A $P_H$ 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

By
Santi Chrisanti, B.S

****
The Ohio State University
2003

Master’s Examination Committee:

Approved by

Dr. Henk Verweij, Adviser
Dr. Charles Drummond

Adviser
Department of Materials Science and Engineering
ABSTRACT

In this report, the experimental work for the project “A pH electrode, based on melt-oxidized iridium oxide” is presented and discussed. A metal oxide pH sensor was fabricated by oxidation of iridium metal wire (usually 0.25 mm diameter, Ø) via a melt oxidation route, in which lithium carbonate is used as oxidizing agent. Sensors were tested and characterized by using XRD, TGA, Raman Spectroscopy, FIB-SEM, TEM, and ICP. After oxidation a black oxide coating with thickness of ~25 µm was formed around iridium wire. A columnar type of structure is observed growing perpendicular from the iridium wire core. For some wires the oxide consists of two layers: The outer layer consists of grains which are mostly crystalline with an amorphous grain boundary phase. The inner layer is dense and amorphous. Aging in water or air causes a transformation in the iridium oxide as observed in Raman and XRD spectra, and may explain the drift observed. The XRD spectrum of non-treated, non-hydrated melt-oxidized wire matches best with the known XRD pattern of Li₈IrO₆. Hydrolysis, for instance by aging in water, dramatically changes the solid structure from Li₈IrO₆ to another structure which is not yet identified. It is also possible that part of the Li₈IrO₆ dissolves completely and that other, more Ir-rich phases are present between the Ir wire core and the Li₈IrO₆ surface layer.
Dedicated to my parents and husband
ACKNOWLEDGMENTS

I wish to thank my adviser Dr. Henk Verweij for his patience, support and encouragement, especially for giving me a chance to work on this project.

I thank Dr. Charles Drummond for his time and willingness to serve as committee member.

Materials characterization could not have been accomplished without the help of Hendrik O. Colijn, Steven Bright and Cameron Begg.

Finally, I am grateful to Belinda Hurley (Department of Chemistry) for Raman experiment and all my colleagues at the Center for Industrial Sensors and Measurements (CISM), especially Jingyu Shi, Chonghoon Lee, Samuel Shian, Nick Szabo, and Osvaldo Figueroa. Above all, I cannot express my thanks to my parents and husband in Indonesia for their love, support and understanding.
VITA

<table>
<thead>
<tr>
<th>Year</th>
<th>Event</th>
</tr>
</thead>
<tbody>
<tr>
<td>December 25, 1976</td>
<td>Born – Bandung, Indonesia</td>
</tr>
<tr>
<td>1998</td>
<td>B.S Chemistry, Bandung Institute of Technology</td>
</tr>
<tr>
<td>1998 - 2000</td>
<td>Laboratory/Process Engineer, TOTAL Indonesie</td>
</tr>
<tr>
<td>2001 – present</td>
<td>Graduate Research Associate, The Ohio State University</td>
</tr>
</tbody>
</table>

FIELDS OF STUDY

Major Field: Materials Science and Engineering
Symbols and abbreviations

\( \gamma_i \): Activity coefficient of species ‘i’
\( \Delta \): Reading potential (Volts)
\( \epsilon_{R(T)} \): Fermi energy at temperature T
\( \epsilon_{i(0)} \): Fermi energy at temperature 0 K
\( \Phi_{ph} \): Electrical potential in phase \( ph \) (V)
\( \bar{\mu}_{i,ph} \): Electrochemical potential of \( i \) in \( ph \) (J/particle or J/mole)
\( \mu_{i,ph} \): Chemical potential of \( i \) in \( ph \) (J/particle or J/mole)
\( \mu^0_{i,ph} \): Reference chemical potential of \( i \) in \( ph \) (J/particle or J/mole)
\( \Omega \): Resistivity (Ohm)
\( \pm \): Positive or negative ion with similar characteristics
\( [i]_{ph} \): Concentration of \( i \) in phase \( ph \)
\( \nabla f \): grad \( f = \frac{\partial f}{\partial x} i^{+} + \frac{\partial f}{\partial y} j^{+} + \frac{\partial f}{\partial z} k \)
\( \Delta f \): \( \frac{\partial^2 f}{\partial u^2} \)
\( ph \): Phase variable
\( A_{ph} \): Characteristic cross-section in phase \( ph \).
\( a_Y \): Activity of the ionic species ‘Y’.
\( e' \): Electron
\( b_{i,ph} \): Mechanical mobility of \( i \) in \( ph \) (s/kg)
\( D_i \): Field diffusion coefficient of phase \( i \)
\( E_{ph} \): Electric field in phase \( ph \) (V/m)
\( E \): Observed potential (Volts)
\( E^0 \): Standard potential (Volts)
\( F \): Faraday constant, 96487 C mol\(^{-1}\)
\( h \): Planck’s constant (6.6261×10\(^{-34}\)J)
\( \hbar \): Planck’s constant divided by 2\( \pi \) (1.0546×10\(^{-34}\) J )
\( H^+ \): Hydrogen ion
\( i \): Particle variable
\( I_{i,ph} \): Electric current due to species \( i \) in phase \( ph \) (A)
\( J_{i,ph} \): Particle flux of \( i \) in \( ph \) (1/m·s)
\( k_B \): Boltzmann constant, 1.3806x10\(^{23}\) J/K
\( k_p \): Parabolic rate constant
\( n \): Number of electrons transferred at the electrode
\( N_A \): Avogadro’s number, \( 6.022 \times 10^{23}/\text{mol} \)
\( p_{\text{CO}_2} \): Partial pressure of \( \text{CO}_2 \)
\( p_{\text{O}_2} \): Partial pressure of \( \text{O}_2 \)
\( p_H \): \(-\log[H^+]\)
\( q_{\text{el}} \): Elementary charge, \( 1.6 \times 10^{-19} \, \text{C} \)
\( q_i \): Charge of \( i \)
\( R \): Gas constant, \( 8.314 \, \text{JK}^{-1}\text{mol}^{-1} \)
\( T \): Absolute temperature (K)
\( t \): Time
\( x_{ph} \): Linear distance in phase \( ph \)
\( Z_M \): Valency of the metal
\( z_i \): Ion charge of \( i \) in units of elementary charge.
AIROF: Anodic Iridium Oxide Film
DTA: Differential Thermal Analysis
FET: Field Effect Transistor
Ir: Iridium
IrO\(_x\): Iridium Oxide
IROF: Iridium Oxide Film
SIROF: Sputtered Iridium Oxide Film
SCE: Standard Calomel Electrode
SHE: Standard Hydrogen Electrode
TGA: ThermoGravimetric Analysis.
XPS: X-Ray Photoelectron Spectroscopy.
EDS: Energy Dispersive X-Ray analysis.
SIMS: Secondary Ionic Mass Spectrometry.
ICP: Inductively Coupled Plasma.
SEM: Scanning Electron Microscope.
TEM: Transmission Electron Microscope.
FIB: Focused Ion Beam.
# TABLE OF CONTENTS

Abstract                          ii  
Dedication                        iii 
Acknowledgment                   iv  
Vita                             v  
Symbol and abbreviations        vi  
Table of contents                viii 
List of tables                   xi  
List of figures                  xii  

Chapters:

1. Introduction                  1  
2. Literature review             4  
   2.1. Iridium and iridium oxide 4  
   2.2. Iridium oxide fabrication methods 8  
      2.2.1. Electrochemical growth 8  
      2.2.2. Electrodeposition 10  
      2.2.3. Sputtering 10  
      2.2.4. Sol-gel deposition 11  
      2.2.5. Thermal deposition 11  
   2.3. $p_H$ electrode based on melt-oxidized iridium oxide 12  
      2.3.1. Lithium carbonate as oxidizing agent 12  
      2.3.2. Iridium oxidation mechanism in lithium carbonate melt 17  
   2.4. Lithium insertion 18  
      2.4.1. Lithium insertion with 2-phase product of IrO$_2$ and Li$_x$IrO$_2$ 18  
      2.4.2. Lithium insertion into single-phase Li$_2$IrO$_3$ 19  
   2.5. Role of gold in iridium oxidation 22  
      2.5.1. Reaction of alkali metal carbonate with aluminum oxide 22  
   2.6. $p_H$ sensing mechanism of IROF 23  
3. Thermodynamic theory          27  
   3.1. Definitions and assumptions 27  
      3.1.1. Buffering 27  
      3.1.2. Reference electrode 27
3.1.3. Salt bridge
3.1.4. Relevant phases
3.1.5. Relevant equilibria
3.1.6. Voltmeter
3.1.7. Space charge
3.1.8. Electrode morphology
3.2. Quantitative expression for the overall electrochemical potential
3.2.1. Relevant equilibria
3.2.2. Quantitative relation
3.2.3. Junction and interface
3.2.4. Expression for reading potential $\Delta_{\text{reading}}$
3.3. Potential drop across salt bridge by Henk Verweij
3.3.1. Assumptions
3.3.2. Derivations
3.3.3. Case 1: 3.3.3. Case 1: $I_{e,Cu} = 0$ and H$^+$ exchange penetration over $x_p$
3.3.4. Case 2: 3.3.4. Case 2: stationary and absence of H$^+$ exchange

4. Procedure
4.1. General preparation of iridium oxide and electrode
4.2. EMF measurement
4.3. Characterization
4.3.1. Thermogravimetry analysis (TGA)
4.3.2. Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM)
4.3.3. Energy Dispersive X-ray (EDX)
4.3.4. Inductively Coupled Plasma (ICP)
4.3.5. Secondary Ionic Mass Spectrometry (SIMS)
4.3.6. Raman spectroscopy

5. Sensor Testing
5.1. Effect if Hydration
5.2. Stability test
5.2.1. Reference electrode stability test
5.3. Effect of oxide surface on sensor’s properties
5.4. Effect of the presence of oxide
5.5. Role of gold foil
5.6. Importance of high impedance voltmeter

6. Sensor Characterization
6.1. Lithium carbonate
6.1.1. Lithium carbonate in air (oxidizing) atmosphere
6.1.2. Lithium carbonate in 5% H$_2$ – 95% N$_2$ (reducing) atmosphere
6.2. Surface and cross-sectioned SEM micrographs
6.3. Focused Ion Beam (FIB) cross-sections, coupled with SEM and TEM for phase identification 72
6.4. Focused Ion Beam cross-sections to investigate porosity 75
6.5. Raman Spectroscopy 76
6.6. X-Ray Diffraction (XRD) 82
6.7. Chemical composition 88
   6.7.1. Inductive-coupled plasma (ICP) 88
   6.7.2. Thermogravimetry analysis (TGA) 91
   6.7.3. Energy Dispersive X-ray (EDX) analysis 93
   6.7.4. Secondary Ionic Mass Spectrometry (SIMS) 94

7. Summary 96

Bibliography 98

Appendix A. Conversion charge calculation 101
LISTS OF TABLES

Table 2.1: Possible forms of iridium oxide and oxyhydroxides [22] .......................... 24
Table 5.1: Effect of surface condition ........................................................................ 59
Table 5.2: Gold effect on sensors performance ............................................................. 61
Table 6.1: Raman peaks position of iridium wire before and after transformation .. 81
Table 6.2: Lithium and iridium content from ICP ...................................................... 89
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>The rutile structure viewed along the c axis [c]</td>
<td>6</td>
</tr>
<tr>
<td>2.2</td>
<td>Iridium (IV) oxide structure[5]</td>
<td>7</td>
</tr>
<tr>
<td>2.3</td>
<td>A drawing which depicts the arrangement of the atoms inside a unit cell of tetragonal IrO$_2$</td>
<td>8</td>
</tr>
<tr>
<td>2.5</td>
<td>DTA and TG results for Li$_2$CO$_3$ during heating at 10 K/min [12]</td>
<td>13</td>
</tr>
<tr>
<td>2.6</td>
<td>Dependence of ΔT and T on time during consecutive heating of Li$_2$CO$_3$</td>
<td>14</td>
</tr>
<tr>
<td>2.7</td>
<td>DTA and TG results for Li$_2$CO$_3$ during heating and cooling process [12]</td>
<td>15</td>
</tr>
<tr>
<td>2.8</td>
<td>Schematic diagram of oxidation in carbonate melts via O$_2^{2-}$ ions [13]</td>
<td>16</td>
</tr>
<tr>
<td>2.9</td>
<td>XRD pattern for Li$_2$CO$_3$ synthesized in air at 1223 K for 48 h. The hkl indexed by the pseudo-hexagonal lattice are indicated in the figure [16]</td>
<td>19</td>
</tr>
<tr>
<td>2.10</td>
<td>The ab plane projection of the structure of Li$_2$RuO$_3$, showing successive (Ru$_2$Li) layers. Filled circles: Ru ions, open circles: Li ions. Anions are omitted in the figure [16].</td>
<td>34</td>
</tr>
<tr>
<td>3.1</td>
<td>Copper I/iridium junction</td>
<td>35</td>
</tr>
<tr>
<td>3.2</td>
<td>Iridium/Li$_2$IrO$_3$ junction</td>
<td>35</td>
</tr>
<tr>
<td>3.3</td>
<td>Li$_2$IrO$_3$/solution junction</td>
<td>37</td>
</tr>
<tr>
<td>3.4</td>
<td>Ref electrode/Pt junction</td>
<td>37</td>
</tr>
<tr>
<td>3.3</td>
<td>Pt/copper II junction</td>
<td>37</td>
</tr>
<tr>
<td>4.1</td>
<td>IrO$_3$ with gold wire (left) and with cap (right)</td>
<td>48</td>
</tr>
<tr>
<td>5.1</td>
<td>Sensor potential at $p_H$ 4 (left) and $p_H$ 8 (right)</td>
<td>51</td>
</tr>
<tr>
<td>5.2</td>
<td>Calibration curve ($p_H$ vs potential)</td>
<td>52</td>
</tr>
<tr>
<td>5.3</td>
<td>Sensor potential at $p_H$ 4 (left) and $p_H$ 8 (right) after hydration in deionized water for 2 days</td>
<td>53</td>
</tr>
<tr>
<td>5.4</td>
<td>Calibration curve ($p_H$ vs potential) after hydration in deionized water for 2 days</td>
<td>54</td>
</tr>
<tr>
<td>5.5</td>
<td>Stability test at $p_H$ 4</td>
<td>55</td>
</tr>
<tr>
<td>5.6</td>
<td>Reference electrode half cell diagram</td>
<td>56</td>
</tr>
<tr>
<td>5.7</td>
<td>Reference electrode potential difference after external solution re-fill in saturated KCl (left) and $p_H$ 6 (right)</td>
<td>57</td>
</tr>
<tr>
<td>5.8</td>
<td>Sensors with different surface condition potential at $p_H$ 4</td>
<td>58</td>
</tr>
<tr>
<td>5.9</td>
<td>Noble metal potential in buffer $p_H$ 4</td>
<td>60</td>
</tr>
<tr>
<td>6.1</td>
<td>Ir wire before (left) and after oxidation (right)</td>
<td>63</td>
</tr>
<tr>
<td>6.2</td>
<td>TG curve for 99% purity Li$_2$CO$_3$ (left) and 99.999% purity (right)</td>
<td>65</td>
</tr>
<tr>
<td>6.3</td>
<td>Phase diagram of Li$_2$CO$_3$-Li$_2$O [25]</td>
<td>66</td>
</tr>
<tr>
<td>6.4</td>
<td>TG curve for 99.999% Li$_2$CO$_3$ in reducing atmosphere</td>
<td>67</td>
</tr>
<tr>
<td>6.5</td>
<td>Surface micrograph of the sensor</td>
<td>68</td>
</tr>
<tr>
<td>6.6</td>
<td>Cross section micrograph of the sensor with split end</td>
<td>69</td>
</tr>
</tbody>
</table>
Figure 6.7: Cross section micrograph of the sensor
Figure 6.8: Oxide tip with manual cutting (left) and laser cutting (right)
Figure 6.9: Surface micrograph of IROF with gold used during fabrication
Figure 6.10: Surface micrograph of IROF without using gold during fabrication
Figure 6.11: Schematic diagram of figure 6.7
Figure 6.12: SEM micrograph for the inner layer: amorphous phase
Figure 6.13: SEM micrograph for the outer layer: crystalline grains with amorphous phase grain boundary
Figure 6.14: TEM micrograph of the inner layer
Figure 6.15: TEM micrograph of the outer layer
Figure 6.16: Inner layer TEM diffraction pattern
Figure 6.17: Outer layer TEM diffraction pattern
Figure 6.18: TEM micrograph of selected area of figure 6.15, 1: pores, 2: amorphous grain boundary, 3: mostly-crystalline grain
Figure 6.19: FIB-shaved oxide surface layer
Figure 6.20: Pores at ~5 µm depth of figure 6.19
Figure 6.21: Pores at ~15 µm depth of figure 6.19
Figure 6.22: Raman spectra of wires (A, B, C and D) produced via one batch of the melt oxidation method
Figure 6.23: Raman spectra of Lithium carbonate (left) and iridium oxide single crystal (right)
Figure 6.24: Raman spectra of wire C aged in normal air
Figure 6.25: Raman spectra of wire A stored in water
Figure 6.26: Comparison of wire stored in air for 9 days (blue) vs. stored in water for 4 days (red)
Figure 6.27: XRD for IrOx wire stored in air for 4 days (Red lines: Li$_8$IrO$_6$ pattern, green lines: MgO pattern)
Figure 6.28: Lithium carbonate XRD peaks (PDF # 22-1141)
Figure 6.29: XRD for IrO$_x$ wire stored in air
Figure 6.30: XRD for IrO$_x$ wire stored in water over 23 days
Figure 6.31: XRD for IrO$_x$ wire stored in air for 4 days (Red lines: Li$_8$IrO$_6$ pattern, green lines: MgO pattern)
Figure 6.32: TG curve for IrO$_x$
Figure 6.33: TG curve for blank crucible
Figure 6.34: EDX spectrum for grain in figure 6.15
Figure 6.35: SIMS spectra for iridium oxide
CHAPTER 1

INTRODUCTION

Due to limitations in the use of the glass electrode for $p_H$ sensing, alternative $p_H$ sensors have been intensively studied [1]. One of the options is to use metal oxides, such as PtO$_2$, IrO$_2$, RuO$_2$, OsO$_2$, Ta$_2$O$_5$ and TiO$_2$. These oxides, mainly from the high valence acid-oxide formers and transition metal groups, can be insoluble and stable in various aqueous environments. They have electronic conductivities due to a slightly non-stoichiometric composition. Generally these oxides show particular point-defect structures such as oxygen deficiency or cation interstitials and a corresponding deviation (reduction) of the ideal oxidation state of the predominant metal. The stoichiometry of the oxide can be changed slightly or significantly by heating to generate a greater deficit of oxygen with a simultaneous generation of a lower valence oxide or the metal itself when no lower oxide exists. Mixed valence oxides can also be formed by addition of foreign metal dopants, such as Sb added to SnO$_2$ [2].

Five different explanations of the electrode mechanism for these oxides have been formulated [2]:

- Simple ion exchange on a surface layer containing –OH groups. This mechanisms is known from the common glass electrode.
• A redox equilibrium between two different solid phases, i.e. a lower and a higher valence oxide, or an oxide and a pure metal phase, such as the antimony electrode:

\[
\text{Sb}_2\text{O}_x + 6\text{H}^+ + 6\text{e}^- \rightleftharpoons 2\text{Sb} + 3\text{H}_2\text{O}
\]  

(1.1)

• A redox equilibrium involving only one solid phase whose hydrogen content can be varied continuously by passing current through the electrode. This is known as a solid solution or intercalation reaction. The process scheme may be written as:

\[
\text{H}_x\text{MO}_n + y\text{H}^+ + ye^- \rightleftharpoons \text{H}_{x+y}\text{MO}_n
\]  

(1.2)

A single phase oxygen intercalation electrode may similarly be envisaged, though no examples of \(p_H\) electrodes involving oxygen-deficit phases have been demonstrated.

• A steady-state corrosion of the electrode material may, in some cases, cause a \(p_H\) - dependent potential.

Iridium oxide (IrO\(_x\)) electrodes have received considerable attention in recent years. Their advantages over conventional glass electrodes and other metal oxide electrodes were shown to include good stability over a wide \(p_H\) range, even at high temperatures up to 250ºC, at high pressure, and in aggressive environments, with fast response time even in non-aqueous solutions [1]. Besides its use as a \(p_H\) electrode, IrO\(_x\) is also well known as an anode material for oxygen and chlorine evolution and as an electrochromic material. For all these application, the characteristics of IrO\(_x\) are generally very sensitive to its structure and composition, which depends on the fabrication methods and conditions. This is the main reason why IrO\(_x\) \(p_H\) electrodes prepared by different methods show various characteristics [1].
Many IrO$_x$ synthesis routes have been proposed in the literature. Recently the route of IrO$_x$ formation on an Ir wire by Li$_2$CO$_3$ melt oxidation route was claimed to result in highly reproducible and reliable $p_H$ sensors [1]. Unfortunately this result has not been reproduced by other researchers. The objectives of the present work is to obtain a method for reproducible and reliable IrO$_x$ sensors using the Li$_2$CO$_3$ melt oxidation route and to obtain a better understanding of the relation between processing and properties of IrO$_x$ sensors.

In this thesis, IrO$_x$ sensors were fabricated by melt-oxidation method. Characterization included:

- **Chemical composition** of the oxide including an attempt to determine the valence of the iridium ions. Inductively Coupled Plasma (ICP) was used for elemental analysis of iridium and lithium. Thermogravimetric Analysis (TGA) was initially used to measure the oxygen content, but apparently this method was not suitable for such measurements due to lithium evaporation at high temperature (above 900ºC).

- **Crystal structure, microstructure and porosity.** Scanning Electron Microscopy (SEM) was used to reveal the surface and cross-section microstructure, while Transmission Electron Microscopy (TEM), together with a Focused Ion Beam (FIB) method were used to determine the phase(s) of the oxide. FIB in combination with SEM were used to detect any porosity in the oxide. Raman Spectroscopy and X-Ray Diffraction (XRD) were used to study any change that may occur during sensor aging in water and air. XRD was also used to identify the oxide structure before and after aging.
2.1. *Iridium and iridium oxide*

M. Pourbaix [3], described iridium as a very noble metal. It is stable in the presence of aqueous solutions of all \( \rho H \)'s, and free from complexing substances. At temperatures around 25°C it is unaffected by water, aqueous solutions of caustic alkalis, acids and oxidizing agents (including aqua regia). The resistance of iridium to aggressive chemical reagents is noteworthy. For the metal to be attacked and converted to iridates it must be fused with an alkaline oxidizing mixture (molten KOH and KNO\(_3\)). Some of the iridates formed are soluble and some are insoluble in water.

In finely divided state (“iridium black”), iridium is soluble in hot concentrated aqua regia. The dissolution most probably takes place through the formation of complex ions in which iridium has a valency of +3 or +4. At atmospheric pressure and 25°C iridium can absorb 807 times its own volume of hydrogen. When used as an anode, iridium is not usually attacked, even in the presence of chlorine liberated by electrolysis. Oxygen is adsorbed onto the metal surface when an iridium anode is polarized in the presence of dilute sulfuric acid or dilute caustic soda, even when the potential is low (i.e. below the oxygen
overpotential). When used as a cathode, iridium absorbs hydrogen, which gradually penetrates into the metal [3].

On heating in air or oxygen, iridium is tarnished owing to superficial oxidation to IrO₂; at temperatures above ~1130°C the oxide decomposes, and the metal becomes shiny again. IrO₂ is insoluble in acid solutions, and soluble in alkaline, oxidizing solutions. At temperatures of 750-1000°C, iridium loses weight through volatilization, most likely as IrO₄. In practice anhydrous IrO₂ (blue to black) can be prepared by heating a mixture of iridium, KOH and KNO₃ to red heat, or by heating finely divided iridium in air. It is insoluble in acids (including aqua regia), and in bases. On the other hand, when it is freshly prepared (e.g. by treating a boiling alkali metal iridochloride solution with KOH or NaOH in the presence of air), the hydrate IrO₂·2H₂O or Ir(OH)₄ (blue-black) is soluble in hydrochloric acid, nitric acid and sulphuric acid [3].

The anhydrous oxide Ir₂O₃ is practically impossible to prepare. Its hydrated form Ir₂O₃·xH₂O (yellow-green to blue-black) is readily soluble in acids and alkali, and is easily oxidized to IrO₂·2H₂O by the common oxidizing agents, including air [3].
IrO$_2$ crystallizes in the rutile structure. Two parameters describe the rutile structure, namely the axial ratio $c/a$ and the anion position parameter $x$. The rutile structure has edge-sharing octahedrally coordinated metal ions which form chains along the [001] direction. The chains are cross-linked by shared corners so that each chain is connected to four neighbouring chains. The MO$_6$ octahedra do not have equal M-O bond distances, but rather are tetragonally distorted with both the apically compressed and apically elongated geometry being known. A feature of the rutile structure is that the O-O bonds within the MO$_6$ also are not equal, so the base of the octahedron is not square, the shared edge being shorter than the edge parallel to the $c$ axis [4].
The IrO$_2$ rutile space group is P4$_2$/mm and there are two molecules in a unit cell of dimensions $a = b = 0.4498$ nm and $c = 0.3154$ nm. The distance from the Ir to each of the four oxygens on a (110) or a (11$ar{1}$0) plane is 0.202 nm, whereas the distance is 0.190 nm to the oxygens on the [110] or the [11$ar{1}$] axis. The point symmetry at the Ir site is 2/m2/m2/m, with the [001], [110] and [11$ar{1}$] axes as the twofold axes. The point symmetry at the oxygen site is mm, with the (001) plane and the (110) or (11$ar{1}$0) plane as the mirror planes [6].
2.2. Iridium oxide fabrication methods

Possible fabrication methods for iridium oxide films are: electrochemical growth, electrodeposition, reactive sputtering, sol-gel, and thermal preparation methods.

2.2.1. Electrochemical growth

A hydrous oxide layer is grown on the surface of iridium when it is electrochemically activated in an electrolyte. This oxide is porous and can assume several oxidation states, which gives it a very high charging capacity as well as the ability to deliver charge to an aqueous solution. This material is also exceptionally resistant to dissolution and corrosion during in vitro and in vivo stimulation [7].

Figure 2.3: A drawing which depicts the arrangement of the atoms inside a unit cell of tetragonal IrO$_2$ [6].
Figure 2.4 describes the build up of the multi-layer iridium oxide film formed by cyclic voltammetry. In this context it is interesting to note that, while in principle an oxidized electrode could be prepared by cycling its potential in a solution of any $pH$, in practice it is found that only a limited range of solutions, such as $H_2SO_4$ and NaOH, lead to the desired result. Dissolution of the electrochemically formed oxide occurs with very acidic electrolytes (e.g. 5M $H_2SO_4$). The morphology of the hydrous films also depends on the electrolyte. An electrochemically prepared $pH$ electrode is probably best formed by cycling in dilute acid [7].
2.2.2. Electrodeposition

In the electrodeposition method, Iridium Oxide Film (IROF) can be deposited on a variety of electronically conducting substrates, such as glassy carbon, Ti, Pt or Pt/Krypton film. This method is useful to produce ultramicroelectrodes and is less expensive than the electrochemical method since it does not require Ir substrates.

M.A. Petit and V. Plichon [8] deposited IrO$_x$ films on conducting transparent SnO$_2$-coated glass substrates by using K$_3$IrCl$_6$ as a soluble iridium precursor. The electrochemical cell contained an IrO$_x$-coated electrode as a working electrode, a platinum wire as counter electrode and a KCl-saturated calomel electrode as a reference.

IrO$_x$ was deposited by driving a fixed anodic current density of about 35 $\mu$A/cm$^2$. Typical charge densities in the range of 35-350 mC/cm$^2$ were used, corresponding to deposition times between 1,000 and 10,000 s. The potential rapidly increased to a plateau value of 0.57 V (SCE).

2.2.3. Sputtering

Thin-film metal oxides have also been investigated for use as $p_{H^+}$ electrodes. K.G. Kreider, et al. [9] studied reactive sputtering of iridium metal targets in argon-oxygen atmospheres to produce 1 $\mu$m thick electrodes on alumina and silicon substrates.

At room temperature the films appear amorphous using XRD and a distinctive rutile pattern emerges from films deposited at 200ºC and above. The most stable films are generally deposited at very slow rates (<2 nm/min) and at room temperature. Freshly deposited films show little hysteresis and a near Nernstian potential-$p_{H^+}$ response. A decrease in standard potential difference, $E^0$, of approximately 200 mV was observed for electrodes
immersed in buffer solutions of $p_H$ 2, 7, and 12 over a period of 1-2 days. This aging effect could be largely reversed by exposing electrodes to air. Iridium oxide films deposited using water-saturated oxygen exhibit a lower redox sensitivity than annealed or dry sputtered-deposited films.

### 2.2.4. Sol-gel deposition

K. Nishio, et al. [10] established a method for the preparation of iridium oxide thin films by the sol-gel dip-coating process where iridium chloride was used as a starting material. The coating solution was prepared by reacting iridium chloride, ethanol and acetic acid. The iridium oxide coating was formed at a 2.0 cm/min withdrawn rate. Films heat-treated at 300ºC did not contain impurities. Iridium oxide crystallized at temperatures above 450ºC.

### 2.2.5. Thermal deposition

The most popular thermal deposition method is based on the pyrolysis of IrCl$_3$ on a Ti substrate at 400-500ºC. Other thermal methods include oxidation of Ir wire in molten KNO$_3$ at 420ºC, or direct oxidation of Ir metal (previously wetted in a NaOH solution) in air at 800ºC. Thermally oxidized iridium electrodes for $p_H$ monitoring showed a wide variation in equilibrium potential values: as much as 120 mV in aqueous buffer solution even though their potential-$p_H$ responses were all essentially Nernstian (i.e., 59 mV/$p_H$ at room temperature) [11].

Thermally prepared IROFs can be made much thicker than Anodic Iridium Oxide Films (AIROFs), and provide more reliable potential values. Generally, thermally prepared IrO$_x$ films are comparable in nature to the Sputtered Iridium Oxide Film (SIROF). Both are
called dry oxide films. Usually the hydrolysis of dry oxide films in water in a very slow process, which can take more than 2 months. Therefore, dry film-based electrodes often exhibit large aging effects, usually with the potential moving in a negative direction. [11].

2.3. \( p_H \) electrode based on melt-oxidized iridium oxide

Many approaches, as describe above, have been proposed and have been proven to be effective for improvement of the \( \text{IrO}_x \) electrode stability, oxygen-induced drift, and selectivity. However, the potential drift, which causes errors in \( p_H \) measurement, remains a serious obstacle to the widespread application of IROF-based \( p_H \) electrodes. To solve these problems, most likely, the key is to produce a high quality IROF.

A new approach to prepare \( \text{IrO}_x \) \( p_H \) electrodes by the high temperature oxidation method was recently developed [1]. In this method iridium wire is oxidized by using lithium carbonate in an alumina crucible with gold foil lining at the bottom of the crucible. The oxidation occurred at 870ºC for 5 hours, with heating and cooling rates of 5ºC/m. The electrode based on this oxide film exhibited very promising \( p_H \) sensing performance, with an ideal Nernstian response in the tested \( p_H \) range of 1 to 13. However efforts to reproduce the result of the paper [1] have not been successful yet.

2.3.1. Lithium carbonate as oxidizing agent

The behavior of lithium carbonate during heating is a subject of some controversy. Some authors claim that there are no thermal reactions before fusion begins at about 679ºC [12]. On the other hand, other authors postulate a phase transition at 405-415ºC. Barin [12] reports two polymorphic phase transitions at 350 and 410ºC with transformation enthalpies of transformations of 0.561 and 2.238ºkJ/mole, respectively [12].
P. Pasierb, et al. [12] studied the binary system of Li$_2$CO$_3$-BaCO$_3$, in which Li$_2$CO$_3$ was dried to constant weight at 200ºC. Standard TGA and Differential Thermal Analysis (DTA) measurements were done with heating rates of 10 or 3 K/min in air with flow rate of 6 dm$^3$/h.

Figure 2.5: DTA and TG results for Li$_2$CO$_3$ during heating at 10 K/min [12].

Figure 2.5 shows the DTA and TG curves determined during heating of Li$_2$CO$_3$ in the temperature range 25-777ºC. As seen in the inset of this figure, no thermal effects have been observed at the postulated phase transitions temperatures. This may be due to the rather small heat of phase transition. The sharp peak near 727ºC is due to Li$_2$CO$_3$ melting. According to Barin [12] Li$_2$CO$_3$ melts at 725ºC.
Figure 2.6 presents DTA curves in the coordinate systems: $\Delta T$ (right axis) and $T$ (left axis) versus time for Li$_2$CO$_3$ during subsequent heating and cooling runs. Two sharp peaks due to melting and solidification can be observed. However the characteristic temperatures of these peaks differ considerably. The melting peak starts at 694°C and achieves an extreme value at 732°C, the cooling peak starts at 675°C and its extreme value is at 679°C. This difference may be explained by analyzing a TG curve. As seen in Figure 2.6 and 2.7, the melting process is accompanied by a 3% weight loss [12].
The actual extent of decomposition will largely depend on $p_{\text{CO}_2}$. In addition the cooling peak is always at lower T due to supercooling effects regardless of compositional changes.

The Li$_2$O formed decreases the melting temperature of lithium carbonate. In the binary system Li$_2$O-Li$_2$CO$_3$ a eutectic mixture (containing 13 mole % of Li$_2$O with $T_{\text{melt}} = 705^\circ\text{C}$) exists [12].

In the carbonate melt the following equilibria are thought to exist [13]:

\[
\text{CO}_3^{2-} \rightleftharpoons \text{CO}_2 + \text{O}^2^- \quad (2.2)
\]

\[
\text{CO}_2 \rightleftharpoons \text{CO}^+ + \frac{1}{2}\text{O}_2 \quad (2.3)
\]
or

\[ \text{CO}_3^{2-} \rightleftharpoons \text{CO} + \frac{1}{2}\text{O}_2 + \text{O}^2- \quad (2.4) \]

Two different oxidative oxygen species were proposed [13]:

- **Superoxide ions** \( (\text{O}_2^\cdot) \)

  The formation of superoxide ions is given by:

  \[ 3\text{O}_2 + 2\text{CO}_3^{2-} \rightleftharpoons 4\text{O}_2^\cdot + 2\text{CO}_2 \quad (2.5) \]

  In contact with metal the superoxide ions may be reduced to peroxide ions:

  \[ \text{O}_2^\cdot + \text{e}^- \rightleftharpoons \text{O}_2^{2-} \quad (2.6) \]

**Figure 2.8**: Schematic diagram of oxidation in carbonate melts via \( \text{O}_2^{2-} \) ions [13].
and subsequently to oxide ions:

\[ \text{O}_2^2^- + 2e^- \rightleftharpoons 2\text{O}^{2-} \]  \hspace{1cm} (2.7)

- Peroxide ions (\(O_2^{2-}\))

The formation of peroxide ions is given by:

\[ \text{O}_2 + 2\text{CO}_2^3^- \rightleftharpoons 2\text{O}_2^{2-} + 2\text{CO}_2 \]  \hspace{1cm} (2.8)

In contact with metal, peroxide ions may also be reduced according to:

\[ \text{O}_2^{2-} + 2e^- \rightleftharpoons 2\text{O}^{2-} \]  \hspace{1cm} (2.9)

In the case of oxidation, the electrons necessary for the reduction reactions are delivered by the oxidation of metal M.

\textbf{2.3.2. Iridium oxidation mechanism in lithium carbonate melt}

Molten carbonate oxidation was intensively studied under Molten Carbonate Fuel Cell (MCFC) conditions. The species which play a role in the electrochemical reaction in the gas-molten carbonate-cathode system are \(\text{O}_2\), \(\text{CO}_2\), and \(\text{H}_2\text{O}\) [14].

The oxygen reduction mechanism under MCFC cathode conditions has been described in terms of several elemental reactions as follows [14]:

\[ \text{O}_{2\text{,gas}} + \text{CO}_{2\text{,gas}} \rightleftharpoons \text{O}_{2\text{,dissolved}} + \text{CO}_{2\text{,dissolved}} \]  \hspace{1cm} (2.10)

\[ \text{O}_2 + 2\text{CO}_2^3^- \rightleftharpoons 2\text{O}_2^{2-} + 2\text{CO}_2 \]  \hspace{1cm} (2.11)

\[ \text{O}_2 + \text{O}_2^{2-} \rightleftharpoons 2\text{O}_2\]  \hspace{1cm} (2.12)

\[ \text{O}^{2-} + e^- \rightleftharpoons \text{O}_2^{2-} \text{ (superoxide limiting reaction)} \]  \hspace{1cm} (2.13)
\[ O_2^2^- + e^- \rightleftharpoons O_2^2- + O^- \quad \text{(peroxide limiting reaction)} \]  
\[ (O^-) + e^- \rightleftharpoons O^2^- \]  
\[ O^2^- + CO_2 \rightleftharpoons CO_3^{2-} \]

The oxygen reduction mechanism is composed of two slower reactions (2.13) and (2.14) that limit the oxygen reduction rate. These reactions are the reduction of the peroxide ions and the reduction of the superoxide ions [14].

**2.4. Lithium Insertion**

**2.4.1. Lithium insertion with 2-phase product of IrO\(_2\) and Li\(_x\)IrO\(_2\)**

I.J. Davidson et. al., [15]. studied lithium insertion in the IrO\(_2\) structure by neutron and XRD powder methods. IrO\(_2\) was prepared by oxidation of Ir sponge in a stream of dry O\(_2\) at 1000°C for 24 h, 1190°C for 2 weeks, and 1190°C for 2 days in a higher pressure of O\(_2\). Lithium insertion was obtained by exposure at ambient temperature of the host rutile type MO\(_2\) to a 0.2 M solution of n-butyl lithium in hexane under argon in a glove box. After 1 to 2 weeks reaction, the hexane solution was decanted and the material was then rinsed twice with about 25 ml of hexane and dried under vacuum for about 2 h. The quantity of n-butyl lithium that had reacted was used to control the amount of lithium inserted. Maximum insertion was achieved at the Li\(_{0.87}\)IrO\(_2\) composition. Attempts to prepare samples with a larger lithium content by increasing the concentration of lithium in the solution had the effect of lowering the quantity of lithium inserted.

The intercalation product, Li\(_x\)IrO\(_2\) was reported to decompose very rapidly on exposure to air or moisture [15]. Compositions in the 0<x<1 range of were two-phase materials con-
sisting of unreacted host, \( x = 0 \), and the limiting composition with \( x = 0.87 \). Li\(_{0.87}\)IrO\(_2\) has an orthorhombic cell with \( a = 0.4962 \), \( b = 0.4758 \) and \( c = 3.108 \) nm. Compared to the host rutile (tetragonal) cell, the insertion compound is largely expanded along [100] and [010], and contracted along [001], in all cases by \( \sim 0.05 \) nm. The space group appears to be \( Pnnm \), a subgroup of the rutile space group \( P4_{2}/mnm \).

The Li\(_x\)RuO\(_2\) structure was determined from neutron diffraction data in which Li\(^+\) was found to be present in octahedral sites. The overall structure is essentially of the ordered Ni-As type. Attempts to solve the structure of Li\(_{0.87}\)IrO\(_2\) from either XRD or neutron powder diffraction data were unsuccessful, presumably due to severe preferred orientation effects [15].

### 2.4.2. Lithium insertion into single-phase Li\(_2\)IrO\(_3\)

![XRD pattern for Li\(_2\)IrO\(_3\)](image)

**Figure 2.9:** XRD pattern for Li\(_2\)IrO\(_3\) synthesized in air at 1223 K for 48 h. The \( hkl \) indexed by the pseudo-hexagonal lattice are indicated in the figure [16].
Hironori Kobayashi et al [16] prepared single phase Li$_2$IrO$_3$ by heating pre-dried, mixed and pelletized Li$_2$CO$_3$ and IrO$_2$ at 923-1223 K for 24-48 h. All the XRD peaks could be indexed by a pseudo-hexagonal cell with $a = 0.5169$ and $c = 1.446$ nm. The XRD pattern of Li$_2$IrO$_3$ shows characteristics peaks corresponding to those of Ru$^{4+}$ hexagonal networks in Li$_2$RuO$_3$. This suggests that Ir$^{4+}$ hexagonal network exists in LiIr$_2$ layers.

![Figure 2.10](image)

**Figure 2.10:** The ab plane projection of the structure of Li$_2$RuO$_3$, showing successive (Ru$_2$Li) layers. Filled circles: Ru ions, open circles: Li ions. Anions are omitted in the figure.

I. Felner et al [17] prepared a ternary oxide of Li$_2$IrO$_3$ by mixing Li$_2$CO$_3$ and iridium metal powder and preheating at 800°C for 24 h. The materials were then pulverized, pelletized and fired again at 800°C for 12 h. The pellets were pulverized and washed in hot distilled water to remove the excess Li$_2$CO$_3$ and then heated at 800°C for 24 h in air. XRD
studies confirmed a monoclinic structure (space group of C2/c) with no secondary phase detected. This material is paramagnetic down to 5K.

Based on the above references ([16] and [17]), Li$_2$IrO$_3$ can be prepared by mixing either iridium metal or iridium oxide with lithium carbonate, but different structures are reported.

In K$_x$IrO$_2$, the structure is found to be of the hollandite-type, with a mean Ir-O distance of 0.2-0.3 nm, in agreement with the presence partially reduced iridium [18]. Oxides with the hollandite structure, corresponding to the general formula $A_xM_8O_{16}$ ($A =$ Ba, Pb, K, Rb, Tl, Na; $M =$ Ti, Mn, Fe, Mg, Mo) form a large family and have been extensively studied for their ionic conductivity and as encapsulants for radioactive waste. At first sight the $[M_8O_{16}]^\infty$ host lattice is very simple. It consists of infinite rutile chains sharing the edges and the corners of their MO$_6$ octahedra and forming large square tunnels where the A cations are located. In general, however, the actual structure of these compounds is more complicated. A large number of these oxides exhibit superstructures, which have not yet been completely elucidated. This is the case, for instance, for the non-stoichiometric hollandites Ba$_x$Ti$_{8-x}$Mg$_x$O$_{16}$ and Ba$_x$Ti$_{8-2x}$Ga$_{2x}$O$_{16}$ with $0.8 < x < 1.33$, which exhibit a continuous variation of superlattice periodicity and multiplicity [19].

Ir oxide films grown in aqueous LiClO$_4$ solutions ($pH$~9) have been found to exhibit excellent charge capacities, charging and discharging kinetics, and stability in acetonitrile and propylene carbonate with LiClO$_4$ as supporting electrolyte. Discharging and charging of the oxide appears to involve Li$^+$ insertion and expulsion from the oxide [20].

In neutral aqueous solution, Li$^+$ insertion can occur rapidly during oxide reduction, although these ions are replaced by protons over time [20].
\[
\left[ \text{Ir(IV)oxide} \cdot x\text{H}_2\text{O} \right]_5 + 5e^- + 4\text{H}_2\text{O} + \text{Li}^+ = \left[ \text{Li}^+ \right] \left[ \text{H}_4\text{Ir(III)oxide} \cdot x\text{H}_2\text{O} \right]^- + 4\text{OH}^- \quad (2.17)
\]

or

\[
e^+ + \text{Ir}_n^+ + \text{Li}^+ \rightleftharpoons \text{Ir}_n^- + \text{Li}^- \quad (2.18)
\]

### 2.5. Role of gold in iridium oxidation

The role of gold in the oxidation process is not yet clear. Gold is generally regarded as being the least catalytically active noble metal. This is ascribed due to the d-band being completely filled, with the result that gold is unable to chemisorb small molecules. During the oxidation process alumina crucibles are generally used. Without a gold foil separating alumina from lithium carbonate, a meta-aluminate forming-reaction may occur as described in the paragraph below.

#### 2.5.1. Reaction of alkali metal carbonate with aluminum oxide

Reaction of lithium carbonate with aluminum oxide crucible material during sensor fabrication may occur. S. Gal et al. [21] studied the reaction of binary and ternary alkali metal carbonate mixtures with aluminum oxide under different conditions. Reaction products were identified by XRD. In the presence of binary and ternary carbonate mixtures, containing \( \text{Li}_2\text{CO}_3 \) the product was always \( \alpha \)-lithium meta-aluminate, transforming to the \( \gamma \)-form at higher temperatures, while the use of only \( \text{Li}_2\text{CO}_3 \) resulted in the formation of ortho-dialuminate as well [21]. Depending on the particle size, the ratio of mixing and the temperature reached, the chemical reactions described by the following equations can proceed between alkali metal carbonates and aluminum oxide:
\[
M_2CO_3 + Al_2O_3 \rightleftharpoons 2MAIO_2 (metalaluminate) + CO_2 \tag{2.19}
\]

\[
M_2CO_3 + 2MAIO_2 \rightleftharpoons M_4Al_2O_5 (orthodialuminate) + CO_2 \tag{2.20}
\]

\[
M_2CO_3 + M_4Al_2O_5 \rightleftharpoons 2M_3AlO_3 (orthoaluminate) + CO_2 \tag{2.21}
\]

The chemical reaction started on the surface of the solid material at about 500ºC in both air and CO\(_2\) atmospheres. In CO\(_2\) atmosphere the chemical process was suppressed and became slower. At 700ºC lithium carbonate melted. The chemical reaction occurred between the solid and molten phases and became complete only at about 950ºC, producing \(\gamma\)-lithium meta-aluminate [21].

### 2.5. \(p_H\) sensing mechanism of IROF

M. Pourbaix [3] gave three equilibria involving iridium oxide and protons:

\[
Ir_2O_3 + 6H^+ + 6e^- \rightleftharpoons 2Ir + 3H_2O \tag{2.22}
\]

\[
E^0 = 0.926 - 0.0591p_H \tag{2.23}
\]

\[
IrO_2 + 4H^+ + 4e^- \rightleftharpoons Ir + 2H_2O \tag{2.24}
\]

\[
E^0 = 0.926 - 0.0591p_H \tag{2.25}
\]

\[
2IrO_2 + 2H^+ + 2e^- \rightleftharpoons Ir_2O_3 + H_2O \tag{2.26}
\]

\[
E^0 = 0.926 - 0.0591p_H \tag{2.27}
\]

It is not immediately obvious which of the three equilibria is responsible for \(p_H\) response of the iridium oxide electrode. For thermally oxidized iridium electrode some workers have suggested that reaction (2.26) is the dominant equilibrium. On theoretical grounds
the equilibrium with the highest exchange current density would be expected to be the dominant one, but for equilibria with comparable degrees of reversibility, mixed control of the rest potential could be expected.

For electrochemically grown iridium oxide in which the growth was accomplished by pulsing of the potential between -0.25 and 1.25 V at 0.5 Hz in a 0.5 H₂SO₄ solution, the oxide may possibly be a hydrated oxyhydroxide [22].

\[
\begin{array}{l|l}
\text{Ir}^3 & \text{Ir}^4 \\
\hline
\text{IrO(OH)} & \text{IrO}_2 \\
\text{Ir(OH)}_3 & \text{IrO(OH)}_2 \\
\text{Ir}_2\text{O}_3 & \text{Ir(OH)}_4 \\
\text{Ir}_2\text{O(OH)}_4 & \text{Ir}_2\text{O}_3\text{(OH)}_2 \\
\text{} & \text{Ir}_2\text{O(OH)}_6 \\
\end{array}
\]

**Table 2.1**: Possible forms of iridium oxide and oxyhydroxides [22].

Between the reduced and oxidized forms of the oxide or oxyhydroxide, many redox reactions are possible. The exact stoichiometric composition is difficult to determine, especially for the hydrous electrochemically grown film.
Hydroxidation of the oxide during growth of the porous, hydrous AIROF causes the presence of many hydroxyl groups. These groups can be considered as amphoteric sites, according to the site-binding theory, which can accept or donate a proton, for example:

$$\text{IrO(OH)} \rightleftharpoons \text{IrOO}^- + \text{H}^+ \quad (2.28)$$

$$\text{IrO(OH)} + \text{H}^+ \rightleftharpoons \text{IrO(OH)}_2^+ \quad (2.29)$$

These reactions, which do not require electron transfer, may be the cause of the deviation of the $p_H$ sensitivity from $59 \text{ mV} / p_H$ only if space charge is formed. If protons are adsorbed in bulk amounts, charge compensation by electrons must take place. Significant space charge can be developed only if extensive surface/interface area are available [22]. Sensitivity deviation can be illustrated by the following example. Consider the redox system:

$$2\text{Ir(OH)}_2 + \text{H}_2\text{O} \rightleftharpoons \text{Ir}_2\text{O(OH)}_6^- + 2\text{H}^+ + 2e^- \quad (2.30)$$

The experiments to determine the open-circuit potential to $p_H$ response could be carried out in a mildly acidic or alkaline solution. Then, the amphoteric character of the hydroxyl groups can be neglected, and the film can be considered only as an acidic oxyhydroxide, each state of the film having its own degree of proton dissociation, for example:

$$\text{Ir(OH)}_3 \rightleftharpoons \text{Ir(OH)}_2\text{O}^- + \text{H}^+ \text{ (reduced form)} \quad (2.31)$$

$$\text{Ir}_2\text{O(OH)}_6^- \rightleftharpoons \text{Ir}_2\text{O(OH)}_3\text{O}_3^+ + 3\text{H}^+ \text{ (oxidized form)} \quad (2.32)$$

Substitution of reaction 2.31 and 2.32 into reaction 2.30 yields:

$$2\text{Ir(OH)}_2\text{O}^- + 4\text{H}_2\text{O} \rightleftharpoons \text{Ir}_2\text{O(OH)}_3\text{O}_3^+ + 3\text{OH}^+ + 2e^- \quad (2.33)$$
The $p_H$ sensitivity of this system is, according to the Nernst equation, 
$(3/2)(RT/F) = 88.5 \text{ mV}/p_H$ at room temperature. This example indicates the theoretical 
possibility of a sensitivity $>59 \text{ mV}/p_H$.

The different measured sensitivities are believed to be caused by a mixed potential from 
the two different states of the oxyhydroxide present in the AIROF, the reduced form hav-
ing a less acidic character than the oxidized form. Depending on the oxidation state of the 
film, one of the forms is dominant and mainly determines the $p_H$ -sensitivity behavior. 
The oxidation state also determines the composition of the film that causes the electrode 
potential shift at a fixed $p_H$ [22].
CHAPTER 3

THERMODYNAMIC THEORY

3.1. Definitions and assumptions

3.1.1. Buffering

A component is considered to be buffered if it has a concentration and mobility sufficiently high so that its chemical potential does not change drastically with small changes in concentration.

3.1.2. Reference electrode

To simplify the discussion the reference electrode is assumed to be a Pt-H₂ electrode. That electrode is buffered for electrons and protons. The standard electrode is immersed in largely immobilized water (gel) with buffered protons with a fixed concentration, or $p_{H}$. This solution is called the reference electrode solution.

3.1.3. Salt Bridge

Salt bridge connects test solution with reference electrode solution. To simplify the initial discussion, the salt bridge is assumed to have a zero potential drop. A more rigorous approach can be found in section 3.3.
3.1.4. Relevant phases

- Cu wires, buffered for electrons that connect electrodes to the volt meter. Cu wire I connects voltmeter with Ir metal. Cu wire II connects voltmeter with reference electrode.
- Ir metal, buffered for electrons and protons.
- \( \text{Li}_x\text{IrO}_y \), buffered for electrons and protons. The proton buffering is still questionable. The mobile electrons are treated as localized on \( \text{Ir}_x \) sites.
- Test solution and reference electrode solution, buffered for protons and counter ions.
- Reference electrode, assumed to be buffered for protons and electrons.
- Salt bridge connects reference electrode solution and test solution, assumed to be buffered for protons and counter ions.

3.1.5. Relevant equilibria

With high-impedance voltage measurements the following quasi-equilibria can exist:

- Electronic equilibrium I between Cu wire I, Ir metal and \( \text{Li}_x\text{IrO}_y \).
- Electronic equilibrium II between Cu wire II and reference electrode metal.
- Protonic equilibrium between Ir metal, \( \text{Li}_x\text{IrO}_y \), test solution, salt bridge, reference electrode solution and reference electrode.
- Counter ion equilibrium between test solution, salt bridge, and reference electrode solution.

Equilibrium implies that:

- The electrochemical potential of electrons I is the same in the Cu wire I, Ir metal and \( \text{Li}_x\text{IrO}_y \).
- The electrochemical potential of electrons II is the same in the Cu wire II and reference electrode metal.
- The electrochemical potential of protons is the same in the Ir metal, Li$_x$IrO$_y$, test solution, salt bridge, reference electrode solution and reference electrode.
- The electrochemical potential of counter ions is the same in test solution and salt bridge.

### 3.1.6. Voltmeter

The voltmeter measures the difference in potential between copper wires I and II, connected to the Ir metal and the reference electrode, respectively. This voltage difference can be translated into a difference in electrochemical potential by multiplying it with the elementary electron charge, $-q_{el}$. The actual voltmeter can be represented by a Cu resistor in which the electrons are not buffered; the actual voltage drop that is measured is equal to the (non-equilibrium) drop of electrochemical potential of electrons across the resistor.

### 3.1.7. Space charge

We assume that the electrochemical potentials of buffered species are such that space charge layers have subatomic thickness. This has the consequence that the voltage in each phase is constant and changes step-wise at phase boundaries. In addition charge neutrality is assumed for the bulk of all phases.

### 3.1.8. Electrode morphology

We distinguish the cases of:
- A dense Li$_x$IrO$_y$ layer around the Ir metal.
• A porous Li$_x$IrO$_y$ layer around the Ir metal in which case charge transfer (equilibration) can take place at triple-phase boundaries and proton buffering in the Li$_x$IrO$_y$ phase is not needed.

### 3.2. Quantitative expressions for the overall electrochemical potential

To understand the sensing behavior, a quantitative expression for overall electrochemical potential is derived. The system consists of several relevant phases which are described in section 3.1.4. Electron and/or proton equilibrium is assumed to exist within the system, which means that electron/protons in one phase will have the same electrochemical potential with electron/protons in the other phase if those phases are in equilibrium (section 3.1.5). Each phase within the system will have a certain potential value ($\Phi$). Electrons in metal have a chemical potential close to the Fermi level, which may vary with the proton concentration. The voltmeter reading potential is obtained by adding all junction potentials, resulting in an overall expression with $p_H$ and defect concentration [equation 3.70].

• The copper electrochemical potentials are

\[
\tilde{\mu}_{e,Cu} = \mu_{e,Cu} - q_{el} \Phi_{Cu}
\]  

(3.1)

\[
\tilde{\mu}_{e,Cu II} = \mu_{e,Cu II} - q_{el} \Phi_{Cu II}
\]  

(3.2)

For non-zero temperatures, the chemical potential is almost the same as the Fermi energy as long as the thermal energy is much less than the Fermi energy ($\epsilon_{f(0)} \gg k_B T$), since $\epsilon_{f(T)}$ is only weakly temperature dependent.
\[ \varepsilon_{f(0)} = \frac{\hbar^2}{2m_e} \left(3\pi^2 [e]\right)^{2/3} \]  

\[ \mu_{e,Cu} \approx \varepsilon_{f(T),Cu} \]  

- The Platinum electrochemical potentials are

\[ \tilde{\mu}_{e,Pt} = \mu_{e,Pt} - q_{el} \Phi_{Pt} \]  

\[ \tilde{\mu}_{H_i^*,Pt} = \mu_{H_i^*,Pt}^0 + kT \ln \left( \frac{[H_i^*]}{[V_i] + [H_i^*]} \right) \]  

- The Iridium electrochemical potentials are

\[ \tilde{\mu}_{e,Ir} = \mu_{e,Ir} - q_{el} \Phi_{Ir} \]  

\[ \tilde{\mu}_{H_i^*,Ir} = \mu_{H_i^*,Ir}^0 + kT \ln \left( \frac{[H_i^*]}{[V_i] + [H_i^*]} \right) \]  

- The electrochemical potentials for protons and electrons in Li\textsubscript{y}IrO\textsubscript{y} are

\[ \tilde{\mu}_{H_i^*,Li, IrO_y} = \mu_{H_i^*, Li, IrO_y}^0 + kT \ln \left( \frac{[H_i]}{[V_i] + [H_i]} \right) + q_{el} \Phi_{Li, IrO_y} \]  

\[ \tilde{\mu}_{e,Li, IrO_y} = \mu_{e,Li, IrO_y}^0 + kT \ln \left( \frac{[Ir'_r]}{[Ir_r] + [Ir'_r]} \right) - q_{el} \Phi_{Li, IrO_y} \]  

- The electrochemical potentials of ions in the test solution are

\[ \tilde{\mu}_{Cl^-,Sol} = \mu_{Cl^-,Sol}^0 + kT \ln \left( \frac{[Cl^-]}{[Cl^-]_{Sol}} \right) - q_{el} \Phi_{Sol} \]  

\[ \tilde{\mu}_{H^+,Sol} = \mu_{H^+,Sol}^0 + kT \ln \left( \frac{[H^+]}{[H^+]_{Sol}} \right) + q_{el} \Phi_{Sol} \]  

- The electrochemical potentials of ions in the reference electrode solution are
\[ \tilde{\mu}_{\text{CT},\text{Ref}}^0 = \mu_{\text{CT},\text{Ref}}^0 + kT \ln \left[ \frac{\text{Cl}^-}{\text{Ref}} \right] - q_e \Phi_{\text{Ref}} \] (3.13)

\[ \tilde{\mu}_{\text{H}^+,\text{Ref}}^0 = \mu_{\text{H}^+,\text{Ref}}^0 + kT \ln \left[ \frac{\text{H}^+}{\text{Ref}} \right] + q_e \Phi_{\text{Ref}} \] (3.14)

- The voltmeter reading, \( \Delta \text{reading} \), is proportional to the difference in electron electrochemical potential between the voltmeter terminals. The voltmeter is represented here as a Cu resistor. Cu I is connected to the negative terminal of the voltmeter while Cu II is connected to the positive terminal of the voltmeter.

\[ q_e \Delta \text{reading} = \tilde{\mu}_{\text{e,CuI}}^0 - \tilde{\mu}_{\text{e,CuII}}^0 \] (3.15)

### 3.2.1. Relevant equilibria

- Electron equilibrium I between Cu wire I, Ir metal and Li\(_x\)IrO\(_y\).

\[ \tilde{\mu}_{\text{e,CuI}} = \tilde{\mu}_{\text{e,Ir}} = \tilde{\mu}_{\text{e,Li,IrO}_y} \] (3.16)

\[ \mu_{\text{e,CuI}} = \mu_{\text{e,Ir}} = \mu_{\text{e,Li,IrO}_y} + kT \ln \left( \frac{[\text{Ir}']}{[\text{Ir}]} \right) - q_e \Phi_{\text{Li,IrO}_y} \] (3.17)

- Electron equilibrium II between Cu wire II and reference electrode metal.

\[ \tilde{\mu}_{\text{e,CuII}} = \tilde{\mu}_{\text{e,Pt}} \] (3.18)

\[ \mu_{\text{e,CuII}} = \mu_{\text{e,Pt}} - q_e \Phi_{\text{Pt}} \] (3.19)

- Proton equilibrium between Li\(_x\)IrO\(_y\) and test solution.

\[ \tilde{\mu}_{\text{H}^+\text{,Li,IrO}_y} = \tilde{\mu}_{\text{H}^+,\text{Sol}} \] (3.20)
\[
\mu_{i,H_{2},Li_{2}O_{x}}^{0} + kT \ln \left( \frac{[H_i]}{[H_x]} \right) + q_{el} \Phi_{Li_{2}O_{x}} = \mu_{H^{+},Sol}^{0} - 2.3kT \rho_{H} + q_{el} \Phi_{Sol}
\]  

- Proton equilibrium between Li$_{i}$IrO$_{y}$ and Ir metal

\[
H_{i,ir}^{x} = H_{i,Li_{2}O_{x}}^{x} + e'_{Li_{2}O_{x}}
\]

\[
\mu_{H_{i,ir}} = \tilde{\mu}_{H_{i,ir}} + \tilde{\mu}_{e',Li_{2}O_{x}}
\]

- Proton equilibrium between reference electrode solution and reference electrode (platinum metal)

\[
H_{i,Pt}^{x} = H_{Ref}^{x} + e'_{Pt}
\]

\[
\mu_{H_{i,Pt}} = \tilde{\mu}_{H_{i,Pt}} + \tilde{\mu}_{e,Pt}
\]

### 3.2.2. Quantitative relation

- Voltmeter

\[
q_{el} \Delta_{reading} = \tilde{\mu}_{e,CuII} - \tilde{\mu}_{e,CuI}
\]

\[
q_{el} \Delta_{reading} = \mu_{e,CuII} - q_{el} \Phi_{CuII} - \mu_{e,CuI} + q_{el} \Phi_{CuI}
\]

\[
\Delta_{reading} = \frac{\mu_{e,CuII}}{q_{el}} - \Phi_{CuII} - \frac{\mu_{e,CuI}}{q_{el}} + \Phi_{CuI}
\]

\[
\Delta_{reading} = \Phi_{CuI} - \Phi_{CuII}
\]

- \(\rho_{H}\) in test solution

\[
\tilde{\mu}_{H^{+},Sol}^{0} = \mu_{H^{+},Sol}^{0} + kT \ln \left[ \frac{H^{+}}{Sol} \right] + q_{el} \Phi_{Sol}
\]
\[ \tilde{\mu}_{\text{H}^+,\text{Sol}} = \mu^0_{\text{H}^+,\text{Sol}} - 2.3kT \rho_{\text{H}^+,\text{Sol}} + q_{\text{el}} \Phi_{\text{Sol}} \]  

(3.31)

- Lithium concentration in Li_{x}IrO_y: \( \left[ \text{Li}_i \right] \) results from chemical analysis

- Proton concentration in Li_{x}IrO_y

\[
\left[ H_i^+ \right] = \left[ \text{Ir}^0_\text{ir} \right] - \left[ \text{Li}_i^- \right]
\]  

(3.32)

3.2.3. Junction and interface

\[
\begin{array}{c|c}
\mu_{e,\text{Cu}I} & \mu_{e,\text{Ir}} \\
\tilde{\mu}_{e,\text{Cu}I} & \tilde{\mu}_{e,\text{Ir}} \\
-q_{\text{el}} \Phi_{\text{Cu}I} & -q_{\text{el}} \Phi_{\text{Ir}} \\
\end{array}
\]

Figure 3.1: Copper I/iridium junction.

- Copper I and iridium

\[
\begin{align*}
\text{electron equilibrium} \\
\tilde{\mu}_{e,\text{Cu}I} &= \tilde{\mu}_{e,\text{Ir}} \\
\mu_{e,\text{Cu}I} - q_{\text{el}} \Phi_{\text{Cu}I} &= \mu_{e,\text{Ir}} - q_{\text{el}} \Phi_{\text{Ir}} \\
\Phi_{\text{Cu}I} - \Phi_{\text{Ir}} &= \frac{\mu_{e,\text{Cu}I} - \mu_{e,\text{Ir}}}{q_{\text{el}}} \\
\end{align*}
\]  

(3.33)  

(3.34)  

(3.35)
\[ \mu_{e,Ir} \approx e_{e,Ir} \]
\[ \mu_{e,Cu} \approx e_{e,Cu} \]

\[ \Phi_{Cu} - \Phi_{Ir} \approx \frac{e_{e,Cu} - e_{e,Ir}}{q_{el}} \]

- Iridium and Li$_x$IrO$_y$

Electron equilibrium
\[ \tilde{\mu}_{e,Ir} = \tilde{\mu}_{e,Li_xIrO_y} \] (3.38)

\[ \mu_{e,Ir} - q_{el} \Phi_{Ir} = \mu_{e,Li_xIrO_y}^0 + kT \ln \left( \frac{[Ir'_x]}{[Ir_x] + [Ir'_y]} \right) - q_{el} \Phi_{Li_xIrO_y} \] (3.39)

\[ \Phi_{Ir} - \Phi_{Li_xIrO_y} = \frac{\mu_{e,Ir}}{q_{el}} - \frac{\mu_{e,Li_xIrO_y}^0}{q_{el}} - \frac{kT \ln \left( \frac{[Ir'_x]}{[Ir_x] + [Ir'_y]} \right)}{q_{el}} \] (3.40)
\[
\Phi_{\text{Ir}} - \Phi_{\text{Li}_x\text{IrO}_y} \approx \frac{\varepsilon_{\text{Ir}} - \mu_{\text{Li}_x\text{IrO}_y}^0}{q_{\text{el}}} - \frac{kT \ln \left( \frac{[\text{Ir}_y]}{[\text{Ir}_y] + [\text{Ir}_y']} \right)}{q_{\text{el}}}
\]  

(3.41)

Proton equilibrium

\[
\mu_{\text{H}_x\text{Ir}_y} = \tilde{\mu}_{\text{H}_x\text{Ir}_y} + \tilde{\mu}_{\text{Li}_x\text{IrO}_y}
\]

(3.42)

\[
\mu_{\text{H}_x\text{Ir}_y}^0 + kT \ln \left( \frac{\left[ \text{H}_x \right]}{\left[ \text{V}_x \right] + \left[ \text{H}_y \right]} \right) = \mu_{\text{H}_x\text{Ir}_y}^0 + kT \ln \left( \frac{\left[ \text{H}_y \right]}{\left[ \text{V}_y \right] + \left[ \text{H}_y \right]} \right) + \mu_{\text{Li}_x\text{IrO}_y}
\]

(3.43)

- \text{Li}_x\text{IrO}_y and solution

\[
\tilde{\mu}_{\text{H}_x\text{Ir}_y} = \tilde{\mu}_{\text{H}^+\text{Sol}}
\]

(3.44)

\[
\mu_{\text{H}_x\text{Ir}_y}^0 + kT \ln \left( \frac{\left[ \text{H}_y \right]}{\left[ \text{V}_y \right] + \left[ \text{H}_y \right]} \right) + q_{\text{el}} \Phi_{\text{Li}_x\text{IrO}_y} = \mu_{\text{H}^+\text{Sol}}^0 - 2.3kT p_{\text{H}} + q_{\text{el}} \Phi_{\text{Sol}}
\]

(3.45)

\[
\Phi_{\text{Li}_x\text{IrO}_y} - \Phi_{\text{Sol}} = \frac{\mu_{\text{H}^+\text{Sol}}^0 - \mu_{\text{Li}_x\text{IrO}_y}^0}{q_{\text{el}}} - \frac{2.3kT p_{\text{H}}}{q_{\text{el}}} - \frac{kT \ln \left( \frac{\left[ \text{H}_x \right]}{\left[ \text{V}_x \right] + \left[ \text{H}_y \right]} \right)}{q_{\text{el}}}
\]

(3.46)
• Reference electrode solution and reference electrode (platinum)

\[
\tilde{\mu}_{e,\text{Pt}} + \tilde{\mu}_{H^+,\text{Ref}} = \tilde{\mu}_{\text{Ph,n}} 
\]

\[
\mu_{H^+,\text{Ref}}^0 - 2.3kT\mu_{\text{ref}} + q_{el}\Phi_{\text{Ref}} + \mu_{e,\text{Pt}} - q_{el}\Phi_{\text{Pt}} = \mu_{H^+,\text{Pt}}^0 + k7\ln \left( \frac{[H^+]^n}{[V]^n + [H^+]^n} \right) \tag{3.48}
\]

\[
\Phi_{\text{Ref}} - \Phi_{\text{Pt}} = \frac{\mu_{H^+,\text{Pt}}^0}{q_{el}} + k7\ln \left( \frac{[H^+]^n}{[V]^n + [H^+]^n} \right) = \frac{\mu_{H^+,\text{Ref}}^0}{q_{el}} + \frac{2.3kT\mu_{\text{ref}}}{q_{el}} - \frac{\mu_{e,\text{Pt}}}{q_{el}} \tag{3.49}
\]

\[
\Phi_{\text{Ref}} - \Phi_{\text{Pt}} \approx \frac{\mu_{H^+,\text{Pt}}^0}{q_{el}} + k7\ln \left( \frac{[H^+]^n}{[V]^n + [H^+]^n} \right) = \frac{\mu_{H^+,\text{Ref}}^0}{q_{el}} + \frac{2.3kT\mu_{\text{Ref}}}{q_{el}} - \frac{\varepsilon_{e,\text{Pt}}}{q_{el}} \tag{3.50}
\]

• Reference electrode (platinum) and CuII

Electron equilibrium

\[
\tilde{\mu}_{e,\text{Cull}} = \tilde{\mu}_{e,\text{Pt}} \tag{3.51}
\]
\[ \mu_{e,\text{CuII}} - q_{el} \phi_{\text{CuII}} = \mu_{e,\text{Pt}} - q_{el} \phi_{\text{Pt}} \quad (3.52) \]

\[ \phi_{\text{CuII}} - \phi_{\text{Pt}} = \frac{\mu_{e,\text{CuII}}}{q_{el}} - \frac{\mu_{e,\text{Pt}}}{q_{el}} \quad (3.53) \]

\[ \mu_{e,\text{Pt}} \approx \varepsilon_{f,\text{Pt}} \]
\[ \mu_{e,\text{CuII}} \approx \varepsilon_{f,\text{Cu}} \quad (3.54) \]

\[ \phi_{\text{CuII}} - \phi_{\text{Pt}} \approx \frac{\varepsilon_{f,\text{Cu}}}{q_{el}} - \frac{\varepsilon_{f,\text{Pt}}}{q_{el}} \quad (3.55) \]

- Voltmeter, CuI and CuII

\[ q_{el} \Delta_{\text{reading}} = \mu_{e,\text{CuI}} - \mu_{e,\text{CuII}} \quad (3.56) \]

\[ q_{el} \Delta_{\text{reading}} = \mu_{e,\text{CuI}} - q_{el} \phi_{\text{CuI}} - \mu_{e,\text{CuII}} + q_{el} \phi_{\text{CuII}} \quad (3.57) \]

\[ \mu_{e,\text{CuII}} \approx \varepsilon_{f,\text{Cu}} \quad (3.58) \]

\[ \Delta_{\text{reading}} \approx \phi_{\text{CuI}} - \phi_{\text{CuII}} \quad (3.59) \]

### 3.2.4. Expression for reading potential \((\Delta_{\text{reading}})\)

\[ \Delta_{\text{reading}} = (\phi_{\text{CuI}} - \phi_{\text{Ir}}) + (\phi_{\text{Ir}} - \phi_{\text{Li},\text{IrO}_3}) + (\phi_{\text{Li},\text{IrO}_3} - \phi_{\text{Sol}}) \]

\[ + (\phi_{\text{Ref}} - \phi_{\text{Pt}}) + (\phi_{\text{CuII}} - \phi_{\text{Pt}}) \]

- Junction potentials

\[ (\phi_{\text{CuI}} - \phi_{\text{Ir}}) \approx \frac{\varepsilon_{f,\text{Cu}}}{q_{el}} - \frac{\varepsilon_{f,\text{Ir}}}{q_{el}} \quad (3.61) \]
\[
\left( \Phi_{\text{Ir}} - \Phi_{\text{Li}_2\text{IrO}_3} \right) \approx \frac{\epsilon_{\text{IrLr}}}{q_{\text{el}}} \cdot \frac{\mu_{0}^{0}}{q_{\text{el}}} \cdot \frac{kT \ln \left( \frac{\left[ \text{Ir}^{0}_r \right]}{\left[ \text{Ir}^{0}_l \right] + \left[ \text{Ir}^{0}_l \right]} \right)}{q_{\text{el}}}
\]
(3.62)

\[
\left( \Phi_{\text{Li}_2\text{IrO}_3} - \Phi_{\text{Sol}} \right) = \frac{\mu_{0}^{0}}{q_{\text{el}}} \cdot \frac{\mu_{0}^{0}}{q_{\text{el}}} - \frac{kT \ln \left( \frac{\left[ \text{H}^{0}_l \right]}{\left[ \text{V}^{0}_l \right] + \left[ \text{H}^{0}_l \right]} \right)}{q_{\text{el}}}
\]
(3.63)

\[
\left( \Phi_{\text{Ref} - \Phi_{\text{Pt}}} \right) \approx \frac{\mu_{0}^{0}}{q_{\text{el}}} \cdot \frac{\mu_{0}^{0}}{q_{\text{el}}} + \frac{kT \ln \left( \frac{\left[ \text{H}^{0}_l \right]}{\left[ \text{V}^{0}_l \right] + \left[ \text{H}^{0}_l \right]} \right)}{q_{\text{el}}} + \frac{2.3kT_{\text{Ref}}}{q_{\text{el}}} - \frac{\epsilon_{\text{Pt}}}{q_{\text{el}}}
\]
(3.64)

\[
\left( \Phi_{\text{CuII} - \Phi_{\text{Pt}}} \right) \approx \frac{\epsilon_{\text{Cu}}}{q_{\text{el}}} - \frac{\epsilon_{\text{Pt}}}{q_{\text{el}}}
\]
(3.65)

- Defining $\Sigma \epsilon_{f}$

\[
\Sigma \epsilon_{f} = 2 \frac{\epsilon_{\text{Cu}}}{q_{\text{el}}} - 2 \frac{\epsilon_{\text{Pt}}}{q_{\text{el}}}
\]
(3.66)

- Defining $\Sigma \mu^{0}$

\[
\Sigma \mu^{0} = \frac{\mu_{0}^{0}}{q_{\text{el}}} \cdot \frac{\mu_{0}^{0}}{q_{\text{el}}} - \frac{\mu_{0}^{0}}{q_{\text{el}}} \cdot \frac{\mu_{0}^{0}}{q_{\text{el}}} + \frac{\mu_{0}^{0}}{q_{\text{el}}} \cdot \frac{\mu_{0}^{0}}{q_{\text{el}}}
\]

if \[
\frac{\mu_{0}^{0}}{q_{\text{el}}} = \frac{\mu_{0}^{0}}{q_{\text{el}}}
\], then

\[
\Sigma \mu^{0} = \frac{\mu_{0}^{0}}{q_{\text{el}}} \cdot \frac{\mu_{0}^{0}}{q_{\text{el}}} - \frac{\mu_{0}^{0}}{q_{\text{el}}} \cdot \frac{\mu_{0}^{0}}{q_{\text{el}}}
\]
(3.67)

- Defining $C$

39
Expression containing the solution $p_H$

$$\frac{2.3kTq_H}{q_{el}} = 0.059 p_H$$ at $25^\circ C$ (293 K) \hspace{1cm} (3.69)

Overall expression

$$\Delta_{\text{reading}} \approx \varepsilon_t + \mu^0 + kT \ln[C] - 0.059 p_H + 0.059 p_{H, \text{Ref}}$$

Since $p_{H, \text{Ref}} = \text{constant} = a$ \hspace{1cm} (3.70)

$$\Delta_{\text{reading}} \approx \varepsilon_t + \mu^0 + kT \ln[C] - 0.059 p_H + a$$
3.3. Potential drop across salt bridge

Ideally salt bridge couples the electrical potential in the test solution with the potential in the standard solution such that there is no measurable voltage difference between the test solution and the standard reference solution. Salt bridges are generally designed with a nearly immobilized saturated KCl solution. The higher the KCl concentration, the lower the voltage difference. A disadvantage of higher KCl concentrations is that they tend to contaminate the test solution. The immobilization should be such that diffusion exchange with the solutions is minimized but that normal circuit currents does not cause any resistive potential drops over the salt bridge.

The objective of this chapter is to understand at which conditions the salt bridge effectively couples the electrical potential in the test solution with the potential in that standard solution of the reference electrode.

We should consider a salt bridge between the aqueous HCl test solution of variable concentration, corresponding to the $p_H$ range to be measured and the standard [HCl] solution around the Pt reference electrode. Ideally the salt bridge connects the potential in the test solution with that of the standard solution without measurable potential drop.

3.3.1. Assumptions

In the derivation below we make the following assumptions:

1. At the solution/salt bridge interface there is a shallow (non-stationary) inter-diffusion zone between $H^+$ from the solution and $K^+$ from the salt bridge. $Cl^-$ may also diffuse in or out of the salt bridge, depending on the relative chemical potentials in the solutions and the salt bridge.
2. The solution concentrations equilibrate completely at the interface; [K\(^+\)] in the test solution is ignored.

3. The expressions for chemical potentials in the solutions and the salt bridge are assumed to be ideal with the same standard potential.

4. The (Onsager) mobilities of K\(^+\) and Cl\(^-\) in the salt bridge are assumed to be equal.

5. The (Onsager) mobilities are assumed to be independent of concentration.

6. Onsager cross coefficients are assumed to be negligible.

7. Effects of space-charge build-up on concentrations are expected to be negligible.

Of these assumptions 1, 2, 4, 6 and 7 are very plausible.

Assumption 3 can be partly eliminated with more sophisticated expressions for chemical potentials, based on well-known solutions approaches or experimental data. Assumption 3 now implies the absence of any jumps in junction potential (liquid phase junction potentials).

Assumption 5 can be partly eliminated with microscopic considerations, based on well-known solutions approaches or experimental data.

**3.3.2. Derivations**

Assumption 5 leads to 
\[
\tilde{\mu}_{i,\text{sol}|SB} \equiv \mu_{i,\text{sol}}^0 + k_B T \ln[i] + q_i \Phi_{\text{sol}|SB}
\]

so that, with assumption 6, the Onsager flux equations become as follows
\[ J_{H^+,SB} = -b_{H^+,SB} \left[ H^+ \right]_{SB} \cdot \nabla \bar{\mu}_{H^+,SB} \]
\[ = -b_{H^+,SB} \left[ H^+ \right]_{SB} \left\{ k_B T \nabla \ln \left[ H^+ \right]_{SB} + q_d \nabla \Phi_{SB} \right\} \]
\[ = -b_{H^+,SB} \left[ H^+ \right]_{SB} \left\{ k_B T \frac{1}{H^+} \nabla \left[ H^+ \right]_{SB} - q_d E_{SB} \right\} \]
\[ = -b_{H^+,SB} k_B T V \left[ H^+ \right]_{SB} + b_{H^+,SB} q_d \left[ H^+ \right]_{SB} E_{SB} \] (3.71)

And likewise with assumption 4 \( b_{K^+,SB} = b_{CT,SB} = b_{x,SB} \)

\[ J_{K^+,SB} = -b_{x,SB} k_B T V \left[ K^+ \right]_{SB} + q_d b_{x,SB} \left[ K^+ \right]_{SB} E_{SB} \] (3.72)

\[ J_{CT,SB} = -b_{x,SB} k_B T V \left[ Cl^- \right]_{SB} - q_d b_{x,SB} \left[ Cl^- \right]_{SB} E_{SB} \] (3.73)

\( J, [i], \Phi \) and \( E \) all depend on \( x_{SB} \) in which \( x \) is measured from the solution (left)-salt bridge (right) interface.

Assumption 7 leads to

\[ \left[ Cl^- \right]_{SB} = \left[ H^+ \right]_{SB} + \left[ K^+ \right]_{SB} \] (3.74)

And also, considering there is no charge being built-up locally at any \( x_{SB} \)

\[ I_{CT,SB} - I_{H^+,SB} - I_{K^+,SB} = I_{e,Cu} \] (3.75)

The ion currents in the salt bridge are obtained from

\[ I_{i,SB} = z_i q_d A_{SB} \cdot J_{i,SB} \] (3.76)

Equation (3.75) is actually the consequence of a diffusion field that is quickly built-up by minimal space charge that affects ion transport fluxes such that (3.75) becomes valid.

Combination of (3.71), (3.72), (3.73), (3.75) and (3.76) leads to
\[-b_{\pm,SB}k_BT\nabla\left[ Cl^- \right]_{SB} - q_{el}b_{\pm,SB}\left[ Cl^- \right]_{SB} E_{SB} + b_{H^+,SB}k_BT\nabla\left[ H^+ \right]_{SB} - q_{el}b_{H^+,SB}\left[ H^+ \right]_{SB} E_{SB} + b_{\pm,SB}k_BT\nabla\left[ K^+ \right]_{SB} - q_{el}b_{\pm,SB}\left[ K^+ \right]_{SB} E_{SB}\]

(3.77)

Solving for the diffusion field yields

\[E_{SB} = \frac{\left\{ k_BT\nabla\left( -b_{\pm,SB}\left[ Cl^- \right]_{SB} + b_{H^+,SB}\left[ H^+ \right]_{SB} + b_{\pm,SB}\left[ K^+ \right]_{SB} \right) \right\} + \frac{I_{e,Cu}}{q_{el}A_{SB}}}{q_{el}\left\{ b_{\pm,SB}\left[ Cl^- \right]_{SB} + b_{H^+,SB}\left[ H^+ \right]_{SB} + b_{\pm,SB}\left[ K^+ \right]_{SB} \right\}}\]

(3.78)

Substitution of (3.74) leads to

\[E_{SB} = \frac{\left\{ k_BT\nabla\left( -b_{\pm,SB}\left[ H^+ \right]_{SB} + b_{H^+,SB}\left[ H^+ \right]_{SB} \right) \right\} + \frac{I_{e,Cu}}{q_{el}A_{SB}}}{q_{el}\left\{ b_{\pm,SB}\left[ H^+ \right]_{SB} + b_{H^+,SB}\left[ H^+ \right]_{SB} + 2b_{\pm,SB}\left[ K^+ \right]_{SB} \right\}}\]

(3.79)

The solution of the complete time- and location-dependant diffusion problem follows from substitution of (3.79) in (3.71) and (3.72), two continuity relations and the concentration profile in the salt bridge at \(t=0\):

\[\frac{\partial\left[ H^+ \right]_{SB}}{\partial t} = b_{H^+,SB}k_BT\left\{ \nabla\left( \frac{b_{H^+,SB} - b_{\pm,SB}}{b_{H^+,SB} + b_{\pm,SB}}\right)\nabla\left[ H^+ \right]_{SB} + \frac{I_{e,Cu}}{q_{el}A_{SB}}/\left[ H^+ \right]_{SB} \right\} - \Delta\left[ H^+ \right]_{SB}\]

(3.80)

\[\frac{\partial\left[ K^+ \right]_{SB}}{\partial t} = b_{\pm,SB}k_BT\left\{ \nabla\left( \frac{b_{H^+,SB} - b_{\pm,SB}}{b_{H^+,SB} + b_{\pm,SB}}\right)\nabla\left[ K^+ \right]_{SB} + \frac{I_{e,Cu}}{q_{el}A_{SB}}/\left[ K^+ \right]_{SB} \right\} - \Delta\left[ K^+ \right]_{SB}\]

(3.81)

Detailed solution of these equations is likely to require a numerical approach.

To make an estimate of possible potential drop we consider the cases of:

1. \(I_{e,Cu} = 0\) and an effective \(H^+\) exchange penetration over a distance \(x_p\).
2. Stationary situation with $I_{e,Cu} > 0$ and absence of proton exchange with the salt bridge.

### 3.3.3. Case 1: $I_{e,Cu} = 0$ and $H^+$ exchange penetration over $x_p$

1. $\nabla \left[ H^+ \right]_{SB}$ is expected to be steepest at the equilibrated test solution/salt bridge interface at $x = 0$. With $I_{e,Cu} = 0$, assumptions 2, and 3 and introducing $\beta_{H^+,SB} = \frac{b_{H^+,SB}}{b_{2,SB}}$, (3.79) at $x = 0$ simplifies to

$$E_{SB} = \frac{k_B T}{q_{el}} \left( \beta_{H^+,SB} - 1 \right) \nabla \left[ H^+ \right]_{SB} (x = 0)$$

(3.82)

$\nabla \left[ H^+ \right]_{SB} (x = 0)$ can by definition be made equal to $-\frac{[H^+]_{SB}}{x_p}$ so that (3.82) becomes

$$E_{SB} = -\frac{k_B T}{q_{el}} \left( \beta_{H^+,SB} - 1 \right) \left( \beta_{H^+,SB} + 1 \right) (x = 0)$$

(3.83)

$E_{SB}$ can be expected to have an extreme value at $x = 0$. For a worst case estimate of the diffusion potential drop we assume that $E_{SB}$ is constant over $x_p$ and after that equals zero. This leads to the very simple result of:

$$\Delta \Phi_{sol,SB} = \frac{k_B T}{q_{el}} \left( \beta_{H^+,SB} - 1 \right) = 0.026 \left( \beta_{H^+,SB} - 1 \right) \left( \beta_{H^+,SB} + 1 \right)$$

(3.84)

2. The electrical mobilities $\nu_i = b_i q_i^2$ of $H^+$, $K^+$ and $Cl^-$ in aqueous systems at room temperature are reported as 31.5, 6.4 and 6.5 m$^2/(V\cdot s)$, respectively [23]. This leads to a
value of $\beta_{H^+,SB} = 4.85$ and hence a maximum value of $\Delta \Phi_{Sol,SB} = 0.017 \, V$. This value represents the maximum possible drift due to diffusion potential development in the salt bridge, disregarding liquid junction potentials. This diffusion drift can be largely compensated by application of a reference cell with a standard HCl solution that will develop a similar diffusion potential at the salt bridge/standard reference solution interface but with opposite sign. The net value of $\Delta \Phi_{Sol,SB,Ref}$ follows in that case from a detailed solution of the complete diffusion problem as mentioned in section 3.3.2.

### 3.3.4. Case 2: stationary and absence of H$^+$ exchange

If the concentration of mobile protonic species in the salt bridge can be neglected a simple estimate can be made of resistive voltage drop vs circuit. For this case (3.79) simplifies to

$$E_{SB} = \frac{I_{Cu}}{2q_{ef}b_{\pm,SB}A_{SB}\left[K^+\right]_{SB}} = \frac{I_{Cu}}{2\nu_{\pm,SB}A_{SB}\left[K^+\right]_{SB}}$$  \hspace{1cm} (3.85)

Substitution in (3.85) of a typical measurement current of $10^{-9} \, nA$, $\nu_{\pm,SB} = 6.4 \, m^2/(V\cdot s)$, $A_{SB} = 1 \, mm^3$ and $\left[K^+\right]_{SB} = 1 \, mole/m^3$ leads to $E_{SB} = 78 \, \mu V/m$. Assuming a salt bridge length of 10 cm, this field strength would lead to a voltage drop of 7.8 $\mu V$. Taking into account the choice of numerical values we may safely assume that for any practical situation, the resistive voltage drop can be ignored as compared to the diffusion potential due to H$^+$ penetration.
CHAPTER 4

PROCEDURE

4.1. General preparation of iridium oxide and electrode

Preparation of $p_H$ electrodes, based on melt-oxidized iridium oxide is described in [1]. Iridium metal wire (0.25 mm diameter, Ø, >99% purity from Alfa AESAR) was received in 10 cm length. It was cut into pieces of about 10 mm in length with a cutting tool. Pieces of wire were then ultrasonically cleaned in 6 M HCl, followed by deionized water.

The clean wires were positioned in a gold foil lined alumina crucible (cylindrical, flat base, H×OD×ID 40×30×26 mm) and covered with ~1-3 g Li$_2$CO$_3$ powder (anhydrous, purity >99%, from Alfa AESAR). The oxidation of the Ir wires was performed at 870°C for 5 hours in a furnace (Fisher Scientific Isotemp programmable muffle furnace) in air.

After cooling to room temperature, the solid carbonate in the crucible was dissolved in 0.01 M HCl solution overnight. The oxidized wires were transferred to a 100 ml beaker, then washed with deionized water dried at 120°C overnight.

As a result of the oxidation process, a 25 µm thick black oxide is formed. The oxide is expected to be a mixed valance oxide with lithium intercalated in the lattice structure.
As a result of manual cutting of the wire, the sensors showed some length variation, and consequently, different oxide surface area. Such differences may influence the sensor signal as each electrode will have different area in contact with the electrolyte.

To fabricate the $p_H$ electrode, a small area (about 1 mm in length) of the iridium oxide at one end of the oxidized wire was scraped off, and a gold wire (0.1 or 0.25 mm Ø from Alfa AESAR) was wound around this bare end to form a good physical and electrical connection as shown in figure 4.1 (left). A small cap such as shown in figure 4.1 (right) was also used as an alternative for the connection method. Both connections worked well, although scraping off the tip of the wire manually could not be avoided.

Figure 4.1: IrO$_x$ with gold wire (left) and with cap (right).
4.2. **EMF Measurement**

EMF measurements was taken at uncontrolled room temperature by using HP 34970A data acquisition/switch unit with a HP 34908A 40-channel single-ended multiplexer and an Ag/AgCl electrode as reference electrode. Buffer test solutions of \( p_H \) 1-12 were used.

4.3. **Characterization**

4.3.1. **Thermogravimetry analysis (TGA)**

Lithium carbonate and IrO\(_x\) oxygen content were evaluated using a Perkin Elmer TGA 7 Thermogravimetric Analyzer with TAC 7/DS Thermal Analysis Instrument Controller. Platinum crucible was used.

4.3.2. **Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM)**

Iridium oxide surfaces and cross-sections were characterized by Field Emission Scanning Electron Microscopy (FESEM) on a Philips XL-30 FESEM (accelerating voltage 0.2-30.0 kV). For surface SEM imaging, no gold/carbon coating was applied.

The iridium oxide surfaces and cross-sections were also characterized by TEM, using a Philips CM200 TEM with a maximum accelerating voltage of 200 kV (LaB6 cathode) and point-to-point resolution of 0.27 nm, equipped with a light element EDS X-ray detector with digital beam control. TEM was performed on an iridium oxide membrane prepared by the Focused Ion Beam (FIB) technique, using a Dual Beam 235 FIB.
4.3.3. Energy Dispersive X-Ray (EDX) analysis

Energy Dispersive X-Ray analysis (EDS) is used in conjunction with Scanning Electron Microscopy (SEM) or Transmission Electron Microscopy (TEM).

4.3.4. Inductively Coupled Plasma (ICP) analysis

Elemental analysis was done in Microscopic and Chemical Analysis Research Center by using a Perkin Elmer Optima 3000 Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) and a Sciex Elan 6000 Inductively Coupled Plasma Mass Spectrometer (ICP-MS).

4.3.5. Secondary Ionic Mass Spectrometry (SIMS)

For Secondary Ionic Mass Spectrometry analysis the Cameca IMS 6F Magnetic Sector SIMS with 1-12 kV Cs source of the North Carolina State University Analytical Instrumentation Facility (AIF) was used.

4.3.6. Raman Spectroscopy

Raman spectra were acquired with a 514.5 nm laser on an f/1.5 Kaiser spectrograph with a holographic grating, 180° backscattered geometry, and a laser spot size of ~50 um. A video CCD camera was used to focus the laser. Spectra were acquired with 0.5 mW of laser power at the sample and the intensity were not corrected for instrumental response. The spectrograph was equipped with a liquid nitrogen cooled CCD detector cooled to -110°C. Integration times for all spectra were 60 seconds or less.
Figure 5.1: Sensor potential at $p_H$ 4 (left) and $p_H$ 8 (right)

Figure 5.1 (left) shows the sensor signal over 20 minutes in $p_H$ 4. The maximum initial potential value is 493 mV for sensor ‘new4’ and minimum initial potential value is 473 mV for sensor ‘new2’. All of these sensors came from one batch. During this period ~3 mV drift was observed.
Figure 5.1 (right) shows the sensor signal during 20 minutes measurement in $p_{\text{H}}$ 8. The maximum initial potential value is 225 mV for sensor ‘new3’ and the minimum initial potential value is 216 mV for sensor ‘new2’. During this period up to ~9 mV drift was observed.

![Calibration curve](image)

**Figure 5.2**: Calibration curve ($p_{\text{H}}$ vs potential)

Figure 5.2 shows the calibration curve for the sensors. EMF measurements were taken in buffer solutions 2, 4, 6, 8, and 10 (results were not shown here). The EMF slope was found to be in the range of 60 to 62 mV/ $p_{\text{H}}$. These values are slightly higher than the theoretical value of 59 mV/$p_{\text{H}}$. 
5.1. Effect of Hydration

Figure 5.3: Sensor potential at \( p_H \) 4 (left) and \( p_H \) 8 (right) after hydration in deionized water for 2 days.

To study the effect of hydration all sensors were stored in deionized water for 2 days before the measurements were taken again. The results can be found in figure 5.3. The signal after hydration was more stable, although drifts were still observed.

Figure 5.4 shows the calibration curve for the sensors after hydration. The EMF slope was found to be in the range of 57 to 62 mV/\( p_H \). For sensor ‘new2’ the EMF slope remained unchanged (60 mV/\( p_H \)) while the EMF slope for the other sensors did changed.
The above result indicates that a new calibration curve may have to be generated every time a $p_H$ measurement is taken if the sensors have been stored in aqueous solution (either deionized water or buffer solution).

**Figure 5.4**: Calibration curve ($p_H$ vs potential) after hydration in deionized water for 2 days

5.2. Stability test

Figure 5.5 shows a stability test of the sensors at $p_H = 4$ for 50 hours. The measurement was taken every 10 minutes. A drift of ~50 mV was observed. All sensors tended to stabilize.

An Ag/AgCl electrode was used as reference electrode during the potential measurements. If such electrode is not stable over a long period of time, reference electrode as well as room temperature fluctuations will contribute to the observed sensor potential drift.

5.2.1. Reference electrode stability test

Two Ag/AgCl reference electrodes were tested against one another in buffer solutions with $p_H = 8$ and 10. For a short period of time (10 minutes) fluctuations in the range of 0.6 to –1.5 mV were observed.
Another experiment was performed to observed the effect of adding Ag/AgCl reference electrode filling solution (Ag/AgCl SURE-FLOW reference electrode filling solution from ORION).

![Diagram of reference electrode half cell](image)

Figure 5.6: Reference electrode half cell diagram.

During $p_H$ measurements the reference electrode external solution will diffuse from the reference electrode and contaminate the testing solution, in this case the buffer test solution. It is therefore necessary to re-fill the electrode external solution from time to time. The filling solution contains 70% wt deionized water and 30% wt KCl. It was added through the filling hole as shown in figure 5.6. After refilling, the potential difference between two reference electrodes was measured in a buffer with $p_H = 2$ and 6, and in a saturated KCl solution. During a 20 minute test period, the reference electrodes were drifting ~0.3 mV at $p_H = 6$ and ~2 mV at $p_H = 2$. In the saturated KCl solution, the reference electrode tended to stabilize after 6 minutes as shown in figure 5.7 (left).
5.3. Effect of oxide surface on sensor’s properties

The effect of the sensor surface condition on $p_H$ response was investigated to answer the question whether the surface has to be completely smooth to obtain the $p_H$ response. This question arises because, if the sensor is connected with a gold contacting wire, the oxide has to be locally scraped off the wire. This process is done manually which may damage the adjacent part of the oxide tip.
Figure 5.8: Sensors with different surface condition

potential at $p_{\text{H}_2} 4$

Oxide surfaces were made with different conditions such as smooth, damaged, or even completely bare. To get a bare surface, a potential of ~1 V was applied to the sensor by using a Gamry DC105 potentiostat (DC Corrosion Techniques Software from Gamry). This resulted in detachment of the oxide from the Ir wire that was in contact with the electrolyte. This treatment was used to obtain half-bare wire and completely bare wires. To obtain a damaged oxide surface, one sensor was scrapped off but not until completely bare. These preparations gave four type of iridium oxide sensor:

- good sensor: no voltage was applied,
- bare (clean) sensor ~1 V was applied
- half-bare sensor ~1 V was applied
- poor sensor some sensor’s surface were scrapped off manually.

The bare/clean sensor had a little oxide on its tip.
Sensor sensitivity was found to be in the range of 55 to 59 mV/pH, as shown in table 5.1. All types of surfaces were found to be sensitive to pH.

The observations suggested that sensors with a smooth, bad or even clean (bare) surface are all sensitive to pH, so relatively large and perfect surfaces are not needed. Stability however may be affected, as ~50 mV drift was found and it gets worse for the bare (clean) wire in which the drift was found to be ~450 mV. Stability tests were performed at pH 4 over a 100 hour period.

Sensors with half-bare surface gave different responses, depending on which part of the sensor was in contact with the electrolyte, i.e. the oxide part or the bare iridium part. This result indicated that the electrical connector such as gold wire has to be isolated completely from the electrolyte during potential measurements. Further study to find a sealing material, such as glass, which is inert and stable over a long period is needed.

<table>
<thead>
<tr>
<th>Sensor</th>
<th>Sensitivity (mV/pH)</th>
<th>Calibration curve linearity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Good</td>
<td>57</td>
<td>Good</td>
</tr>
<tr>
<td>Bare/clean</td>
<td>57</td>
<td>Good</td>
</tr>
<tr>
<td>Half-bare</td>
<td>59</td>
<td>Poor</td>
</tr>
<tr>
<td>Poor</td>
<td>55</td>
<td>Good</td>
</tr>
</tbody>
</table>

Table 5.1: Effect of surface condition.
5.4. Effect of the presence of oxide

This experiment was performed to determine the effect of the oxide absence to $p_H$. Clean/bare wire from the previous experiment which still had a little oxide on its tip was cut so that the wire was completely bare. In this case an EMF slope of 51.52 mV/$p_H$ was obtained. It was concluded that this bare iridium wire is still active as $p_H$ sensor even though its surface is completely bare.

Further experiments showed that as-received gold, platinum and iridium metals are sensitive to $p_H$. No calibration curve ($p_H$ vs mV) could be drawn, as the data points showed considerable scatter. This response could be related to solution of atomic hydrogen in the metals.
5.5 Role of gold foil

Besides protecting the crucible, the role of the gold during the oxidation process is not clear. Sensors produced with and without gold are both sensitive to $p_{\text{H}}$, as shown in table 5.2.

<table>
<thead>
<tr>
<th>Sensor</th>
<th>Sensitivity (mV/$p_{\text{H}}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gold 1</td>
<td>58.8</td>
</tr>
<tr>
<td>Gold 2</td>
<td>56.6</td>
</tr>
<tr>
<td>No Gold 1</td>
<td>60.37</td>
</tr>
<tr>
<td>No Gold 2</td>
<td>60.12</td>
</tr>
</tbody>
</table>

Table 5.2: Gold effect on sensors performance

5.6. Importance of high impedance voltmeter

With the glass electrode, a Donnan [24] potential is established on both sides of the glass membrane. The potential on one side is kept constant by the internal reference solution. The resistance (impedance) of this sensor is very high because of the bulk resistance of the glass layer so that the input impedance of the $p_{\text{H}}$ meter must be very high (normally $>10^{12}$ Ω). Such a very high impedance can result in noise measurements [24]. One motivation to study metal oxide $p_{\text{H}}$ sensor is to avoid the need of such high impedance $p_{\text{H}}$ meter. However, in case of lithium iridium oxide with a mixed valance at the iridium ions (+3 and/or +4), the $p_{\text{H}}$ meter impedance must still be sufficiently high to avoid complete conversion of one ion to another.

$$\text{Ir}^{4+} + e^- \rightleftharpoons \text{Ir}^{3+} \quad (5.1)$$
With an oxide thickness of 25 \( \mu m \) and a sensor length of 1 cm, a charge of 0.25 mC is sufficient to convert all \( \text{Ir}^{+3} \) to \( \text{Ir}^{+4} \) and vice versa (the calculation is shown in appendix A). Using the assumption that a mixed valence iridium oxide is required for \( p_\text{H} \) sensing, the sensor will have a limited life time (i.e. \( \sim 1 \) year based on calculation in appendix A).
6.1. Lithium carbonate

6.1.1. Lithium carbonate in air (oxidizing) atmosphere

Lithium carbonate was used to thermally oxidize the iridium wire for 5 hours at a temperature of 870°C.

Figure 6.1: Ir wire before (left) and after oxidation (right).
Lithium carbonate with 99% and 99.999% purity from Alfa AESAR was evaluated. Li₂CO₃ melting is accompanied by weight loss. The actual extent of decomposition will largely depend on $P_{CO_2}$. At low $P_{CO_2}$ the decomposition occurs mainly according to the reaction

$$Li_2CO_3 \rightleftharpoons Li_2O + CO_2 \hspace{1cm} (6.1)$$

The degree of decomposition is defined by the formula:

$$\text{degree of decomposition} = \frac{\Delta m}{\Delta m_{\text{theoretical}}} \times 100\% \hspace{1cm} (6.2)$$

where $\Delta m$ denotes experimental mass change, $\Delta m_{\text{theoretical}}$ corresponds to the maximum value of mass change when total amount of lithium carbonate in the sample decomposes to lithium oxide, calculated by percentage mole weight change of Li₂CO₃ (MW = 74 g/mole) to Li₂O (MW = 30 g/mole).

$$\Delta m_{\text{theoretical}} = \frac{74 - 30}{74} \times 100\% = 59.46\% \hspace{1cm} (6.3)$$

The Li₂O formed decreases the melting temperature of lithium carbonate. In the binary system Li₂O-Li₂CO₃ a eutectic mixture (containing 13 mole % of Li₂O with $T_{\text{melt}} = 705^\circ C$) exists [12].

The TG curve was measured from 30°C to 800°C with heating and cooling rates of 5°C/min in air with a flow rate of 20 ml/min. The level of carbon dioxide pressure in air is 0.03 vol.%. The TG curve can be found in figure 6.2.
In figure 6.2. (left), weight loss during heating in the range of 30-200ºC could be caused by the release of physically bound water, while the weight loss during heating in the range of 233-482ºC could be caused by the release of chemically bound water. Weight loss of ~7% which corresponds to 11.8% carbonate decomposition was observed starting at 677ºC. This temperature is lower than the reported values for the \( \text{Li}_2\text{CO}_3 \) melting temperature (725ºC according to Barin [12]), which may be explained by eutectic temperature and difference in \( p_{O_2} \) used in the experiment.

![Figure 6.2.](image)

**Figure 6.2.** TG curve for 99% purity \( \text{Li}_2\text{CO}_3 \) (left) and 99.999% purity (right)

For high purity \( \text{Li}_2\text{CO}_3 \) [figure 6.2. (right)], weight loss which could be caused by the release of physically and chemically bounded water was observed during heating in the range of 30 to 500ºC. Weight loss of ~6% which corresponds to 10.1% carbonate decomposition was observed to start at 653ºC.
Weight gain towards the end of the experiment (h = 3) which is observed in both figure 6.2 (left) and 6.2 (right) is also observed for the blank crucible as observed in figure 6.34 (h = 30). This weight gain is probably caused by platinum crucible reaction with the gas used in the experiment.

The TG results suggest that Li$_2$CO$_3$ is melted completely at oxidation temperature of 870°C, although an increasing degree of decomposition can be expected during 5 hours dwell time.

![Figure 6.3: Phase diagram of Li$_2$CO$_3$-Li$_2$O [25]](image)

The lithium carbonate melting temperature increases with the increase of CO$_2$ concentration in ambient while mass loss decreases. These effects can be explained taking into consideration the phase diagram of Li$_2$CO$_3$-Li$_2$O. The increase of $p_{CO_2}$ shifts the equilibrium (6.1) towards the carbonate side.

If during the oxidation process pure oxygen is used instead of air, an increase of the decomposition degree of lithium carbonate as well as a decrease of melting point can be expected.
Heating the Li$_2$CO$_3$ to a constant mass at 200ºC and then storing them over activated silica gel in a desiccator will result in a dry starting material before oxidation begins.

**6.1.2. Lithium carbonate in 5%H$_2$ - 95%N$_2$ (reducing) atmosphere**

![Figure 6.4: TG curve for 99.999% Li$_2$CO$_3$ in reducing atmosphere.](image)

Figure 6.4 shows the TG curve for Li$_2$CO$_3$ (99.999% purity) in a 20 ml/min flow of (reducing) forming gas (5%H$_2$-95%N$_2$). The TG measurement was taken with a heating rate of 1ºC/min from 30 to 1000ºC, 12 hours dwell time, and then cooling to 30ºC at a rate of 10ºC/min.

Weight loss was observed to start at 685ºC. A slope change was observed at 967ºC which may be due to the onset of lithium evaporation.
With lithium volatilization starting at 967°C it will be difficult to use TG curves of Li-doped iridium oxide in reducing atmosphere to determine the oxygen content of the oxide. As will be shown later, oxygen is not completely released at such temperatures while lithium starts to volatilize.

### 6.2. Surface and cross section SEM micrographs

![Surface micrograph of the sensor.](image_url)

**Figure 6.5**: Surface micrograph of the sensor.
A surface micrograph of the sensor is shown in figure 6.5. A columnar (finger) type of structure was observed growing perpendicular from the iridium wire core, with a total oxide thickness of ~25 µm. In figure 6.5 (right) the fingers seemed to be flattened, possibly due to direct contact with crucible’s bottom.

![Image of a surface micrograph of the sensor](image)

**Figure 6.6**: Cross section micrograph of the sensor with split end

Figure 6.6 shows a cross-sectioned micrograph of the sensor with a split end. The oxide has grown in between the iridium metal.

Figure 6.7 (left) shows a cross section micrograph of the sensor, in which a gap is observed between the iridium wire and the oxide.
Figure 6.7: Cross-sectioned micrograph of the sensor.

In figure 6.7 (right) no gap is observed between the iridium wire and the oxide. The oxide consists of one layer. It is possible that such gap as observed in figure 6.7 (left) was produced during polishing process. The gap may indicate weak adhesion of the inner oxide layer to the Iridium wire.

Figure 6.8: Oxide tip with manual cutting (left) and laser cutting (right)
Figure 6.8 shows the tip of the sensor wire after oxidation. Laser cutting gave a relatively flat tip surface compared to manual cutting.

**Figure 6.9:** Surface micrograph of IROF with gold used during fabrication.

**Figure 6.10:** Surface micrograph of IROF without using gold during fabrication.

**Figure 6.11:** Schematic diagram of figure 6.7 (left)
6.3. Focused Ion Beam (FIB) cross-sections, coupled with SEM 
and TEM for phase identification

Sensors as shown in figure 6.7 (left) consisted of two layers (i.e. inner and outer layer). The schematic diagram of the oxide structure is shown in figure 6.11.

To have a better picture of the oxide morphology, FIB was used to cut two membranes from both the inner and outer layers. The SEM micrographs of the membranes are shown in figure 6.12 and 6.13. Those membranes were characterized by TEM for diffraction analysis. TEM micrographs were shown in figure 6.14 and 6.15.

The inner layer such as shown in figure 6.12 and 6.14 consists of a dense oxide layer, which was found to be amorphous based on the diffraction pattern of figure 6.16.

---

**Figure 6.12:** SEM micrograph for the inner layer: amorphous phase.

**Figure 6.13:** SEM micrograph for the outer layer: crystalline grains with amorphous phase grain boundary.
The outer layer of the oxide consisted of a columnar type of structure grown in the direction perpendicular to the iridium wire core, shown as grains and grain boundaries in figure 6.13 and 6.15. The porosity is also observed in those figures. A zoom in for a selected area in figure 6.15 is shown in figure 6.18.
Figure 6.16: Inner layer TEM diffraction pattern.

Figure 6.17: Outer layer TEM diffraction pattern.

Figure 6.18 shows the diffraction pattern of the grain in figure 6.15. The grains consist mostly of a crystalline phase based on diffraction in figure 6.18. The grain boundaries consist of an amorphous phase (diffraction pattern is not shown here).

For oxides with two layers it can be concluded that the outer layer consist of grains which are mostly crystalline and grain boundary areas which are amorphous. The structure is not perfectly dense as some pores were observed.
It is believed that the hydration process either dissolved the outer layer causing pores or
inducing a phase transformation from crystalline to amorphous. The inner layer consists
of a dense, amorphous phase. Which of these two phases is active as a sensing material
needs further study.

6.4. **Focused Ion Beam cross-sections to investigate porosity**

This experiment was performed to investigate the internal porosity of the oxide which
could play a role in the sensing behavior. There are two possible mechanisms for sensing
behavior: a triple phase boundary mechanism or a two phase boundary mechanism. If
connected porosity is present, the IrO$_x$ does not have to be buffered for protons and elec-
trons since, in that case, proton and electron transfer can take place at the metal-oxide-
liquid triple-phase boundary.
Figure 6.20: Pores at ~5 µm depth of figure 6.19 with excess lithium carbonate.

Figure 6.21: Pores at ~15 µm depth of figure 6.19.

In figure 6.20 porosity is observed. Excess lithium carbonate is present between grains. Less pores are observed at ~15 µm depth. Further experiment is needed to study whether connected porosity is present.

6.5. Raman Spectroscopy

Raman scattering is results from phonon modulation due to optical polarizability. It can give information about the material structure in terms of molecular units and is probably one of the most useful methods available for studying lattice vibrations and their interactions with other excitations [26]. Figure 6.22 shows Raman spectra of 4 wires (A, B, C and D) produced in one batch by the melt oxidation method. These wires were not hy-
drated. Excess lithium carbonate is still present and can be observed as a strong peak at 1089 cm\(^{-1}\) and a small peak at 1459 cm\(^{-1}\). A gaseous O\(_2\) peak is observed at 1556 cm\(^{-1}\).

![Raman spectra of wires (A, B, C and D) produced via one batch of the melt oxidation method.](image)

**Figure 6.22:** Raman spectra of wires (A, B, C and D) produced via one batch of the melt oxidation method.

For comparison, a lithium carbonate spectrum was taken and is shown in figure 6.23 (left). Iridium oxide single crystal Raman spectrum from the literature [26] is shown in figure 6.23 (right). The laser penetration depth was reported to be about 40 nm for IrO\(_2\).[26] The three major Raman peaks, namely the E\(_g\), B\(_{2g}\) and A\(_{1g}\)-modes for single crystal IrO\(_2\) are located at 561, 728, and 752 cm\(^{-1}\). These peaks do not match our observed values of 532 cm\(^{-1}\), 610 cm\(^{-1}\), 705 cm\(^{-1}\) in figure 6.22, because IrO\(_x\) structure is not
a single crystal IrO$_2$ structure. In addition, a peak at 1126 cm$^{-1}$ which is caused by room light was observed in figure 6.22.

![Raman spectra of Lithium carbonate (left) and iridium oxide single crystal (right)](image)

**Figure 6.23:** Raman spectra of Lithium carbonate (left) and iridium oxide single crystal (right)

Figure 6.24 shows Raman spectra of wire C stored in air over a 9 days period. The lithium carbonate peak at 1089 cm$^{-1}$ is observed for all spectra. Starting at day 9 the strong peak at 705 cm$^{-1}$ has disappeared, while another peak at 627 cm$^{-1}$ appears.
Figure 6.24: Raman spectra of wire C aged in normal air.

Figure 6.25 shows wire A which is stored in water over a 9 days period. For the purpose of clarity, the curves were shifted vertically. The strong peak found on day 0 at 705 cm\(^{-1}\) weakened after day 2 and had finally disappeared at day 4. The peak at 627 cm\(^{-1}\) appears strongly on day 2. The weak peak at 1126 cm\(^{-1}\) due to room light was also observed. Most of the lithium carbonate had dissolved during water storage, as can be seen in the day 2 and 4 spectra. The lithium carbonate peak was observed only in the day 6 and 9 spectra. This may be due to the fact that for each measurement a different location on the sample was taken. Between experiments the wire was taken in and out from the instru-
Figure 6.25: Raman spectra of wire A stored in water.

ment sample holder, which makes it difficult to focus on exactly the same spot of ~50 µm size. An in-situ aging experiment may be the best way to monitor the changes more accurately.

Figure 6.26 shows a comparison of water storage vs. air storage. After 9 days aging in air Raman spectra of iridium oxide wire shows the same peaks of iridium oxide wire which was aged in water for 4 days, expect for lithium carbonate peak at 1089 cm⁻¹.

Raman spectra suggested that structure transformation occurred in iridium oxide wires which were aged in water and air. Such transformations occur more rapidly in water compare to in air. It is suspected that hydration caused such transformation.
**Figure 6.26:** Comparison of wire stored in air for 9 days (blue) vs. stored in water for 4 days (red).

<table>
<thead>
<tr>
<th>Initial (cm$^{-1}$), day 0 in air</th>
<th>Final (cm$^{-1}$), day 9 in water</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>532</td>
<td>532</td>
<td></td>
</tr>
<tr>
<td>610</td>
<td>627</td>
<td>Blue shift</td>
</tr>
<tr>
<td>705</td>
<td>-</td>
<td>Li$_2$CO$_3$, dissolved</td>
</tr>
<tr>
<td>1089</td>
<td>-</td>
<td>Li$_2$CO$_3$, dissolved</td>
</tr>
<tr>
<td>1126</td>
<td>1126</td>
<td>Room light scattering</td>
</tr>
<tr>
<td>1459</td>
<td>1459</td>
<td>Li$_2$CO$_3$, dissolved</td>
</tr>
<tr>
<td>1556</td>
<td>1556</td>
<td>O$_2$</td>
</tr>
</tbody>
</table>

**Table 6.1:** Raman peaks position of iridium wire before and after transformation
Table 6.21 shows a comparison of peak positions at extreme conditions. At day 0 when the wire was removed from the furnace, excess lithium carbonate was present around the wire, so lithium carbonate peaks are to be expected. The O$_2$ peak appears due to relatively long integration time (60 seconds). After 9 days aging in water most lithium carbonate is dissolved.

6.6. X-Ray Diffraction (XRD)

![XRD for IrO$_x$ wire stored in air for 4 days (Red lines: Li$_8$IrO$_6$ pattern, green lines: MgO pattern)](image)

**Figure 6.27:** XRD for IrO$_x$ wire stored in air for 4 days (Red lines: Li$_8$IrO$_6$ pattern, green lines: MgO pattern)
Figure 6.27 shows the XRD pattern of a wire stored in air for 4 days. Li$_8$IrO$_6$ is found to be the best match (red pattern, PDF #26-0849). MgO contamination from the crucible is also found (green pattern, PDF #01-1235). Lithium carbonate peaks were not prominently present. Figure 6.28 shows the lithium carbonate XRD pattern. The highest peak of lithium carbonate only appears as a small peak at 20~31.8° in figure 6.27.
Figure 6.29: XRD for IrO$_x$ wire stored in air
Figure 6.29 shows XRD spectra of IrO$_x$ wire stored in air for a 30 days period. No change is observed in peak position, although intensity ratio changes were observed. Initially sharp peaks between 72-75° 2θ seemed to be broaden at day 30. The MgO [200] peak (43°2θ) to Li$_8$IrO$_6$ [101] peak (20°2θ) intensity ratio was found to be inverted at day 30.

Figure 6.30 shows IrO$_x$ wire stored in water for a 23 days period. No change is observed in peak position, although peak shape and intensity ratio changes were observed.
Figure 6.30: XRD for IrO$_x$ wire stored in water over 23 days
Figure 6.14 shows a comparison between wire which was stored in air vs wire which was stored in water. The magnesium oxide [200] peak at 43°2θ is still observed after 2 days storage in water.

Figure 6.31: XRD for IrOx wire stored in air for 4 days (red lines: Li₆IrO₆ pattern, green lines: MgO pattern) and stored in water for 2 days.
The XRD for wire stored in water could not be identified. The pattern does not match either IrO$_2$, Li$_8$IrO$_6$, or Li$_2$IrO$_3$. Some of the peaks tend to be broad which may be due to amorphous nature of the oxide phase formed.

Based on the previous results, it is expected that IrO$_x$ wire produced via melt oxidation method consists of more than one oxide layer, as shown in figure 6.151. The outermost oxide consists of the lithium rich Li$_8$IrO$_6$ compound. Upon contact with water some of the lithium and iridium are dissolved, and the oxide is transformed into another structure which is not yet identified.

It is important to note that the wire XRD pattern was taken with a rotating capillary sample holder. The iridium oxide wire does not have a smooth surface which makes it difficult to focus the X-ray beam.

6.7. Chemical composition and oxidation state

6.7.1. Inductive-coupled plasma (ICP)

In plasma mass spectroscopy, the inductive-coupled argon plasma (ICP) is used as an excitation source for the elements of interest. The plasma in ICP-MS is used to generate ions which are then introduced to the mass spectrometer. These ions are then separated and collected according to their mass to charge ratios. The constituents of an unknown sample can then be identified and measured. ICP-MS offers extremely high sensitivity for many elements and can also be successfully applied to a wide range of elements [27].

For iridium oxide analysis the digestion process is as follows: a piece of as-recieved Ir wire (6.1 mg) and a piece of Ir wire with oxide coating (19 mg) were each placed in sepa-
rate microwave digestion vessels. Three mL concentrated HCl and 1 mL concentrated HNO₃ were added to each vessel. The vessels were heated to 180°C for 10 minutes, and then held at 240°C for 70 minutes. The acid solution from each vessel was diluted to 50 mL with deionized water. Wire remained in each vessel. The as-received Ir wire was shiny before and after the acid treatment. The wire with the oxide coating was dark/dull before the acid treatment but shiny afterwards. The wires were rinsed with deionized water, dried and weighted again. The final weight of as-received Ir wire was 6.3 mg, the final weight of Ir wire with oxide was 16.8 mg. The uncertainty of the weights are likely to be ±0.2 mg or more. There appears to have been a loss of material from the wire that had the oxide layer but not from the as-received Ir wire.

<table>
<thead>
<tr>
<th>Concentration in dilute solution (µg/mL)</th>
<th>Mass in original solution (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>0.35</td>
</tr>
<tr>
<td>Ir</td>
<td>16.8</td>
</tr>
</tbody>
</table>

*Table 6.2:* Lithium and iridium content from ICP

The Ir and Li concentration in the diluted acid solution, obtained with the as-received Ir wire were not detectably higher than solutions obtained with blank vessels. The results for the wire with the oxide layer are presented in table 6.2.
From ICP analysis we obtained a Li to Ir ratio of 1 to 1.736. During digestion 2.2 mg of oxide was dissolved. This oxide probably contained lithium, iridium, oxygen, hydrogen, and water unless the oxide was perfectly dry. For the digestion method as described above there is a risk that some oxide remained undissolved.

To avoid the risk of uncompleted digestion a S-405D Branson digital sonifier (input power 115 V, 60 Hz, output power 400 Watts was used to remove the oxide from the wire. Wires were cut in 5 mm pieces and placed in a 25 mL plastic bottle. The bottle was filled with water. The sonic probe was inserted into the bottle and maximum power applied. The plastic bottle was immersed in water to minimize the increase of temperature. After 30 minutes a black deposit was found at the bottom of the bottle. This sample was sent to Microscopic and chemical Analysis Research Center (MARC) for analysis. Unfortunately with ~30 pieces of wire only ~4 mg powder was obtained. This amount of sample was not sufficient since a microbalance was not available in MARC.

With this process the sample dry weight is unknown unless it can be dried completely.
6.7.2. Thermogravimetry analysis (TGA)

Figure 6.32: TG curve for IrO$_x$

Thermogravimetric analysis (TGA) is a common technique to determine oxygen content in oxide. This method is most often used due to its simplicity and accuracy. The TGA method measures changes in weight as a function of temperature in a reducing atmosphere, and the weight loss is assumed to be related to oxygen content. The measured values of oxygen content may be in error if there are other volatile components present.
Figure 6.33: TG curve for a blank crucible.

Figure 6.32 shows a TG curve of iridium oxide with a heating and cooling rate of 1 C/min and dwelling time of 12 h at 900°C in 5% H₂-95%N₂ atmosphere. Only ~0.45 mg weight loss was observed as compared to a maximum possible weight loss of ~4.5 mg if all oxygen were released, assuming a stoichiometric IrO₂ structure. The weight increase which is observed as a hump during the early stage (~1 hour) and the final stage (30 h) of the experiment was caused by atmospheric density changes as observed in the TG curve for a blank crucible as shown in figure 6.33. A weight decrease during dwell at temperature of ~900°C in figure 6.33 may indicate that some platinum were reduced by hydrogen gas.

A more suitable method for oxygen determination is needed since the temperature could not be increased higher than ~967°C where lithium evaporation starts to become significant.
6.7.3. Energy Dispersive X-Ray (EDX) analysis

The energy of the electron beam in SEM is typically in the range 10-20keV. This causes X-rays to be emitted from the material. The energy of the X-rays emitted depends on the material under examination. The X-rays are generated in a region about 2 microns in depth, and thus EDX is not a surface technique. By moving the electron beam across the material an image of each element in the sample can be acquired. Due to the low X-ray intensity, images usually take a number of hours to acquire. Elements of low atomic number are difficult to detect by EDX. The Silicon Lithium detector (SiLi) is often protected by a beryllium window. The absorption of the soft X-rays by the Be precludes the detection of elements below an atomic number of 11 (Na). In windowless systems, elements with an atomic number as low as 4 (Be) have been detected, but the in any case detection becomes progressively more difficult as the atomic number is reduced [29].

Figure 6.34: EDX spectrum for grain in figure 6.15
Inspection of the grain in figure 6.15 by EDX shows that the grain consists of iridium and oxygen. Copper and carbon shown in this figure is from the TEM sample holder grid. Quantification with EDX requires a standard sample with a known composition.

The amorphous layer in figure 6.14 also contains iridium and oxygen (the spectrum is not shown here). A composition map by EDX or EPMA is needed to observe composition variations.

6.7.4. Secondary Ionic Mass Spectrometry (SIMS)

In SIMS analysis, a focused beam of "primary" ions (a few μm in diameter) bombards a solid sample to obtain a localized (near-) surface analysis. The bombardment or "sputtering" removes atoms from the polished surface of the specimen, some of which are ionized and can be accelerated into the entrance slit of a mass spectrometer [30].

SIMS is found to be the best method for elemental analysis as it can detect all elements of interest at one run. This method however also requires a standard of a known composition.
Figure 6.35: SIMS spectra for iridium oxide
CHAPTER 7

SUMMARY

Sensor testing showed that sensors produced via the melt oxidation method were sensitive to changes in $p_H$ but tended to be irreproducible. Sensors produced in one batch gave drifts as high as ~50 mV over 50 hours although these sensors tended to stabilize over time. Hydration changed sensors sensitivity.

Sensors might have a limited operational time due to complete conversion of Ir$^{+3}$ to Ir$^{+4}$ and visa versa. The sensors can possibly be regenerated by reverse voltage application.

Sensors microstructure characterization by FIB, SEM and TEM showed that a columnar structure was present perpendicular from the iridium wire core. For some wires the oxide consisted of two layers. The outer layer consisted of grains which were mostly crystalline with an amorphous grain boundary phase. The inner layer was dense and amorphous. Identification by EDX showed that grain and grain boundary consisted of iridium and oxygen.

Sample aging in water or air caused a transformation in the iridium oxide as observed in Raman and XRD spectra, and could probably explained the observed drift.

The XRD spectrum of non-treated, non hydrated melt-oxidized wire matched best with the known XRD pattern of Li$_8$IrO$_6$. Hydrolysis, for instance by aging in water, dramati-
cally changed the solid structure from Li$_8$IrO$_6$ to an unidentified structure. It was also possible that part of the Li$_8$IrO$_6$ dissolved completely and that other, more Ir-rich phases were present between the Ir wire core and the Li$_8$IrO$_6$ surface layer.

Compositional quantification by EDX and SIMS required a standard sample with a known composition. A suitable preparation method is needed.
Bibliography


17. Felner and I.M. Bradaric, “The Magnetic Behavior of \( \text{Li}_x\text{MO}_3 \) (M=Mn, Ru and Ir) and \( \text{Li}_2(\text{Mn}_{1-x}\text{Ru}_x)\text{O}_3 \)”, \textit{Physica B} \textbf{3} 11, 195-99 (2002).


27. [http://www.chemex.com/tech/t-sec2_4.htm#sec2_4_1_4](http://www.chemex.com/tech/t-sec2_4.htm#sec2_4_1_4)


30. [http://earth.agu.org/revgeophys/neal00/node7.html](http://earth.agu.org/revgeophys/neal00/node7.html)
A Conversion charge calculation

Lithium iridium oxide is assumed to consist of a mixture of mostly iridium (IV) (90% wt) and iridium (III) (10% wt). The IrO$_2$ density is 11700 kg/m$^3$ (data from MSDS) assuming IrO$_2$ dense structure.

For sensor fabrication, 1 cm length of iridium wire with diameter of 0.25 mm was used. After melt oxidation process, the oxide thickness of 25 µm was found.

The calculated oxide volume was 4.9×10$^{-12}$ m$^3$, so Ir$^{+3}$ weight was 4.92×10$^{-9}$ kg.

To convert 4.92×10$^{-9}$ kg Ir$^{+3}$ to Ir$^{+4}$ the charge of 2.47×10$^{-4}$ coulomb was needed. With typical multimeter internal impedance of 50×10$^9$ Ω and potential of 400 mV, the Ir$^{+3}$ will be totally converted to Ir$^{+4}$ after ~1 year.