



# Analyzing the Properties of Iridium Oxide(IrOx) Derived Electrochemical Sensors

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## Introduction:

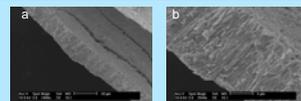
The IrOx pH sensor is an inexpensive, miniaturized, and versatile electrochemical sensor that poses great industrial and biological potential. The standard glass pH electrodes used today are expensive, fragile, and difficult to miniaturize based on current manufacturing technologies. Due to these limitations, glass pH electrodes cannot be used for many applications such as implantable devices, patient blood testing, and foods. In past years, melt-oxidized iridium wires have shown considerable promise in overcoming these limitations. Recently SensIrOx, a company producing these sensors, has made progress in manufacturing these sensors. IrOx sensors obtained from SensIrOx were tested in our lab and compared to initial claims that have not been reproducible by other researchers.<sup>2</sup>

## Formation of melt-oxidized Ir sensor:

Ir metal wires are positioned in a gold foil lined aluminum crucible covered with a Li2CO3 powder within a furnace at 870 °C for 5 hours. They are then dried at 120 °C overnight. One end is bombarded with small glass beads and a gold contact is secured at the tip with a silver epoxy.



Figure 1. Iridium electrodes (1 cm) attached to gold contact purchased from SensIrOx. Left most probes shows destruction of oxide layer of flawed probes by hydration



SEM images of scraped oxide layer (20–25 μm) Figure 2.a) Shows amorphous oxide layer of a scraped probe

b) High magnification picture of dense and amorphous oxide layer

## Initial Claims:

Melt-oxidized IrOx sensors were initially claimed to have:

- Excellent mechanical stability (In the presence of strong reducing agents and oxygen)
- Very fast response times and stability in a wide variety of mediums (Wet or Dry, High temperature/ pressure, wide pH range)
- Excellent reproducibility (In slope and drift [i.e. 0.1 mV/day])

## Theory:

When the potential of an electrode is measured against a suitable reference electrode (e.g. a standard Ag/AgCl electrode), its relationship to ionic activity is logarithmic. Using the Nernst equation, the slope and E values can be derived by:

$$E = E^{\circ} + 2.3 \frac{RT}{\nu F} \log a$$

Applying the Nernst equation to an iridium oxide chemical equation gives:



$$E = E^{\circ} + \frac{2.303RT}{F} \log[\text{H}^+] = E^{\circ} - 59.15 \text{ pH}$$

There is a 59.15 mV difference for every power of ten change in ionic activity. Thus, there is an expected -59.15 mV slope for every change in pH.

## Experiment:

Open-circuit potential of IrOx electrodes were measured as a function of the pH of the test solution vs. a single junction Ag/AgCl reference electrode (with 4 M KCl internal solution, obtained from Fisher Scientific). These measurements were done using Gamry PC4/750 Potentiostat/Galvanostat/ZRA and Gamry DC Corrosion Potential Software. The tests were first run using dry, un-soaked, probes in pH buffers of pH 2, 3, 6, 8, 10, 11, 12. Tests were then done using probes soaked in a commercial pH 7 buffer solution (obtained from Fisher Scientific) for a several day break-in period. Attempts were made to isolate the possible drift due to hydrophilic interaction by layering the contact with different low viscosity coatings. A mixture of toluene and polystyrene (200ml per 0.026g) with added isopropanol (25% of mixture) was created, soaked and air dried onto IrOx/gold contact. Another attempt to prevent upwards creep used Flash super glue (cps 1-3) while contact was encapsulated by a glass capillary tube. When in the presence of .5 M ferricyanide, stability was observed indicating resistance to strong reducing agents. Extended exposure to pH 12 Buffer appears to greatly affect probe readings.

## Data:

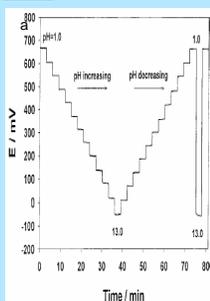


Figure 3. Potential response of an IrOx electrode (batch 1) to pH changes at a series of pH buffer solutions from pH 1 to 13.

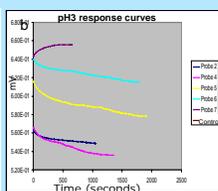


Figure 3b. Dry probes produced slow response times for the potential to level off and high drift was observed. Response times took anywhere from a few minutes to 35+ minutes

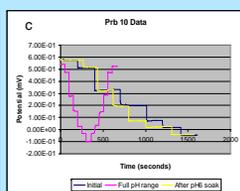


Figure 3c. When hydrated, response curves were near instantaneous and drastically little or no noticeable drift was observed in the span of several minutes

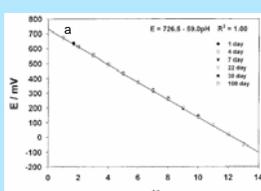


Figure 4. Long-term stability of the IrOx pH electrode (batch 2) in pH buffer solutions. Between the tests, the pH electrode was stored in air, in a pH buffer, or in a 4 M KCl solution.

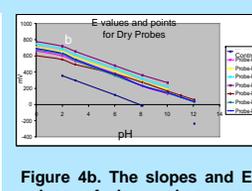


Figure 4b. The slopes and E<sup>0</sup> values of dry probes were different among each other and themselves

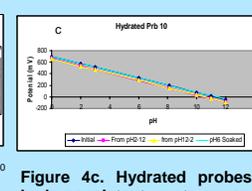


Figure 4c. Hydrated probes had consistent, yet super-Nernstian slopes. E<sup>0</sup> values however, varied

Even with a hydrated probes that yielded best responses(4c), the perfectly consistent results of original claims(4a) (extreme reproducibility and consistency) is lacking with our current data. Dry probes yielded scattered E<sup>0</sup> values and slopes around expected value

## Possible Causes of Drift:

The hydrophilic nature of IrOx may potentially cause the solution to creep up and measure the potential of the gold contact. Despite attempts to block solution contact, drift was still present. Other sources of drift include possible porosity (figure 5b) serving as pinholes resulting in current leakage; possible aging in water or air dramatically transforms the iridium oxide solid structure from Li8IrO6 to another not yet identified structure (figure 5a) and may explain the observed drift.<sup>2</sup> According to the original publications, drift should be ~1mV/day. It is presently uncertain why this discrepancy exists, however the general progress thus far does not fully support most of the initial claims made regarding the IrOx pH sensors made in a lithium carbonate melt bake.

Figure 5 illustrates probably causes of drift due to third outer layer(5a) or porosity(5b).

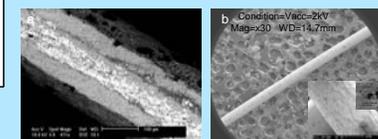


Figure 5. a) BSE scan showing outer hydrated layer, oxide, and iridium b) SEM of outer IrOx surface

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S. Yao, M. Wang and M. Madou, "A pH Electrode Based on Melt-Oxidized Iridium Oxide", *Journal of the Electrochemical Society*, 148 [4] H29-H36 (2001).  
Santi Christanti, "A pH Electrode Based on Melt-Oxidized Iridium Oxide", A Thesis Presented in Partial Fulfillment of the Requirement for the Degree Master of Science in the Graduate School of The Ohio State University (2003).