

Electrode Materials for the Electrolysis of Metal Oxides

by

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Submitted to the Department of Materials Science and Engineering
in Partial Fulfillment of the Requirements for the Degree of

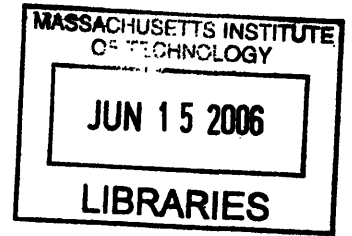
Bachelor of Science

at the

Massachusetts Institute of Technology

May 2006

[June 2006]



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Abstract

Carbon, tungsten, platinum, and iridium were examined as candidate anode materials for an electrolytic cell. The materials were pre-selected to endure high process temperatures and were characterized for inertness and high current density during electrolysis using voltammetric techniques. Inertness is viewable through current discrepancies dependent on voltage scan direction at low voltage, consumption of current by metal oxide formation, and ease of surface oxide electro-stripping. Conductivity during electrolytic oxidation is observable as current density maximization at high voltages. While carbon, tungsten, and platinum formed surface oxides, iridium remained quite inert. In addition, the voltage hold-time was found to affect the leading current density, as platinum performed best during cyclic voltammetry, but iridium performed best during potentiostatic electrolysis. The intermediate potentiodynamic scan-rate displays the transition from platinum to iridium dominated current density.

Introduction: Economic Background

Titanium has long been a high-performance metal of choice due to its mechanical and corrosion-resistant properties. Titanium maintains a strength-to-weight ratio equal to magnesium, 1.5 times that of aluminum, and 2 times that of stainless steel [1]. These advanced mechanical properties have brought titanium to common use in aerospace (jet engines, airframes) and consumer/medical products (golf clubs, bike frames, prosthetic bones). Its high melting point around 1700°C and general temperature stability also make it a superior candidate for temperature-sensitive applications. As for corrosion, titanium forms a self-limiting oxide surface layer that regenerates when the bare metal is exposed and is resistive to oxidizing and reducing conditions.

Given this impressive set of materials properties, it is no surprise that demand for titanium is high. Since titanium is the 9th most abundant element in the earth's crust and the 4th most abundant structural element, the demand for titanium should be as easily met as the demand for aluminum, iron, copper, tin, lead, or many other metals [2]. However, the same reactive metal properties that make titanium attractive for high temperature and anti-corrosion applications, cause it to be found as a natural oxide (FeTiO₃ ilmenite or TiO₂ rutile) and make it difficult to process and refine to the pure metal. The current processes are capital intensive, energy intensive, and environmentally hazardous, which have made it impossible to expand production to meet the market demand for titanium.

The inability to expand the production capacity of titanium metal has caused the price to skyrocket from around \$7 to over \$25 dollars per pound over the last year, and the market capitalization of the 3 major titanium manufacturers in the United States (Titanium Metals Corporation, Allegheny Technologies, and RTI) has soared under these

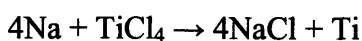
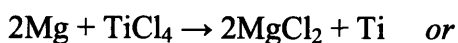
economic conditions. There is a great need for titanium processing methods that are (a) more efficient from a manufacturing standpoint and (b) environmentally safe for the government to permit the construction of new facilities.

In response to these requirements, Sadoway et al [2] has conceived of a 1700°C electrolytic process which would directly reduce rutile ore into liquid titanium and oxygen gas. The process could be also used to economically produce a range of pure specialty metals from their natural oxides, including beryllium, uranium, and tantalum. One of the main challenges in this new approach is the characterization of optimal materials for the electrodes. The 1700°C atmosphere is very harsh on materials and is capable of facilitating a large number of reactions between the electrode and the melt through oxidation and dissolution, particularly at the anode where oxygen gas forms. Indeed the aluminum industry, which also uses electrolytic methods, has been using and replacing consumable carbon electrodes for decades. Here we investigate the electrical characteristics of alternate anode materials for use in electrolytic metals processing. The candidate materials need all display high-temperature stability and inertness to an oxidizing environment.

Current Practice for Titanium Production

Rutile is routinely carbochlorinated to TiCl_4 and oxygenated back to TiO_2 particles for use as white pigment, primarily in white paint. Ilmenite refinement to titanium dioxide requires a sulfate process that produces twice the product weight of sulfuric acid, but it is uncommon to be used for titanium manufacture. Rutile is the dominant choice since it can be directly combined with petroleum coke at 1000°C to form titanium-carbide sponge which is chlorinated into the titanium tetrachloride [3].

The titanium tetrachloride is then fed into a furnace containing magnesium (Kroll process) or sodium (Hunter process) for reduction into solid titanium [4, 5]. The Kroll magnesium process is by far the most commonly used and occurs at the melting point of magnesium around 950°C , such that the liquid magnesium chloride can be gradually taken out of the reaction batch (Figure 1). The Hunter process is carried out similarly to remove molten NaCl . The respective reactions:



after several days result in titanium sponge that is removed from the furnace, mechanically and thermochemically purified, and plasma-arc-remelted into pure titanium products. The MgCl_2 of the Kroll process is reclaimed back into magnesium and chloride gas to be reused in successive batches. The long time-frame and multi-step discontinuity of the process lead to manufacturing inefficiencies, while the carbochlorination processes contribute to environmentally hazardous waste products, such as dioxins and furans. Yet these are the most economical manufacturing methods for titanium to date, with the Hunter process existing from 1910-1940 and the Kroll process supplanting it afterwards.

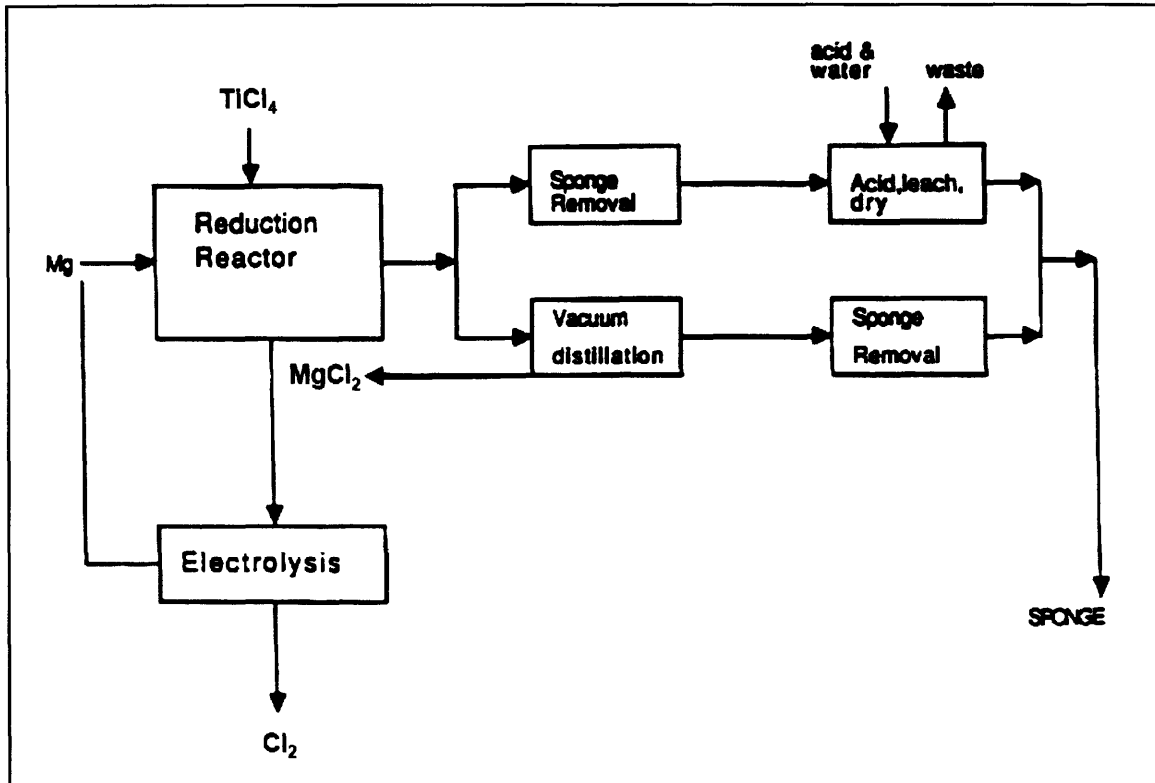
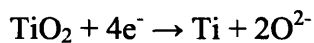
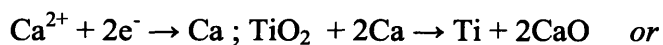


Figure 1: The Kroll process for processing titanium chloride into titanium sponge by reduction with magnesium, which is tapped out of the reactor as $MgCl_2$. The $MgCl_2$ is recycled into Mg and chloride gas for reuse in the next batch. After several days, the titanium sponge is fully reduced, removed from the reactor, and subjected to thermo-mechanical and chemical purification methods before plasma arc melting into usable titanium products.

The most successful electrochemical attempts to produce titanium have been reported by Fray et al and are known as the FFC Cambridge process [6-13]. By holding TiO_2 pellets at the cathode in a $CaCl_2$ melt, the oxygen (in the metal) was dissolved into the salt, leaving behind pure titanium. The oxygen is reacted with deposited calcium into CaO , which can be moved away from the titanium surface by its solubility in $CaCl_2$, in principle allowing for a continuous titanium reduction process. Alternatively, oxygen ionization may be more energetically preferable than calcium deposition, so direct reduction of the metal transpires. These respective reactions are:

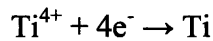


However, the FFC Cambridge process used a graphitic carbon anode that was consumed where the oxygen gas is discharged, and given the presence of oxygen, carbon, and chlorine, dioxin and furan generation may still occur, although on a much lower scale than the Kroll or Hunter processes. Furthermore, the solid-state reaction has not yet been able to scale up the laboratory findings to a manufacturable level.

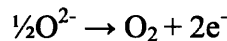
The Sadoway process under investigation would also be a direct electrochemical reduction of TiO_2 to titanium metal. In order to ensure compliance with environmental standards, the scheme would use an all-oxide melt of BaO with TiO_2 , eliminating the potential for any emissions other than oxygen gas (except for CO_2 burn off in cases where a carbon electrode is used). The Sadoway process also calls for processing at 1700°C , such that liquid titanium is formed and can be drained out in a continuous manufacturing process, opposed to the previously discussed solid-state reactions. Although more electrical power is needed to achieve the high temperature, the cost of manufacturing titanium via the Sadoway process should be less expensive because it is a one-step process without the need for the carbochlorination preparation of the TiO_2 feedstock.

Scientific Background

A molten metal-oxide melt is similar to any other solution in that individual species will ionize to full valence states leaving them charged with respect to their compound electronic structure. Thus, solid TiO₂ dissolves into the “like” liquid BaO as Ti⁴⁺ and O²⁻. By introducing electrodes to the system and running a current from the positively charged anode to the negatively charged cathode, the ionic species will migrate to the oppositely charged electrode and donate or receive electrons to neutralize to an uncharged valence structure. The titanium reduces at the cathode as:



while the oxygen is oxidized to gas at the anode as:



to complete the ionic current. In order for the process to successfully harvest the liquid titanium, the molten oxide must be of a lesser density, so the titanium can sink to the bottom. Also, the process would use a conductive crucible as the cathode, so that the titanium forms at the bottom of the cell. Typically, if solid metal is drawn out of the solution at temperatures below the melting point of the metal, it will electroplate the cathode as a solid, which will continue to conduct and grow layers of the deposited metal.

The mass of the metal produced (m) can be calculated by Faraday’s law of electrolysis:

$$m = \frac{1}{F} \frac{QM}{n} \qquad \text{Equation 1}$$

where F is the Faraday constant, Q is the total charge passed through the system, M is the molar mass of the metal, and n is the valence number of the metal ions in solution. The charge can be obtained by measuring the current passing through the cell and multiplying by the time the current was held (amperes = coulombs per second). The valence number

of electrons for titanium would be 4, although multivalent states are common with titanium and are a main reason for redox looping. The Faraday theory is not equipped to handle systems where multivalent states are as abundant and unpredictable as titanium. Still, the positive relationship between charge and metal production remains, so higher operating current densities would lead to higher throughput of metals production.

Reversible electrolysis occurs when for every charge-unit entering the system, one *electrolytic* reaction occurs that does not impair the electrode surface where the reaction occurs. In the TiO₂-BaO system, this would mean that 4 electrons arrive at the cathode, reduce one titanium ion, and by electrical neutrality that titanium ion's oxygen partners give up 4 electrons to be taken away by the anode and complete the circuit. Reversible electrolysis displays linear potential-current (VI) characteristics where there is a simple resistance in the system from the ionic conduction. More electrical potential directly induces more reactions, which can be observed as an electrical current flowing in the cell through the anode and out of the cell through the cathode. In practice, however, electrolytic reactions do not regularly scale linearly with the flow of available charge present, as there are other unwanted reactions capable of consuming the charge flow. For example, the titanium can cycle between subvalent electron states, at the worst having ions consuming the uncharged liquid Ti product in redox looping. In addition, reactions affecting the electrodes can alter the current level between deposition and electrostripping. This can include dissolution of the electrode (especially at the oxidizing anode), corrosion, or burn off as with carbon electrodes into CO₂.

The electrolytic voltogram is non-linear in most cases, with critical potentials required to activate the electrolytic reaction and unlock current flow. The metal may

reduce and deposit above a certain potential, with the molten oxide species (e.g. barium in the titanium system) actually reducing and depositing on the cathode at another higher potential. The same behavior is observable for oxygen formation at the anode. However, while metal deposition at the cathode still allows for conduction of electrons into the melt to continue the electrolysis, oxygen formation at the anode occurs as a gas which covers and *insulates* the anode, preventing electrical current flow (uptake of electrons from oxygen anions). Anodic destabilization by the oxygen products can be a strong constraint on the metal-producing efficiency of the electrolytic system. Therefore, the identification of optimal materials for the cell anode is critical to the success of the electrolytic system.

The candidate materials must be capable of (a) enduring the high temperature hold-points that accompany the Sadoway process, (b) remaining as minimally reactive and consumable as possible to the melt and the products, (c) maintain high current density to maximize the metal production throughput (Equation 1), and (d) match price and supply levels that will not jeopardize the economic feasibility of the electrochemical cell. Noble metals such as platinum and iridium are extremely expensive (roughly \$14,000 a pound for platinum and \$4,000 a pound for iridium), but are high temperature stable and non-reactive [14]. Molybdenum, tungsten, and carbon are cheap (\$25 a pound for molybdenum, \$15 a pound for tungsten, and \$0.25 a pound for graphite) and have sufficiently high melting temperatures, but could form oxides too easily (MoO_3 & WO_3 solids and CO_2 gas) to serve as continually conductive or non-consumable anodes.

Experimental Procedure

The experiments concerning electronic characteristics were not conducted on the BaO-TiO₂ system, but rather with a less harsh system to give a clearer indication of individual electrode behavior. A physical model melt of sodium borosilicate (Na₂O-B₂O₃-SiO₂) was used as a low-temperature surrogate. No metal oxide feed was included, since our investigation revolves around the anode process where only oxygenation is the dominant factor. The composition of the melt was 15.0 g Na₂O, 15.0 grams B₂O₃, and 10.5 grams SiO₂ and was held at a temperature of 850°C. This temperature was sufficient to melt the sodium borosilicate. A running stream of water with a welded-on copper tube cooled the neck of the furnace to prevent corrosion of the steel furnace (made by Mellon). In addition, a slight overpressure of argon was kept in the furnace atmosphere, also to prevent corrosion. A graphite crucible was used to hold the melt.

The electrodes consisted of wires of varying materials types that were encased within an alumina shell, such that only the very end of the bottom tip was exposed with a diameter of approximately 0.5 mm. The wire was inserted into the hollow alumina tube and sealed with MgO cement, then allowed to dry for 24 hours in ambient conditions. The candidates for anode materials were: carbon, tungsten, iridium, and platinum.

The potentiostatic, galvanostatic, cyclic voltametry, and open circuit measurements were all acquired by Schlumberger Solarton 1200 series electrochemical analyzer and impedance/gain phase analyzer and Cordata software. The data acquisition scan rates were 20mV/s for cyclic voltametric data and 10mA/s for galvanostatic data. A three electrode system was used for measurements, whereby instead of measuring electrical properties with respect to the oppositely charged electrode (e.g. anode with

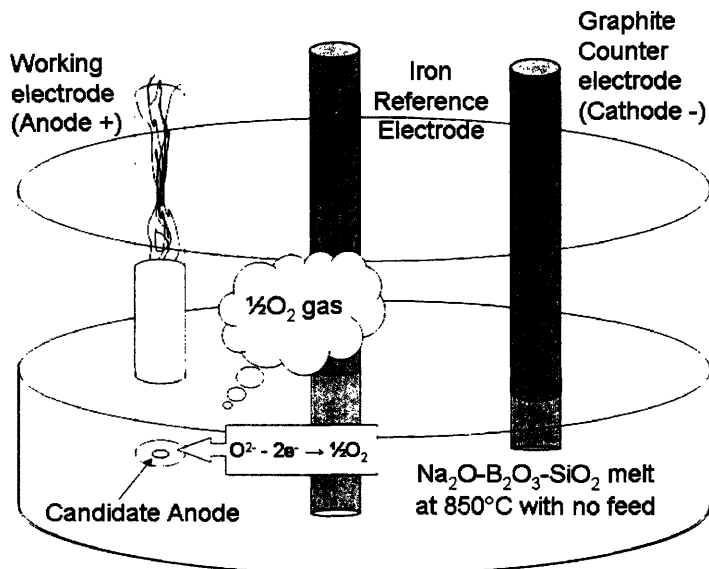


Figure 2: Schematic of the electrolysis cell for voltammetric experiments. The candidate anode materials were small, flat disks in alumina housing. Measurements were taken with respect to the iron reference electrode and the graphite counter electrode was used to modulate current or voltage. The low-temperature surrogate sodium borosilicate was used at 850°C with no metal feed.

respect to cathode), measurements were captured with respect to a grounded reference electrode (Figure 2). The reference electrode method results in more accurate data by eliminating offset effects. An industrial electrolytical cell for metals production would only require a cathode and anode (the reference is only for experimental measurements). An iron reference electrode was used, and a graphite counter electrode. The working electrode was varied between the 5 candidate materials.

Results and Discussion: Cyclic Voltammometry

Voltammometric techniques were used to analyze the effectiveness of the candidate electrode in our cell. These techniques treat the cell as an electrical device, whose IV curve is capable of describing its efficiency and functionality. In cyclic voltammometry, the current is measured while voltage is scanned repeatedly from a rest potential to a higher potential and back. The data used here is from the second such cycle in the voltammometric measurements. The upward potential scan reveals a smaller peak where the primary reaction is the oxidation of the electrode into a metal oxide. The reactions in this region are limited by electron transfer, such that the oxygen anions arrive at the electrode faster than their electrons can be directly stripped to produce oxygen gas. Instead, the oxygen reacts with the metal and the electrons are donated via that process. This voltage and current should be as low as possible, so that the transition into the mass transport limited regime is favored, where the desired oxygen gas evolution is the dominant reaction. The longer the cell is in the metal oxidation regime (when the upward scan is at a local peak), the less efficient the electrode for the electrolytic reaction.

At high enough potential during the upward scan (typically around 2V), oxygen gas evolution can be observed as the current becomes highly volatile and reaches a maximum value. The oxidation of the oxygen anions to gas allows for the removal of oxygen from the cell and the accompanying electrons, facilitating the uptake of electrons and reduction of titanium at the cathode. A high terminal current during oxygen gas evolution enables more electrolytic activity and metals production on the opposite end. At these high potentials, the oxygen gas forms at the surface of the electrode and

insulates it from conduction between the oxygen anions and anode. As bubbles form and depart, the current of the cell can range greatly in value.

After this threshold, the voltammogram scans downward back to the rest potential. The current on the down scan is less than the upward scan due to the difference in surfaces at which the reactions take place. In the upward scan, the oxidation reaction is occurring on a mostly metal surface that may form a metal oxide barrier as the scan progresses. During oxygen gas evolution, some metal oxide layer formation may still occur as well. On the downward scan, the oxide layer is being stripped off as oxygen moves back into the melt as anions. The energy required to oxidize and reduce the metal surface should be conserved in either direction of the reaction. However, since the downward scan has a thicker oxide barrier that produces more electrical resistance in the cell, the downward scan current is always less than the upward scan current. The cyclic voltammogram (CV) therefore displays some hysteretic characteristics, with the least hysteresis denoting the least reactivity of the metal with oxygen to form an oxide surface layer. The best candidate anodes should have as narrow a CV as possible to suggest low reactivity with the melt. Also during the downward scan, there is another local peak (similar to the upward scan) where the electron transfer limited regime is reentered. This signifies the recovery of the metal to a non-oxidized surface. The better anodes will be stripped of the surface oxide more quickly (less negative current at higher voltage) to signify low affinity for metal oxide surfaces and little energy to accomplish the oxide stripping. In light of the ideal CV properties discussed, the anode materials' performance can be analyzed.

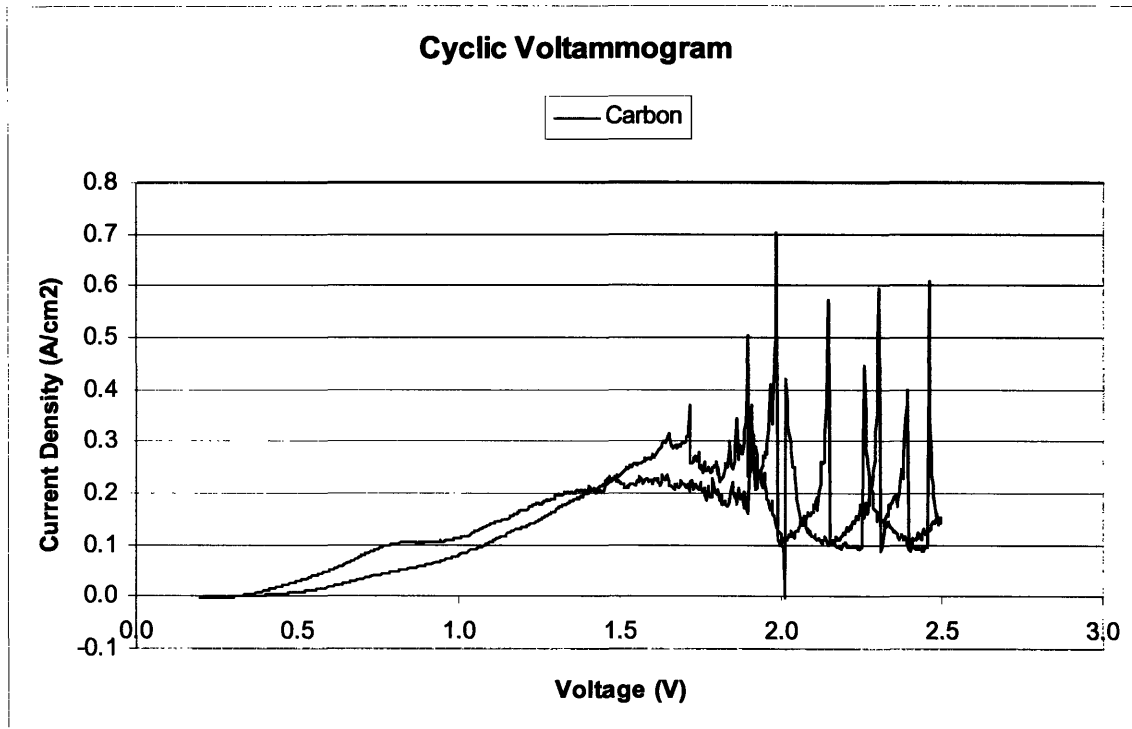


Figure 3: Cyclic voltammogram of a carbon anode. The current density for oxide formation (in the electron transfer limited regime) is 0.10 A/cm^2 occurring at 0.8 V . The current density during oxygen gas evolution was 0.16 A/cm^2 over 2.0 to 2.5 V . The recovery (oxide stripping) does not occur for carbon since oxidized CO_2 departs the system as a gas (bubble departure can be observed in the sharp spikes above 2.0 V). Hence, the upward and downward scans are very close in current since the reactions always take place on a newly exposed graphitic surface.

Carbon

The graphite anode exhibits some effects that counter the intuition stated above. Unlike the other metals, the oxide layer formed by oxidation of graphite is a gas, CO_2 . The gas can depart from the metal surface, whereas the solid oxide layers of the other candidate anode are fixed in place. Therefore, the graphite anodes are consumed by the electrolytic reaction, always leaving a metal surface layer. Since the reactions always take place on the freshly bare graphitic layers, very little hysteresis is observed in the carbon CV. The surface during the upward scan is nearly identical compositionally to the downward scan. Here, low hysteresis does not denote low reactivity, but rather high reactivity into a species that can actually escape the anode. The CO_2 also wets the

surface of the graphite electrode, so the bubble sticks around and insulates the anode from achieving optimal conduction. CO₂ molecules, because of their higher degree of polarity than oxygen gas molecules, form larger bubbles- which not only further retards conduction by eliminating anode surface area, but also impede release of the bubble so there are less high conduction spikes. The frequency of the bubble release can be observed from the CV spikes above 2.0V, but even more so from potentiostatic measurements, which are analyzed in an upcoming section.

Due to the interference of the CO₂ bubble with the electrical conduction of the anode, the graphite displayed the lowest current density during gas evolution. This would limit the metal formation at the cathode by creating a current bottleneck, resulting in slower, less efficient metal production. The graphite is actually well conducting – it exits the electron transfer regime first of all the candidate metals and is a performance leader at low voltages – unfortunately, the CO₂ consequences outweigh the inherent metal properties and it is the laggard at current density for high voltages. The current density for oxide formation (J_{MOX}) was 0.10 A/cm² at 0.8V and the current during gas evolution was 0.16 A/cm² over 2.0 to 2.5V (Figure 3). The recovery of an oxide layer into metal is non-existent since the CO₂ has departed and only the underlying graphitic layer remains.

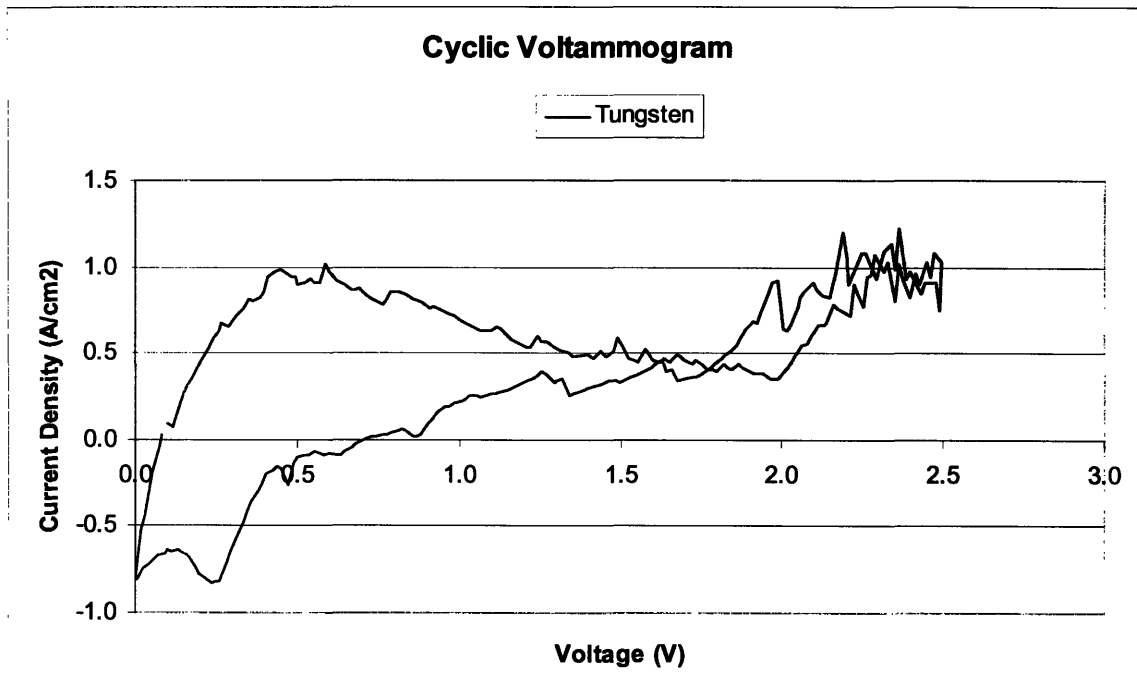


Figure 4: CV of a tungsten anode. Tungsten's tendency to form a surface oxide leads to a large conductance of charge in the electron transfer regime (1.0 A/cm² at 0.5V) and nearly as large current densities to strip the oxide on the downward scan (-0.83 A/cm² at 0.24V). The current density during oxygen gas evolution is 0.87 A/cm².

Tungsten

Of the non-graphitic metals, tungsten forms a metal oxide layer (WO₃) the most readily, which drives its anodic behavior in the cell. Tungsten has a lot of low voltage hysteresis, meaning its oxide layer forms readily and is not easily stripped off. Tungsten is the most conductive anode below 1.0V, as it accepts electrons easily and soon enters the mass transport limited stage at just over 0.5V. However, much of this current goes into oxide formation as the upward scan local peak approaches 1.0 A/cm² before falling back down as electron transfer becomes less relevant (Figure 4). The current density during oxide formation is 0.87 A/cm² over 2.0 to 2.5V. Oxygen bubbles still limit current flow in this regime, but the smaller size of oxygen bubbles and quicker frequency of formation and release contribute to better conduction than graphite (with its CO₂) in

this mode. The tungsten takes a long time to recover to the metal, with a downward scan peak at -0.83 A/cm^2 and 0.24 V which is quite far into the downward scan (low potential). Tungsten is initially conducting and draws in current, but much of it goes into oxide formation. The WO_3 is not very conductive, so it is difficult for the anode to reabsorb enough current during the downward voltage scan to strip that oxide and recover the tungsten metal surface.

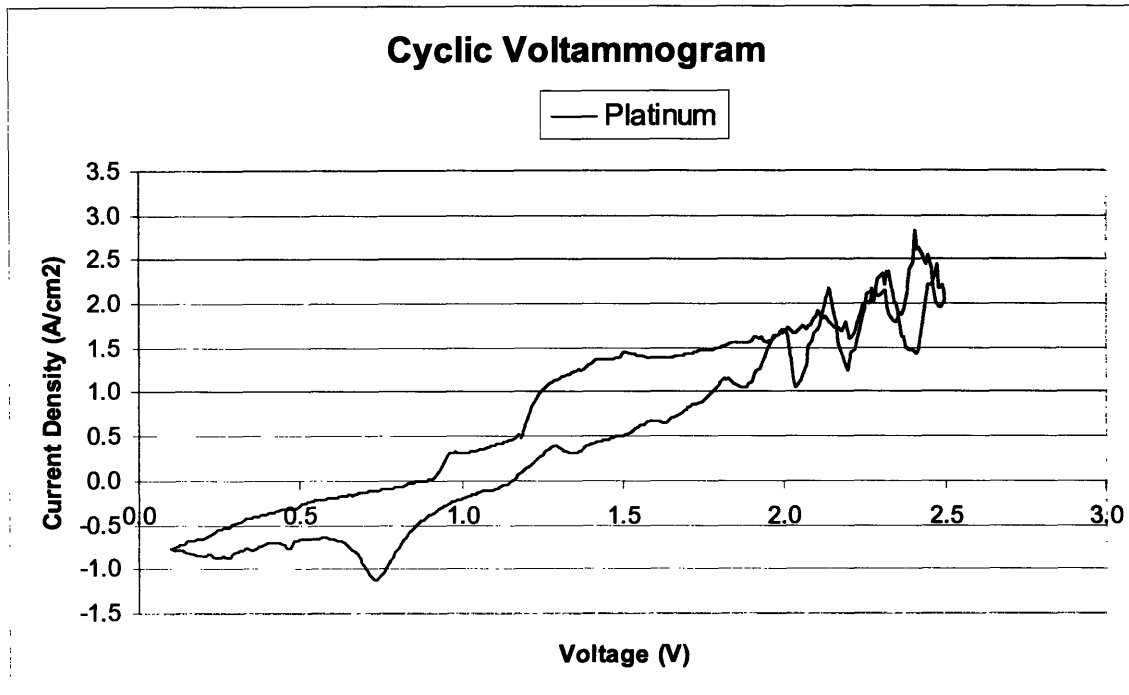


Figure 5: CV of a platinum anode. Platinum has a current density peak for PtO_2 formation of 1.46 A/cm^2 at 1.5V , followed by a current density during O_2 gas evolution at 1.87 A/cm^2 . The oxide stripping peak is -1.1A/cm^2 at 0.7V on the downward scan. The hysteric nature of the CV suggests a difference in the surfaces of the upward vs. downward scan due to oxide formation.

Platinum

While platinum has some undesirable oxide forming properties, it conducts very well during oxygen gas evolution. Platinum exits the electron transfer limited regime the latest at 1.5V at a current of 1.46 A/cm^2 . This may be explainable by the conductivity of platinum, even in an oxide form (PtO_2). Although platinum draws current into oxide formation, the PtO_2 remains conductive so the transfer mode remains electron limited until 2.0V when oxygen gas evolution begins and is carried out a current density of 1.87 A/cm^2 (Figure 5). Platinum's current density during oxygen evolution surpassed the other anode candidates for CV measurements. This current level could potentially result in the best metal production efficiency in a functional cell. In the downward voltage

scan, platinum recovers to non-oxidized metal at 0.7V at a current density of -1.1A/cm^2 .

While the recovery voltage is acceptable, the current required is much larger than the other candidate anodes. Again, the rationale may be that the conductivity of PtO_2 allows it to pass current without breaking up and being stripped back into the melt. The reentrance of the voltage scan into the electron transfer regime occurs quickly, but the electrolytical removal of oxygen (a regime which is not the favored mode of the system) requires more current for charge to allocate to the recovery reaction. There is a fair amount of hysteresis from low voltages all the way up through oxygen gas evolution. The ready formation of a conducting oxide enables high current density during oxygen gas evolution, but there is still some amount of resistive loss from the oxide layer, so the difference in surfaces during the reactions (Pt on the upward scan, PtO_2 on the downward scan) is observable in the hysteretic nature of the CV curve.

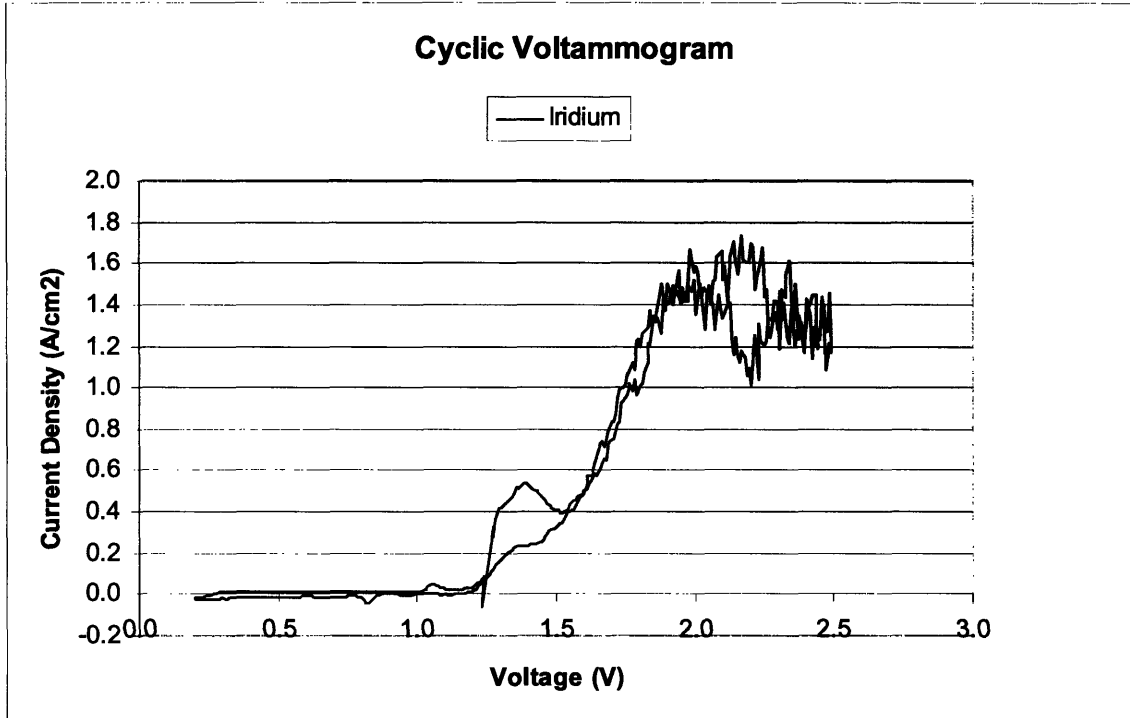


Figure 6: CV of an iridium anode. Iridium displays exceptional inertness through (a) its equitability of scan direction, indicating that the metallic surface is maintained and (b) minimal down-scan current of -2.0 mA/cm² for oxide stripping. The electronic transfer regime peak is 0.54 A/cm² at 1.4 V and the current density during O₂ evolution is 1.37 A/cm².

Iridium

Iridium combines the best qualities of low oxide formation and high conductivity during oxygen gas evolution to make it a strong anode candidate. There is little observable hysteresis between the upward and downward scans, signaling that the surface properties are consistent in that very little oxide forms. The oxidation reactions taking place in the upward scan occur on the metal surface and the reduction during the downward scan also occurs on the metal surface. Iridium also displays very little current (around 14 mA/cm²) during the electron transfer regime where metal oxide formation (IrO₂) would be the dominant reaction (Figure 6). The only exception is the very start into the mass transfer limited regime, where some hysteresis is observable. In the 1.2 to 1.5 V range, there is enough current for metal oxide to form, but after 1.5 V the dominant

conduction mode is channeled into oxygen gas evolution. The current density for oxide formation maximizes at 0.54 A/cm² at 1.4V before moving into oxygen gas evolution at a current density of 1.37 A/cm². In the downward scan, there is little hysteresis, even within the mass transfer limited regime until the 1.2 to 1.5V region where oxide formation was evident. The oxide recovery current density was -0.02V, a low for all the candidate anodes, at 0.8V. The IrO₂ is easily stripped by very little current, and quicker (at higher downward scan voltages) than other anodes as well. Iridium is very inert: it displays minimal hysteresis, forms minimal oxide, and strips off what little oxide does form very easily. However, in its only shortcoming, iridium's current during oxygen gas evolution was less than platinum for these CV measurements.

Potentiostatic and Galvanostatic Electrolysis Voltammometry

Although CV measurements are useful for picking out electrical and kinetic properties as they relate to metal reactivity and oxide formation, they do not represent the steady-state conduction properties that would govern an always-on electrolytic cell. CV scans return the knee-jerk current density that a voltage is capable of producing in the cell. However, as the cell electrolyzes metal oxides feedstock, it maintains a consistent setting over a long time-frame. Therefore, potentiostatic (PS) or galvanostatic (GS) measurements, in which constant voltage or current is maintained, give greater insight into the actual current densities that can be obtained during oxygen gas evolution periods. Inertness is also more rigorously tested in these measurements, although not quantitatively as in CV. Oxide layers are given the opportunity to form (to continually building or self-limiting thicknesses) and some effects on later-in-time conduction can be observed. The GS data should, in large, be consistent with the PS data, as both are merely holding one parameter constant and measuring the other which is a direct function of the constrained parameter. Fortunately, the GS and PS data agree such that the current densities are very similar for comparable voltages (Figure 7).

While the two bottom performers, graphite and tungsten, retained their conductivity rank, platinum was passed by iridium, which became the highest conducting steady-state anode during oxygen evolution. Graphite actually matched its CV with its PS scan, which can be understood from the fact that the surface is incessantly oxidized into departing CO₂ gas. Since each set of reactions takes place on a freshly revealed graphite layer, no long term steady-state oxide effects exist (or rather they are reached

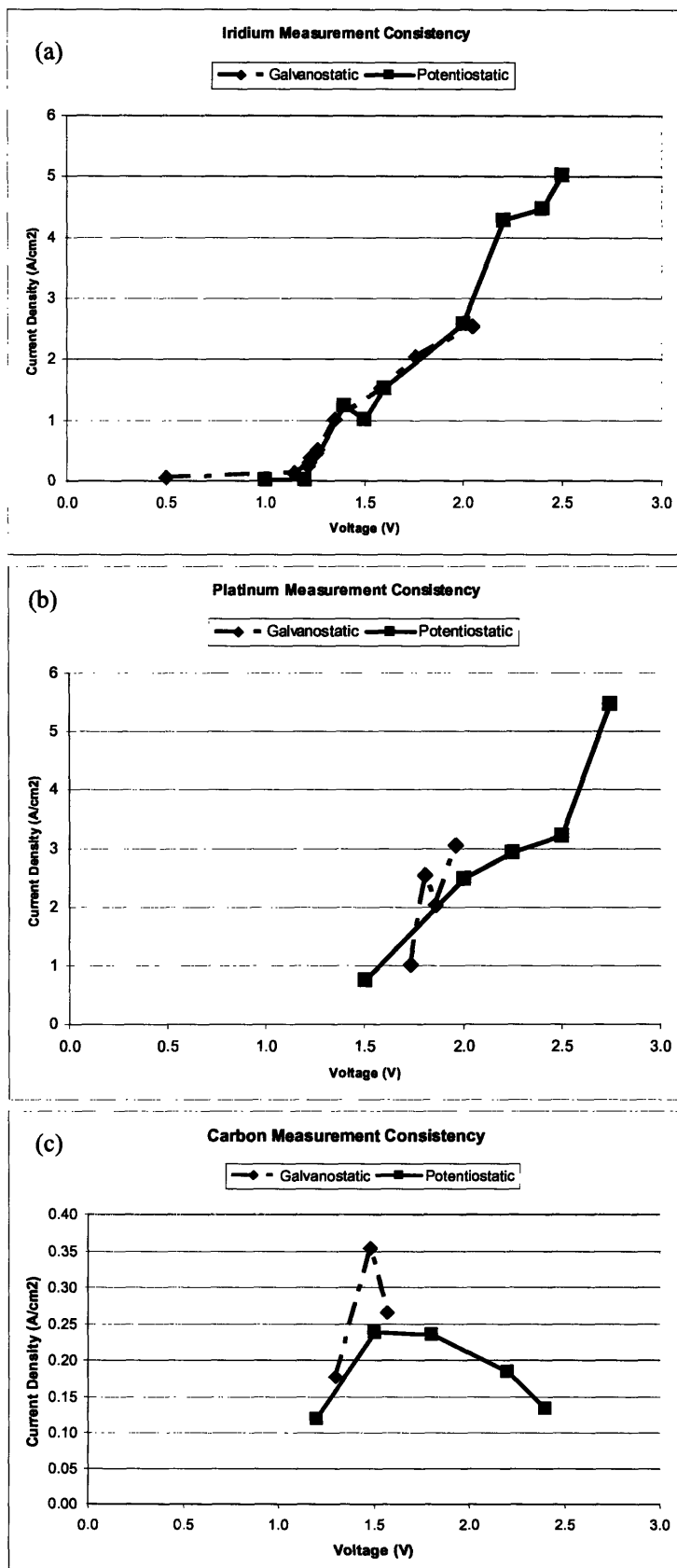


Figure 7: Comparison of potentiostatic (constant voltage) and galvanostatic (constant current) measurements for (a) iridium, (b) platinum, and (c) carbon. Galvanostatic measurements were not taken for tungsten.

These measurements should be very similar, since they perform the same electrolytic function. Any differences indicate erratic behavior of the system or limitations on the accuracy of measurements.

The iridium measurements were very consistent, while the platinum and carbon measurements were mostly consistent (although not entirely). The performance of the iridium anode may be due to minimal oxide formation across all measurements. Platinum and carbon are more reactive with the oxygen anions, which may lead to alternative oxide thicknesses or reaction rates that are subject to fluctuation.

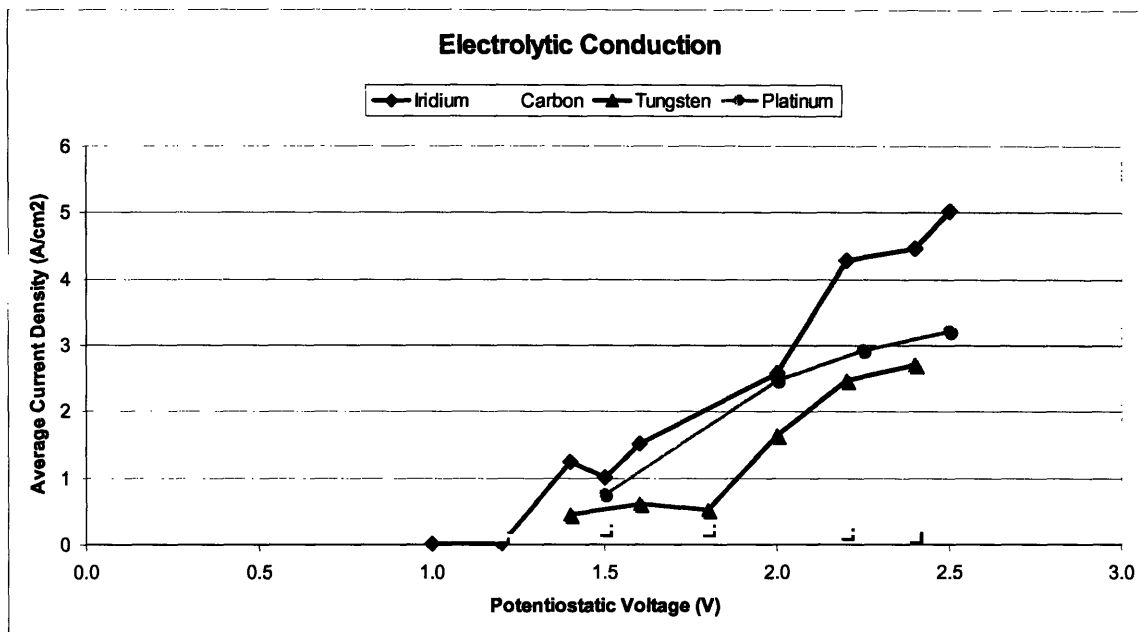


Figure 8: Potentiostatic voltammogram of iridium, carbon, tungsten, and platinum. Instead of automatic scanning at a rate around 1 volt each minute, as in CV, target voltages were manually held for about 10 minutes and average values were measured. This more closely simulates performance in a metal-producing electrolytic cell. Iridium maintained the highest current density during O₂ evolution, whereas platinum was the lead performer in CV. The steady-state quality of PS electrolysis may favor the more inert iridium over the relatively more reactive platinum.

instantaneously, depending on the point-of-view). Tungsten was comparable CV-to-PS until 1.8V, but the PS current density outperformed the CV counterpart significantly. This may be due initial energy allocation into WO₃ formation (as shown by CV), but the oxide layer self-limits after some time that allows redistribution of charge into conduction during oxygen gas evolution. Platinum also shifted to higher current density during oxygen gas evolution and could be exhibiting the same effects as the tungsten. Iridium achieved the highest PS current density at high voltages, reaching 5 A/cm² at 2.5 V. Carbon, tungsten, and platinum all display deceleration of current density with respect to higher voltages. Although the amount of points in the data set is not optimally dense, the PS measurements show decreasing slopes for carbon, tungsten, and platinum conduction as higher voltages are reached. In fact, carbon reaches a peak conduction of 0.3 A/cm² at

1.7V and worsens at higher voltages. This behavior (for W and Pt as well) could be due to increased bubble formation and impedance of current. However, iridium does not display this deceleration; the explanation may be that iridium's surface properties have lower affinity to oxygen gas (oxyphobic) so it forms smaller bubbles that depart quicker. Alternatively, just graphite faces the CO₂ bubble problem, while tungsten and platinum form self-limiting layers of oxides that are resistive barriers and eventually cap out conduction at distinct current densities. Iridium might display such a high level of inertness that it never forms such an oxide barrier and current density continues to climb. Irrespective of the kinetics behind iridium's high-V conduction, it vastly outperformed the other candidate anodes during steady-state oxygen gas evolution occurring above 2V. In functional electrolytic cell, this would enable the highest degree available of metals production efficiency.

Potentiodynamic Voltammometry

Potentiodynamic (PD) scans fall in between CV and PS in terms of instant electrical response versus steady-state measurements. PD is basically the same as CV in that voltage is ramped up while the resulting current is measured. However, a much slower data acquisition rate is used (0.2 mV/s) so that the hold-time at each particular voltage is longer to simulate steady-state current. The PD hold-time is automatically more precise than PS, but PS hold-times are on the order of minutes, whereas PD is still at seconds (with CV at fractions of a second). Indeed the PD data more closely resembles the steady-state PS data in terms of the ranking of current density during oxygen gas evolution for the candidate anodes. Carbon performed the worst, while tungsten improved greatly to fall just short of matching platinum, and iridium was the

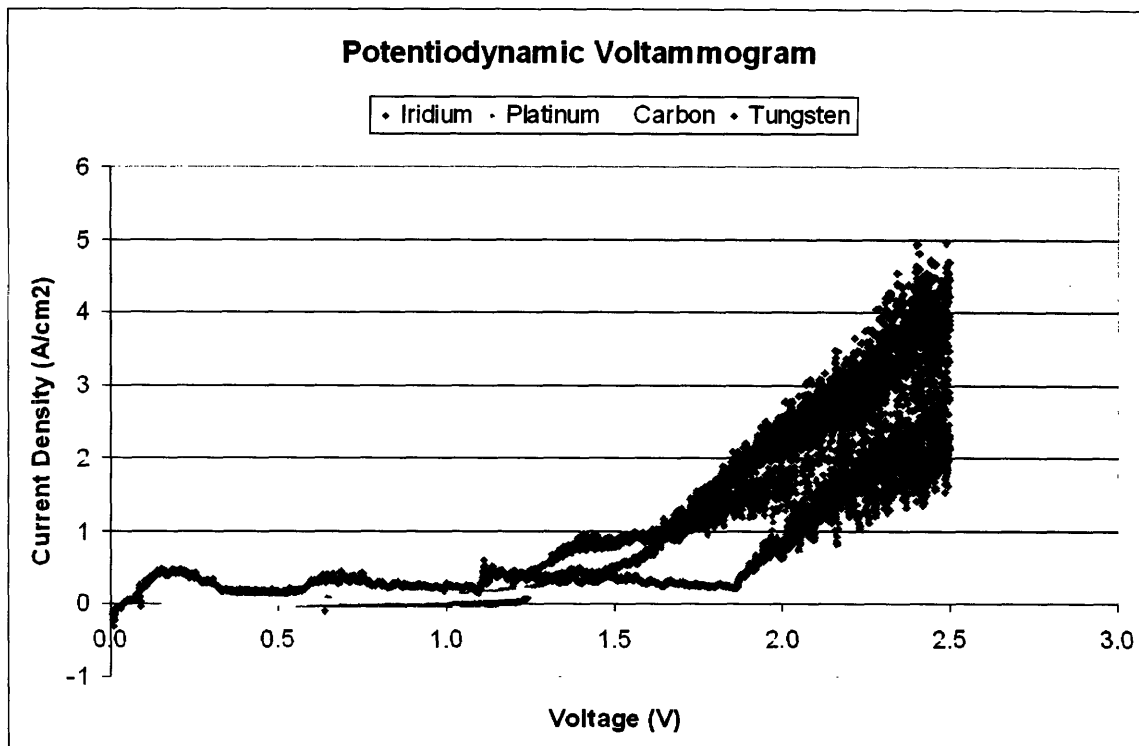


Figure 9: Potentiodynamic voltammogram of iridium, platinum, carbon, and tungsten. The intermediate voltage scan rate elucidates some of the effects of short-run vs. long run measurements. Tungsten is the most conductive in the electron transfer limited regime, as it forms oxide the most readily (least inert). Platinum is the lead performer (in current density) from 1.2 to 1.7V as its oxide hasn't had sufficient time to form over the scan-time required to reach that voltage. After 1.7V, however, the PtO₂ layer becomes thick enough to limit conductivity and iridium is the most conductive in the steady-state electrolytic O₂ evolution regime.

best conductor above 1.7V. The graphite anode still demonstrates a peak where current density is maximized at 0.28 A/cm² at 0.65V (very near to the PS peak of 0.3 A/cm² at 0.7V). Tungsten is actually the best low voltage conductor up to 1.25V (within the electron transfer limited regime), since the dominant reaction in the regime is metal oxide formation. Tungsten draws much current for the formation of a substantial WO₃ layer. This is similar to the CV data in which tungsten also was the most conductive in the low voltage electron transfer limited regime (which lasted until 1.18V in CV). The tungsten PD measurements display the anode remaining in the electron transfer mode through 1.87V, comparable to the 1.8V value in the PS and CV data.

In PD, however, platinum actually is the most conductive upon entrance to the mass transport limited regime (1.25 to 1.67V). Deeper into the mass transport limited regime, when serious oxygen gas evolution begins as evidenced by the increasing volatility of the current, iridium's current density passes that of platinum (above 1.67V). This symbolizes the short-run versus long-run observations of CV versus PS quite well. The quick scan rate of CV gives the immediate reaction of the anode to a certain voltage, while the long scan rate of PS gives the steady-state reaction. In CV measurements of anode conductivity during oxygen gas evolution, platinum was the highest; in PS measurements, iridium was the highest. PD data, with the intermediate scan rate, contains a region of platinum as the most conductive, followed by a region of iridium as the most conductive. The latter region occurs after the anode properties have had enough time to develop their steady state current (at higher voltage), while the former region occurs before such development has had sufficient time to occur. This is due to two factors. Firstly, platinum enters the mass transfer limited regime before iridium (at lower voltages), allowing it to pass greater current from oxygen gas forming reactions, while iridium has not yet reached oxygen gas evolution. Secondly, while platinum is the better natural conductor, platinum oxide forms after a certain amount of time [or current] to limit the total current that can be passed during oxygen gas evolution. In the short-run measurements (CV, mid-voltage PD) that oxide has not had time to materialize, so the platinum performs better. Iridium forms very little oxide in the long-run, so it is able to pass more current in measurements that reflect its inertness despite the opportunity for oxidation (PS, high voltage PD).

Conclusion

Four candidate anode materials were accessed for use in an electrolytic cell. The main criteria for selection included (a) inertness and (b) high current density during electrolysis. The electrolytic cell can be treated as an electrical device describable by voltage and current characteristics. These properties were measured through cyclic, potentiostatic, galvanostatic, and potentiodynamic voltammometry. The main difference between these techniques is the voltage scan speed. CV scans fairly quickly to give the immediate reaction of the cell to certain voltages. PD scans slowly to give a better idea of the long-term behavior of the cell as a steady-state electrolyzer. PS is even more long term as individual voltages are held for up to 10 minutes and the average current is assessed based on that time-frame.

There is little difference [in terms of rank] over the short-run or long-run measurements for carbon and tungsten. Carbon oxidizes into CO_2 , which adheres to the anode surface as bubbles and insulates the anode from further conduction until it releases (Figure 10). Tungsten is too reactive in forming surface WO_3 , so it underperforms platinum and iridium in terms of current density during oxygen gas evolution (J_{O}^2). Platinum achieved the highest J_{O}^2 during the short-run CV measurements, but iridium achieved the highest J_{O}^2 during the long-run PS electrolysis. In the intermediate PD data, the transition from short-run to long-run conductivity is observable at 1.7V as iridium overtakes platinum. The short-run performance of platinum is not explainable by a higher conductivity of its bare metal since iridium is more conductive at 900°C ($\sigma_{\text{Pt}} = 2.48 \text{ S}/\mu\text{m}$, $\sigma_{\text{Ir}} = 4.42 \text{ S}/\mu\text{m}$) [15].

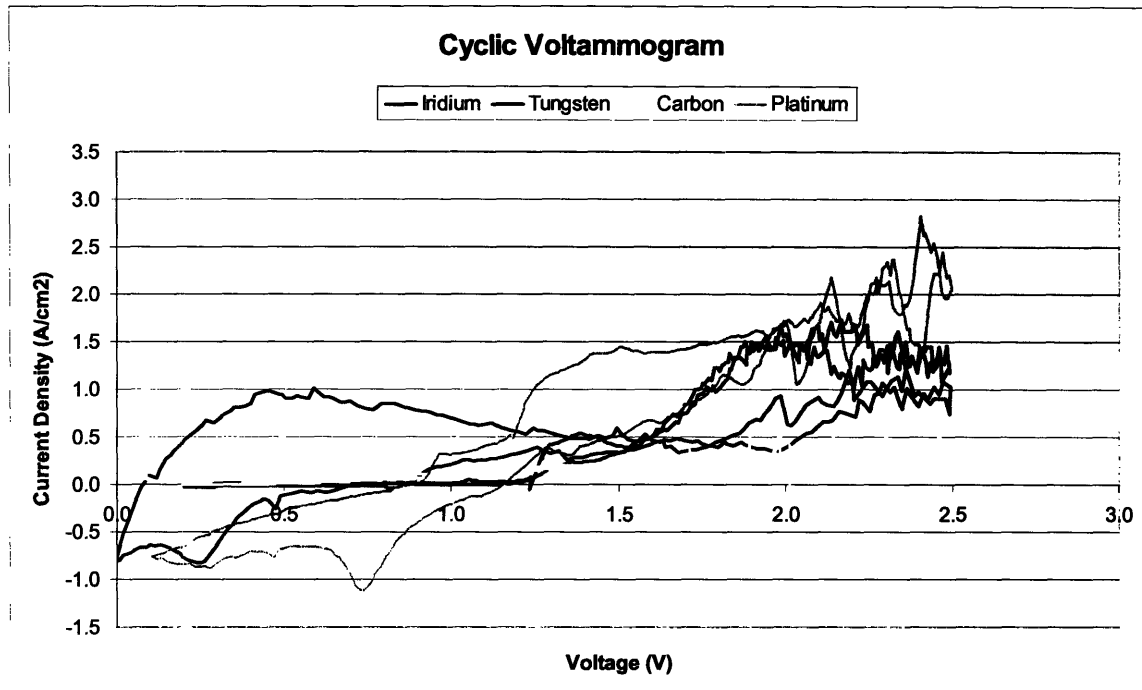


Figure 10: Combined CV of iridium, tungsten, carbon, and platinum. Carbon oxidizes into CO₂, which adheres to the anode and insulates it. The tungsten surface reacts into WO₃ at low voltages, consuming charge in the process (observed as high current density and scan hysteresis). Platinum displays some oxide formation (hysteresis), but high current density during oxygen gas evolution. Iridium appears inert (low hysteresis) and conducts nearly as well as platinum at high voltages. Iridium outperformed platinum in steady-state electrolysis measurements.

Instead, the electron transfer barrier may be lower between platinum and the oxygen anions (seems feasible as platinum does form an oxide easier than iridium). The reactivity of bare Pt leads to higher conduction in the short-run of CV, but also results in a PtO₂ layer in the PS and PD measurements that allows the inert iridium to surpass it in the long-run. This is also observable with tungsten: it is reactive, so it conducts well in the short-term CV up to 1.2V, but that reactivity is also manifested in oxide formation that leads to eventual J_O² under-performance. Of the four candidate anode materials, iridium consistently displayed the best features of inertness and high current density during electrolysis. Indeed, iridium has been shown to be an excellent electrochemical oxidation catalyst with clear differentiation between low-current electrochemical reaction rate-control and higher-current surface adsorption and mass transfer rate-control [16-19].

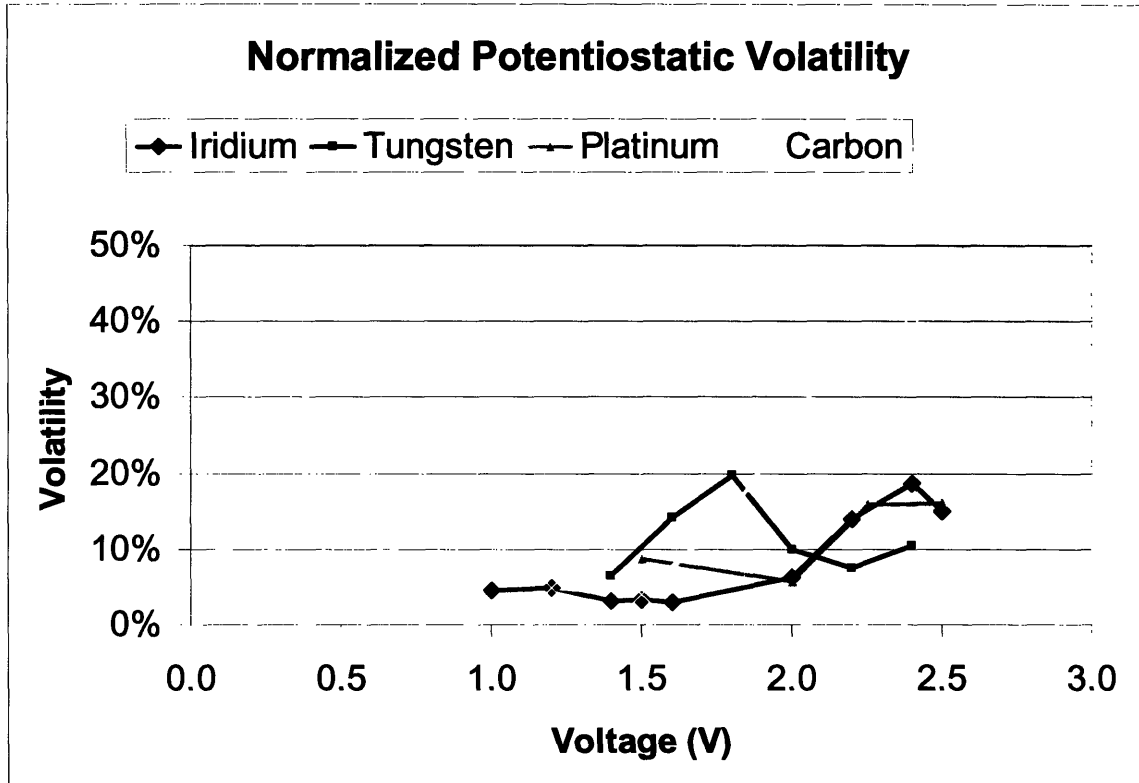


Figure 11: Volatility (standard deviation normalized by average current) for PS measurements. Tungsten's volatility is centered at 10%, platinum and iridium increase from 5-7% below 2.0V to 15-20% above 2.0V [during oxygen gas evolution], and carbon's volatility increases from 5-7% below 1.5V to nearly 40% above 2.0V. This volatility in PS data stems from the insulating effects of the oxygen gas products of electrolysis as bubbles nucleate on the anode surface, expand, and eventually depart.

The evolution of oxygen [or CO₂] bubbles on the anode introduces much volatility into current density measurements. The bubbles nucleate, grow, and become of enough size that their surface energy is lowered by departing from the anode surface. During this process, the anode surface is partially blocked by bubbles, which insulate it from electrolysis, and cause the current measurements to fluctuate. For the PS measurements that simulate electrolysis, these variations could be averaged out to arrive at the operating current for each voltage. The PS volatility (standard deviation normalized by average current) caused by the bubbles was typically around 10% over the 1.0 to 2.5V range for tungsten, iridium, and platinum. The kinetics of graphite's CO₂ product led to even more volatility approaching 40% at 2.4V (Figure 11).

Other CV effects include the polarization of the IV curve due to mass transport kinetics. The three basic steps of electrolysis at the anode are: (1) O^{2-} anion arrives at the anode surface, (2) electrons transfer from the anion to the anode (oxidation), and (3) oxygen departs the anode surface as a gas. If one of these steps is slower than the others, it will limit the electrolysis reaction and prevent the system from reaching equilibrium. For low voltages, the electron transfer step is slowest (as there is inadequate charge flow). Thus, as the voltage is increased (more access to charge), the current increases as well. For higher voltages (above 2.0V), the electron transfer is sufficient, but the mass transport of oxygen to and from the surface is insufficient, so increasing the voltage does not increase the current significantly (only faster oxygen movement would increase current). Since alternate steps can hinder the electrolysis, the electrical characteristics tend to shift to more extreme voltages to accomplish the same reaction (positive voltage quadrant to the right and negative voltage quadrant to the left).

As this work was carried out on a low temperature surrogate of sodium borosilicate, these voltammometric techniques may further be applied towards the determination of anode properties [for titanium production] in the target molten oxide of BaO and/or at high processing temperatures of 1700°C. Effects of the anode geometry on electrochemical properties should also bear impact. There are further materials not discussed here that may be of some relevancy to anode selection (molybdenum, nickel chromium, tantalum).

Acknowledgements

This work was performed in the MIT Department of Materials Science and Engineering towards the author's fulfillment of the thesis requirement for a Bachelor of Science. The author would like to thank Professor Donald Sadoway for supervising the thesis and Professor Dihua Wang of Wuhan University and Dr. Chanaka Dealwis for laboratory aid and supervision.

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