

# Small Scale Bio Fuel Cells for Long Duration Unattended Ground Sensor Applications

Christopher Apblett<sup>1\*</sup>, David Ingersoll<sup>1</sup>, Gregory Roberts<sup>1</sup>, Shelley Minter<sup>2</sup>, Plamen Atanassov<sup>3</sup>

<sup>1</sup>Sandia National Laboratories, 1515 Eubank SE, Albuquerque, NM 81785 USA

<sup>2</sup>St. Louis University, Department of Chemistry, 3501 Laclede Ave., St. Louis, MO 63103-2010 USA

<sup>3</sup>University of New Mexico, Department of Chem. & Nucl. Engineering, 247 Farris Center, Albuquerque, NM 87131 USA

## Abstract

The development of small, sustainable power sources for continuous monitoring applications requires a power source that is independent of a logistical supply, and therefore necessarily requires some form of environmental harvesting for long term operation. This paper outlines efforts to develop a chemical harvesting power source, where fuel is harvested from local flora, and oxygen reductant is taken from the air. A fuel cell running on glucose, sucrose, and tree sap is explored, with a conclusion that noble metal catalysis is difficult for these natural fuels, and that enzymatic catalysis is preferred for the anode. The requirements of such an enzymatic anode in terms of stabilization and mediator performance are discussed in the context of a continuous flow, long term operation fuel cell.

*Keywords: Miniature Fuel Cell, Enzymes, Energy Harvesting, Glucose/Sucrose Fuel*

## 1. INTRODUCTION

The use of electrochemical fuel cells that take fuel from their immediate environment for implantable devices has been suggested for more than 40 years[1, 2], but real progress toward such devices has been hampered by the capability of the anode and cathode to operate for long periods of time on environmentally available fuels. In contrast to the majority of the literature, the performance of electrochemical cells on environmentally harvestable ex-vivo fuels (such as sucrose, saps, and pinenes derived from flora) have been unreported.

Yet, it is this application which promises to provide small, continuous operation power sources for use as unattended ground sensor (UGS) systems, as such a device can harvest both its fuel and reductant (oxygen) directly from the environment. Such a power supply, however, requires significant advances to overcome engineering limitations prior to being realized. On the anode side, oxidizing environmentally available fuels using traditional noble metal catalysts suffers from catalyst poisoning by the byproducts of the oxidation reaction.[3, 4] On the cathode side, reduction of oxygen from the air is limited by somewhat sluggish kinetics on platinum.[5, 6] In addition, crossover of fuel from the anode delivers some level of poisoning byproduct to the cathode resulting in lowering performance of the cathode over time.[7]

Enzyme based fuel cells have been developed by several workers.[8, 9, 10] These fuel cells are based on enzymatic catalysts for the oxidation of glucose, and produce small amounts of power. Understanding the limitations of enzyme fuel cells, particularly as these limitations pertain to lifetime of the cell, then become important. While the limitations for

noble metal based anodes are well understood, the limitations for enzymatic catalysts are less clearly understood. We developed fuel cells based on both types of systems, and looked at the comparison between the two anode types.

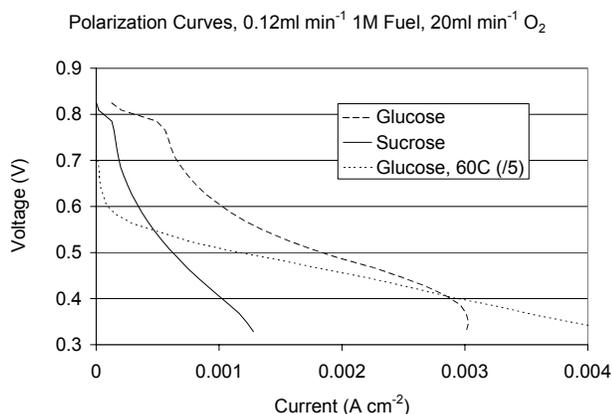
## 2. EXPERIMENTAL

The fuel cell assemblies in this work are similar to those reported in the literature[11], and follow the standards set by the direct methanol fuel cell literature when possible.[12] Cathodes are 5mg cm<sup>-2</sup> of platinum black loaded with Nafion™ and supported by a Teflon™ binder, and backed by a gas diffusion layer (GDL) of Toray® paper. Separators were 7 mil thick Nafion™ thermally bonded to the cathode and anode in the case of metal anodes, or compression bonded in the case of enzymatic anodes. Flow plates on both anode and cathode are pyrolytic graphite (POCO Co.) that have been ultrasonically milled with a single serpentine channel and are internally manifolded to an external fuel pump and oxygen pressure regulator. Due to the hydrophobic nature of the machined graphite, the functional region of each plate (the center 1cm x 1cm region in direct contact with the Toray® GDL were coated with 1µm of gold through thermal evaporation. Channel width for all assemblies on both anode and cathode are 1mm wide and 800µm thick, and are separated by 500µm wide ribs between channels. Supply rates for fuels are 0.12 ml min<sup>-1</sup> to the anode and 20ml min<sup>-1</sup> for oxygen or air to the cathode. Fuel was glucose (Sigma-Aldrich) at 1M concentration in deionized water for the noble metal anodes, and at 50mM concentration in phosphate buffer pH 7 for the enzyme anodes. The enzyme anode fuelstock also contained approximately 20mM of mediator in solution, either

\*Contact Author: Tel. 505-844-3497, Fax: 505 284-7690, email: caapble@sandia.gov

Ferricenyltrimethylundecylammonium bromide salts (FTMAB) or phenazine or its substituted derivatives (all from Sigma Aldrich). Sucrose fuels for the metal anodes were also 1M concentration (Sigma Aldrich). Tree saps were harvested from a sugar maple during sapping season from a representative host in New Mexico.

Assembled cells using metal anode catalysts used  $6\text{mg cm}^{-2}$  platinum ruthenium (Pt-RuO<sub>2</sub>) blacks with Teflon™ and Nafion™ binders, and were broken in using  $20\text{ ml min}^{-1}$  of atmospheric pressure hydrogen on the anode and a similar rate of atmospheric pressure oxygen on the cathode. Break in was performed over 24 hours at 80C and  $0.5\text{A cm}^{-2}$  current prior to testing with glucose. Due to the hydrophobic nature of the channels, switching from hydrogen to glucose necessitated an intermediate step of  $0.12\text{ml min}^{-1}$  flow of 1M methanol to wet the channels, prior to introducing the 1M glucose fuel for testing.



**Figure 1: Polarization curves for Pt-RuO<sub>2</sub> catalysts for Glucose and Sucrose, and Glucose at 60C (the 60C data is divided by 5 to scale it to the other two curves). Conditions:  $0.12\text{ml min}^{-1}$  1M fuel,  $20\text{ml min}^{-1}$  O<sub>2</sub>**

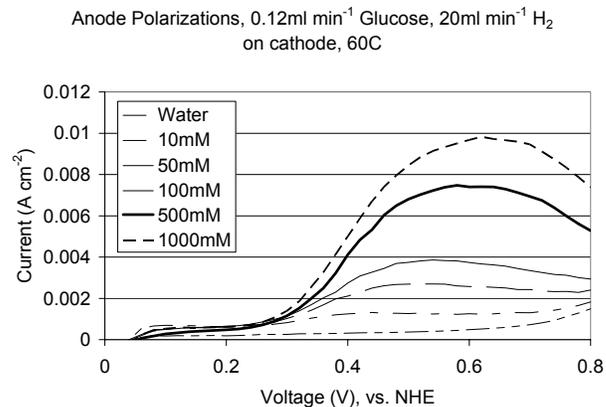
Assembled cells using enzyme anode catalysts were exposed directly to glucose without break in, due to the risk of denaturation of the enzymes from a high temperature or methanol based break in. The enzyme used was glucose oxidase (Biozyme) and the enzyme was placed into solution using a pH 7 phosphate buffer. It was subsequently deposited and air dried onto a high surface area Monarch 880 carbon electrode backed by Toray® paper for a GDL. Loadings of the enzyme solution and the total amount of solution precipitated on the Toray® paper, assuming no loss during the drying process. Most anode enzyme loadings were approximately  $200\mu\text{g cm}^{-2}$

### 3. RESULTS AND DISCUSSION

#### 3.1. Noble Metal Anode Performance

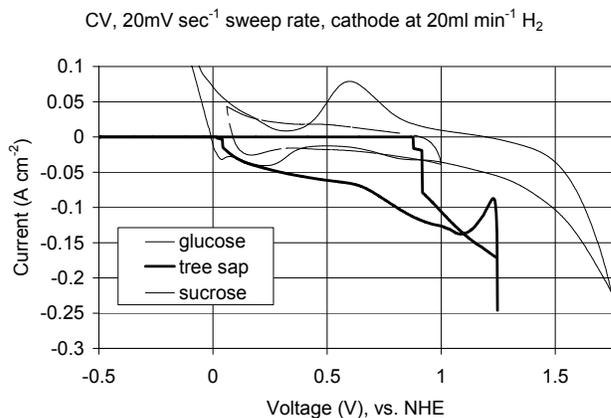
The polarization curves for glucose and sucrose on Pt-RuO<sub>2</sub> are shown in Figure 1 for temperatures at 60C and at room temperature. The power generated from the cell is highly dependent on the temperature, as is expected of a first order

catalytic process. Note that the performance curve exhibits a nontraditional mass transport limitation region, where with continued polarization of the anode, the current decreases rather than increases. This region of the curve is consistent with the generation of a 2-electron oxidation of glucose to form glucono-1-lactone.[13] As the anode is polarized into



**Figure 2: Anode Polarization Curves of Glucose on Pt-RuO<sub>2</sub>, showing the advent of the glucose to glucono-1-lactone byproduct formation and subsequent poisoning at +550mV vs. NHE.**

this potential region, the rates of glucose oxidation and byproduct formation both increase. The environment is not sufficiently oxidizing to remove the byproduct from the surface. As a result, the byproduct glucono-1-lactone remains on the catalyst surface, blocking further catalysis at that site. Because of poisoning of the catalytic surface, polarization of the anode more negatively than this value results in decreases in current, rather than an increase. The actual potential at which this happens can be seen in Figure



**Figure 3: Cyclic voltammograms of glucose, sucrose, and tree sap. Sucrose and glucose behave similarly, with a stripping current available near 0V vs. NHE. Tree sap does not exhibit any stripping current, even when polarized to -500mV vs. NHE, indicating strongly bound poisons.**

2, where the cathode of the cell is held under hydrogen, making it a pseudoreference at the normal hydrogen

electrode (NHE) potential.[14] Since the NHE is always a constant potential under normal voltage conditions, all polarizations for this cell are therefore at the anode. As can be seen, independent of the fuel concentration, the anode exhibits an oxidation wave at about 550mV vs. NHE, which is in agreement with the potentials for the formation of glucono-1-lactone reported in the literature.[3]

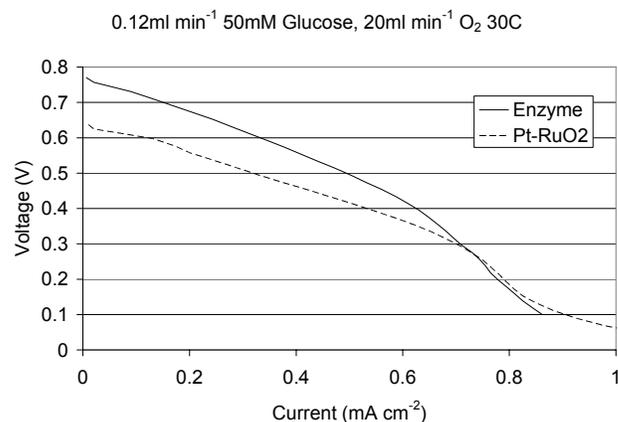
The poisoning of the anode can be reversed with a sufficiently positive potential applied to the anode, as seen in the cyclic voltammograms shown for glucose, sucrose, and tree sap, shown in Figure 3. In this case, the cathode is once again held under hydrogen, providing a reference potential for the anode. The anode is polarized through the entire stability window, and both glucose and sucrose show a stripping current at +250 mV vs. NHE, consistent with the values for gluconolactone being oxidized to gluconic acid and removed from the platinum surface.[15] The same is not true when the cell is run on tree sap, although the oxidation peak is still present during the oxidative sweep for tree sap, the oxidation current goes to zero near NHE, and even significant negative potentials are insufficient to strip this poison from the platinum surface. In the reductive sweep, the anode requires almost a volt of polarization before any reducing current appears again, as the poisons from the tree sap are finally stripped from the platinum. It is unknown currently what these poisons are, but there is no method by which they may be stripped within the normal operating potential of a glucose-oxygen fuel cell. For the cell to operate for a long time, a non poisoning anode is required.

### 3.2. Enzyme Catalyst Anode Performance

Enzymatic catalysis of these fuels does not suffer from poisoning in the same way that noble metal catalysts poison, but these catalysts require additional effort in preparation to render them stable on the time frames required for long term unattended ground sensor type of applications. In particular, stabilization of the enzyme against the electrode to protect from denaturing and diffusive loss is required. Several methods of achieving stabilized enzymes have been reported.[16, 17] Performance on whole cell enzyme fuel cells have been reviewed[18] and show that stability of the enzyme electrodes are of particular concern for long term operation. Performance of these electrodes in the short term, however, is quite good if the electron transport is mediated, and can actually exceed the performance of the noble metal catalysts if both are under the same (relatively unpoisoned) conditions. This can be seen in Figure 4, where a fuel cell built with a traditional platinum cathode is mated to either a Pt-RuO<sub>2</sub> or an enzyme anode and undergoes a traditional voltage polarization. The enzyme anode cell shows approximately a 100mV higher initial open circuit potential when compared to the noble metal catalyst, and continues to show increased polarization over the entire current window.

Both cells eventually start to show decreased performance over the course of the next several hours, however. In the

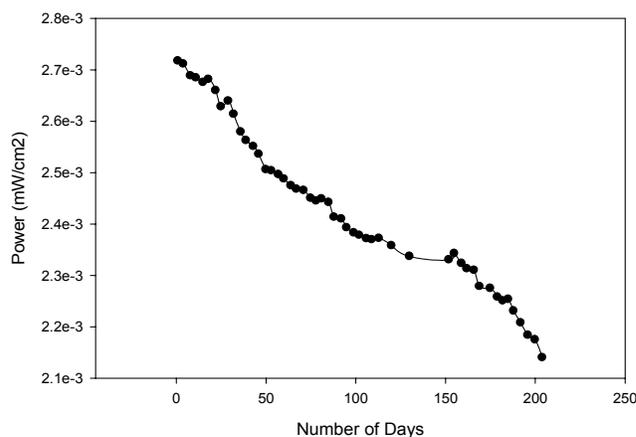
case of the noble metal catalyst, poisoning due to glucono-1-lactone formation and poisoning, as previously discussed, is the likely cause of this loss in performance over time. In the case of the enzyme electrode, however, it is unlikely poisoning that is causing the loss in performance, as the enzyme in use, glucose oxidase, is unreactive to the lactone



**Figure 4: Performance of noble metal anode vs. enzyme anode with Pt cathode. Conditions: 30C, 0.12ml min<sup>-1</sup> 50mM glucose (with 20mM phenazine methosulfate mediator for enzyme), 20ml min<sup>-1</sup> O<sub>2</sub> cathode.**

byproduct. It is likely, then, that loss of the enzyme to the fuelstock over time in flowthrough conditions is depleting the anode of enzyme catalyst, resulting in lower performance. This effect is well documented in the literature[8] and is, along with loss of mediator and denaturation of the enzymes themselves, the ultimate limiter of enzyme cell lifetime.

Testing in a whole cell under flow through conditions requires immobilization of the enzymes to the electrode surface. A long time operation of enzyme anode that retains



**Figure 5: Lifetime operation of Glucose Oxidase anode in quiescent conditions. 0.046mg anode loading, room temperature, 10mM glucose, Pt-air cathode.**

good power performance is shown in Figure 5 using the method of Minteer.[10] In this cell, the glucose oxidase was

held in a micellar network within the Nafion™ separator and resulted in good stability of the enzymes for significant lengths of time. This performance, it should be noted, was under quiescent conditions, however, with 10mM fuel being intermittently spiked into the fuel solution, rather than being continually replaced as would occur in a flow through fuel cell anode. Still, losses from the anode over the course of this experiment (either diffusional or other mechanisms) resulted in only a 25% drop in power over the course of 200 days. In the case of this cell, the fuelstock was spiked with mediator and the performance was limited by physical diffusion of the mediator within the system. In a harvesting system, the mediator will not be present in the feedstock, and will also need to be immobilized on the electrode in order to provide long term operation.

### 3.3. Mediator design and performance

Mediator molecules are needed in enzyme based anodes to transport electrons from the active redox site of the protein to the electrode, where it is reduced, and recycled back to the enzyme redox site. While some work has demonstrated the possibility of direct electron transfer from glucose oxidase to an electrode[19], the currents generated by such devices remain low, and more efficient power can be achieved through the use of a mediator. A covalently linked mediator has been demonstrated partially by Heller[8], but the redox site of this mediator is not covalently linked, and loss of mediator to solution is reported by this group as one of the loss mechanisms over time. Mediators such as FTMAB, with a long alkyl chain terminating in a binding amine group, could be used to tether the mediator covalently to the electrode, while the alkyl chain would still provide enough mobility to the redox center to allow for interaction with both the redox site of the protein and the electrode surface. Phenazine based derivatives provide excellent reversibility at a functionally attractive potential for a glucose-oxygen fuel cell, with an operating potential roughly -200mV vs. Ag/AgCl. Organic synthesis of a phenazine derivative with the alkylation present in the ferricenyl derivatives resulted in a mediator molecule with covalent attachment capability, but at the cost of significant performance (+100mV vs. Ag/AgCl) in the operating potential of the phenazine active site. Since a stable mediator is a requirement of long term operation in a harvesting cell, however, this tradeoff may be acceptable, provided sufficiently high activity can be maintained in the enzyme itself to produce acceptable currents.

## 4. CONCLUSIONS

Continuous operation of a fuel cell based on harvested fuel and reductant is far from commercial realization, but the technical developments needed to realize such a device are now well understood, and should in principle be achievable. Due to the poisoning nature of most naturally derived fuelstocks, it is unlikely that a platinum based catalyst will provide an adequate solution for long term operation of a

device. This requires the development of an enzyme based anode, in which poisoning effects are more tractable. Stabilization of the enzyme for long periods of continuous operation has been demonstrated, but the operation in the absence of a dissolved mediator is yet to be demonstrated. Modification of known good mediators to accept an alkylation tether for covalent attachment to the substrate was demonstrated, but resulted in significant (~300mV) loss in redox potential for the anode mediator. Significant progress towards stability of enzymes and direct electron transfer, as well as stabilized mediated transfer, may bring such a device within the realm of practical theater operations in the not-to-distant future.

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