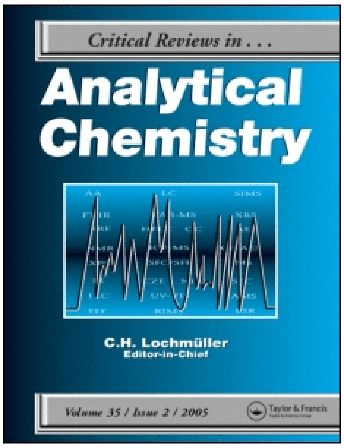

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Metal-Metal Oxide and Metal Oxide Electrodes as pH Sensors

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Metal-Metal Oxide and Metal Oxide Electrodes as pH Sensors

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I. INTRODUCTION

The pH is one of the most important parameters for characterizing the chemical properties of an aqueous solution. The glass electrode is by far the most commonly used pH sensor. The determination of pH in special situations, e.g., *in vivo* applications where the fragility of the glass electrode is a drawback, requires pH sensors that can easily be miniaturized and built into physically rugged sleeves. Also, for other applications where the volume of solution is very restricted miniaturization of pH sensors is very important. The glass electrode does not respond properly to pH in some corrosive environments (e.g., in hydrogen fluoride [HF] solutions). At present, among alternatives to the hydrogen-selective glass electrode group of sensors, potentiometric metal-metal oxide pH sensors respond to pH, ideally due to an equilibrium involving the metal and its oxide. In the case of metal oxide electrodes, the metal is not involved in the potential-determining reaction. This distinction is of course not clear in many cases because the mechanism giving the pH response is not always unequivocal.

II. METAL-METAL OXIDE ELECTRODES

Ideally metal-metal electrodes respond to pH, changing their potential by RTln10/F volts for each unit of pH change in the solution into which they are immersed.[1] According to Ives,[1] they may be regarded as pH electrodes of the second kind, i.e., the hydrogen ion response does not depend on only one simple reaction, but also on a second reaction which succeeds or accompanies the primary electrochemical process. For a reversible metal-metal oxide electrode $M/M_xO_yH^+$ (aq), the potential determining reaction can be represented by:

$$M_xO_y + 2yH^+ + 2ye^- = xM + yH_2O \qquad (1)$$

The potential of the electrode will change linearly with pH:[1,2]

$$E = E^\circ_{M,M_xO_y,H^+} - RT\ln 10\ pH/F - RT/F\ \ln a_{H_2O} \qquad (2)$$

where $E^\circ_{M,MxOy,H+}$ is a standard electrode potential and a_{H2O} is the activity of water in the solution. The last term can in most cases be ignored for diluted aqueous systems and, consequently,

$$E = E^\circ - RT\ln 10/F\ pH \qquad (3)$$

where RTln10/F is 0.059 V at 25°C.

Ives[1] discussed the properties of the metal and its oxide which are necessary in order to obtain a properly working metal-metal oxide electrode.

1. The metal (M) must be sufficiently noble over a usefully wide pH range to resist attack by all solutions in which it is to be used.
2. It must be possible to obtain the metal in a reproducible state of minimum energy.
3. The oxide (M_xO_y) must be stable. This is contradictory to the first statement because the more noble the metal, the less stable its oxide.
4. It must also be possible to obtain the oxide in a reproducible state, preferably of minimum free energy.
5. The oxide should be very sparingly soluble. At the same time, the oxide must be able to participate in the equilibrium reaction, thereby giving the electrode reaction an adequate exchange current density.

Ives[1] also discussed the possibilities of forming a working metal oxide with the above-mentioned properties. Various possible electrode systems have been investigated. These have been critically reviewed by Ives,[1] Cater and Silver,[2] and Bates and Covington.[3] No ideal metal-metal oxide electrode system has yet been found,[1-3] however, a few systems have been studied and often used. They promise to be good pH sensors. The antimony electrode belongs to this group and was the first metal-metal oxide alternative to the glass hydrogen-sensitive electrode. Recently, palladium and iridium electrodes of the metal-metal oxide type have become the center of interest.

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Other systems are rarely used and have been critically reviewed by Ives.[1] No real progress can be reported at this time. Of course, some papers concerning other systems have appeared in the literature, but these systems were used only as indicator electrodes (e.g., ample Ta/Ta_2O_5 electrode[4,5] in acid-base titration. The proper working of a pH sensor as an indicator electrode in titrations does not mean it is suitable for measuring pH values.

A. Antimony

The antimony electrode is an electrode of the metal-metal oxide type. The use of the antimony-antimony oxide system as a pH-sensing electrode was initiated more than 60 years ago by Uhl and Kestranek,[6] who employed it as an indicator of potential in the titration of acids and bases. The first use in medical pH determinations *in vivo* was reported 60 years ago by Buytendijk.[7] The electrode has generally been the first alternative to the glass electrode when the latter fails, for instance in hydrofluoric acid which attacks the glass membrane. For 6 decades, antimony electrodes have been the subject of continuing investigation and exploitation.

The electrode potential of polycrystalline antimony is unstable, irreproducible, sensitive to stirring, etc. These properties have obviously hampered the widespread use of antimony electrodes as pH sensors. During the last few decades, the situation has changed, especially the medical use of antimony electrode which has experienced a renaissance. This is due to improved properties obtained with capillary-shaped antimony electrodes used in kidney research.[8,9] Nevertheless, much confusion remains as to whether pH values obtained with antimony electrodes *in vivo* reflect the true pH value.[10-14] Edwall[15-18] was the first to show that most of the disadvantages of polycrystalline antimony electrodes can be avoided by using electrodes made of monocrystalline material.

Various possible designs of antimony electrodes and their properties have been reviewed critically by Ives,[1] Cater and Silver,[2] Bates and Covington,[3] and Stock et al.[19] The early work on antimony electrodes is almost completely covered in Reference 20. In the metal-metal oxide group of pH sensors, the antimony electrode is the most often investigated and also the one most frequently used in practical measurements of pH.

1. Methods of Preparation

The antimony surface is spontaneously covered by an oxide layer in an atmosphere of air, and no drastic methods are needed in this case in order to form an oxide phase on the surface. Three types of antimony electrodes — namely the cast electrodes, the plated electrodes, and the antimony powder electrodes — have been mainly used. Cast antimony electrodes in the form of a metal stick are the type most commonly used. This form of electrode was used as the first pH-sensitive antimony electrode by Uhl and Kestranek.[6] It has the advantages of being relatively rugged and of having a low electrical resistance. Furthermore, it can be made into various forms, suitable for the intended application. Some authors preferred to add some antimony(III) oxide to the antimony melt before casting the electrode in the form of a cylindrical rod.[19]

Antimony-plated electrodes were produced by electrolytical deposition of antimony from a solution containing antimony chloride on platinum, copper, or mercury previously deposited on platinum.[1] Regarding plated electrodes, as Ives[1] summarizes in his review, they are only occasionally well behaved and in general are irreproducible and have a limited useful lifetime. The antimony stick and the plated electrodes are polycrystalline, must be used in aerated solutions, and do not exhibit a stable electrode potential for any long period of time. This is an indication for a nonequilibrium electrode reaction. The response time of the electrodes, i.e., the time for the potential to reach a state where the potential drift is less than some specified value (this state being considered to be a "quasiequilibrium"), is long. The response time and "quasiequilibrium" potential depend on the pretreatment of the electrode and on the purity of the antimony.[1,15-18] In this respect, the ingenuity appears to be immense.

In short, most methods include polishing the metal surface with fine emery paper followed by some treatment to obtain a superficial oxidation. The results claimed for various pretreatments are indeed contradictory. In general, an oxide layer must be present on the surface for proper functioning. On the other hand, the sensitivity to pH changes is gradually lost. Ives[1] considers this to be due to the gradual covering of the surface with inactive corrosion products. Renewal of the surface by polishing and surface oxidation restores the former sensitivity. Consequently, this treatment has to be repeated. After polishing, a resting period of a few days has been recommended. The physical effect of this storage might be to relieve strain in the metal surface.[1] The electrode potential values of polycrystalline electrodes are, at best, reproducible to within 3 mV.[20] Special methods for preparing the electrodes are often claimed to give more reproducible results. However, in this respect the reported results are contradictory. According to Edwall,[15-18] the following trends can be abstracted from the literature:

1. Electrolytically produced electrodes have a fast response, but a limited useful lifetime.
2. For cast electrodes, using pure metals may improve the characteristics of the electrode.
3. During casting, oxygen should be excluded to avoid oxides in the bulk material.
4. The way of casting the electrodes is important. Accordingly, slowly cooled electrodes are said to have a faster response than those that were rapidly cooled.
5. Electrodes, tapering off into a constriction, prepared according to the method originally described by Levin,[21] are reported to have good stability. Varieties of this method

have been used to produce microelectrodes with improved stability and reproducibility.[8,9,22]

6. Electrodes with only one exposed plane surface are claimed to have faster response.

Edwall noticed that antimony-antimony oxide electrodes with only a few crystal grains exposed to the measuring solution in a plane polished electrode surface are preferable for reasons of stability[16] and he was the first to make and use monocrystalline antimony electrodes.[17] These electrodes, especially crystallographically oriented monocrystyalline electrodes presenting a close-packed crystallographic plane to the solution,[18] have a very fast response and their potentials are stable for a very long time. Also, the reproducibility of the potential between individual electrodes is very good. Antimony electrodes of this type hold much promise as pH sensors.

The antimony powder electrode was used by Roberts and Fenwick.[23] This electrode contained a mixture of antimony and antimony(III) oxide in powdered form and electrical contact was made by a platinum wire plated with antimony. Powder electrodes attain their equilibrium slowly (12 h or more to within 0.2 mV). This type of antimony electrode is not used in practice.

2. *The pH Response*

Numerous workers have experimentally investigated the potential-pH relation of antimony electrodes. Their results have been critically reviewed by Ives[1] and Stock et al.[19] Linear potential-pH relations have been reported by several investigators. However, there are great variations both regarding the slope and the standard electrode potential among the values reported. To examine any correlation between the results, obtained at 7 temperatures (T) by 17 independent workers, a least-squares calculation has been applied to the E° values and to the potential-pH slopes by Ives.[1] The following results were obtained[1] (temperature given in Kelvin):

$$E^\circ = 0.245 - 0.00225(T - 298) \text{ volt} \quad (4)$$

$$dE/dpH = 0.0565 + 0.000145(T - 298) \text{ volt/pH} \quad (5)$$

The standard potential value obtained from these calculations is quite different from the value corresponding to equilibrium:

$$Sb_2O_3 + 6H^+ + 6e^- = 2Sb + 3H_2O \quad (6)$$

The antimony oxide (Sb_2O_3) has been shown by X-ray diffraction studies to exist in two crystalline forms: the cubic form found in nature as the mineral senarmontite, and the orthorhombic form, which appears as the mineral valentinite.[24] A difference in the free energy of formation exists between the oxides, the cubic being more negative. Accordingly, as also pointed out by Roberts and Fenwick,[23] the cubic form is more stable at temperatures below 570°C, but at room temperature the orthorhombic oxide is metastable for long periods. Due to the difference in free energy, the solubility in water is different and consequently different E° values for the above given equilibrium were obtained from calculations.[25,26] For the Sb/Sb_2O_3 couple, the standard electrode potential is +152 mV (for the cubic form of antimony) or +167 mV (if the antimony is in a metastable equilibrium with its orthorhombic oxide). The electrode potential-pH relation should obey the Nernst equation, independent of the oxide form. The value of the standard potential of the antimony stick electrode as given previously, calculated from experimental data (245 mV[1]) is higher than expected by calculation using thermodynamic data, independent of which oxide form exists. Only Roberts and Fenwick[23] obtained experimentally a value for the standard electrode potential (150.4 mV) in close agreement with the one calculated from thermodynamic data (152 mV for the cubic oxide form). The reason for the outstanding results obtained by Roberts and Fenwick[23] seems to be the careful procedure which they used to prepare the Sb powder in a thermodynamic standard state and to mix it with Sb_2O_3 powder in which the oxide is in its lower (cubic) free energy state. The authors concluded that the maximum accuracy of the potential of the antimony-antimony oxide electrode is obtained only when unstable solid phases, notably orthorhombic antimony(III) oxide, are carefully avoided. The potential of their powder electrodes follows a straight line with the Nernstian sensitivity from pH 1 to pH 10.

Electrodes made in the form of massive stick electrodes are more useful than powder electrode from a practical point of view. It is clear that it is not possible to make such electrodes where the metal and its oxides are in the reproducible state of minimum free energy required for the stable electrode performance. The experience of various investigators[1] shows that the potential is neither stable nor reproducible between different polycrystalline stick electrodes. Edwall[17,18] showed that monocrystalline electrodes possess a more stable potential, regarding both short-term and long-term stability, than polycrystalline electrodes. Also, the reproducibility of potential between different electrode samples is excellent (for six oriented antimony electrodes, the value of the potential at pH 7.4 was −370.4 ± 0.8 mV against an Ag/AgCl reference electrode).[27] For newly polished monocrystalline antimony electrodes, it was shown[17,18] that at pH 1.9 in an HCl-SbOCl measuring solution at 20°C a stable potential of 154 mV (SHE) is obtained. The potential is stable to within 1 mV for more than 100 h. The electrode potential after the period of good stability has a continuous drift to about 170 mV and then the potential started to drift irregularly in the 170 to 230 mV region, usually centered around 210 mV. However, the value of the potential for newly polished monocrystalline electrodes of 154 mV at pH 1.9, as for the polycrystalline electrode case, does not agree with the value corresponding to the Sb/Sb_2O_3 system (40 mV at pH

1.9). It is obvious that the potential-pH relation for solid antimony electrodes cannot be explained by the simple reaction given earlier for the Sb/Sb_2O_3 system. Several hypotheses have been presented in order to explain the electrode response of cast and plated antimony electrodes.[1,19] A common characteristic of all antimony electrodes, except powder electrodes, is that they are made of massive antimony with superficial oxidation. The theories for these electrodes try to explain why their electrode potential is about 100 mV more positive than the theoretical value for the Sb/Sb_2O_3 reaction.

The most obvious explanation of the "overvoltage" effect is that another equilibrium reaction, other than the Sb/Sb_2O_3 reaction discussed above, controls the electrode potential. This reaction may be set up by a metal-metal oxide couple or by two metal oxides. However, Ives[1] in his critical review of different theories negates this, basically because no pure antimony-antimony oxide couple or any couple formed by different antimony oxides can be found having a standard electrode potential value corresponding to that experimentally obtained with the electrodes. However, accepting that the potential of the antimony electrode can be under mixed control by two or more reactions, possibly including higher order oxide reactions, Edwall[17,18] discussed this theory somewhat further. From potential values for various antimony-antimony oxide couples, the value of the Sb/Sb_2O_4 ($E° = 333$ mV,[25] which gives $E = 221$ mV at pH 1.9) is in fair agreement with the potential level experimentally found by the author when the electrodes were in a state of a less-controlled potential drift. Mehta and Kulkarni Jatkar[28] also suggested that the Sb/Sb_2O_4 couple was the effective one in cast antimony electrodes. According to Edwall,[15-18] the electrode potential in its stable or continuously drifting state cannot depend solely on higher oxides. However, we cannot disregard the possibility that the antimony electrode potential may also be controlled by the Sb/Sb_2O_4 couple under conditions when uncontrolled drift is observed.

At present, it seems that the local cell action theory of metal corrosion provides a plausible explanation for all experimental findings concerning electrode behavior. The idea that the antimony electrode constitutes a corroding system[1] was strongly supported by Edwall,[17,18] who correlated the electrode potential behavior to the observed surface structure of the electrodes. The potential of the antimony electrode is a corrosion potential. This means that the electrode potential is determined by at least two reactions, presumably the anodic metal dissolution

$$2Sb + 3H_2O = Sb_2O_3 + 6H^+ + 6e^- \qquad (7)$$

and the cathodic oxygen reduction reaction

$$O_2 + 4H^+ + 4e^- = 2H_2O \qquad (8)$$

In a corrosion diagram (Figure 1), the influence of the two reactions on the corrosion potential (E_{corr}) can be visualized.[29]

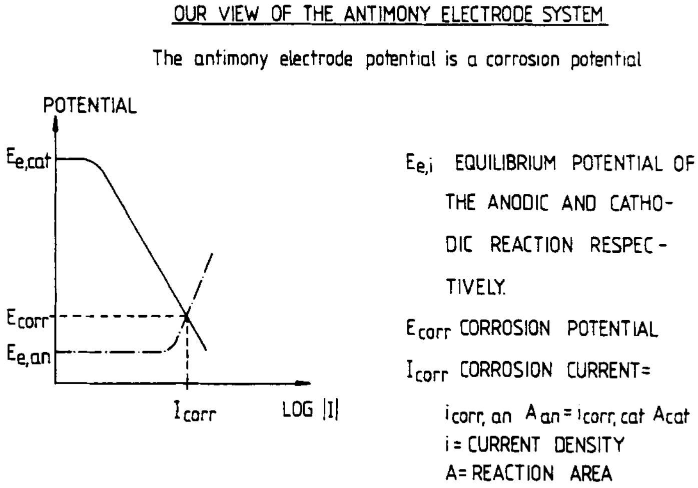

FIGURE 1. Evans diagram for antimony.

The equilibrium potentials for the two reactions are

$$E_{e,cath} = 1.23 - k\,pH + k/4 \log pO_2 \qquad (9)$$

$$E_{e,an} = 0.15 - k\,pH \qquad (10)$$

where k is equal to 2.3RT/nF. The corresponding corrosion current I_{corr}, however, is the product of the current density i_{corr} and the accessible reaction surface area A for each reaction, respectively. Therefore, the conditions for a stable and reproducible corrosion potential can be formulated as: (1) either both the current density and the reaction surface area for both the anodic and the cathodic reaction must remain constant in time, (2) or they change with the same relative velocity so as to keep their product constant with time.

In a corrosion process, however, these surface properties often change in rapid and irreproducible ways. In this aspect, a monocrystalline surface is superior to a polycrystalline one. The changes are slower, and the antimony surface is corroded in a more uniform way. Therefore, a potential that is stable and reproducible for a sufficiently long period of time for several applications can be gained. Pits, cracks, and other inhomogeneities in the surface have to be avoided since they will give rise to local corrosion cells. These cells result in rapid and irreproducible changes in current densities and in reaction area and cause instability in the potential level. This theory seems to be valid with antimony electrodes and explains why their potential values are higher than expected from the standard potential value for the Sb/Sb_2O_3 couple. The corrosion theory can also explain why these electrodes are sensitive to stirring because the diffusion equilibria at the surface will be perturbed by stirring.

Antimony electrodes in unbuffered solutions or containing TRIS [tris-(hydroxymethyl)aminomethane] as a buffer system show a linear potential-pH dependence over the pH range of

2 to 10, with a response slope of about 52 mV/pH.[27] Oriented monocrystalline electrodes have an especially excellent response, and only negligible differences in the potential values were observed between individual electrodes at constant pH. Monocrystalline electrodes respond as rapidly as glass electrodes. Unfortunately, their pH response is affected by different factors. Several authors have published work concerning these problems, including Bishop and co-workers,[30-33] who studied factors affecting the response. Among the factors investigated was the influence of oxygen on zero current and polarized antimony electrodes. Caflish et al.[13] reported work on the manufacture and utilization of antimony electrodes. Their observation that antimony electrode potentials changed when nitrogen was passed through the solution was suggested to be the result of small amounts of rare gases in the nitrogen. A much more likely explanation is that the oxygen concentration in the solution decreased. This would be in accordance with the findings of both earlier and more recent research.[34,35]

Oxygen affects the response of antimony electrodes. The monocrystalline antimony electrodes have a fast, stable, and reproducible oxygen response. They can in fact be used as oxygen electrodes if the pH of the measuring solution can be kept constant. The oxygen response was not significantly different from that for a four-electron oxygen reduction process.[35] Various authors have studied the influence of carbonate and phosphate on the potential of antimony electrodes. One of the early contributions was made by Gysinck,[36] who observed a kink in the calibration curves between pH 7.12 and 8.17. In this pH region, phosphate buffers were used for calibration and the effect observed has been named the "Gysinck effect". Other workers, such as Karlmark and Sohtell,[37] reported results that suggest that bicarbonate can affect the antimony electrode potential. Glab et al. performed experiments on the bicarbonate system[27] and found no marked effect of bicarbonate ions on the measured antimony potential. These results support a suggestion by Quehenberger[12] that the Karlmark and Sohtell "bicarbonate effect" could in fact be a phosphate effect. Phosphates affect the pH response of antimony electrodes[27,38] but, in contrast to results by Green and Giebisch,[11] measurements show very little dependence of the Sb-potential on the phosphate concentration.

The effect of phosphates on the potential vs. the pH curve may be connected with the complexation of antimony by the phosphates.[27,38] Other ligands known to form soluble complexes with antimony(III) are tartrate, citrate, oxalate, and EDTA. These ligands also have a great effect on the E vs. pH curves of polycrystalline as well as monocrystalline antimony electrodes in the acidic and neutral pH ranges.[27,38] In the alkaline pH range, all ligands except EDTA exhibit a negligible effect on the potential-pH dependence of the antimony electrode. This could mean that no complex can compete with the hydrolysis of antimony in this pH range. The exception is again EDTA, which has been suggested to form mixed complexes with antimony and one or two hydroxide ions. Unfortunately, the pH response of the antimony electrode is strongly affected by redox systems present in the measuring solution.[34]

B. Iridium

Iridium has been used for many years as a material for electrodes.[39] The electrochemistry of iridium electrodes and iridium monolayer oxide electrodes is well known,[40-42] and their potential for use as pH sensors was pointed out more than 40 years ago by Perley and Godshalk.[43] They were the first to use pure and uncoated iridium to measure pH in solution. However, such electrodes have low sensitivity (43 mV/pH unit) and their stability could be better.[44] No evidence could be found in the literature about the successful use of plain iridium electrodes for the practical measurement of pH.

During recent years, there has been a growing interest directed toward thick iridium oxide films deposited on iridium or on some other support as a pH-sensitive coating. According to Katsube et al.,[45] iridium oxide coatings are potentially attractive as pH sensors because of (1) their stability in aqueous solutions over a wide range of temperature and pressure and their low rate of dissolution even in corrosive fluids, (2) their low impedance, and (3) their fast response. Various kinds of pH-sensitive iridium/iridium oxide and iridium oxide electrodes have been described in the literature. The iridium oxide layers were formed on the iridium or on another substrate in many different ways. The properties of the pH-sensitive iridium electrodes depend on the method used in their preparation because different methods result in different composition and structure of the oxide layer. This is one reason for the different characteristics of electrodes prepared by using different procedures. The mechanism of the iridium/iridium oxide as well as the iridium oxide electrodes is not fully understood despite many investigations.

1. Methods for Making the Electrodes

The formation of the iridium oxide layer on the iridium is not simple because iridium is a noble metal. Different methods for the preparation of the oxide layer have been investigated. Since the pH response and/or the stability of the iridium and the iridium-monolayer oxide electrodes are not good, most papers report on methods for the formation of a thick iridium oxide layer. A thick iridium oxide layer on iridium metal or on another substrate has been formed with a view to producing pH sensors in many ways: (1) thermally on iridium or on some other support, (2) by sputtering, (3) electrochemically, and (4) by using iridium dioxide in a mixture with an inert matrix.

Only the first method, i.e., thermal oxidation of a metallic iridium surface, gives an iridium/iridium oxide couple. The pH-sensitive iridium electrodes obtained by using other methods, including the thermal formation of iridium oxide from iridium(III) salts onto a material other than iridium, belong to the metal oxide or rather metal oxide/metal oxide group of electrodes. For this reason, such electrodes are discussed elsewhere in this paper.

Marcur[44] described three different procedures of forming the oxide layer on an iridium wire:

1. The end of the iridium wire is immersed in an aqueous solution of either potassium hydroxide or sodium hydroxide with a concentration in excess of 1 *M*. The wetted portion of the wire is heated in an oven at 800°C for about 30 min. This process is repeated until a blue-black coating has formed. A wire thus treated is then immersed into distilled water for about 20 h. The coating on the iridium wire consists of oxide and an undertermined amount of hydrate water.
2. The iridium/iridium oxide electrode may be prepared by partial immersion of an iridium wire into a fused mixture (400 to 500°C) of potassium hydroxide and potassium nitrate (1 + 1 by weight). Then the oxide-coated wire tip should be digested in distilled water. The iridium oxide coating thus produced is not so adherent to the iridium as the coating obtained by the first procedure.
3. The iridium oxide layer may be formed on iridium by heating at around 800 to 900°C in a highly oxidizing flame. After digestion in water, the electrode may be used for measuring pH.

According to Marcur, the best method is the first where iridium is immersed in hydroxide solution. These procedures have, with some modifications, been used by other research groups. Papeschi et al.[46] prepared iridium/iridium oxide electrodes by thermal oxidation of iridium after immersing it in 1 *M* sodium hydroxide. The same group of authors[47] also used a thermal procedure to oxidize iridium wire wetted with saturated sodium bicarbonate solution. Dobson et al.[48] prepared electrodes by immersion of iridium wire in melted potassium nitrate. This is a modification of the procedure given by Marcur[44]

All the electrode types prepared by the methods discussed above have iridium dioxide in contact with iridium metal. The presence of iridium dioxide in the oxide layer was confirmed by Dobson et al.,[48] who studied electrodes in a scanning electron microscope equipped with an energy dispersive X-ray analyzer. The most common, as well as the most promising, method for preparing iridium/iridium oxide electrodes seems to be the thermal method of oxidizing iridium metal after immersion in hydroxide solution.

2. The pH Response

The literature data on the pH response of iridium/iridium oxide electrodes are scarce. Dobson et al.[48] and Papeschi et al.,[46] who used electrodes prepared by immersion in a potassium nitrate melt and by thermal formation, respectively, agree that the most likely electrode reaction is

$$IrO_2 + 4H^+ + 4e^- = Ir + 2H_2O \qquad (11)$$

The potential of a freshly prepared electrode initially changes quickly and after 2 or 3 d reaches an equilibrium value of 930 ± 5 mV (SHE) at pH = 0, which remains constant for a long time.[47] This value agrees quite well with the E° value for the reaction given earlier (0.925 V — calculated from thermodynamic data[49]). Papeschi et al.[46] and Marcur[44] reported that iridium/iridium dioxide electrodes show a perfectly linear potential-pH relationship in the pH range of 2 to 9, but unfortunately no statistical data were given. The slope of the potential-pH dependence is given as about 63 mV/pH by both groups of authors. These electrodes are insensitive to stirring of the solution, to most ions such as copper, lithium, sodium, and potassium, and are not affected by oxygen, carbon dioxide, ammonia, and hydrogen sulfide. Molecular hydrogen affects their potential.[46,47] Unfortunately, the effect of most common complex-forming ligands on the pH response has not been checked. The response time is given as 1 s in the pH range of 1 to 8, but it increases in more basic solutions (30 s at pH 12). The electrodes have excellent mechanical properties and can be stored dry over a long period without a shift in potential.[46,47] The impedance of the electrodes is low due to the low impedance of iridium dioxide.[45]

C. Palladium

Electrochemical studies of palladium have been carried out over many years.[50] A very important feature to bear in mind during investigations of the electrochemical behavior of palladium is its capacity to adsorb hydrogen. Palladium is also well known as one of the best catalysts for oxidations. The metal is also used as a material for pH-sensing electrodes. Jasinski[51] used palladium for the construction of a palladium-palladium hydride electrode which was employed for the measurement of pH in solutions containing HF. Another possibility can be to use palladium as electrode material for pH sensors of the metal-metal oxide type. Palladium forms two oxides, PdO and PdO_2, which can exist in both the hydrous and anhydrous forms.

1. Methods of Preparation

Two methods have been used to construct palladium-palladium oxide electrodes. Grubb and King[52] devised a method for preparing electrodes by coating palladium wire with sodium hydroxide and oxidizing them at 800°C for 20 min. The end of the palladium wire was cleaned by dipping it in *aqua regia* for about 20 s, followed by immersion into a 50% aqueous solution of sodium hydroxide. Subsequently, the electrode was dried for about 10 min in a stream of nitrogen while rotating the wire in order to even out the coating of NaOH. The coated end of the wire was then placed in an oxygen-flushed furnace at 800°C for 20 min. Kinoshita et al.[53] recommend the same method, but at a slightly lower temperature of oxidation (750°C). Simple air or oxygen oxidation of palladium wire at high temperatures without using hydroxide for coating is not recommended because electrodes produced in this way are not stable over time.[52] The composition of the oxide layer was studied by using X-ray diffraction,[52,54] ESCA,[53] and cyclic voltammetry.[53] The X-ray method shows, for a thermally formed palladium oxide layer, some extra lines in addition to those characteristic of PdO. Cyclic voltammograms obtained for a thermally prepared palladium/palladium oxide electrode suggest the presence of some amounts of PdO_2 in oxide film. This was not confirmed by ESCA measurements, but according to Kim et al.,[54] PdO_2 may decompose in vacuum and consequently not be detectable of ESCA. This suggestion was confirmed by a cyclic voltammetric experiment, which, for the thermally prepared electrode after storage in vacuum, shows no presence of peaks corresponding to the compound believed to be palladium dioxide.[53] Cyclic voltammetric experiments showed that the thickness of the oxide layer increased with the temperature used for oxidation up to 750°C, then decreased when the temperature was increased further.

Liu et al.[55] used electrochemical oxidation of the palladium surface in a mixed melt of sodium nitrate and lithium chloride (98 + 2 by weight) at a temperature >310°C. The authors found that the best performing Pd-PdO pH electrodes were formed with an anodic potential of 5.9 to 6.2 V (vs. a platinum cathode) and an oxidation time of 90 s. The authors also compared the two methods of preparation and concluded that both methods yield good electrodes having very similar properties. The electrochemical formation of oxides in aqueous solutions on palladium has been investigated by several research groups. Hickling and Vrjosek[56] presented cathodic charging curves indicating that both PdO and PdO_2 are being formed in sulfuric acid when the oxide layer becomes thicker than a few molecules. According to Hoare,[57] when palladium is anodized at a high potential (>2 V) in 1 *M* sulfuric acid, a Pd/PdO_2 electrode is formed first. This electrode with time transforms into a Pd/PdO electrode. This was confirmed by the experiments of Kinoshita et al.,[53] which also showed that, during the first hours of life of an electrochemically prepared Pd/PdO_2 electrode, this electrode responds to pH. After 2 d, the electrode had ceased to respond to pH.

Gossner and Mizera[58] and Chierchie et al.[59] studied the formation of palladium oxides by cyclic voltammetry in acidic solutions (1 *M* sulfuric acid and 0.5 *M* perchloric acid, respectively). Both groups of authors, as well as Kinoshita et al.,[53] showed that at low anodization potentials (<1.05 V) PdOH is being formed. When the potential is increased, this is transformed to PdO. Unfortunately, only a thin layer of PdO is obtained during anodization of palladium electrodes at potential values corresponding to its formation. The pH response of electrodes prepared in this way disappears after using them for a few pH measurements. The thermal method for preparing palladium-palladium oxide electrodes therefore seems to be the one to recommend.

2. The pH Response

For palladium-palladium oxide electrodes made by thermal oxidation for 20 min at 750°C,[53] the pH response is linear over the pH range of 2.5 to 8.5, with a slope of 59.6 mV/pH. At pH values higher than 8.5, the potentials of the Pd/PdO electrodes are of the order of a few millivolts more positive than expected from the linear potential vs. pH plot in the pH range of 2.5 to 8.5. The E° value for these electrodes decreased by about 20 mV during the first days after preparation, but then remained unchanged for at least a few months. The slope varied slightly (59.5 to 59.8 mV/pH) from electrode to electrode. The potential value extrapolated to pH = 0 is typically about 820 mV. The E° values differ between individual electrodes. In a group of 15 electrodes, the greatest difference between their E° values was 50 mV. The potential values for thermally prepared palladium/palladium oxide electrodes fell between the values that could be calculated for the reaction.

$$PdO + 2H^+ + 2e^- = Pd + H_2O \qquad (12)$$

from an E° value of 0.79 V (determined experimentally by Hoare[57]) and an E° value of 0.917 V (calculated from thermodynamic data[49]).

The mechanism of the palladium/palladium oxide pH-sensitive electrodes is still not clear. It seems that the oxide phase which is formed by thermal oxidation contains both PdO and PdO_2 and that both oxides are anhydrous.[34] The potential of an electrode may be controlled by either or both oxides reduction reactions. There are no kinetic data for the reduction of the oxides of palladium, but neither reaction is likely to be much faster than the other. Thus, the potential of the electrode is probably controlled by both reactions, perhaps with the dioxide system as the more important one since it seems necessary to have PdO_2 present in order for the electrode to perform well as a pH sensor.[34] The oxide activities may differ from one electrode to another, which may explain the difference in potential between individual electrodes. The pH response is not affected by the direction of the pH change, and the response time is 5 to 10 s for a 95% signal change. At pH values >8, the response is slower.

Complex-forming ligands such as orthophosphate, ammonia, borate, and acetate do not affect the potential of the palladium/palladium oxide electrode. Oxalate, however, being a strong reducing agent, shifts the potential of Pd/PdO electrode by about 1 to 5 mV (the oxalate concentration was 0.02 *M*).[34] Redox systems present in the solution strongly affect the pH response of this sensor. The palladium/palladium oxide electrode is insensitive to oxygen. The potential change 2 h after switching from air to 8% oxygen in nitrogen was only 3 mV. Consequently, oxygen is probably not directly involved in reactions with the electrode material.

The palladium/palladium oxide electrodes prepared by electrochemical oxidation in a mixed melt of sodium nitrate and lithium chloride exhibit super-Nernstian behavior and give a mean pH response of 71.4 mV/pH.[54] The potential values seem to be less reproducible for the electrochemically than for the thermally prepared electrodes. The mechanism of the pH response is unknown and seems to be different from the one proposed for thermally obtained palladium/palladium oxide pH sensors.

III. METAL OXIDE pH SENSORS

The electrochemistry of oxides is of practical interest in many applications, e.g., in batteries, as electrode materials for electrosynthesis, in the corrosion of ceramics, for the passivity of metals, in electrochromic displays, etc.[60] Different properties of oxides are exploited in these applications.

Another possibility for a practical application of some metal oxides is connected with their pH sensitivity. These oxides (insoluble and stable in water) may work as metal oxide pH electrodes on electronically conducting substrates (not necessarily on the metal from which they are formed). This group of pH sensors is distinguished from metal/metal oxide pH-sensitive electrodes by a different kind of reaction determining their potential-pH response. It is believed that in this case a metal oxide/metal oxide (higher and lower valency) couple instead of a metal/metal oxide couple is involved in the pH-dependent equilibrium. The oxide layer which covers the electronic conductor contains a mixture of both oxides or one with some oxygen deficiency.

The metal oxides (e.g., iridium dioxide) which are mostly employed as receptors in metal oxide pH sensors usually display more or less electronic conductivity due to a slightly nonstoichiometric composition.[61] The composition of the pH-sensitive metal oxide phase depends strongly on the method used for its formation. Potential candidates investigatged for use as pH-sensing materials include TiO_2, RuO_2, RhO_2, Ta_2O_5, IrO_2, PtO_2, and ZrO_2.[62-64]

Thick zirconium dioxide films have high impedance at room temperature and unfortunately the open circuit potential of thick-layer zirconium dioxide electrodes is insensitive to pH.[64] However, ZrO_2 is utilized in ceramic membranes (ZrO_2 + 17% Y_2O_3) forming excellent pH sensors which are very useful at high temperatures.[65-73] The working principle of the zirconia pH sensors is quite different from the so-called metal oxide electrodes and is based on their reversibility to oxygen (on their internal surface) and on the oxygen ion conductivity of the zirconia membrane.[71,72] Among metal oxides electrodes, the iridium oxide electrode is by far the most widely investigated and has found the widest use as a pH sensor.

A. Methods of Preparation

The most often used iridium oxide electrodes have been prepared by different methods, i.e., by thermal decomposition of iridium(III) salts on a conducting substrate, by sputtering, and by electrochemical methods. Also, chemically prepared iridium dioxide in mixture with a conducting inert matrix was investigated for use in pH sensors.[62]

A thermal procedure to obtain the iridium oxide layer was described by Ardizzone et al.[74] and used also by others.[63,75,76] Iridium chloride was dissolved either in water or in isopropanol and the resulting solution was "painted" onto a titanium support. After each deposition, the film was dried at about 60 to 70°C for 10 min. This procedure was repeated three times, and then a final heat-treatment in air in an oven was conducted at a temperature of 400 to 500°C for 3 h. Both X-ray diffraction analysis[63] and scanning electron microscopy[74] indicated that iridium dioxide was obtained by this procedure.

Katsube et al.[45] described the results of an extensive series of measurements of the pH response of electrodes consisting of DC reactively sputtered iridium oxide onto a variety of substrates. According to the authors, pH-sensitive iridium oxide coatings prepared by reactive sputtering from an iridium target in pure oxygen plasma have the following advantages over the other film preparations: (1) bath manufacture of electrodes is simple; (2) only a direct deposition technique offers sufficient processing flexibility to be compatible with multiple probe microelectrode manufacture; (3) in particular, one is not constrained to using iridium substrates. Sputtered iridium oxide films on tantalum, stainless steel, and iridium adhered well. For the preparation of pH sensors, stainless steel and tantalum were used.

The electrochemical methods of forming the oxide layer on the metal are probably the simplest in scope for readily controlling the rate of growth and the thickness of the film. It is interesting that oxide film growth does not occur even after more than 2 h,[77,78] if the potential is held constant at up to 1.6 V (SHE); beyond this, some dissolution occurs. When an iridium electrode is continuously cycled between the appropriate potential limits (usually between the potentials corresponding to hydrogen and oxygen evolution), an oxide film having a thickness of several hundred nanometers develops. This oxide film is a so-called anodic iridium oxide film (AIROF). It is suggested that the growth originates from an accumulation of incompletely reduced oxide left after completion of the cathodic sweep, following each anodic sweep. In the course of potential cycling, this oxide film exhibits a reversible reflectivity behavior[79] and reversible oxidation/reduction currents in cyclic voltammetry. These currents originate in a redox process Ir(III)/Ir(IV) taking place within the thick film.[80-83] During the first years of investigating this system, the corresponding reaction was assumed to be[80]

$$\underset{\text{colored}}{2\,IrO_2\,(\text{hydrated})} + 2H^+ + 2e^- = \underset{\text{colorless}}{Ir_2O_3\,(\text{hydrated})} + H_2O \qquad (13)$$

This reaction suggests that the potential-pH dependence for such films is close to 59 mV, i.e., 2.303 RT/F per pH unit at 25°C, but in practice, several authors[76,78,81-85] have observed a potential/pH shift of 80 to 90 mV/pH unit at 25°C in the cyclic voltammetric experiments for the highly reversible Ir(III)/Ir(IV) transition in AIROF films. This means that the reaction describing the Ir(III)/Ir(IV) transition is more complicated than the one given above. An important factor is the structure and the degree of hydration.[82] Some literature suggestions about the composition of the hydrated species and about the stoichiometry of the reaction connected with the Ir(III)/Ir(IV) transition are reported later when discussing the pH response.

The rate of growth of AIROF during continuously cycling of an iridium electrode depends on various experimental parameters:[78]

1. On the anodic and cathodic end potentials in a repetitive sweep. The electrode should be cycled between the potentials corresponding to hydrogen and oxygen evolution, and this depends on the type and the concentration of electrolyte used. If the anodic potential is too high, the growth rate decreases, presumably due to corrosion of the film and degradation due to oxygen evolution.[86]
2. On the type and concentration of the supporting electrolyte used in the experiment. The rate of growth depends on the anodic end potential and decreases in the order 0.5 *M* H_2SO_4 > 1 *M* $HClO_4$ >> 0.5 *M* Na_2CO_3 >> 0.5 *M* NaOH. When the proper anodic end potentials are used, the rate growth in 0.5 *M* H_2SO_4 and 0.5 *M* Na_2CO_3 is practically the same. Growth rates for NaOH are very slow.[78] Very acidic solutions (e.g., 4 to 5 *M* H_2SO_4) cannot be used because they inhibit the development of a thick film.[80,87,88] The morphology of AIROF also depends on the type of the electrolyte used for cycling. The degree of dispersion of the oxide is considerably greater in the case when acid is used as an electrolyte compared with oxide grown in alkali solutions, but the films grown in alkaline solutions are less adherent than their analog formed in acid.[88]
3. On the sweep rate (s). The rate of growth is fairly constant as long as s < 100 mV/s; it decreases linearly with log s when s is increased.
4. On the temperature. The growth rate decreases with temperature up to 50°C, after which it decreases, probably due to an increase of the dissolution rate.[89]

The electrolyte used most frequently in preparing AIROF is 0.5 *M* H_2SO_4. De Rooij and Bergveld[90] were the first to use the AIROF electrode for measuring pH. Their electrodes were made by continuously cycling the potential of the iridium electrode between −0.25 and + 1.25 V (SCE) for around 200 cycles with a scan rate of 150 mV/s. The present group of authors has used AIROF electrodes prepared by the same method using a scan rate of 100 mV/s.[34] The investigations were carried out using electrodes made of poly- and monocrystalline iridium using 100, 200, and 400 potential growth cycles.

Burke et al.[76] formed AIROF on iridium by initial fast cycling (usually 5000 cycles) at 6 V/s in 1.0 *M* H_2SO_4, subsequently stopping the sweep during the course of a slow scan (130 mV/s) at the maximum of the main positive sweep. After a suitable aging period, during which the electrode was immersed in distilled water for about 12 h, the electrode may be used as pH sensor.

Recently, Hitchman and Ramanathan[91,92] studied AIROF electrodes which were cycled between −0.25 and 1.25 V (SCE) at 3 V/s for 8000 cycles. They used and investigated a pretreatment procedure of the electrode suggested by Burke et al.[76] This consisted of a slow scan (30 mV/s) terminating at the potential maximum on the anodic part of the sweep.

Other metal oxide electrodes have been less extensively studied than the iridium oxide pH sensors. Fog and Buck[62] prepared OsO_2, RuO_2, Ta_2O_5, PtO_2 as well as IrO_2 electrodes by mounting the appropriate oxide on a Ruzicka Selectrode from Radiometer. The same method was used for making a palladium oxide electrode.[53]

B. The pH Response

The potential-pH response of iridium oxide electrodes depends on the method used for making them. Table 1 lists the potential-pH characteristics of iridium oxide electrodes obtained by various authors using different preparation methods.

Table 1

Characteristic Values of Potential at pH = 0 and Slope of AIROF Electrodes Prepared by Different Methods

Method of preparation	Potential at pH = 0 (mV)	Slope of E = f (pH) (mV/pH)	Ref.
Thermally on Ti support	950	59	74
	982 (new)	59	63
	902 (aged)	59	63
IrO_2 in mixture with inert matrix	925-930	59.8	62
Sputtered on stainless steel or titanium	1040 (new)	59.5	45
	820 (aged)	59.5	45
AIROF obtained with			
200 cycles	900	67.4	90
100—400 cycles	920	62—68	34
5000 cycles	1170	72—77	76
8000 cycles	1025 (new)	76.3	92
	990 (aged)	75.6	92

Iridium dioxide electrodes prepared by thermal decomposition of iridium chloride on a titanium support respond to pH with a Nernstian sensitivity of 59 mV/pH unit.[63,74] The slope of the potential-pH dependence for sputtered iridium oxide electrodes on stainless steel and tantalum[45] as well as for iridium dioxide on an inert electrode of the Ruzicka Selectrode type (Radiometer, Copenhagen)[62] is also 59 mV/pH. Significantly different behavior has been reported for AIROF electrodes (iridium oxide electrodes obtained by continuously cycling the potential of the iridium electrode between −0.25 and +1.25 V [SCE] in

0.5 *M* H_2SO_4). These exhibit a linear super-Nernstian response. The slope of the response differs within this group of electrodes and depends on the thickness of the oxide film (number of growth cycles used during the preparation of the AIROF), on the iridium surface state, and, consequently, on the composition of the oxide layer.

Hitchman[91] investigated the influence of the thickness of the oxide film (proportional to the number of cycles) on the slope and the E° value of AIROF pH sensors. The electrodes were made by cycling with a scan rate of 3 V/s. The slope increases with the number of cycles up to around 80 mV/pH; when the number of cycles is increased up to 3000 to 4000, then it is fairly constant. The potential value of the AIROF electrodes at a constant pH also increases with the number of cycles used in the preparation procedure. These results were obained using a pretreatment procedure consisting of a slow scan (30 mV/s) terminating at the potential maximum on the anode excursion. The slope of the response of AIROF electrodes prepared without this pretreatment procedure was significantly lower. Such electrodes, even with a thick oxide layer (corresponding to 8000 cycles), exhibited a pH sensitivity not in excess of around 65 mV/pH.

Generally, for polycrystalline AIROF electrodes, the response slope varies from 65 to 80 mV/pH in the range of 100 to 8000 cycles. It should be kept in mind that the thickness of the AIROF film is not proportional to the number of cycles, especially when the scan rate varies.[78] For AIROF electrodes obtained on monocrystalline iridium, the slope of the response is expected to be slightly higher.[34] This difference in slope between the AIROF electrodes and other iridium oxide electrodes is due to the quite different composition and structure that the oxide phase has in the different sensor types. Iridium dioxide is known to exist both in a "dry" and a "hydrous" form.[93,94] An anhydrous (compact) IrO_2 has a rutile-type structure,[79] and a hydrated (microdispersed) IrO_2 may be represented in various ways,[75] e.g., $IrO_2\,4H_2O$, $Ir(OH)_4\,2H_2O$, $IrO_2(OH)_2$, $2H_2O^{2-}$, $2H^+$, etc. The AIROF is regarded as a hydrated oxide, whereas films prepared by thermal decomposition of iridium(III) salts, by sputtering, or by chemical methods contain anhydrous oxide (at least at the beginning of their use). The voltammograms for the iridium oxide prepared by a thermal decomposition process[74] or by sputtering[45,95] are similar but they differ from that of the AIROF.[76] In the case of "dry" films, the potential/pH response is close to 59 mV/pH unit at 25°C. This suggests that equilibrium for the electrodes with anhydrous iridium oxide film (prepared thermally, chemically, or — probably — by sputtering) may be written as given by Pourbaix:[25]

$$2IrO_2 + 2H^+ + 2e^- = Ir_2O_3 + H_2O, \quad E° = 0.926\ \text{V (SHE)} \qquad (14)$$

The values of the potential of thermally or chemically prepared iridium oxide layers extrapolated to pH = 0 are close to the E° value given by Pourbaix,[25] but there are higher differences in the case of electrodes prepared by sputtering. The differences in the values of the potential for "new" iridium oxide electrodes prepared by using various methods are probably connected with differences in the stoichiometry of the iridium dioxide obtained. This is known to be a slightly nonstoichiometric compound[61] and/or to have a contaminated oxide layer. The equilibrium (Equation 14) can only be expected to be valid for anhydrous oxides. Katsube et al.[45] suggest that the big difference in the E° values for "new" and "aged" sputtered oxide films can be explained by hydration of the oxide layer. For freshly prepared (anhydrous) iridium oxide electrodes (with unknown composition of the oxide) according to Katsube et al.,[45] the potential/pH response is due to a redox equilibrium similar to equilibrium (Equation 14):

$$IrO_{(x+n)/2} + ne^- + nH^+ = IrO_{x/2} + n/2H_2O \qquad (15)$$

The corresponding standard potential for the sputtered iridium oxide electrode was about 800 mV (SCE). The shift in electrode potential for new electrodes is consistent with an increase in the extent of hydration with time. The potential of the hydrated sputtered iridium oxide electrode seems to be determined by the equilibrium:[45]

$$IrO_{(x+n)/2}(H_2O)_{y+m} + ne^- + nH^+ = IrO_{x/2}(H_2O)_y + (m + n/2)H_2O \qquad (16)$$

For the fully hydrated sputtered iridium oxide films (aged electrodes) prepared by Katsube et al.,[45] the slope was also 59 mV/pH, with E° = 580 mV (SCE). This value of the slope indicates a pH-independent structure of the sputtered iridium oxide. This explanation of an aging process seems to be valid for all other iridium electrodes except the AIROF electrodes. The iridium oxide film obtained by continuously cycling the potential of the iridium electrode is hydrous. The AIROF electrodes respond to pH with a super-Nernstian slope. This suggests a pH-dependent hydration structure of the AIROF. The oxide formed on cycling is regarded as a hydrated oxyhydroxide in a cross-linked,[96] open polymeric chain.[76] The potential determining equilibrium for the AIROF electrodes may be written as follows[76,92]

$$2IrO_2(OH)_{(2-x)}(H_2O)_{(2+x)}^{(2-x)-} + (3 - 2x)H^+ + 2e^- = Ir_2O_3(OH)_3(H_2O)_3^{3-} + 3H_2O \qquad (17)$$

The slope of the potential/pH response for equilibrium (Equation 17) at 25°C is 59 (3 − 2x)/2 mV/pH and changes with changing value of x, i.e., with changing composition of AIROF. For example, for an AIROF responding to pH with a slope of 74 mV/pH, the mean charge of the oxyanionic species is −1.75 (x = 0.25) (assuming this model).

Not very much attention has been paid to studying the effect of interferents on the pH response of iridium dioxide electrodes prepared thermally or by applying iridium dioxide onto an inert electrode. Only the effects of redox systems on these electrodes have been reported.[62]

The pH-sensitive sputtered iridium oxide electrodes have been investigated in more detail.[45] The linearity of their pH response is good (correlation coefficient = 0.9984 to 0.9999). Some metal ions influence the pH response. The effect of Pb^{2+}, Fe^{3+}, Fe^{2+}, Cu^{2+}, Ag^+ is negligible at concentrations up to 0.01 *M*. At higher concentrations, typically a positive shift of less than 5 mV was observed. However, detailed experimental conditions (ionic strength, etc.) were not given in the paper. An increase of the electrode potential of the order of a few millivolts was observed at a constant pH when switching between nitrogen bubbling and oxygen in nitrogen. In the worst case, however, there was an increase of 40 mV, resulting from a change of equilibrating gas from reducing gas to pure oxygen.

Sputtered iridium oxide electrodes work well as hydrogen ion sensors in concentrated acids (HF) and in dilute aqueous solutions at $100 < t < 200°C$ and high pressure in an autoclave.[97] The AIROF electrodes can be used in the pH range of 2 to 8.5 (correlation coefficient = 0.9990).[34] The slope of the electrodes increases with increasing film thickness.[76,91,92] From a practical point of view, electrodes having a thicker oxide layer (prepared, e.g., with a few thousands of growth cycles) would be preferred, not only because of the higher sensitivity, but also because a significant degree of oxide loss, e.g., dissolution could be tolerated without a contingent loss of pH resolution. No effect of such commonly used ligands as acetate, borate, phosphate, ammonia, or TRIS was observed.[34] The potential of the AIROF electrode is affected by oxalate in the neutral pH range (10 mV in 0.02 *M* oxalate), probably due to the reducing properties of the oxalates. In the presence of a redox system with high concentration (0.01 *M*), AIROF electrodes respond to redox potential of the solution. Also a change in potential of the order of a few millivolts is observed after switching from air to 8% oxygen in nitrogen.[34] However, Burke et al.[76] reported that the potential of the AIROF electrode (with a much thicker oxide layer) remained unaltered on changing the stirring gas from nitrogen to oxygen.

Several metal oxides which have electronic conductivity due to an oxygen deficiency can be used as pH electrodes.[62] The most promising oxide surfaces, from the accuracy point of view, are those based on Ru(IV), Rh(IV), Pt(IV), and Os(IV). The recommended pH ranges for using oxide electrodes and their characteristic slopes, respectively, are RuO_2 — 2 to 12, 61.8 mV/pH; $RhO_2 \times H_2O$ — 2 to 12, 62.8 mV/pH; PtO_2 — 5 to 10, 46.7 mV/pH; OsO_2 H_2O — 2 to 11, 51.2 mV/pH. The standard deviation of the regression line was of the order of a few millivolts. Reducing and oxidizing agents affect the pH response of these sensors. A palladium oxide electrode[53] prepared by mounting PdO on a Ruzicka Selectrode body gives a pH sensitivity of 45 mV/pH, but if the PdO were heated at 750°C, the slope increased up to 59 mV/pH. The heated palladium oxide would contain anhydrous oxide and some palladium metal from the decomposition[98] of PdO and consequently would be equivalent to the thermally prepared palladium/palladium oxide electrodes.

The utility of electrodes made from other metal oxides for sensing pH has only occasionally been investigated. For example, the potential/pH response for a thermally prepared Co_3O_4 electrode on a titanium support[99] depends on the measuring procedure and is linear if the pH is changed from acidic to alkaline, but is nonlinear if the pH is changed in the opposite direction. The Co_3O_4 electrode is not promising as a potential pH sensor.

IV. COMPARISON AND DISCUSSION

The sensors presented previously are the most frequently used and studied electrodes of the metal/metal oxide or metal oxide types. The distinction between these two groups of pH-sensitive electrodes is not quite clear, and it is sometimes difficult to decide whether a given sensor belongs to the first or to the second type. In this paper, the classification suggested by the authors of the reviewed papers has been used. It is very difficult, or even impossible, to classify a sensor properly if the mechanism of action of the sensor is not well known.

It seems that the antimony electrode should be classified as a metal/metal oxide electrode. This electrode works as a corroding system. Iridium electrodes prepared by sputtering, or thermally by decomposition of $IrCl_3$ on a titanium support, are metal oxide or rather metal oxide/metal oxide electrodes. To this group of electrodes belong also the iridium electrodes of the AIROF type. The situation is more complicated, for example, in the case of iridium electrodes prepared by thermal oxidation of an iridium metal surface. According to the authors who introduced this electrode, it is a metal/metal oxide electrode. The properties of this electrode do not differ much from the properties of an iridium dioxide electrode prepared by thermal decomposition of $IrCl_3$ on a titanium support. The last electrode is classified as being a metal oxide electrode. It seems possible that an iridium electrode prepared by thermal oxidation of iridium metal also acts as a metal oxide electrode and that iridium only plays the role of an electric conductor. However, potentiometric studies are not enough to make it possible to conclude whether the working mechanism of these electrodes is the same.

From a practical point of view, a proper potential-pH dependence is of course the most important property of an electrode, but no real improvement of the performance of these sensors may be expected without understanding their mechanisms of action. One good example of this is the antimony electrode for which improved properties were obtained using monocrystalline antimony after understanding that this electrode acts as a corroding system and that it is very important that pure material be used for its preparation. It is particularly important that other metals which can give cathodic regions be absent. Also, any impurities present should be in solid solution in the antimony matrix and not as precipitated inclusions. We can conclude that until now in most cases the mechanisms of action for the group of pH sensors under discussion were not fully known.

Antimony, iridium, and palladium have been the most frequently used materials for making electrodes of the type under discussion during the past 2 decades. The properties of these electrodes have been steadily improving during this period of time, mainly due to improved preparation procedures. It is impossible to indicate which electrode is the best. The following comparison of this group of pH sensors is presented in a similar way as the present group of authors used before.[34]

A. Preparation

Monocrystalline antimony electrodes are simple to make. Orienting the monocrystals with a tightly packed crystal plane toward the solution requires some skill. There are no problems with the formation of the oxide phase because it is formed in air atmosphere. The preparation of the oxide phase is more difficult in the case of palladium or iridium. It is easier to control and maintain the same conditions during the course of an iridium AIROF electrode preparation than during the thermal preparation of a palladium electrode.

B. The pH Response

Monocrystalline antimony electrodes exhibit a good response over the pH range of 2 to 10, with a response slope of 52 mV/pH. The thermally prepared palladium/palladium oxide electrodes have a linear response in the pH range of 2.5 to 8.5, with a slope of 59.6 mV/pH. In the same pH range, the AIROF electrode shows a linear dependence of potential vs. pH. The response slope depends on the thickness of the oxide film and varies from 62 to 76 mV/pH. The reproducibility of the E° values between electrodes is best for the monocrystalline antimony electrode. Within a group of monocrystalline antimony electrodes, the differences in E° values are very small (<1 mV). The differences between individual electrodes are substantially greater for the thermally oxidized palladium/palladium oxide electrodes than for the antimony electrodes. However, the E° value for a particular electrode is quite stable for a long time. The E° values of the AIROF electrodes differ, too.

C. The Effect of Complexing Ligands

The effect of commonly encountered ligands on the pH response of the discussed electrodes is presented in Figures 2 to 4. Antimony electrodes are very sensitive to several ligands, some of them components of standard buffers. None of the common ligands except oxalate affect palladium or AIROF electrodes.

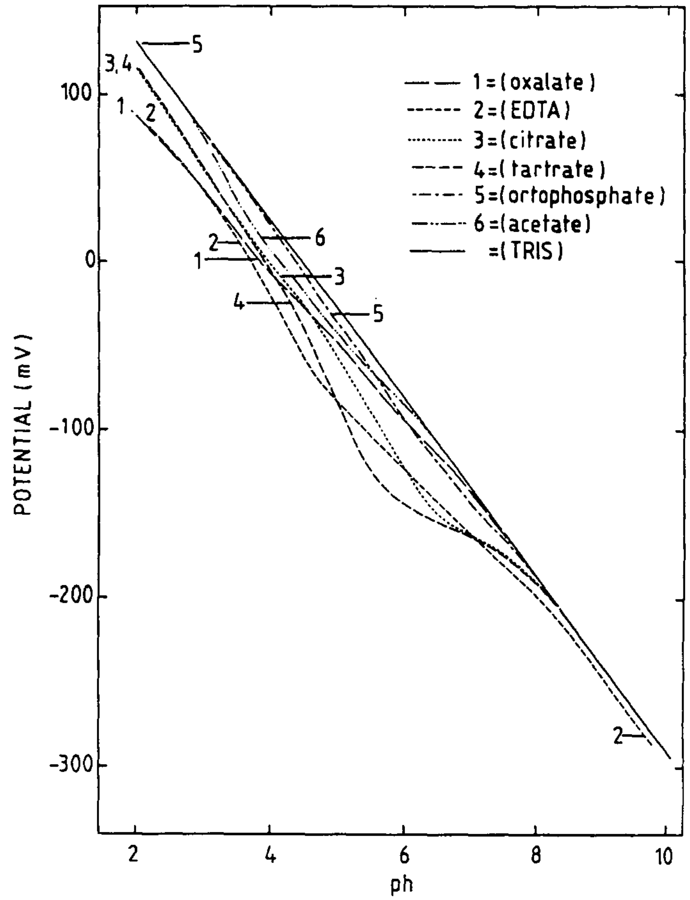

FIGURE 2. The dependence of potential on pH for antimony-antimony oxide electrode in 0.14 *M* $NaNO_3$/0.02 *M* ligand medium.

D. The Effect of Redox Systems and Oxygen Pressure

All three electrode types are affected by redox systems (Figure 5) and can in practice not be used in the presence of redox systems even in relatively low concentrations. The effect of the oxygen pressure on the pH response of this group of electrodes is shown in Figure 6. This effect is greatest for the antimony electrode, and the oxygen response does not differ significantly from what is to be expected for a four-electron oxygen reduction process. The monocrystalline antimony electrode can in fact be used as a potentiometric oxygen electrode if the pH of the measuring solution can be kept constant.[35]

V. TYPICAL APPLICATIONS

The metal/metal oxide and metal oxide electrodes, similar to other groups of pH sensors, are used in pH measurements when the use of the hydrogen-selective glass electrode is inconvenient or impossible. This is connected with the fragility

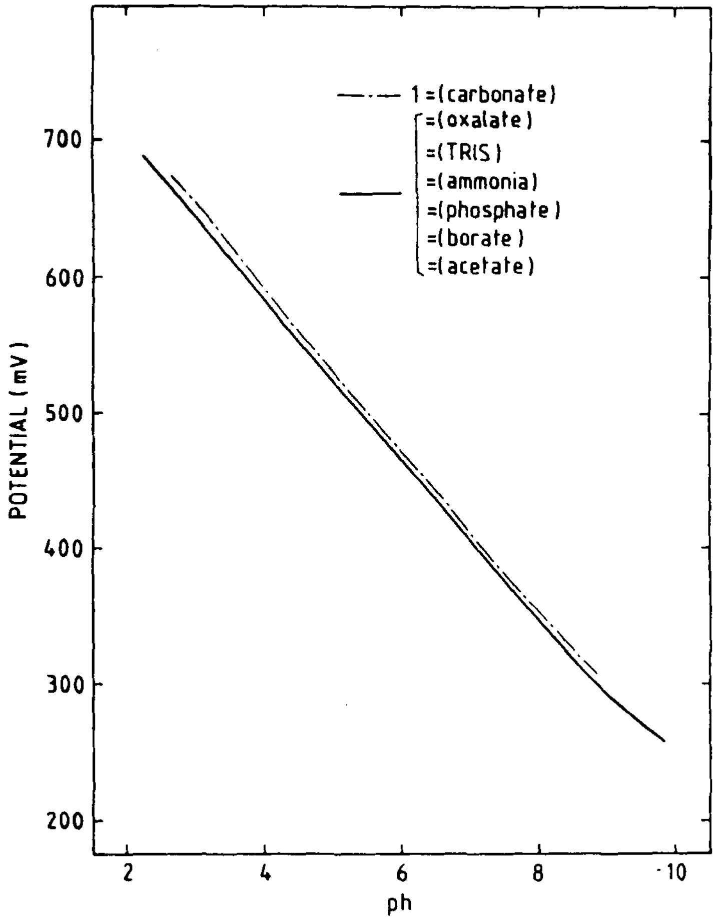

FIGURE 3. The dependence of potential on pH for palladium-palladium oxide electrode in 0.1 M $NaNO_3$/0.02 M ligand medium.

of the glass electrode and with difficulties which arise when miniaturization is needed. Also, the high impedance of the glass microelectrode is a great disadvantage.

The miniaturization of pH sensors and reference electrodes is very important when pH is determined in a very restricted volume. *In vivo* measurements of pH in biological samples also require small-sized pH sensors. Similarly, small pH sensors are required as indicator electrodes in microelectrodes. Other fields of application of this class of pH sensors are in cases when the studied object is corrosive to the glass membrane or when pH is to be measured in ranges of acidity, temperatures, or pressure at which the glass electrode does not respond properly.

Some special sensors, e.g., enzymatic sensors and the carbon dioxide sensor, employ a pH sensor as an internal sensor (transducer) because hydrogen ions are involved in the reaction forming the base of the sensor. The pH sensors used in such cases should be designed with the proper size and shape. Also, in the case of enzymatic sensors, the pH-sensitive surface should be suitable for immobilization of the enzyme. This is the next field of application for the discussed group of pH sensors.

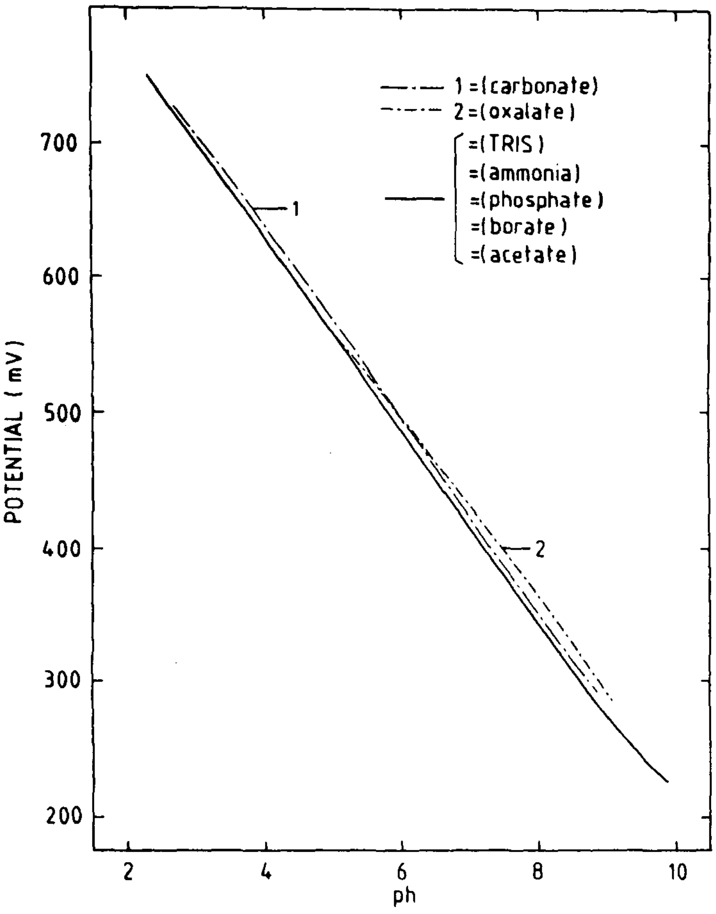

FIGURE 4. The dependence of potential on pH for anodic iridium oxide film (AIROF) electrode in 0.14 M $NaNO_3$/0.02 M ligand medium.

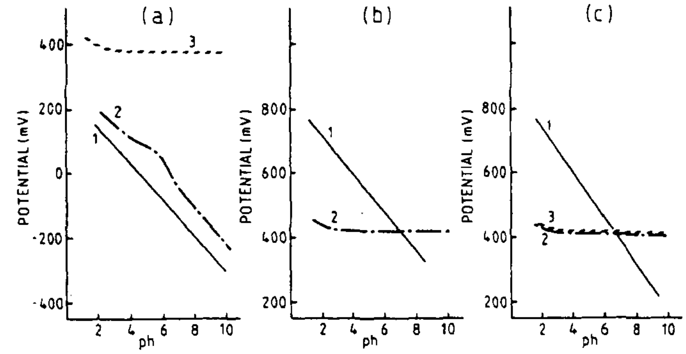

FIGURE 5. The redox sensitivity of the metal-metal oxide electrodes recorded for curves 1, 0.02 M TRIS/0.14 M $NaNO_3$; curves 2, the same solution, containing also (a) 0.09 M $Fe(CN)_6^{4-}$ + 0.001 M $Fe(CN)_6^{3-}$ for the Sb-electrode, (b) 0.01 M $Fe(CN)_6^{4-}$ + 0.01 M $Fe(CN)_6^{3-}$ for the Pd-electrode, and (c) 0.001 M $Fe(CN)_6^{4-}$ + 0.001 M $Fe(CN)_6^{3-}$ for the AIROF electrode. A platinum-wire electrode was used as a check of the redox response (curves 3; for Pd, curves 2 and 3 coincided).

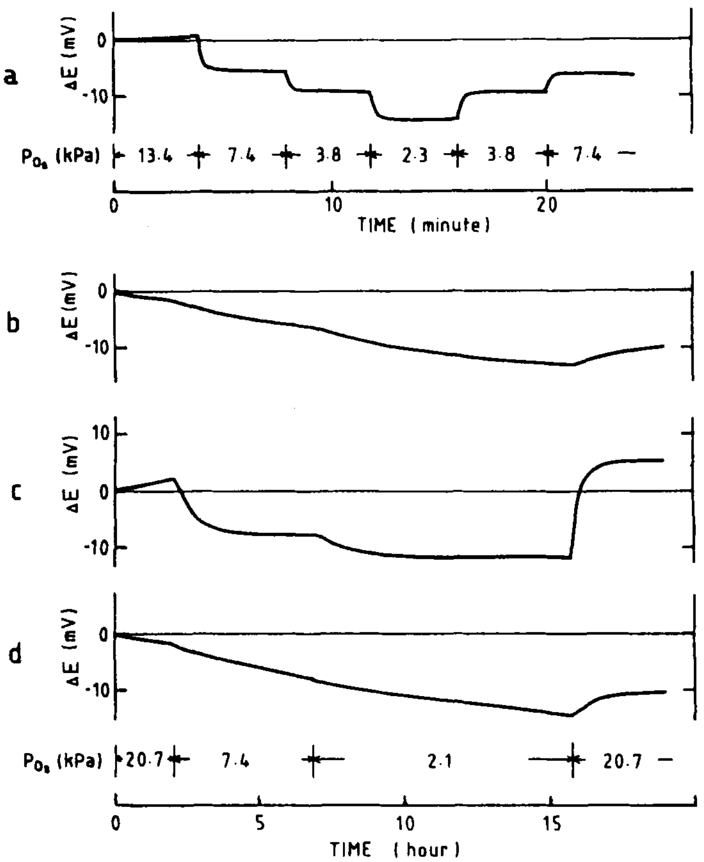

FIGURE 6. The change of electrode potential of the various types of electrodes when changing the pressure of oxygen above the test solution, as a function of time. The oxygen pressures are indicated. (a) The antimony electrode, (b) the palladium electrode, (c) the polycrystalline, and (d) monocrystalline AIROF electrode.

The applications of metal/metal oxide electrodes (mainly antimony) electrodes have been reviewed by Stock et al.,[19,100] Bates and Covington,[3] and Cater and Silver.[2] The two last mentioned reviews[2,3] focused on biological applications, whereas Stock reviewed general applications of the antimony electrode[19] and its use as an indicator electrode in acid-base titration in nonaqueous media.[100]

The metal/metal oxide and the metal oxide electrodes are mostly used for measurements of pH in samples important from a medical or a biological point of view. Buytendijk[7] was the first to use an antimony electrode in medical pH determinations *in vivo*. In the polycrystalline form, its measuring accuracy has been limited to approximately 0.1 pH units. The potential of the polycrystalline antimony electrode is unstable and depends on the presence of oxidizing, reducing, and complex-forming substances. These properties have obviously hampered the widespread use of antimony electrodes *in vivo*, and Fosbinder[101] claimed early that "apparently the electrode is not applicable for the determination of pH in blood." During the last 20 years, there has been a strong revival of the medical use of the antimony electrode. This has been due to the improved properties obtained with the earlier-mentioned capillary-shaped microelectrodes used in kidney research.[8,9,22]

Recent development of the microelectrode technique for measuring the ionic environment in the body has made possible the determination of pH in ultraminute amounts of sample, such as in the intracellular fluid of giant-sized cells, in the intraluminal fluid of glandular tissues, and in the interstitial fluid of general tissues.[102] Among other kinds of pH-sensitive microelectrodes which have served for physiological measurements are the metal/metal oxide electrodes. The construction of this type of microelectrode is not very difficult. Matsumura et al.[102-105] studied in detail the effects of different parameters on the antimony electrode in application to measurements in biological fluids. They used an antimony microelectrode with a pH-sensitive tip as small as 1 to 2 μm. The effect of plasma protein was found to be relatively small, and the practical application of the antimony microelectrode to biological samples such as blood plasma would be tenable.[103] The authors reached this conclusion after having studied the effects of oxygen and temperature and of different methods of calibration on the pH response of an antimony microelectrode.[104-105] The same group of authors[102] used antimony microelectrodes for pH measurements in whole blood and plasma samples. The results were practically the same as those obtained by a glass microelectrode. The toxicity of the monocrystalline antimony electrodes was discussed by Nilsson and Edwall.[106]

Matsumura et al.[14] also used a pencil-shaped antimony electrode with a double-barreled design having a tip <1 μm to measure intracellular pH on frog sartorius muscle and renal tubular cells. The measurement of intracellular pH using microelectrodes have been greatly advanced during the last decade, principally through the work of Thomas.[107] The glass microelectrodes are difficult to manufacture, especially if a very fine tip is desired, and difficult to use due to high impedance. Very often an indication of the intracellular pH at rest or a rapid response to pH shifts is needed. In these cases, according to Giaume and Kado,[108] an antimony electrode is an alternative to the glass electrode. Also, Nair et al.[109] and Bicher and Ohki[110] used an antimony microelectrode for measuring intracellular pH.

The antimony electrode provides a stable and reproducible means for the determination of intramuscular pH. Dhalla et al.[111] employed the antimony electrode to monitor intramuscular pH in isolated perfused rat heart. Levine and Kelly[112] used an antimony microelectrode to measure pH in rat seminiferous tubules and epididymides *in vivo*. Harrison and Walker[113] have discussed requirements for an electrode to be used successfully in tissue and concluded that an antimony microelectrode can be used in this case. Tissue pH measurements with antimony needle electrodes have been reported by Haljamae et al.[114] and Wenberg et al.[115] The importance of tissue pH has been pointed out by Hagberg[116] and Raskin et al.[117] A multipoint pH antimony microelectrode for tissue surface measurements enables improved and more detailed monitoring of the acid-base status of the tissue.[118,119]

Continuous intra-arterial studies in nonheparinized dogs have been performed by Nilsson and Edwall,[120,121] using catheter-shaped monocrystalline antimony electrodes. The monocrystalline antimony electrode has been used for long-term registration of gastroesophageal reflux, for the esophageal acid clearing test, and for identification of pH-gradient zone between the gastric and esophageal mucosa.[122,123] The antimony microelectrode has been used for the measurement of the isoelectric points of proteins after isoelectric focusing in polyacrylamide gel.[124]

For the same purpose, Papeschi et al. used a thermally prepared iridium/iridium oxide electrode.[46,125] The same authors[126] used an iridium/iridium oxide electrode for *in vivo* monitoring of blood pH changes and compared the results with those obtained by using a glass electrode. They concluded that the iridium electrode provides a means of studying the changes in hydrogen ion activity induced by a variety of physiological, pathological, and pharmacological interventions and that it seems to be a useful tool for monitoring blood pH changes in animals during acutate experiments. Also Marcur,[44] in a patient, described the application of an iridium-iridium oxide electrode for measurement of blood pH.

Another area of applications for the group of electrodes under discussion is also connected with miniaturization. Antimony microelectrodes have been used in acid-base titration procedures. The principles for acid-base titration in nanoliter samples using miniaturized pH-sensitive antimony electrodes were first described by Solomon and Alpert.[127] The method was subsequently improved and extended to include, in addition to the measurement of titratable acid, the analysis of bicarbonate and ammonium ions in the same nanoliter sample.[9,37] (Titratable acid is defined as the amount of OH-ions used to titrate a bicarbonate-free sample from its actual pH up to pH 7.4.)

The use of an iridium oxide electrode obtained by sputtering onto alumina (Al_2O_3) for measuring the acidity in HF solutions is an example of measurements in environments that are corrosive to the glass electrode.[97] Other applications of this type of pH sensor have been described by the same group of authors.[45,128,129] Bordi et al.[47] reported the use of thermally prepared iridium/iridium oxide electrodes for measurements of pH in hydroorganic solutions (among them dimethylsulfoxide) at subzero temperatures. In this case, measurements using the glass electrode would be difficult.

Another application of pH-sensitive electrodes is their use to measure the pH of an internal solution in gas-sensing probes, e.g., CO_2, NH_3, SO_2. The working principle of gas-sensing electrodes is simple. Dissolved gas (e.g., CO_2) from the sample diffuses through a gas-permeable membrane until a reversible equilibrium is established between the gas level of the sample and the internal filling solution ($NaHCO_3$ solution in the CO_2 probe case). The hydrogen ion activity of the internal filling solution is measured by the internal pH sensor and is directly proportional to the level of gas in the sample. This internal pH sensor should be easy to miniaturize and design to proper shape. Mascini and Cremisini[130] used an antimony electrode obtained by thermomolding a mixture of powdered antimony and a thermoplastic polymer in gas-sensing probes for NH_3, CO_2, and SO_2. The antimony electrodes have appeared to be useful as internal electrodes in these probes. The monocrystalline antimony electrode was also used in CO_2 probe by Markdahl-Bjarme and Edwall.[131] Other researchers have also designed and used carbon dioxide gas-sensing electrodes employing an antimony electrode as the internal pH sensor.[132-135]

An application of the palladium/palladium oxide electrode in a sensor for *in vivo* CO_2 measurements has been described by Niedrach and Grubb.[136] A very interesting application is in a combination electrode for *in vivo* application. The CO_2-permeable membrane in a CO_2 sensor is replaced by a pH-sensitive polymer membrane.[137] An internal Pd/PdO electrode measures CO_2 by sensing the pH change against an internal reference electrode. The pH is measured against an external reference electrode. This works because the pH-sensing membrane and the Pd/PdO electrode cancel internal pH changes with respect to the external reference electrode and only the external pH affects the potential with respect to the external reference electrode. The pH-sensitive electrodes of this group are also used in enzymatic sensors when hydrogen ions are involved in an enzymatic reaction of the analyte. Alexander and Joseph[138] prepared and studied an enzyme electrode in which urease immobilized in polyvinyl chloride was used to coat an antimony electrode in order to detect changes in pH when the electrode was immersed into the urea solution. Also, a miniature enzyme sensor sensitive to urea employing an antimony electrode (tip diameter, 50 to 500 μm) was prepared by Joseph.[139]

Ianniello and Yacynych[140] used an iridium dioxide electrode in an enzymatic sensor for urea. A similar miniaturized palladium-palladium oxide enzyme electrode was used for urea determination by Szuminsky et al.[141]

The iridium dioxide electrode was also used in the design of proteolytic enzyme sensors utilizing chymotrypsin and trypsin which were immobilized via cyanuric chloride to the NaOH-activited hydroxyl groups of IrO_2.[142]

VI. CONCLUSIONS

The antimony-antimony oxide electrode (particularly the monocrystalline ones) can be used for the measurement of pH in special cases. Examples are measurements in body fluids *in vivo* or when a low impedance measuring system is desirable. The purity of the antimony is very important since the working principle is based on a corrosive process. Impurities would lead to pit formation and memory effects.

- More work is needed to elucidate the working mechanisms of the palladium and iridium electrodes. It is clear, however, that the AIROF iridium electrode can be used with advantage for the measurement of pH, especially in cases where the antimony electrode cannot be used because of its sensitivity to oxygen or phosphates.
- Among the metal-metal oxide electrodes, both the AIROF electrode and the sputtered iridium electrode hold promise for the future as pH-sensing devices.
- Once the working mechanisms have been elucidated, it is likely to become possible to draw more detailed conclusions about optimization of measurements using these devices. A good example of this is the antimony-antimony oxide electrode.

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