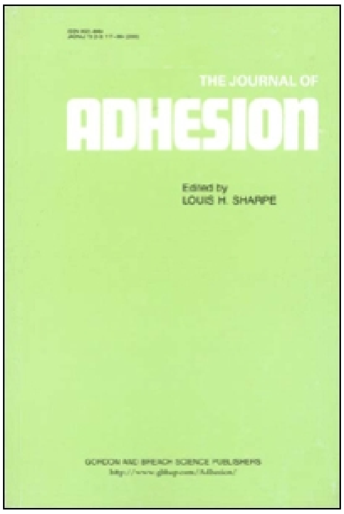

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Determination of the Isoelectric Point of Planar Oxide Surfaces by a Particle Adhesion Method*

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A particle adhesion method for the determination of the isoelectric point (iep) of planar oxide surfaces in aqueous media is described. The experiment consists in measuring the rate of deposition of latex particles as a function of pH. We have measured the iep of fused silica, soda-lime silicate glass and thin films of different metal oxides: tin, aluminum, iridium and tungsten. We find our results in good agreement with data from the literature obtained with other experimental techniques.

KEY WORDS isoelectric point; particle adhesion; oxide surface; glass surface; latex particles; acid-base properties of surfaces; pH; colloids.

INTRODUCTION

It is now well established that the acid-base interaction plays an important role in the mechanism of polymer adhesion.[1] Planar surfaces of oxide materials are of major technological importance and, therefore, it is of crucial interest to develop experimental methods for the characterization of their acid-base properties. The usual description of the Brϕnsted acidity of an oxide surface is based on the complexation of the M-OH amphoteric surface hydroxyl groups.[2] In this model, when the oxide is immersed in an aqueous solution, its surface becomes electrically charged because M-OH groups can exchange protons with the solution to give M-O$^-$ if the solution is basic or M-OH$_2^+$ if the solution is acidic. Two equilibrium constants K^+ and K^- are defined, for the surface hydroxyl acting as a proton donor or a proton acceptor, respectively. The point of zero charge (pzc) is defined as the pH of the solution required to achieve zero net surface charge. It is easy to show that the pzc value is equal to the quantity $(\mathrm{pK}^+ + \mathrm{pK}^-)/2$. The surface charge is positive (resp. negative) when the pH of the electrolyte is smaller (resp. larger) than the pzc. The oxide can also be characterized by the isoelectric point (iep) which corresponds to the pH at which the zeta potential is

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zero. If there is no specific adsorption of ions other than H^+ or OH^-, the iep is simply equal to the pzc.

Electrophoretic measurements and potentiometric titration have been used to measure the iep or pzc of oxide particles in suspension. Most of the experimental data concerning the iep or the pzc of oxide surfaces found in the literature[3] are obtained in this way. Few data related to the iep or pzc of planar oxide surfaces have been obtained by streaming potential measurements,[4,5] zeta-potential measurements in the plane interface technique[6,7] and, in the case of thin films, flat-band potential measurements in electrolyte/oxide/semiconductor structures.[8] Recently, we have shown that it is possible to use an Atomic Force Microscope (AFM) operated in an aqueous medium to measure the iep of oxide substrates with a precision of about 0.4 pH unit and with the capability of studying acid-base heterogeneities with a resolution of about 40 nm.[9] The iep of alumina has, thus, been found equal to 8.1.[10]

In this paper, we propose a simple method for the determination of the iep of planar oxide substrates. It is based on the measurement of the deposition rate of latex colloidal particles in suspension in an aqueous solution as a function of the pH of this electrolyte.

PRINCIPLE

The adhesion of fine particles at solid/solution interfaces has attracted the attention of many scientists because of its relevance to the stability of colloidal suspensions. The subject has been recently reviewed by Kallay.[11] The adhesion is influenced by two processes: the convective diffusion of particles in solution and the particle-substrate interaction. The convective diffusion can be precisely controlled by using the disk-shaped rotating substrate method introduced by Levich[12] and first used for particle adhesion studies by Kitchener and coworkers.[13,14] First general formulations of the problem, in the case of an interaction energy presenting an energy barrier, have been given by Hull and Kitchener[14] and by Ruckenstein and Prieve.[15] A large amount of theory and experimental data have been reported subsequently,[16] which improve upon these earliest theories. As our purpose is not to analyze quantitatively the rate of deposition, but to discuss semi-quantitatively the influence of the barrier height upon the deposition rate (the variation is exponential: equations (1–3) below), it will be sufficient to make use of the simple analysis of References 14 and 15. From the latter, the overall deposition rate, j, can be written as:

$$\frac{1}{j}=\frac{1}{Kc_0}+\frac{\eta^{1/6}}{0.62\,D^{2/3}\,\omega^{1/2}c_0} \tag{1}$$

where c_0 and D are the particle concentration and diffusion coefficient, respectively, η is the viscosity of the solution and ω is the substrate rotation speed. The adhesion rate constant, K, is thermally activated:

$$K \propto \exp(-E/kT) \tag{2}$$

where E is the energy barrier. Equations (1) and (2) reveal that two limiting regimes may exist. If K is very small (high energy barrier), the first term of the right-hand side of equation (1) is predominant and the deposition is controlled by the particle-surface interaction. If K is very large (small or zero energy barrier), the second term is predominant and the deposition is controlled by convective diffusion.

The existence of an energy barrier can be easily understood from a qualitative discussion of the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory.[17] Two contributions to the interaction energy are considered: the van der Waals energy and the electrical double-layer energy. The van der Waals interaction is predominant at short distance (below 10 nm) and is attractive. It creates an energy sink for the particle at the substrate-solution interface. The range of the double-layer interaction is large compared with the typical van der Waals distance; depending on the ionic strength of the solution, the so-called Debye length can go from 10 nm to 1 µm. Because it is of electrostatic origin, the double-layer interaction can be attractive or repulsive, depending on the relative signs of the two charged surfaces. It is attractive if the surface charges are of opposite signs (in the present context, this will happen for pH values intermediate between the iep values of the particle and the substrate) and repulsive if the surfaces are of the same sign. When considering the total interaction (van der Waals + double-layer), an energy barrier is then expected in the only second case. Thus, a change from slow deposition rate to fast deposition rate is expected, as it can be seen from Eqs. (1) and (2). Note that the same basic principles have been used in a different experimental context by Kallay and coworkers to develop a method for measuring the iep of small particles.[18, 19]

In order to make these arguments more quantitative, we have calculated the energy barrier height, E, using the analytical approximation derived by Hogg *et al.* for the sphere-plane interaction in the case of dissimilar materials.[20] The physical parameters that are needed to calculate the energy-*versus*-distance curve are the particle radius, r, the Hamaker constant, A, for the three-media system, solid 1 (substrate)/water/solid 2 (particle), the ionic strength of the solution, I, and the two surface potentials, ϕ_1 and ϕ_2, which play a symmetrical role in the Hogg *et al.* expression. In other words, our calculation refers to a situation where the iep of the substrate is smaller than that of the particle. It suffices to change the sign of both ϕ_1 and ϕ_2 to describe the opposite situation. The energy barrier has been calculated as a function of ϕ_1, for three values of I: 10^{-3} mol/l, 10^{-2} mol/l and 10^{-1} mol/l. A is kept equal to 10^{-20} J, a typical value of the Hamaker constant for an oxide/water/polymer system, and r is 0.3 µm, the radius of the particles used in this work. A value of + 60 mV has been taken for ϕ_2. It corresponds to the limit of validity of the Hogg *et al.* expression and is high enough to represent the physical situation when the pH of the solution differs significantly from the iep of the particle.

Hull and Kitchener[14] have given the following approximation for the ratio of the deposition rates $j(E=0)$ and $j(E \neq 0)$, *i.e.* in the presence and in the absence of an energy barrier, respectively:

$$\frac{j(E=0)}{j(E \neq 0)} \approx 1 + 10^{-3}\left[\frac{\exp(E/kT) - 1}{E/kT}\right] \tag{3}$$

From this expression, it is easy to show that the slowing down of the deposition becomes effective when $E > 10\,\mathrm{kT}$. Figure 1 indicates that this occurs when the surface potential, ϕ_1, is larger than a given value ϕ_{1c} which depends on the ionic strength of the

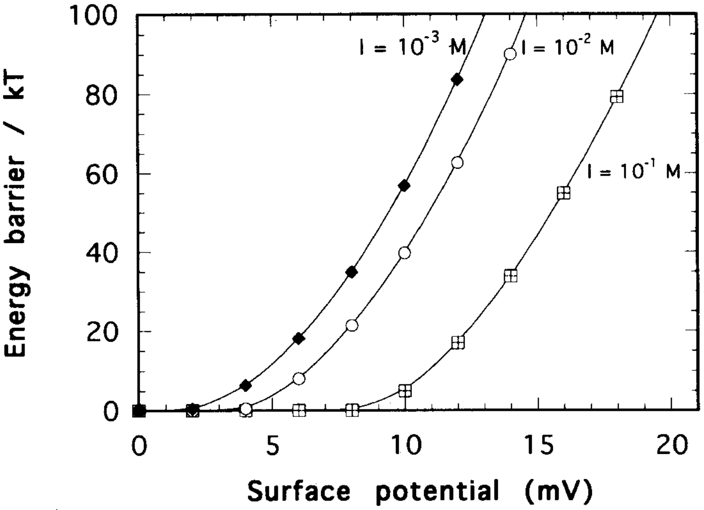

FIGURE 1 Variation of the energy barrier of the particle-substrate interaction calculated from the expression of Hogg *et al.*[20] as a function of the surface potential, ϕ_1, for three values of the ionic strength, I. The surface potential, ϕ_2, is set at 60 mV. Hamaker constant: 10^{-20} J, particle radius: 0.3 μm.

electrolyte: $\phi_{1c} \approx 4\,\mathrm{mV}$ for $I = 10^{-3}\,\mathrm{mol/l}$, $\phi_{1c} \approx 6\,\mathrm{mV}$ for $I = 10^{-2}\,\mathrm{mol/l}$, and $\phi_{1c} \approx 10\,\mathrm{mV}$ for $I = 10^{-1}\,\mathrm{mol/l}$.

The variation of ϕ with pH has been discussed in the framework of the theory of the surface complexation of the amphoteric hydroxyl groups. If the solid/solution interface has a Nernstian behavior, the surface potential varies linearly with the pH: $\phi(\mathrm{mV}) = \beta(\mathrm{pH_{iep}} - \mathrm{pH})$, with $\beta = 59.2\,\mathrm{mV/pH}$.[21] Many surfaces do not present a Nernstian behavior, however. For silica, which is typical of a very strongly non-Nernstian surface, it has been shown theoretically and experimentally[21] that the above relation is still valid for pH values close to the iep, but with β depending on the ionic strength I. The β values are approximatively 40 mV/pH, 15 mV/pH and 5 mV/pH for $I = 10^{-3}\,\mathrm{mol/l}$, $I = 10^{-2}\,\mathrm{mol/l}$ and $I = 10^{-1}\,\mathrm{mol/l}$, respectively. We conclude from this discussion that the pH value expected for the transition from slow to fast deposition must give an estimate of the substrate iep with a precision of ϕ_{1c}/β, *i.e.* 0.1 pH unit, 0.3 pH unit and 2 pH units, for $I = 10^{-3}\,\mathrm{mol/l}$, $I = 10^{-2}\,\mathrm{mol/l}$ and $I = 10^{-1}\,\mathrm{mol/l}$, respectively.

Because the surface potentials of the substrate and the particle play a symmetrical role in the discussion above, we expect to observe an associated transition from fast to slow deposition when the pH is close to the particle iep.

EXPERIMENTAL SECTION

In our experiments, the rotating-disk technique is used. The pH is gradually changed and two transitions are observed between fast and slow deposition for the two pH's which correspond to the iep's of the particle and the substrate. The particle iep being measured independently, this provides us with a measurements of the substrate iep.

The colloidal particles are amidine-grafted polystyrene latex particles obtained from Interfacial Dynamics Corp. (USA). The particle diameter is given as $0.60 \pm 0.04\,\mu m$. The iep of the particles is measured in a $HNO_3 + KOH$ aqueous solution of ionic strength $I = 10^{-3}$ mol/l for pH values between 3 and 11 by use of a Malvern zeta-meter. The variation of the experimental zeta-potential with pH is given in Figure 2. The iep value obtained from these measurements is 6.0 ± 0.2.

Disk-shaped samples, 1 cm in diameter, are cut from flat sheets of pure fused silica (WKS, Germany) and soda-lime silicate glass (Saint-Gobain Vitrage, France). Some of these samples are directly used as substrates for the latex adhesion experiments. Thin films of iridium oxide, tungsten oxide, tin oxide and indium (90%)-tin(10%) oxide (ITO) are deposited on glass disks by radio-frequency sputtering. The alumina thin film is chemically deposited from a $KNO_3 + Al(NO_3)_3$ solution as described in Ref. 6. All substrates are carefully cleaned and dried before running the adhesion experiments.

The adhesion experiments are carried out in an aqueous solution (Millipore water) of HNO_3 and KOH. The pH and ionic strength are controlled by adjusting the concentrations of HNO_3 and KOH. For pH between 3 and 11, the ionic strength is kept constant at 10^{-3} mol/l. For pH ≤ 3, no KOH is used and I is simply equal to 10^{-pH}. The disk-shaped sample is mounted on a rotating equipment and immersed in the solution with latex particles in suspension (concentration $c_0 = 3.85\ 10^7$ particles/ml) for a given period of time. The rotation is then stopped and the sample is removed from the suspension and immediately rinsed in an identical solution but without latex particles. The surface is examined using an optical microscope in dark field and the deposited particles are counted over areas of $100 \times 100\,\mu m^2$. The deposited density, N_t, is obtained by taking the mean value over 20 such areas. The deposition is found homogeneous and the particles are well dispersed, as can be seen in Figure 3.

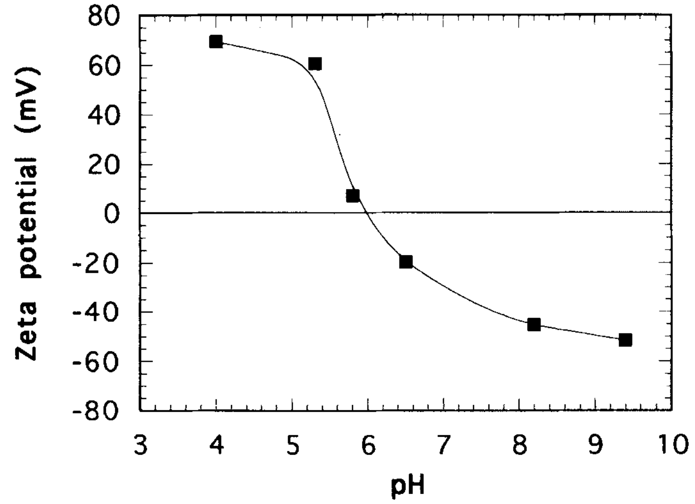

FIGURE 2 Zeta potential measurements of the probe amidine latex in a $KOH + HNO_3$ solution of constant ionic strength 10^{-3} mol/l.

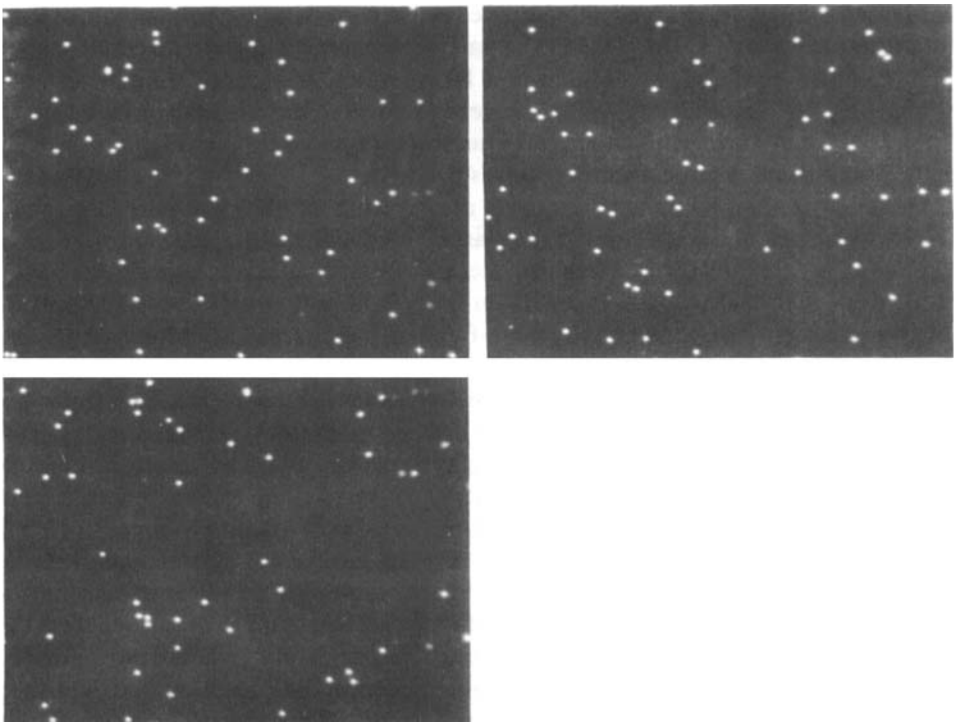

FIGURE 3 Optical micrographs in dark field of three different regions of the same glass substrate after deposition of amidine latex particles in a $HNO_3 + KOH$ solution. The dimension of each picture is $125 \times 100\,\mu m^2$. Experimental deposition parameters: pH = 3; ionic strength $I = 10^{-3}$ mol/l; immersion time $t = 10$ mins; substrate rotation speed $\omega = 31.4$ rad/s.

RESULTS AND DISCUSSION

In a series of preliminary experiments the deposited particle density, N_t, has been measured as a function of the immersion time, t, and of the sample rotation speed, ω. For immersion times up to 30 min, N_t is found proportional to t, so that a deposition rate, j, can be defined by $j = N_t/t$. Also, the variation of j as a function of ω obeys Equation (1). These results validate the experimental approach. For all the experiments discussed below, the substrate rotation speed ($\omega = 31.4$ rad/sec) and the deposition time ($t = 10$ min) are kept constant.

As an example, Figure 4 shows the variation of the deposition rate of amidine latex particles onto the ITO substrate as a function of pH. As expected, three successive regimes can be distinguished, for which slow, fast and slow deposition rate may be defined. The transitions occur at pH values of 4.3 ± 0.3 and 5.7 ± 0.1. According to the principle espoused above, these values can be assigned to the two iep's. The latter is consistent with the one measured for the amidine latex by electrophoresis. Therefore, we assign the former to the iep of the ITO thin film. In the intermediate pH regime, no

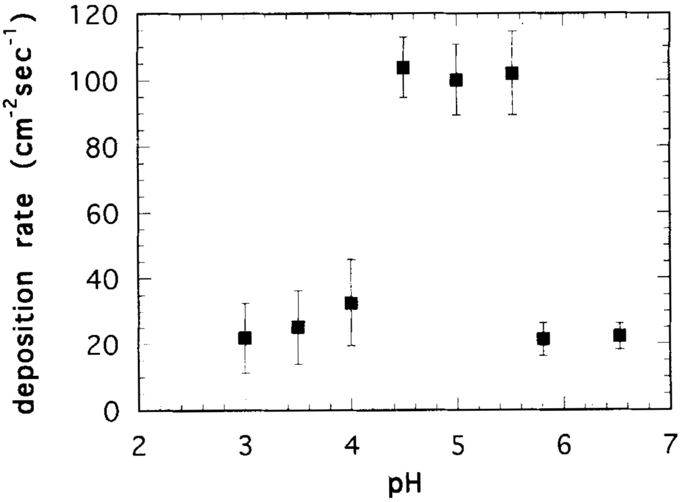

FIGURE 4 Deposition rate of amidine latex particles onto an indium (90%)-tin (10%) oxide thin film in a HNO_3 + KOH solution of constant ionic strength 10^{-3} mol/l. Substrate rotation speed: 31.4 rad/sec.

energy barrier against deposition is expected. This is the regime governed by convective diffusion for which Equation (1) can be reduced to $j = 0.62\, D^{2/3}\, \eta^{-1/6}\, \omega^{1/2}\, c_0$. From the measured value of j and the value $\eta = 8.9 \times 10^{-4}$ cm^2/sec for the kinematic viscosity of water, we obtain $D = 4.5 \times 10^{-9}$ cm^2/sec for the particle diffusion coefficient, in satisfactory agreement with the value $D = 7.3 \times 10^{-9}$ cm^2/sec calculated from the Stokes-Einstein equation.[12] It can be noticed that the observed slow deposition rate is only five times lower than the fast one, although we should expect from equations (1) and (2) a negligible deposition. We think that this is due to the fact that the hydrodynamic conditions are out of control during the rinsing step.

The results obtained with all the other substrates also exhibit three different regimes, allowing for an evaluation of the oxide iep. The measured values are given in Table I. The error limits that are indicated depend on experimental factors (increments of the pH values and statistical error in the estimation of the number of deposited particles)

TABLE I
Isoelectric points of bulk and thin film oxides as obtained by the adhesion method

Iridium oxide[a]	< 1.5
Tungsten oxide[a]	1.5 ± 0.5
Silica[b]	2.0 ± 0.3
Soda-lime silicate glass[b]	2.8 ± 0.2
Tin oxide[a]	4.0 ± 0.5
Indium (90%)-tin (10%) oxide[a]	4.7 ± 0.2
Aluminum oxide[a]	8.0 ± 0.5

[a] thin film,
[b] bulk sample

and on the inherent accuracy of the method, as discussed in the "Principle" section. Some of these results can be compared with data found in the literature.

Among all, silicon dioxide, of various structures and forms, has probably been the most widely investigated oxide. A large number of experimental iep values have been collected by Parks,[3] Ahmed[22] and Bousse and coworkers.[4, 8] The iep of silicon dioxide powders and thin films are in the range 1.5–3.7 and 2.2–3.2, respectively. Electrophoretic measurements on amorphous silica give an iep value of 2.0.[23] Our result is in general agreement with these values, especially with the last one which corresponds to a similar material.

For alumina, data obtained on powders of various crystallographic natures by electrophoretic measurements or by potentiometric titration have been collected by Parks[3] and Bousse.[4] They are widely distributed over the range 6.4–9.4. The values of 8 and 8.1 are reported for a thin film of γ-Al_2O_3[8] and for the (1000) face of a α-Al_2O_3 single crystal,[10] respectively. Our result is in very good agreement with these two last values.

Only a small amount of data exist for tin oxide.[3] They are distributed over the range 3.9–8.5. A recent measurement on monodispersed SnO_2 gives iep = 4.2.[24] Here again, our result is compatible with the published values.

The only two electrophoretic measurements reported by Parks[3] for tungsten oxide have been performed on hydrated powders. They indicate that the iep is very small, around or beyond 0.5. Our measurement confirms that the surface of tungsten oxide is strongly acidic. To our knowledge, the acid-base properties of iridium oxide have not been studied in the past. Our result indicates that this oxide is also strongly acidic.

The case of glass deserves special comments. Our result indicates that the surface is markedly acidic; however, it has been found to be slightly basic after some recent measurements by a colorimetric titration method on samples of the same composition and supplier.[25] Note that zeta-potential measurements on soda-lime silicate glass also show an acidic character.[5, 23] We propose two possible explanations to account for this discrepancy. Firstly, we have to consider that the surface of soda-lime glass is not chemically stable in water, because alkaline and alkaline-earth ions are preferentially dissolved.[26] Then, for experiments done in aqueous solutions, such as electrophoretic measurements or those described in this paper, the composition of the surface might be close to the one of SiO_2. This would explain why the iep that we measure for soda-lime silicate glass is close to the iep of silica. Secondly, it is important to keep in mind that our method, as well as electrophoretic and potentiometric titration methods, probes the Brϕnsted acidity of the hydroxyl surface groups, whereas the colorometric titration method probes the Lewis acidity. Although the relationship between the two definitions is well established for many simple oxides,[25] this might be no more valid in the case of alkaline oxides or alkaline-earth oxides, such as Na_2O or CaO, which are considered to be responsible for the basic character of glass.[25] Anyway, the Brϕnsted surface acidity of these oxides has never been measured, probably because they are soluble in water.

CONCLUSION

A simple experiment, based on the measurement of the rate of deposition of small latex particles in an aqueous solution, has been used to measure the surface Brϕnsted acidity of planar oxides. The accuracy is of the order of 0.1 pH unit for iep's between 3 and 11 and decreases as the iep moves away from this range. Results obtained for silica, alumina, tin oxide and tungsten oxide agree with the values reported in the literature for powders or thin films of the same materials. The surface of iridium oxide has been shown to be strongly acidic. We think that the method could be extended to the case of aprotic electrolytes, which would allow for the study of the surface Lewis acidity of glass.

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