaction 3 is not the rate-limiting step in CO oxidation but rather that OH_{ads} generation by reaction 4 is rate limiting on Pt anodes. An experimental study found that the onset of CH₃OH oxidation shifted about 50 mV negative at 60°C, compared to its value at 25°C on Pt.²¹ This was interpreted to mean that the activation energy for OH_{ads} formation was overcome at lower potentials as the temperature was increased. The theoretical results support this conjecture.

Ru-Pt alloys.—It was found over 30 years ago that upon alloying ruthenium with platinum the efficiency of methanol electro-oxidation could be significantly enhanced.⁸ Recent work shows the reduction in CO oxidation potential for a fixed oxidation current is 0.25 V for surfaces with a 1:1 Ru:Pt ratio.¹⁹ This was attributed to the OH_{ads} oxidant being formed at a lower potential than on

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Pt. For CH_3OH oxidation, the optimal surface Ru atom concentration was found to be about 10%, and this was explained with a hypothesis that ensembles of Pt atoms are needed in the surface to activate the initial stages of methanol decomposition and that isolated Ru atoms react with H_2O to provide OH_{ads} .¹ In agreement, a molecular orbital study showed that H_2O is attracted to substitutional Ru in (111)Pt and dissociated with a low barrier compared to when it is on Pt.²² At this lower Ru concentration the CO oxidation peak was shifted 0.18 V negative relative to pure Pt.¹⁴

Sn-Pt systems.—Not long after Ru-Pt alloys were discovered to be relatively active in electro-oxidizing methanol, tin added to the Pt surface was found to reduce the potential necessary for oxidation by several hundred millivolts, depending on the soluble organic fuel employed.²⁸ To explain this result, initially it was suggested that a Sn(II)/Sn(IV) redox couple at the electrode surface participated in oxidizing the organic residues. It was later suggested that Sn atoms alloyed substitutionally into the surface weaken the adsorption bond of the poisoning residue and attract H_2O molecules which would be converted into the oxidant.²⁴ Recent experimental work²⁵ shows, however, that Sn in an ordered Pt alloy surface is inactive, and does nothing more than block CH_3OH oxidation. Molecular orbital studies demonstrated that Sn atoms in the (111)Pt surface can weaken CO adsorption²⁶ but subsequent molecular orbital work showed that substitutional Sn atoms do not attract H_2O or activate the formation of the OH_{ads} oxidant.²⁷ These findings are in agreement with the experimental observations. It was found in Ref. 25 that Sn(II) in solution seemed to be responsible for catalyzing the removal of the surface poison generated during CH_3OH electro-oxidation and that the optimal concentration was $1 \mu\text{M}$ Sn(II) . The adsorption of Sn(II) as playing a role in CH_3OH residue oxidation had been postulated earlier²⁸ and radio tracer measurements showed the displacement of the ^{14}C -labeled residue formed by oxidation of CH_3OH by ^{121}Sn cations when present in the electrolyte.²⁹ Vibrational measurements showed the displacement of CO by Sn(IV) in solution.³⁰

Very recently it has been found that sputtered Pt_3Sn alloy surfaces oxidize CO in solution at extraordinarily low overpotentials, 0.15 V lower than for any Pt-Ru alloy.³¹ This is suggestive of the operation of an altogether different mechanism.

Thus, for the two known highly effective catalytic additives to Pt anodes the experimental and theoretical indications are that there are different mechanisms for their activity in removing the CO poison by oxidation to CO_2 . The transition metal atom Ru activates H_2O when present substitutionally in the Pt surface, generating the OH_{ads} oxidant at low positive potentials. The valence p element Sn does not activate H_2O when present substitutionally in the Pt surface and the high activity of sputtered alloy surfaces and the apparent activity of Sn in solution implies different mechanisms for Eq. 2.

Other alloys of Pt and surface modifications.—Many other alloy and surface-modified Pt electrodes have been tested for use as organic fuel cell anodes. In the first reports over 30 years ago³² the catalytic activities of quite a number of Pt-based alloys for methanol oxidation were tabulated. The Ti and V groups showed some enhancement; the Cr and Mn groups showed greater enhancement, with Mo being superior and Re quite good. Fe, Co, Ni, and Cu showed no enhancement. Ru was superior, similar to Mo, and Rh and Ir showed less enhancement, but comparable to Re. Ternary alloys combining W, Ta, Zr, or Mo with Pt-Ru were comparable to binary Pt-Ru. A Ru-Rh binary alloy showed good enhancement but Ru or Os with Pd, Ir, or Rh did not, compared to Pt. Of the binary Pt alloys, Mo and Ru looked best and Re almost as good.

Why are Mo-Pt and Re-Pt alloys not used today? Much depends on the conditions of the experiment, i.e., alloy composition, surface treatment, electrolyte pH, and there

are issues of alloy stability. Numerous additional studies of Pt alloy surfaces and Pt surfaces with foreign electrodeposited atoms have been published.³³⁻⁴⁶ Some of these references present continuations or modifications of the earlier work (Ref. 30) such as Ti,³³ Re,³⁵ and Mo⁴¹ on Pt; some give results for new species on Pt which show activity, such as As^{35,37,39} and Pd;³⁶ others discuss the influence of Pt surface structure⁴⁵ and dissolution of the admetal³⁸ or alloying metal;⁴⁶ and finally some deal with the activity of Pt alloys in base^{42,43} and with the question of lack of activity of other metal electrodes such as Rh and Ir.⁴⁷ In most cases (aside from Ru and Sn alloys with Pt on which relatively extensive electrode surface characterization, though still inferential, has been recently completed^{1,19-22,25,27,31}), a full exploration of surface composition and structure lies in the future. Questions to be probed include finding activities of alloy surfaces and Pt surfaces with the metal atoms deposited in adsorbed states and the dependencies of these activities on concentration or coverage of the alloying species. Then there is the question of whether certain surface structures can be made in the electrochemical environment and, if they can be made outside the electrochemical environment, will they retain integrity in it? Will they be stable in potential and pH ranges used in organic fuel cells? Will they perform electro-oxidation at low enough potential?

Goal of this work: trends in $\text{H}_2\text{O}_{\text{ads}}$ activation by alloyed Pt.—The purpose of this paper is to communicate a study of modified, by the presence of substitutional foreign atoms, Pt anodes for the activation of $\text{H}_2\text{O}_{\text{ads}}$ to make the OH_{ads} oxidant (Eq. 5). The (111) surface is chosen for our molecular orbital study, which is made in the same way as the evidently successful studies of Ru and Sn in (111)Pt discussed above.^{20,22,27} The same cluster model is employed, with a single substitutional atom in each case to find out whether or not such an atom, in isolation from others in the surface, which seems to be the optimal surface structure for Ru-Pt alloy catalysts, is likely to make OH_{ads} at a low potential.

We examine the effects of 42 different alloying atoms, 14 from each of period 4 (Sc through Se), period 5 (Zr through Te), and period 6 (Hf through Po). Some trends have been found, and we discuss them in terms of atomic properties, which are also parameters in the molecular orbital theory, namely, valence electronic structures, meaning orbital occupations and ionization potentials, and orbital sizes. This study is carried out with parameters corresponding to the 0 V; if the surface valence band is shifted down on the energy scale, corresponding to increasing the electrochemical potential, it is believed that the activation energies that could be calculated for OH_s generation (Eq. 5) would decrease in the cases when H_2O binds strongly to the substitutional foreign atom. This is what was found for Pt and Ru in Pt in the previous work. As is shown, many transition metals in all three periods bind H_2O strongly when present substitutionally in the (111)Pt surface. But to the right of Pt all elements in all three periods bind H_2O weakly when in the Pt surface and activation is unlikely even for positive potentials. We note that for Sn in Pt the activation energy for $\text{H}_2\text{O}_{\text{ads}}$ decomposition did not decrease but increased as the potential of the model was increased.²⁷ Consequently, we believe our results for the 0 V potential are sufficient for stimulating further experimental research for a number of transition metals, particularly in periods 4 and 5, for which we calculate strong H_2O adsorption and low activation energies for OH_{ads} formation.

Theoretical method.—The model used is structurally identical to the one used in the substitutional Ru and Sn in (111)Pt studies. It consists of a two-layer thick 18 atom cluster with one atom replaced by the foreign atom as shown in Fig. 1. The most stable height of the substitutional atom is determined by minimizing the cluster energy and is then maintained constant when H_2O is allowed to adsorb on it and dissociate, leading to OH_{ads} on the sub-

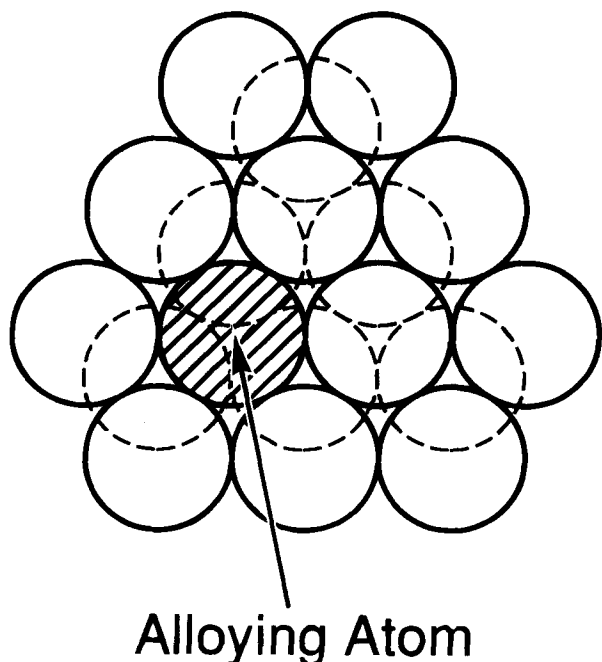


Fig. 1. Cluster model used for the calculations.

stitutional atom. The mechanism for dissociation is in Fig. 2. The energy along with the dissociation reaction pathway is found by selecting stretched OH internuclear distances of 1.1, 1.2, 1.3, 1.4 Å, etc., letting an automatic variational program minimize the energy for each OH distance by varying the remaining positional and internal coordinates for the H_2O molecule. The transition state energy is identified by graphing the energies.

Atom superposition and electron delocalization molecular orbital^{49,50} (ASED-MO) calculations are performed. This is a convenient method for seeking trends across the periodic table because it uses input data that vary in understandable ways across it. These are atom valence orbital occupations, ionization potentials, and Slater orbital exponents.

Earlier work has shown that simple criteria can be applied to systematically perturb the atomic parameters to allow ASED-MO calculations of bond lengths, force constants, and dissociation energies of high numerical accu-

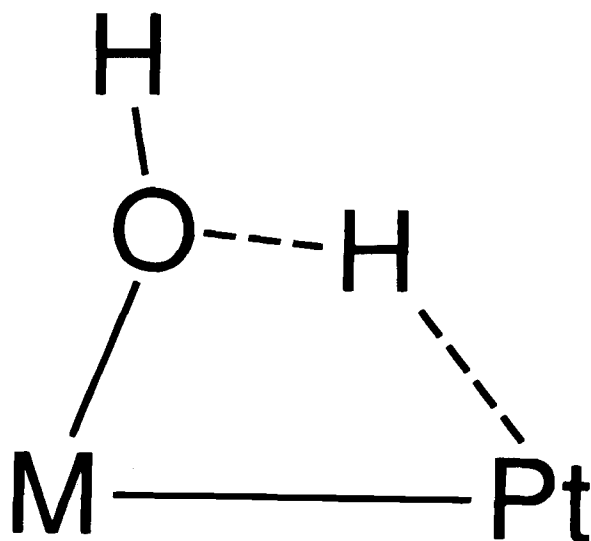


Fig. 2. Dissociation mechanism for H_2O bonded to substitutional metal atom in Fig. 1.

racy for a series diatomic transition metal oxides.⁴⁹ For the alloy systems studied here there are no known structure, force constant, or bond strength data to help in a similar parameterization. Consequently, our main focus is on cluster models of the alloy surfaces and the use of raw literature data, subjected to our standard adjustments of 1.5 eV decreases in experimental valence state ionization potentials (VSIP) for H and O and 1.5 eV increases in the values for Pt. The 1.5 eV increase is applied to all the alloying atoms, too.

The ASED-MO theory is based on a model of partitioning molecular electronic charge distribution functions into rigid free atom atomic and bond forming delocalization components.⁵⁰ As each rigid atom joins the forming molecule all repulsive pairwise forces are evaluated by integrating the electrostatic force on the nucleus of the less electronegative atom of each pair. The electron delocalization charge density distribution provides the attractive force for the bonding of each atom as the molecule forms. These distribution functions are not available. However, the sum of all the electron delocalization energies involved in the atom by atom formation of the molecules is approximated reasonably well by the molecular orbital bonding energy as obtained using a modified extended Hückel hamiltonian. Thus, the diagonal matrix elements are set equal to the negative of the measured VSIP,⁵¹ subject to the above-mentioned adjustments. The off-diagonal matrix elements are calculated as the sums of the corresponding diagonal ones multiplied by $1.125 \exp(-0.13 R)$, where R is the distance between orbital centers, and by the corresponding orbital overlap integral. The overlap integral is evaluated using single-zeta Slater functions for s and p orbitals and double-zeta ones for transition metal d orbitals. Parameters used in this work are in Table I. The H and O ionization potentials were decreased by 1.5 eV and all others were increased by 1.5 eV. Empty orbital ionization potentials were determined from optical tabulations,⁵² assigning them to the lowest ground state ionization potential minus the excitation energy for forming the first excited state with one electron in the originally empty orbital. These values were then treated in the same way as the others. Orbital exponents and linear coefficients (for double- ξ d orbitals) are based on various sources,⁵³⁻⁵⁷ Ref. 53 for O, Ga, Ge, As, and Se, Ref. 54 for first transition series atoms, Ref. 55 for second and third transition series atoms, Ref. 56 for In, Sn, Sb, and Te, and those for Tl, Pb, Bi, and Po were extrapolated from Ref. 57 with adjustments to yield reasonable homonuclear diatomic bond lengths.

In our model, eight electrons are unpaired at the top of the cluster band when there is an even number of electrons and nine are unpaired otherwise. One of the three central Pt atoms is calculated to relax 0.18 Å into the surface. Heights of substitutional atoms are calculated and reported with respect to the central Pt atom. These heights are not allowed to change when H_2O bonds to the substitutional atom. The H_2O structure is completely optimized by energy minimization in these sites. The standard state used for nonadsorbed H_2O is the experimental structure. If the calculated structure were used, with its excessively large bond angle of $\sim 150^\circ$, the adsorption energies reported in Fig. 3 would decrease by 0.5 eV. This might improve their absolute values, but our focus is on the trends in these energies that are observed for binding to substitutional atoms from across the periodic table.

Results and Discussion

H_2O adsorption and activation.—Let us go straight to the calculated adsorption energies in Fig. 3. They are relatively high for the first five transition metal groups (Sc through Fe), around 2 eV, and then trend down to around 1 eV for the Cu group. Rh and Ir appear anomalous, with H_2O calculated to bond weakly to them. This is commented upon below. Continuing across periods 4, 5, and 6, there is, except for Cu, an increase in H_2O adsorption energies

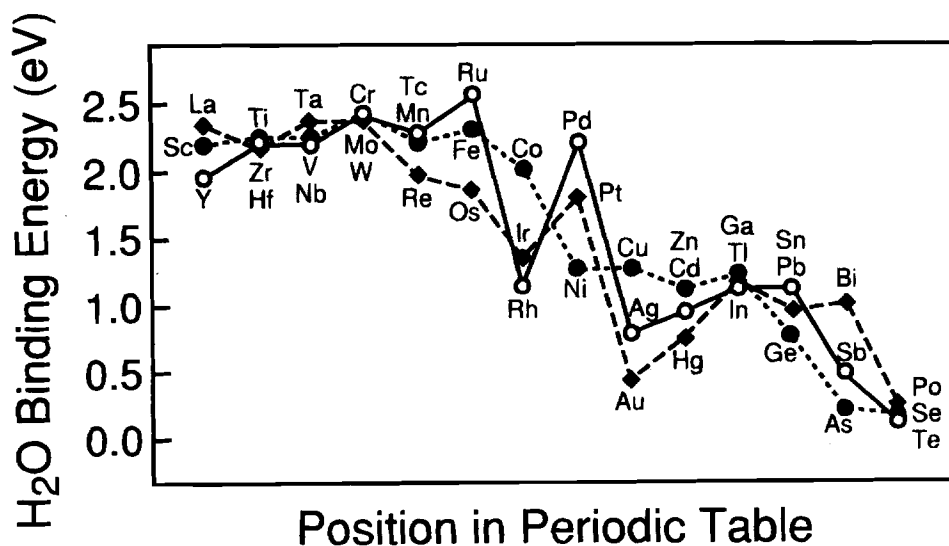
Table I. Parameters used in the calculations: principal quantum numbers, n , diagonal hamiltonian matrix elements, H (eV), orbital exponents, ζ (a.u), and linear coefficients, C , for double ζ d orbitals.

Period 4				s			p			d			
Atom	n	H	ζ	n	H	ζ	n	H	c ₁	ζ ₁	c ₂	ζ ₂	
Sci	4	-8.04	1.35	4	-6.097	1.15	3	-9.5	0.40627	4.35	0.76982	1.50	
Ti	4	-8.32	1.50	4	-6.352	1.20	3	-9.5	0.43903	4.55	0.73966	1.60	
V	4	-8.24	1.55	4	-6.212	1.25	3	-9.5	0.47548	4.75	0.70523	1.70	
Cr	4	-8.265	1.60	4	-5.376	1.30	3	-9.75	0.50579	4.95	0.67472	1.80	
Mn	4	-8.934	1.65	4	-6.653	1.35	3	-10.50	0.53108	5.15	0.64788	1.90	
Fe	4	-9.37	1.70	4	-5.971	1.40	3	-10.50	0.55050	5.35	0.62600	2.00	
Co	4	-9.364	1.75	4	-6.437	1.45	3	-10.50	0.56786	5.55	0.60586	2.10	
Ni	4	-9.135	1.80	4	-5.942	1.50	3	-11.50	0.58172	5.75	0.58902	2.20	
Cu	4	-9.226	1.85	4	-4.388	1.55	3	-12.20	0.59332	5.95	0.57442	2.30	
Zn	4	-10.894	1.90	4	-6.888	1.60	3	-13.10	0.60209	6.15	0.55298	2.40	
Ga	4	-12.50	1.7667	4	-7.50	1.5554							
Ge	4	-15.80	2.0109	4	-9.40	1.6951							
As	4	-18.50	2.2360	4	-10.31	1.8623							
Se	4	-21.65	2.4394	4	-11.25	2.0718							
Period 5				s			p			d			
Atom	n	H	ζ	n	H	ζ	n	H	c ₁	ζ ₁	c ₂	ζ ₂	
Y	5	-7.98	1.76	5	-6.67	1.46	4	-7.83	0.63615	3.350	0.56765	1.30	
Zr	5	-8.34	1.817	5	-6.32	1.517	4	-10.11	0.62104	3.835	0.57964	1.505	
Nb	5	-8.38	1.889	5	-6.05	1.589	4	-8.67	0.62655	4.080	0.56650	1.637	
Mo	5	-8.60	1.956	5	-5.42	1.656	4	-10.06	0.58986	4.542	0.58986	1.901	
Tc	5	-8.78	2.018	5	-6.74	1.718	4	-10.10	0.57280	4.900	0.59998	2.094	
Ru	5	-8.87	2.078	5	-5.61	1.778	4	-10.00	0.53398	5.378	0.63650	2.303	
Rh	5	-8.96	2.135	5	-5.60	1.835	4	-11.06	0.55632	5.542	0.61192	2.398	
Pd	5	-9.25	2.190	5	-5.84	1.890	4	-10.06	0.52644	5.983	0.63733	2.613	
Ag	5	-9.08	2.244	5	-5.42	1.944	4	-12.00	0.55910	6.070	0.60476	2.663	
Cd	5	-10.49	1.8039	5	-6.76	1.5039	4	-15.00	0.56164	5.2126	0.54883	2.7056	
In	5	-11.50	2.0023	5	-7.29	1.7770							
Sn	5	-13.50	2.226	5	-8.84	1.919							
Sb	5	-16.50	2.5228	5	-10.14	2.1986							
Te	5	-19.34	2.7060	5	-10.51	2.3580							
Period 6				s			p			d			
Atom	n	H	ζ	n	H	ζ	n	H	c ₁	ζ ₁	c ₂	ζ ₂	
La	6	-7.08	2.150	6	-4.85	1.850	5	-7.25	0.69054	4.10	0.55243	1.550	
Hf	6	-9.00	2.214	6	-7.26	1.914	5	-8.50	0.69669	4.360	0.53217	1.709	
Ta	6	-9.40	2.280	6	-7.24	1.980	5	-9.80	0.66017	4.762	0.55995	1.938	
W	6	-9.50	2.341	6	-7.10	2.041	5	-10.50	0.66703	4.982	0.54121	2.068	
Re	6	-9.40	2.398	6	-6.95	2.098	5	-11.10	0.63591	5.343	0.56771	2.277	
Os	6	-10.00	2.452	6	-7.09	2.152	5	-11.10	0.63717	5.571	0.55982	2.416	
Ir	6	-10.60	2.504	6	-7.34	2.204	5	-11.10	0.63506	5.796	0.55561	2.557	
Pt	6	-10.50	2.554	6	-6.46	2.250	5	-11.10	0.65581	6.013	0.57150	2.696	
Au	6	-10.73	2.602	6	-6.10	2.302	5	-13.30	0.64418	6.163	0.53558	2.794	
Hg	6	-11.90	2.649	6	-7.23	2.349	5	-14.50	0.64379	6.436	0.52147	3.032	
Tl	6	-9.50	2.4034	6	-7.61	1.6966							
Pb	6	-11.50	2.5953	6	-8.92	1.9863							
Bi	6	-13.50	2.8531	6	-8.79	2.2923							
Po	6	-16.50	2.7949	6	-9.93	2.2649							

up to the $s^2 p^1$ atoms Ga, In, and Tl at a little over 1 eV. Then, on to the chalcogens Se, Te, and Po the trend down to around 0.2 eV.

Generally, Fig. 3 shows that substitutional atoms to the left of Pt in the transition series, except for Ir, Rh, and Ni, will attract water molecules and hold them more strongly

Fig. 3. Calculated H_2O binding energies over substitutional atoms in the cluster shown in Fig. 1.



than the surrounding surface Pt atoms. These atoms may be able to hold and orient H_2O molecules, perhaps disrupting hydrogen bonded clusters, so that they can dissociate as illustrated in Fig. 2. All other substitutional atoms in these periods, from the coinage metals through the chalcogens, have less ability to attract and orient water molecules than do the majority Pt atoms.

Activation energies of OH bond scissions when H_2O is bonded to several substitutional transition metal atoms are shown in Fig. 4. Notably, first transition series metals, with the exception of Ni, are predicted to have exceptionally high activity. H_2O adsorption to the Ni atom is weak (Fig. 3). Second transition series substitutional atoms are predicted to have high activity comparable to that of Ru. Since H_2O bonding to substitutional Rh is weak, its activation of H_2O is likely to be weak, making it an exception. Third transition series substitutional atoms are more or less comparable to Pt by itself though it might be expected that the activity of Ir will be very low because H_2O bonds weakly to it.

Several substitutional atoms to the right of the coinage metals were tried and in some cases H_2O desorption was favored over OH bond cleavage. That is, some substitutional atoms had no activity toward water by this mechanism. H_2O will dissociate over the Sn-Pt site with a calculated activation barrier of 0.70 eV²⁷ but not enough transition states were found for the Zn, Ge, and Se groups to continue Fig. 4.

Structure and electronic factors.—In the earlier work with substitutional Ru²² and Sn,²⁷ electronic factors were identified that explained the activity of Ru for attracting and activating H_2O and the inactivity of Sn. The activity of Ru was traced to acceptor orbitals which could bond H_2O strongly by lone-pair donation, a Lewis acid-Lewis base interaction. These acceptor orbitals had energies just above the top of the occupied cluster band and were antibonding between Ru and the neighboring Pt atoms. They were well-localized on Ru and the bonding counterparts were low in the occupied band. These interactions are shown schematically in Fig. 5. The bracket on the right-hand column indicates energies of orbitals with substantial amplitude on atoms surrounding the vacancy site. They lie in the doubly occupied (hatched) region. The five d orbitals on the left form stable occupied bonding molecular orbitals with the vacancy site orbitals. These orbitals span a region indicated schematically by brackets on the central column of the figure. The antibonding counterpart orbitals lie higher in energy and are empty for the early

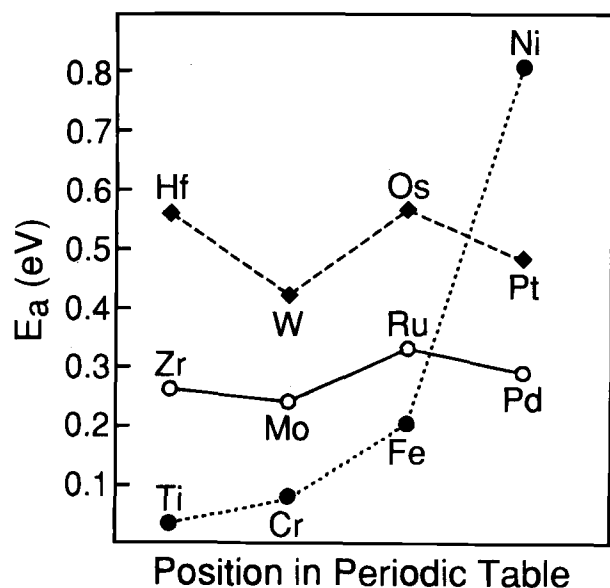


Fig. 4. Activation energies, E_a for OH bond scission (Fig. 2) when H_2O is bonded to a substitutional transition metal atom.

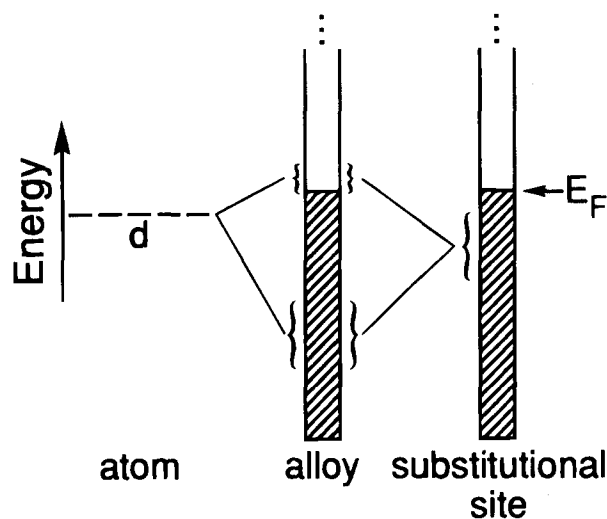


Fig. 5. Electronic structures for substitutional transition metal atoms to which H_2O binds strongly.

transition metal substitutional atoms, which have their d orbital energies near the top of the Pt valence band, such as Ru. The calculations hinted that strong donation bonding of H_2O carried with it strong activation for OH bond cleavage. The current results show that there is another dimension to consider because the activation energy is not strongly related to the adsorption energy. For example, the H_2O absorption energies on Ti, Zr, and Hf are all about the same (Fig. 3) but the activation energies vary from ~0.0 to ~0.5 to ~0.6 eV (Fig. 4) for these respective substitutional atoms. For substitutional Sn the weakness in H_2O adsorption was due to closed-shell repulsion between the lone-pair orbital and filled Sn 5p orbitals at the bottom of the cluster valence band. In this case the empty 5p antibonding counterpart orbitals were spread in a band higher in energy and less available for Lewis acid-base bonding than those of Ru. See Fig. 6. The p^1 through p^4 neighbors of Sn all bond H_2O weakly when in the surface substitutional site and do not activate H_2O bonded to them, so it

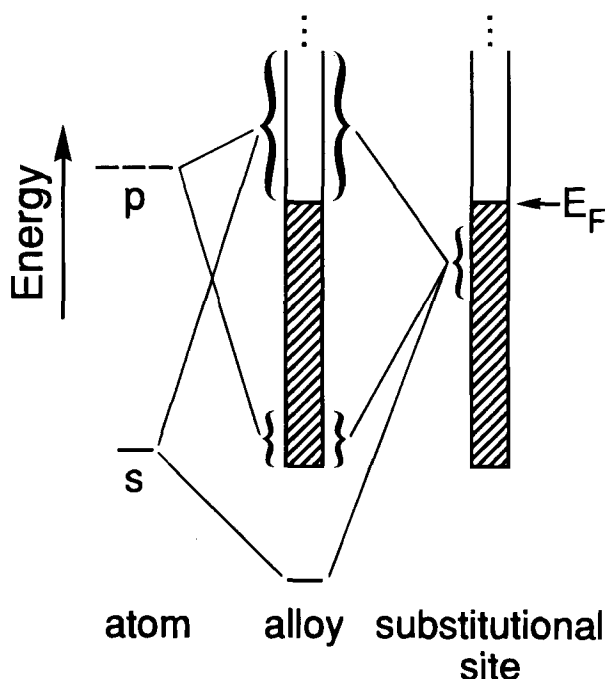


Fig. 6. Electronic structure for substitutional main group atoms to which H_2O bind weakly.

may be asked if there is a closed-shell repulsion in all of these cases and if that alone explains the results.

Considering the transition metals first, it is of interest to compare the valence d orbital energy levels with Ru and the Pt valence band to see which atoms are likely to be better or worse Lewis acids when present substitutionally in the surface. As Fig. 7 shows, the d levels trend down, some of the early ones being above the cluster Fermi energy, E_f , and those for Cd and Hg being below. Looking at the H_2O adsorption energies in Fig. 3 and comparing, there is an evident correlation between d level position and H_2O adsorption energy, excluding the scandium group: the weak adsorption to Os, Ir, Rh, Pt, Ni, and the copper and zinc groups may be associated with the stability of the d levels. Yet, as the d levels rise from the chromium group to the scandium group, the adsorption energies are relatively constant, trending slightly down. Thus it appears that atoms of the scandium group through the ruthenium group have similar substitutional atom electronic structures, with empty acceptor levels just above the Fermi level as in Fig.

5. Rh, Ir, and Ni are evidently different. Might it be that there is a closed-shell repulsion component to their bond to H_2O , a result of approaching the d^{10} configuration by having the antibonding counterpart orbitals in Fig. 5 occupied? This should lead to a negative charge on these atoms, and Fig. 8 indeed shows relatively negative Mulliken charges on Rh, Ir, and Ni as well as on the copper and zinc group atoms which also bond H_2O weakly when in the substitutional site. However, a number of early transition metal atoms to which H_2O bonds strongly also are negatively charged because the atoms have so few d electrons and the bonding orbitals are sufficiently polarized toward the atoms. Overall, there is no correlation between atom charge and attractiveness to H_2O for these systems.

Quite a good correlation is found between substitutional transition metal atom height in the surface, shown in Fig. 9, and attractiveness toward H_2O as shown in Fig. 3. Of the late transition metal groups, Co-Zn, excluding Co, Pd, and Pt, H_2O adsorption is weak and the atoms are displaced above the surface. Zn is not displaced above

Fig. 7. Atomic d energy levels (Table I) compared with the Pt_{18} cluster occupied valence band.

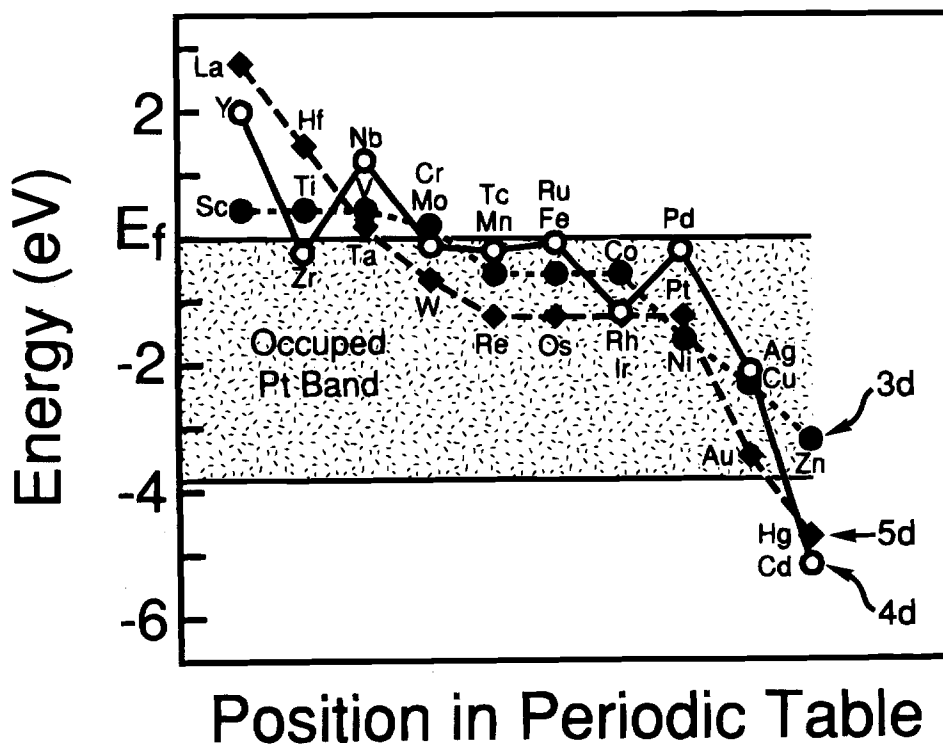
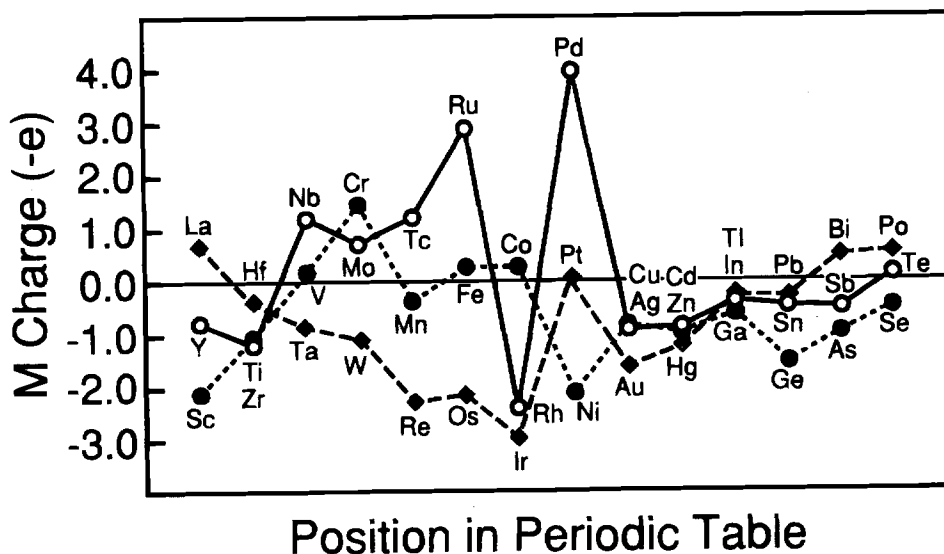


Fig. 8. Substitutional atom charge in Mulliken definition.



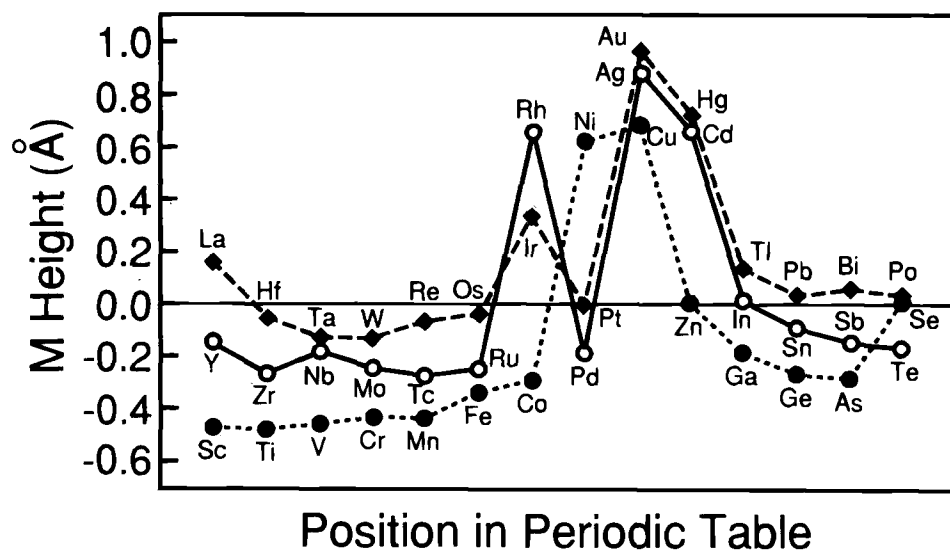


Fig. 9. Heights calculated for substitutional atoms.

the surface but H_2O bonds weakly to it. In all cases of displacement above the surface for these groups, the atom charges are relatively negative, showing that the M d-surface antibonding orbital set (Fig. 5) has become occupied. This reduces the bond orders between these atoms and the substitutional site, allowing the two-body repulsion energy to push the atoms up. Due to its large d orbital exponents, Zn has effectively a small size and is not pushed up like the other $\sim d^{10}$ atoms. The weakness of bonding of H_2O to such atoms is therefore due to closed-shell repulsions involving H_2O lone-pair and filled M d orbitals. For the Cu and Zn groups the atoms are already d^{10} and charge buildup is due to mixing s and p orbitals for the $d^{10}s^1$ Cu group and p orbitals for the $d^{10}s^2$ Zn group.

The activation energies shown in Fig. 4 for H_2O dissociating over substitutional transition metal atoms are quite

closely related to the heights of these atoms on the surface (Fig. 9). The deeper the atom resides in the surface, the lower is the activation energy calculated for the dissociation mechanism shown in Fig. 2, for this presses the OH bond against an adjacent Pt atom, which enhances the OH σ donation and back donation to the OH σ^* orbital interactions that weaken the bond. As support for this explanation, transition states were determined for the Fe atom positioned at heights above the optimized value, and as the Fe atom was moved up, the activation energy increased.

Turning now to the substitutional atoms from the main groups Ga through Se, we see that the donation bond of H_2O is weak because the valence p levels, which lie, on average, about 1 eV above E_f , as shown in Fig. 10, give rise to electronic structures as shown in Fig. 6, for which the

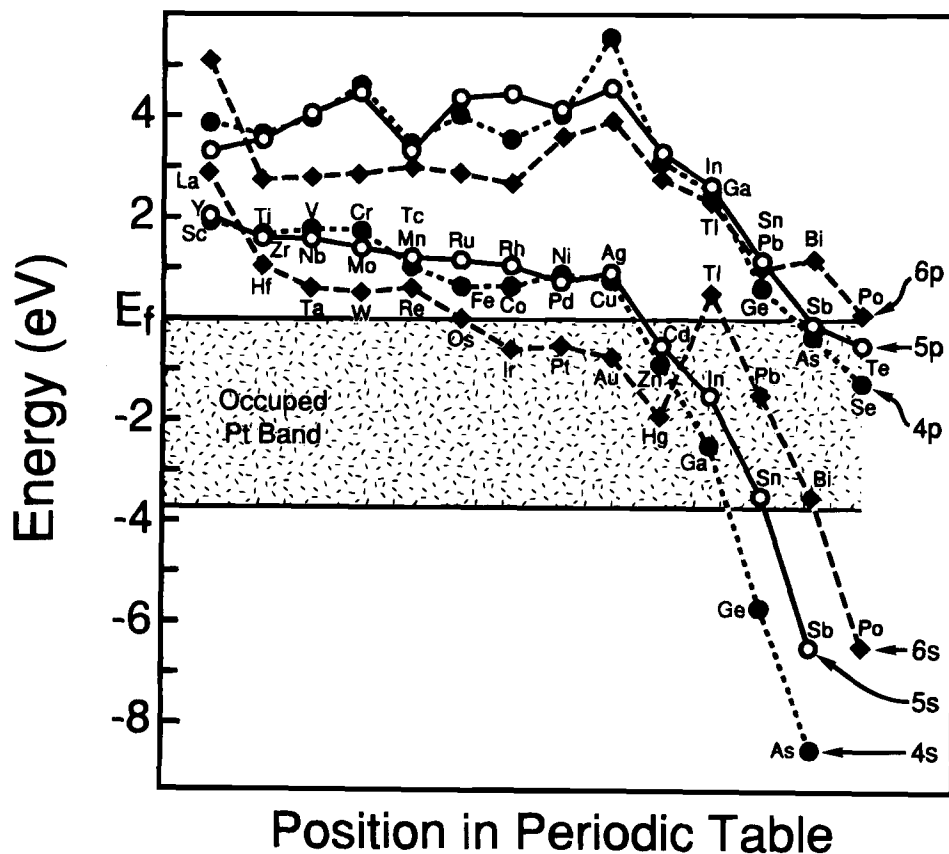


Fig. 10. Atomic s and p energy levels compared with the Pt_{18} cluster occupied valence band.

closed-shell repulsion between H₂O lone-pair orbitals and p-cluster bonding orbitals near the bottom of the occupied cluster band is strong. For these atoms the heights seem to be related to atom sizes.

Reaction of OH_{ads} with CO on an adjacent Pt.—Given the high activity of the first row transition metal atoms when in substitutional sites for attracting H₂O and generating OH bonded to them, we have examined reaction 3 in the case of Cr. OH is found to bond about as strongly to Cr (4.64 eV) as calculated in Ref. 22 for Ru (4.61 eV) and both are higher than for Pt (3.92 eV²¹). Calculated activation energies for reacting OH_{ads} and CO_{ads} for Cr, Ru, and Pt at 0 V are 0.80, 1.03,²² and 0.98 eV.²¹ Thus it again is found that a substitutional atom that is highly active toward H₂O is also able to release the OH bonded on it to oxidize CO that is bonded to an adjacent Pt atom.

Conclusion

We have found that substitutional atoms from periods 4, 5, and 6 of the periodic table when present in the (111)Pt surface seem to form two groups in respect to their activity for forming OH bonded to them from H₂O molecules. From the coinage metals on, H₂O adsorbs weakly to the substitutional atoms and is not activated, a result of closed-shell repulsion between lone-pair orbitals on H₂O and filled d or p orbitals of the substitutional atom. The transition metals to the left of the coinage metals, with the possible exceptions of Ni, Rh, and Ir, show activity for generating OH_{ads}. Of these, the early first transition series metals appear especially promising and the early second transition series metals are also potentially active in attracting and dissociating H₂O. A reevaluation of alloys of these metals in Pt using modern alloy preparation and surface characterization techniques seems warranted. If alloys with well-dispersed monosubstitutional atoms can be formed, they may show high activity in organic fuel cells. Could one be found that is more active than Ru in Pt and stable over time against oxidation and dissolution?

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REFERENCES

- H. A. Gasteiger, N. Markovic, P. N. Ross, Jr., and E. J. Cairns, *J. Phys. Chem.*, **97**, 12020 (1993).
- S. Gottesfeld and J. Pafford, *This Journal*, **135**, 2651 (1988).
- B. Bittins-Cattaneo, S. Wasmus, B. Lopez-Mishima, and W. Vielstich, *J. Appl. Electrochem.*, **23**, 625 (1993).
- S. Wasmus and W. Vielstich, *ibid.*, **23**, 120 (1993).
- S. Gilman, *J. Phys. Chem.*, **68**, 70 (1964).
- P. Shiller and A. B. Anderson, *J. Electroanal. Chem.*, **339**, 201 (1992).
- A. Wieckowski, *ibid.*, **78**, 229 (1977).
- J. O'M. Bockris and H. Wroblowa, *ibid.*, **7**, 428 (1964).
- J. Willsau and J. Heitbaum, *Electrochim. Acta*, **31**, 943 (1986).
- W. Vielstich, P. A. Christensen, S. A. Weeks, and A. Hamnett, *J. Electroanal. Chem.*, **242**, 327 (1987).
- J.-M. Leger and C. Lamy, *Ber. Bunsenges*, **94**, 1021 (1990).
- C. Lamy, *Electrochim. Acta*, **28**, 1589 (1984).
- K. J. Kunimatsu, *J. Electroanal. Chem.*, **145**, 219 (1985).
- B. Bedan, F. Hahn, S. Juanto, C. Lamy, and J.-M. Leger, *ibid.*, **225**, 215 (1987).
- R. J. Nichols and A. Bewick, *Electrochim. Acta*, **33**, 1691 (1988).
- F. H. Feddrix, Ph.D. Thesis, Case Western Reserve University, Cleveland, OH (1989).
- L.-W. Leung and M. J. Weaver, *Langmuir*, **6**, 323 (1990).
- S. A. Lin, Ph.D. Thesis, Case Western Reserve University, Cleveland, OH (1991).
- H. A. Gasteiger, N. Markovic, P. N. Ross, Jr., and E. J. Cairns, *J. Phys. Chem.*, **98**, 617 (1994).
- A. B. Anderson and E. Grantscharova, *ibid.*, **99**, 9143 (1995).
- H. A. Gasteiger, N. Markovic, P. N. Ross, Jr., and E. J. Cairns, *This Journal*, **141**, 1795 (1994).
- A. B. Anderson and E. Grantscharova, *J. Phys. Chem.*, **99**, 9149 (1995).
- K. J. Cathro, *This Journal*, **116**, 1608 (1969).
- M. M. P. Janssen and J. Moolhuysen, *Electrochim. Acta*, **21**, 861 (1976).
- A. N. Haner and P. N. Ross, Jr., *J. Phys. Chem.*, **95**, 3740 (1991).
- P. Shiller and A. B. Anderson, *Surf. Sci.*, **236**, 225 (1990).
- A. B. Anderson, E. Grantscharova, and P. Shiller, *This Journal*, **142**, 1880 (1995).
- B. Bittins-Cattaneo and T. Iwasita, *J. Electroanal. Chem.*, **238**, 150 (1987).
- J. Sobkowski, K. Franaszczak, and A. Piasecki, *ibid.*, **196**, 145 (1985).
- I. T. Bae, S. Takeshi, and D. A. Scherson, *ibid.*, **297**, 185 (1991).
- H. A. Gasteiger, N. M. Markovic, and P. N. Ross, Jr., *J. Phys. Chem.*, **99**, 8945 (1995).
- These are results of O. J. Adlhart and K. O. Heuer as reported in J. O'M. Bockris and H. Wroblowa, *J. Electroanal. Chem.*, **7**, 428 (1964).
- M. M. P. Janssen and J. Moolhuysen, *Electrochim. Acta*, **21**, 869 (1976).
- S. Motoo and M. Watanabe, *J. Electroanal. Chem.*, **111**, 1980 (1960).
- B. Beden, F. Kadirgan, C. Lamy, and J. M. Leger, *ibid.*, **127**, 75 (1981).
- F. Kadirgan, B. Beden, J. M. Leger, and C. Lamy, *ibid.*, **125**, 89 (1981).
- M. Watanabe, M. Shibata, and S. Motoo, *S. ibid.*, **187**, 161 (1985).
- M. Beltowska-Brzezinska, J. Heitbaum, and W. Vielstich, *Electrochim. Acta*, **11**, 1465 (1985).
- M. Shibata and S. Motoo, *J. Electroanal. Chem.*, **209**, 151 (1986).
- L. D. Burke and K. J. O'Dwyer, *Electrochim. Acta*, **34**, 1659 (1989).
- J. Wang, H. Nakajima, and H. Kita, *ibid.*, **35**, 323 (1990).
- L. D. Burke and K. J. O'Dwyer, *ibid.*, **35**, 1821 (1990).
- E. M. Belgsir, E. Bouhier, H. E. Yei, K. B. Kokoh, B. Beden, H. Huser, J.-M. Leger, and C. Lamy, *ibid.*, **36**, 1157 (1991).
- P. N. Ross, Jr., *ibid.*, **36**, 2053 (1991).
- K. Yahikozawa, Y. Fujii, Y. Matsuda, K. Nishimura, and Y. Takasu, *ibid.*, **36**, 973 (1991).
- M. Morita, Y. Iwanaga, and Y. Matsuda, *ibid.*, **36**, 947 (1991).
- A. Aramata, I. Toyoshima, and M. Enyo, *ibid.*, **37**, 1317 (1992).
- M. Watanabe, K. Tsunumi, T. Mizukami, T. Nakamura, and P. Stonehart, *This Journal*, **141**, 2659 (1994).
- A. B. Anderson, R. W. Grimes, and S. Y. Hong, *J. Phys. Chem.*, **91**, 4245 (1987).
- For full discussion of this theory, see A. B. Anderson, *Int. J. Quantum Chem.*, **49**, 581 (1994).
- W. Lotz, *J. Opt. Soc. Am.*, **60**, 206 (1970).
- C. E. Moore, *Atomic Energy Levels*, Vol. 1 (1949), Vol. 2 (1952), Vol. 3 (1958), Natl. Bur. Std. (U.S.) Circ. 1/67 (U.S. Govt. Printing Office, Washington, DC).
- E. Clementi and D. L. Raimondi, *J. Chem. Phys.*, **38**, 2686 (1963).
- J. W. Richardson, W. C. Nieuwpoort, R. R. Powell, W. F. Edgell, *J. Chem. Phys.*, **36**, 1057 (1962).
- H. Basch and H. B. Gray, *Theoret. Chim. Acta*, **4**, 367 (1966).
- E. Clementi and C. Roetti, *Atomic and Nuclear Data Tables*, **14**, 454-455 (1974).
- N. J. Fitzpatrick and G. H. Murphy, *Inorg. Chim. Acta*, **111**, 139 (1986); *ibid.*, **87**, 41 (1984).