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.[3]

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 Oxide electrodes (1 cm) attached to gold contact purchased from SenseIrOx. Left most 3 probes shows destruction of oxide layer of flawed probes by hydration

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 E values can be derived by:

\[ E = E^0 + \frac{2.303RT}{nF} \log a \]

There is a 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.

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 values and slopes around expected value 2.303RT/a

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 Li2Ir6O12 to another not yet identified structure (figure 5a) and may explain the observed drift. 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.

Data:

Contrary to initial claims (3a) that dry probes produced similar results to hydrated probes, only hydrated probes produced fast response times (3c).

Reproducibility of measurements for good probes (3c) were close, but do not fully support initial claims. The different potentials at the same pH indicate that calibration is needed when running new measurements. Long term drift is still an issue for hydrated probes.

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])

Figure 1. pH response curves

Figure 2a. Shows amorphous oxide layer of a scraped probe

Figure 2b. High magnification picture of dense and amorphous oxide layer

Figure 3b. Dry probes produced slow response times for the potential to level off and high drift were 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 4b. The slopes and E values of dry probes were different among each other and themselves

Figure 4c. Hydrated probes had consistent, yet super-Nernstian slopes. E values however, varied

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

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