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Optical and Electrical Experiments
at Some Transition-Metal Oxide Foil-
Electrolyte Interfaces*

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Metal-oxide layers formed from transition-metal foils oxidized by heating in air have been examined for their photoelectrolytic response. The metals examined are Y, Ti, Zr, Hf, V, Nb, Ta, Mo, W, and Pt. Weak photoeffects are observed for oxide layers of all of these metals. Sizable light-dependent oxygen gas evolution rates are found in Ti and also in W oxides. The spectral dependence of the oxygen response in these compounds is investigated, and interpretation is given of these experiments.

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The study of molecular and electrolytic reactions at interfaces has received attention from a number of workers recently.¹⁻⁴⁾ These reaction mechanisms have been studied by photoemission and by other electron spectroscopies at solid-vacuum interfaces,⁴⁾ and at solid-electrolyte interfaces¹⁻³⁾ by examining current-voltage behavior of electrolytic cells both with and without external illumination. Many of these and related surface spectroscopic techniques derive their importance from the basic scientific information obtainable, as well as from their connection to problems of energy conversion.

Some of the emphasis on solid surfaces for use as electrodes in photoelectrolytic cells has centered on certain transition metal oxides. The motivation for this interest is the discovery that some of these oxides, notably TiO_2 ²⁾ and SrTiO_3 ,¹⁾ show a sizable enhancement of oxygen evolution rate when operated under positive electrolytic cell potentials and when simultaneously illuminated. In the case of titanium, electrodes made of oxidized foils have been found to behave similarly to reduced single crystal wafers of the same compound,⁵⁾ a result that we have also observed. It suggests a useful procedure for examination of a number of oxidized foils of various transition metals to determine whether these substances show a sizable light-enhanced photoelectrolytic response. In this paper we report the results of such measurements on oxides of the following metals: Ti, V, Y, Zr, Nb, Mo, Hf, Ta, W, and Pt. The first nine of these metals were chosen from the left-hand portion of the periodic table and are transition metals, and the final noble metal Pt was used as a reference, since no photoresponse was expected in this case.

The conclusion from this survey is that while all oxides yield a weak light-response with respect to oxygen evolution rate under positive cell bias, only two--Ti and W--show comparably sizable responses. For oxidized titanium oxides this occurs in both acid and basic solutions, whereas for tungsten it occurs only for an acid solution, since the oxide is unstable in a strong base.

Experimental Procedure and Results

Samples of each metal in the form of thin sheets about 10 mils thick were cut into strips 0.5 cm wide and 2.5 cm long. These were degreased by scrubbing in acetone and isopropyl alcohol, rinsing in de-ionized water, and blowing dry with nitrogen. They were subsequently placed in a quartz-tube electric furnace open to air. Four samples of each metal were prepared by heating foils for one hour at the temperatures 400, 500, 600, and 700°C. These foils were then submerged to a depth of 2 cm in electrolyte giving a 1 cm² effective electrode area in a cell consisting of a beaker containing either 1 M H₂SO₄ or 1 M KOH in aqueous solution with a Pt counterelectrode. Electrical contact to the foil was made above the water with an alligator clip to a portion of the foil from which the oxide had been scraped away. Current-voltage measurements were obtained with a scanning electronic circuit, monitored using a digital voltmeter, and recorded with an x-y recorder, both with and without illumination. Each metal oxide sample was examined in both 1 M KOH and 1 M H₂SO₄ in the dark, varying the cell voltage continuously from approximately +5 V down to zero and from -5 V up to zero. This procedure was repeated for all oxides examined under illumination with a 150 W Xe arc lamp using the same scanning technique from high absolute voltage

to zero. This approach was necessitated to minimize observed transients thought to be caused by formation and removal of adsorbed species on the electrode surfaces.

The electrolytic behavior of the oxide-liquid interfaces investigated, using 1 M KOH and 1 M H₂SO₄ solutions, was obtained from measurements of current-voltage characteristics for oxide layers formed at 400°C, 500°C, 600°C, and 700°C, as mentioned earlier. A discussion and analysis of these measurements is given separately⁶⁾; however, a number of essential features of these measurements can be summarized here. These are given as follows:

(1) Metallic current-voltage curves were obtained under no illumination for oxidized foils of Y, Ti, Zr, Hf, Nb, and Ta, which were formed at lowest temperatures. These results apply to electrolytic cells with platinum metal counterelectrodes. This behavior means that the current-voltage relations were nearly symmetric under both positive and negative bias, and may suggest an oxide-metal mixture on the oxide electrode surface. For oxides formed on foils at higher temperature, an increasing tendency to form a positive blocking contact was observed. Under a negative bias, relatively small changes from the lower temperature characteristics were obtained, although the current at a given bias voltage tended to decrease. This could occur under more complete oxidation of the metal, assuming the oxide to remain electron excessive (n-type).

(2) For oxide layers that were stable in both acid and basic electrolyte, namely for the cases of Ti, Zr, Hf, Nb, and Ta, we observed that oxides tended to be more blocking under positive bias in acid than in base. This is understood as due to differences in band bending in the

oxide layer, since different interfacial reactions dominate in acid compared to base, as discussed later.

(3) Various instabilities were observed. The cases of M and V show dissolution in both acid and base under positive, anode bias. Y oxide foils were unstable under both positive and negative bias in acid, and oxidized W foils were anodically unstable in basic solution.

4) Certain oxides showed a nonexponential current-voltage response. To understand this we first recall that the current vs voltage at a single electrode-electrolyte interface is given by⁷⁾ $i = i_0 \exp(\beta e \Delta V / kT)$ where β is a transfer coefficient and ΔV is an electrode overvoltage, i.e., the amount of voltage needed above an equilibrium value to induce an electrode current i . If both electrodes of a cell are exponential, then in the equation above, ΔV can be replaced by the cell voltage if

$$\frac{1}{\beta} = \frac{1}{\beta_1} + \frac{1}{\beta_2}, \quad (1)$$

where β_1 and β_2 are the transfer coefficients of each electrode. Thus, the cell response is again exponential. This is no longer true if, say, processes at one electrode are dominated by ohmic conduction or another similar mechanism. In a basic solution a nonexponential response occurred for highly oxidized Y and Hf foils; in acid for highly oxidized Ti and Hf.

Titanium and tungsten oxides are important for their relatively strong photoeffects under positive bias. Other metal foils investigated, as we have previously mentioned, have very weak photoelectrolytic responses. Within this class, however, we should note that Nb oxides showed a slightly stronger photoeffect than other metals. The results of measurements on Ti and W are summarized in Figs. 1 and 2, which show

current-voltage curves for various light intensities for oxides made, respectively, at 600°C and 500°C. Light intensity measurements were made using a calibrated, submersible photodiode. Both figures show similar features. Under negative bias an exponential onset is observed to commence at about -2 V. If the oxide is assumed to have excess electrons (n-type), then the negative voltage behavior is readily given as due to electron exchange from the conduction band with reacting ions in the liquid. The surfaces would tend to become electron degenerate and behave as a metal. This model also accounts for the lack of light-dependence in this bias direction since illumination does little to change the equilibrium carrier density at ordinary intensities. On the other hand, under positive bias the electric field in the oxide layer changes sign. This means that holes in the valence band can now accumulate near the surface. Because these are minority charges, their equilibrium number is small. Since anode reactions involve hole exchange at the electrode, the equilibrium positive current in the dark will be small. Under illumination, however, the change in this minority carrier density can be large and thus large anode photoresponses can be explained. Also, a plateau current proportional to light intensity is reached because the hole generation rate near the surface is proportional to light intensity. At sufficiently high voltages, tunnelling into the conduction band becomes possible causing the plateau current to increase further. The width of the saturation region in this picture is thus on the order of the energy gap of the oxide. The location of the positive onset depends on the magnitude of the net energy difference of reacting states at the interface and on the size of the screening layer at the surface.

Moreover, it depends on the size of the oxide work function, in this case the sum of the oxide electron affinity and energy gap. Unfortunately, the affinity is likely to be a sensitive function of conditions within a few monolayers of the interface, as is observed generally in experiments under vacuum conditions.

Mechanics of Gas Reactions and Surface

Properties at Electrolytic-Oxide Interfaces

In order to describe electrolysis at electrolyte-solid interfaces, it is useful to obtain an energy scale for those reactions that are important at each electrode interface in cells used for gas generation. Such a procedure can be carried out using the Born cycle on room-temperature spectroscopic and chemical information if one assumes a known binding energy for the hydrogen ion H^+ in water.⁸⁾

In the normal structure of a water molecule, four directed valence orbitals are formed around oxygen. The two lowest lying of these states are saturated by bonding to hydrogen atoms. Two additional states consisting mainly of hybridized oxygen p-orbitals are higher lying, filled, and nonbonding. However, these states induce weak bonds (0.21 eV) to adjacent hydrogen atoms on neighboring H_2O molecules to comprise bonding in liquid water. Introduction of an additional hydrogen ion can probably be viewed as producing a resonance on the oxygen bonds of a single molecule, since three hydrogen atoms on four equivalent orbitals can resonate through four degenerate configurations. In this case, the binding of the extra ion is expected to be strong. If this ion were to bond only to one molecule, forming H_3O^+ , the bond energy would probably be on the order of 8 eV.⁹⁾ However, the binding is

likely to create a complex involving some fraction of additional molecules so that the total binding energy is larger. It is believed to be of order 11.5 eV, a value consistent with thermodynamic estimates.^{9,10)}

In Fig. 3 the binding of H^+ in the liquid has been treated as forming the complex H^+X with the binding energy just given. The hydroxyl ion is treated as forming an $H_3O_2^-$ -type complex OH^-X . In this figure we show energy differences for reacting states in both a strong acid and a strong base, which are simply treated as limiting cases. In the former instance, the reactions of importance for decomposition of water into gaseous components are

In a strong base the reactions dominating instead are

These assumptions are consistent with the law of mass action or the equilibrium rate equation for water, since the presence of large concentrations of either ion H^+X or OH^-X suppresses formation of ions of the opposite type. Thus, interfacial collisions of water molecules rather than of ions dominates one of the electrode reactions in either strongly acid or strongly basic solution.

The total one-electron energy necessary to decompose water is 1.47 eV, to be compared to a free energy change of 1.23 eV per electron when entropy changes are included. The potential shift for pairs of cathode

or anode reactions between the two cases of strong acid and strong base is 0.60 eV. This is to be compared to a chemical potential shift of 0.83 eV, the pH shift. Since these energies are difference energies, they are independent of the binding energy assumed for H^+X , as they depend only on energetics of water decomposition. However, the energy gain or loss for each electrode reaction separately will obviously depend on the binding energy of H^+X .

Shown also in Fig. 3 is an additional complication that cannot be treated solely from equilibrium energetics. If we are concerned with details of reaction rate or threshold conditions, then an understanding of the mechanism by which these proceed is important. In the model taken here, this involves a consideration of interactions at the electrode surface and an accounting of the intermediate states likely to be important in each reaction. In the case of the hydrogen ion H^+X shown in Fig. 3, for example, we assume that an electronic transition takes place between this ion and a surface bound state of atomic hydrogen. In the liquid, HX would be repulsive if the charge transfer occurred in the liquid instead of at the interface. This state could subsequently decompose into a surface bound state of H , though this possibility seems less likely. The surface state is taken to be adsorbed by an energy δ . The mechanism and strength of the binding (such as through chemisorption or physisorption) depends on the kind of surface, on its orientation, and on subsidiary reactions that can introduce interfacial layers modifying the interface.¹¹⁾ This bound intermediate state must then relax to give the final molecular state no longer attached to

the surface that emerges as a molecule of gas. The nature of the atomic-to-molecular recombination is unknown, although it probably involves a vibrational exchange or viscous hopping of atoms in the intermediate state until a final molecular recombination takes place. The magnitude of the energy loss due to this inelastic transition would be expected to be a few tenths of an electronvolt.

Using the energy states in the liquid given above, a qualitative picture of the charge exchange for a reaction onset at each electrode requires that $\Delta E + e\Delta V = \phi$ where ΔE is the difference energy between initial and final electronic states for either of the cathode reactions as given in Fig. 3. In other terms, this is the energy change for the electron transfer ignoring inelastic relaxation. If this latter component is small, the practical distinction of these final states makes little difference. However, we believe the physical distinction can be quite important. Here $\Delta V^{12)}$ is the applied interfacial cathode potential difference, and ϕ is the cathode work function. For the anode we obtain $\Delta E' = \phi' + e\Delta V'$ where each quantity is now defined analogously to the cathode case. This picture applies to single atom processes. The statistical nature of current measurements in electrochemical cells requires that energy differences ΔE be replaced by free energy differences $\Delta \mu$ to include the entropy changes occurring in each reaction. The entropy of an electron is usually taken as zero in this treatment.

It is here important to examine aspects of oxide layers that contribute to the electron charge transfer mechanism, particularly in the case of light-induced enhancement of the oxygen evolution reaction in

the case of oxides of titanium and tungsten. The electronic and optical properties of these and related transition metal oxides has been examined by a number of workers.^{13,14)} The structure of many of these oxides may be viewed as intermediate to that of molecular and strongly ionic crystals. For such compounds optical transitions near the fundamental edge involve electron excitations from filled oxygen $O^{2-}(2p^6)$ orbitals to empty d states on the transition metal ion and also possible exciton effects.

In the case of titanium recent band calculations on $SrTiO_3$ ¹⁵⁾ suggest a number of qualitative features that should also be applicable for understanding other similar oxides. The energy gap in this work is calculated using a Madelung-stabilized linear-combination-of-atomic-orbitals model. The results show that most of the energy gap (~75%) is accounted for by the difference between the ionization potential of the Ti^{4+} cation and the electron affinity of the O^{2-} anion and the Madelung correction due to the effective charge transfer from anion to cation. This transfer is about 0.3e to 0.4e less than the full ionic limit. The remaining 25% of the energy gap is due to covalent bond effects and residual electrostatic splitting. Insofar as excitations near the band edge are concerned Sr is inert in $SrTiO_3$ and does not contribute to optical structure until energies about 11.5 eV above the 3 eV gap.¹⁵⁾ We may thus approximately apply these results to the consideration of TiO_2 in the following sense: In the perovskite the Ti site symmetry is cubic whereas it is nearly octahedral in the case of rutile. This crystal field splits the Ti d-levels into threefold t and twofold e states in both cases. Electrostatic repulsion between the Ti and O sites raises the energy of

the e levels with respect to t in each instance (~ 0.6 eV in the perovskite). The oxygen sites have tetrahedral symmetry in SrTiO_3 and approximately the same symmetry in TiO_2 , so we expect a p-splitting into twofold perpendicular and nondegenerate parallel components. The perpendicular components lie higher. The effective charge transfers in TiO_2 yield $\text{Ti}^{3.16}\text{O}_2^{-1.58}$ for a 75% Madelung stabilized 3.0 eV band gap.

In the case of Ti_2O_3 , a direct comparison to a perovskite is not justified. However, we may observe that the Ti sites remain sixfold coordinated and the oxygen sites are fourfold coordinated in a corundum structure. This means that the approximate t,e d-band splitting remains, except that the t-state is split into a bonding and antibonding subband due to cation-cation overlap. This distance decreases as the lattice distorts from cubic to lower symmetry. Moreover, because of a valence change in the oxide, the Fermi level in the lattice now occurs midway between these subbands. This introduces further low-lying states into the optical spectrum near 1.0 eV.^{13,16)} In other TiO_x oxides of lower symmetry the t bonding and antibonding energy difference is likely to increase, since the cation-cation bond energy is thought to make up for the cohesive electrostatic energy loss due to vacancies in the lattice.¹⁴⁾

We have examined optical spectra of light-induced oxygen evolution for comparison to reflectivity spectra and assignments based on the foregoing considerations. This procedure gives information on the excitations of the oxide that are responsible for hole evolution to initiate the oxygen-reaction for which light enhancement is observed. These measurements (see Fig. 4) indicate that the $\text{O}(2p^6)\text{-Ti}(3d)$ gap transition

dominates. No evidence was seen for reaction enhancement for transitions occurring within the $Ti(3d)$ bonding-antibonding complex. These latter effects have also been discussed in relation to surface states on crystalline TiO_2 within its energy gap due to a phase transformation from TiO_2 to Ti_2O_3 due to ion-bombardment to produce disordered surfaces, as seen by photoemission, electron energy loss, and Auger spectroscopy.⁴⁾ Such effects are different from gap states expected on TiO_2 due to truncation of the crystal.¹⁵⁾ Although we may expect any of such effects from mixed crystal phases that may dominate the surface structure of our oxidized layers, they are not seen in Fig. 4. This means that for the samples examined, as shown, charge exchange reactions are apparently dominated by interactions with the TiO_x 2p valence band. However, some indication exists (see arrow) that a small photoelectrolytic onset begins due to localized states at about 2.8 eV about 0.2 eV below the fundamental edge. These states may be formed due to excitations trapped near localized sites in oxide films likely to be disordered. The behavior of WO_x is similar (see Fig. 5) and suggests an onset at ~ 2.8 eV. This appears to be the $O(2p)-W(5d)$ edge of this oxide.

The ordinary normal-incidence reflectivity spectra of the same oxide layers TiO_x and WO_x were also examined. The results show a monotonic rise in the reflectivity of both of these crystals with increasing energy and suggests band edges at about 2.8 to 3.0 eV for each oxide. We made a single measurement to look for d-band complex transitions in the reflectivity spectrum. If these exist, they are small. We wish to emphasize, however, that measurements on the present films are complicated

by the facts that the oxide layers are thin, semitransparent, and somewhat diffuse. Thus, the optical properties determining the reflectivity spectrum will consist of both that of the oxide and of the underlying metal substrate. It will also have a wavelength dependent substructure due to nonspecular scattering.¹¹⁾ Optical structure measurements can only be obtained using a more accurate differential spectroscopy technique. Such experiments are currently in progress.

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FIGURE CAPTIONS

- Fig. 1. Current-voltage response of a photoelectrolytic cell consisting of an oxidized titanium foil and a platinum counterelectrode immersed in 1 M H_2SO_4 . A photoresponse proportional to white light intensity (Xe arc) is observed as shown for the case in which the titanium oxide layer is biased positively to platinum.
- Fig. 2. Current-voltage response of a photoelectrolytic cell consisting of an oxidized tungsten foil and a platinum counter-electrode immersed in 1 M H_2SO_4 aqueous solution in a configuration identical to that in Fig. 1. The photoelectrolytic response of cell current per unit electrode area per unit incident white light intensity is approximately twice that of the titanium oxide in the saturation region between +1 V to +3 V cell bias.
- Fig. 3. Reaction energy diagrams for energy differences of electrolytic reactions in a strong acid and a strong base in aqueous solution. Energy states are determined by the Born cycle from spectroscopic and chemical data assuming a hydrogen ion to be bound to water with an energy of 11.5 eV. Given are energy differences for reactions. These should be distinguished from free energy differences that would be obtained if the statistical effect of entropy were properly included. Interfacial electron transfers are assumed to occur to an intermediate adsorbate level (bound by an energy δ) that can subsequently relax to yield molecular gas (see text). The nature of the intermediate state depends on details of the electron transfer during ion collisions with the surface.

Fig. 4. Dependence of photoelectrolysis current density per unit light intensity (i/I) on the photon energy of the illuminating radiation. An onset is observed at approximately 3.0 eV for an oxidized titanium layer electrode. This energy is taken to be due to the $O^{2-}(2p^6)-Ti(3d)$ energy transition E_g and shows evidence that holes supplied to the oxygen reaction originate from the 2p valence band of the oxide. The cell bias is +2 V. A small reaction onset below 3 eV in photon energy at about 2.8 eV (arrow) may be due to optical transitions from localized states in the oxide layer.

Fig. 5. Dependence of photoelectrolysis current density per unit light intensity versus photon energy for tungsten oxide. Structure obtained is similar to titanium and shows an $O(2p^6)-W(5d)$ onset. Optical onset energy in this case is approximately 2.8 eV.

Fig. 2

ACID

CATHODE REACTION

ANODE REACTION

BASE

CATHODE REACTION

ANODE REACTION

Fig. 3

Fig. 4

Fig. 5