

DOE Inventions & Innovation, Category 1, Final Report

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Antek Inc.

Award #: DE-FG36-06GO16047.A000

Project Title: A Bio-Based Fuel Cell for Distributed Energy Generation

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## **1. EXECUTIVE SUMMARY**

In this report, we describe the results of Antek Inc.'s Inventions & Innovation, Category 1 project: A Bio-Based Fuel Cell for Distributed Energy Generation.

The objective of the project was to further develop a “bio-fuel cell” system, which utilizes the natural ability of certain bacteria to convert renewable hydrocarbons (e.g. glucose, acetate) into electricity. The intent of the project was to improve the power density attributes of a proof-of-principle system in order to make it a viable energy generation strategy. The expected result of the project was a prototype of a functional (laboratory) system that, at minimum, substantiated further development of this approach into a commercially-available product that operates on renewable fuel(s) and is competitive and cost-effective vs. alternative technologies.

Here, we show that our research addressed several important areas of bio-fuel cell design. Specifically, these include: improvements to the growth media, which is a ubiquitous component of such a fuel cell, serving as the conductive electrolyte as well; and the benefit of pre-treating the anodic electrode surface by electro-oxidation. Further, we demonstrated the potential of completely eliminating costly platinum from the fuel cell design, which could eventually lead to a low cost energy generation product for the public; one that produces zero (net) carbon emissions from renewable, domestic fuel sources.

These accomplishments, however, did not immediately lead to the development of a viable product. Further work is needed to address several engineering challenges – which we describe herein, and continue to investigate – although many of the biological questions have been thoroughly researched and satisfactorily answered.

## **2. RESEARCH ACCOMPLISHMENTS AND COMPARISON TO ORIGINAL PROJECT AIMS**

### **2.1. Original Project Aims**

- A) Optimize power density of biofuel cell (BFC) prototype.
- B) Develop appropriate fluidic systems for sustained “real world” applications; build functional prototype unit.
- C) Investigate the use of microorganisms as catalysts in the cathode compartment.

### **2.2. Variance from Original Aims**

As described in section 2.3 below, the work performed during the course of this project followed the original aims with high fidelity. Each aim was worked toward, with varying degrees of success; the main variance from the proposed research being the time-course needed to thoroughly research the extensive variety of approaches one could explore in addressing each aim (see below). Correspondingly, Antek continues work on fully accomplishing the goals set forth, with confidence in the eventual development of a commercially-viable product for distributed energy generation.

## 2.3. Work Performed

### Aim A

The original plan for optimizing the biofuel cell's power density presupposed that the most straightforward part of developing the BFC would be the physical assembly of the electrode housing and fluidic systems. This proved not to be the case (see Aim B below). Nonetheless, with knowledge of the characteristics of the BFC system that directly influence its power generation, we were able to optimize two integral components of the fluid media that constitutes both the growth environment of the bacterial catalysts, and the fuel cell's electrolyte. These are the media's ionic strength (which affects the internal resistance of the electrolyte, and thus power density) and pH level (which directly represents the availability of protons at the cathode reaction).

Typical ionic strength levels used in literature examples of BFCs using bacteria as catalyst are in the range of 100-300mM. As shown in **Figures 1** and **2** (see section 5, Supplemental Information), by incrementally increasing the ionic strength over time from 265mOsm (vial #1) to 465mOsm (vial #9), the growth rate of an electrogenic bacteria culture (here, *Geobacter sulfurreducens*) can be sustained at strengths well above their "recommended" level (see published ATCC recommendation for *Geobacter* growth media ionic strength - approximately 230mM; Note: ATCC also recommends 10mM acetate, whereas we are now using 20mM with no adverse effect on growth; data not shown). Figure 1 shows the increase in optical density of the culture over time (reflecting increasing cell count per mL) until shortly after the available acetate (*Geobacter*'s carbon source) is exhausted (see Figure 2). In these experiments, we've shown that the growth rate of this electrogenic bacterium in media that has an ionic strength as high as 365mOsm is comparable to growth in "control" media. This represents an increase of ~60%, which will significantly lower the internal resistance of the BFC and lead to a sizeable increase in the generation of current per unit volume and, correspondingly, the power density of the fuel cell product. Furthermore, doubling the acetate concentration to 20mM has already significantly increased the available "fuel" to the bacteria for growth and electricity generation.

The pH level of the media used in nearly all publications involving this bacterial strain is just below neutral (see published ATCC recommendation for *Geobacter* growth media; pH = 6.8). The pH is primarily controlled by the amount of sodium-bicarbonate in the media (when the growth headspace atmosphere is kept constant at 80:20 N<sub>2</sub>:CO<sub>2</sub>), which we adjusted in order to determine the lowest pH at which this bacteria can still respire (i.e. donate electrons to an electron acceptor in the media - in this case: fumarate - in order to grow and divide). As shown in **Figures 3** and **4** and **Table 1**, analogous to the ionic strength experiments, an incremental decrease in pH over time (achieved by lowering the amount of sodium-bicarbonate in the media) allowed us to determine the pH at which growth remained robust. Here, we found that the amount of Na-bicarbonate could be reduced to 0.25g/L without adversely affecting growth, which corresponds to a pH of approximately 6.1. Considering the log-scale used in calculation of pH values, this represents a 400% increase in the amount of H<sup>+</sup> ions in solution (as compared to the "control" media), and will further significantly elevate the power density of the ultimate BFC product.

### Aim B

Assembling the prototype unit, complete with associated fluidic systems, posed a number of problems. The nature of the novel anode design that we have developed requires a unique system for flowing media through the device. The circulation of this media is needed to bring acetate,

and other nutrients, to the bacteria catalysts, as well as to transport protons generated in the anode to the cathode compartment. Unfortunately, this stage of development was fraught with difficulties; including problems associated with the uneven pressures in the system that are created with simple peristaltic pumping, caused by the anode being highly resistive to advective fluid flow, as well as the permeability of the cathode (here, Platinum-coated carbon paper) to atmospheric air when fluid is alternatively “pulled” through the anode by placing such a pump downstream of the electrode chambers.

A persistent problem of contamination from unwanted bacterial strains was mitigated somewhat by procuring the use of sterile hood and other procedures, however, the use of off-the-shelf components to construct a air- and leak-tight prototype was unsuccessful and a novel system had to be designed and custom-made at a machine shop. This design itself posed several new problems, and the time associated with modifying the prototype in this way became a major limitation to assembling a device that could operate, problem-free, for extended periods of time (i.e. more than several weeks).

Nevertheless, several incarnations of the BFC were assembled and tested. Although long-term performance was an issue, one metric for evaluating our BFCs against similar bacteria-catalyst designs in the literature is to compare open circuit voltages (VOCs). This value represents the potential difference between the anode and cathode when the electrical circuit is not completed. How much this differs from the operating voltage depends on the load applied, and the internal resistance and capacity of the cell. VOC values from the literature, in publications describing the use of *Geobacter* (or other electrogenic bacteria) as the anodic catalyst are typically in the range of 400mV-600mV (e.g. see Bond & Lovely, “Electricity Production by *Geobacter sulfurreducens* Attached to Electrodes”, *Applied and Environmental Microbiology*, 69:1548-55, 2003; Liu & Logan, “Electricity Generation Using an Air-Cathode Single Chamber Microbial Fuel Cell in the Presence and Absence of a Proton Exchange Membrane”, *Environ. Sci Technol*, 38:4040-6, 2004). With our system, we regularly measure VOC values of over **860mV**. This increase in VOC over other laboratories results is most likely due to our technique of first electro-oxidizing the graphite surface of our anode (note: details available upon request). This process – which is often employed in other fields, e.g. battery design – increases the prevalence of phenol, carboxyl, and quinone groups on the graphite surface, which, in our case, lowers the barrier associated with the attached bacteria transferring electrons to the graphite, thereby raising the VOC as well as power density of the fuel cell.

An example of the very unstable closed circuit voltage measured when operating the BFC with an applied load is shown in **Figure 5**. While the operating voltage generally increases over the first several days after assembly, invariably one or more of the difficulties described above limits the power production from rising to its full potential.

### **Aim C**

Analogous to the “metal-reducing” bacteria present in the anode, a number of “metal-oxidizing” bacteria exist that, heretofore, have not been studied in terms of their potential value to bio-fuel cell applications. The use of microorganisms in the cathode compartment (as opposed to the present “air-cathode” design) could completely eliminate the use of platinum catalyst in the BFC system and reduce the need for a proton exchange membrane. Modifying the system in this way would therefore make the BFC product even less expensive and simpler to construct, and thus more attractive commercially.

In this project, we have focused on the use of *Leptothrix discophora*, which utilizes a manganese oxide based cathode structure in a two-step reaction that first reduces the manganese oxide to ions, using electrons derived from the anode reactant. Since the divalent manganese ions are released in close proximity to the bacteria-colonized surface of the cathode they are reoxidized to manganese dioxide and deposited once again on the cathode surface thus regenerating the cathodic reactant for another round of reaction.

The use of *Leptothrix* as the cathode catalyst precludes circulating media throughout the BFC, as was done with the standard air-cathode design described previously, due to the requirement that manganese ions be isolated in the cathode compartment. Therefore, the two compartments were separated with a standard PEM (Dupont Nafion<sup>®</sup> NRE-211), as in most fuel cell designs. As expected, the VOC achieved when using a bacterial catalyst was somewhat lower than when using platinum in the cathode, and was typically in the range of 700-760mV. The fact that the two compartments' media were stationary, i.e. not well-mixed, as well as the limitations associated with relying on bacteria-catalyzed reactions at both electrodes, should cause one to expect that a similarly-sized *Geobacter/Leptothrix* BFC could not sustain the power output of the *Geobacter/Platinum* BFC, however the voltage achieved with an applied load is actually superior to that of the air-cathode system (as shown in Figure 5). This reflects the afore-mentioned troubles in assembling an effective fluidic system for the original BFC design, but lends confidence that, with further improvements, the *Geobacter/Leptothrix* (non platinum-containing) BFC could be a cost-effective, long-term strategy for low cost, renewable energy generation.

## **2.4. Conclusions and Future Work**

Antek Inc. continues to perform research on the development of a fully functional BFC. We believe that, with sufficient time and effort, the problems encountered – and described above – will be overcome and allow for a more concrete determination to be made as to the possible utility of a BFC as compared to more traditional fuel cells. At this stage, it is not possible to discern whether this strategy will or will not become a viable basis for renewable energy generation. The results to date are encouraging, however more work must be done, primarily on perfecting the associated fluidic system that is critical to BFC performance.

## **3. PRODUCTS/COLLABORATIONS DEVELOPED UNDER AWARD**

A commercially-viable product has not yet been achieved during this Category 1 project, however in conducting the necessary research toward that goal, Antek Inc. has fostered a number of scientific and business collaborations of note. These include a strong relationship with several faculty of the Microbiology Department at the State University of New York – College of Environmental Science and Forestry, where much of this research was, and is still, performed (Note: Antek first secured all IP rights to any technology associated with this project developed in this University's facilities). In addition, a beneficial relationship with the Syracuse Technology Garden – a high-tech business incubator facility – has resulted in numerous opportunities for procuring future investment capital. Although, said opportunities consistently rely on getting a fuel cell product ready for market, which we continually work towards.

## 4. APPENDICES

### 4.1. Appendix A. Final Task Schedule

#### Final Task Schedule

Task Number	Task Description	Task Completion Date				Progress Notes
		Original Planned	Revised Planned	Actual	Percent Complete	
1	Study the use of microorganisms in the cathode compartment	04/13/07	06/30/07	06/30/07	100%	Completed.
2	Optimize power density of “bench-scale” bio-fuel cell	06/08/07	10/12/07	10/12/07	100%	Completed.
3	Prototype Fabrication	07/13/07	12/31/07	12/31/07	100%	Completed.
4	Prototype Testing	08/03/07	03/29/08	03/29/08	100%	Completed.
5	Project Management	09/29/07	03/29/08	03/29/08	100%	Completed.

### 4.2. Appendix B. Final Spending Schedule

#### Final Spending Schedule

Project Period: 09/29/06 to 03/28/08

Task	Approved Budget	Final Project Expenditures
Task 1	34,000	34,000
Task 2	28,000	28,000
Task 3	14,000	14,000
Task 4	14,000	14,000
<b>Total</b>	90,000	90,000
DOE Share	50,000	50,000
Cost Share	40,000	40,000

### 4.3. Appendix C. Final Cost Share Contributions

**Final Cost Share Contributions**

<b>Funding Source</b>	<b>Approved Cost Share</b>		<b>Final Contributions</b>	
	<b>Cash</b>	<b>In-Kind</b>	<b>Cash</b>	<b>In-Kind</b>
DOE - Golden	50,000		50,000	
NYSERDA	30,000		30,000	
Antek Inc.		10,000		10,000
<b>Total</b>	80,000	10,000	80,000	10,000
<b>Cumulative Cost Share Contributions</b>				90,000

### 4.4. Appendix D. Energy Savings Metrics

A ‘single unit’ of the current technology may be considered to be an average household-sized distributed energy generation system (including heat), providing ~3kW of (peak) power. If the consumer is completely ‘off-grid’, approximately  $100 \times 10^6$  “usable” BTUs are needed per year. If half of this goes to heating requirements, and the fuel is oil or natural gas (burning efficiency ~75%, and elect. conversion efficiency ~40%, together yield a total efficiency, depending on consumer’s location, of ~60%), the number of total (chemically-stored) BTUs required is  $\sim 167 \times 10^6$  BTU/yr. While our technology does not directly reduce the final consumption of energy by the customer, an ~90% efficiency of the system would require only  $\sim 111 \times 10^6$  BTU/yr of stored energy. This would conserve fossil fuel supplies for other applications where renewables are less viable.

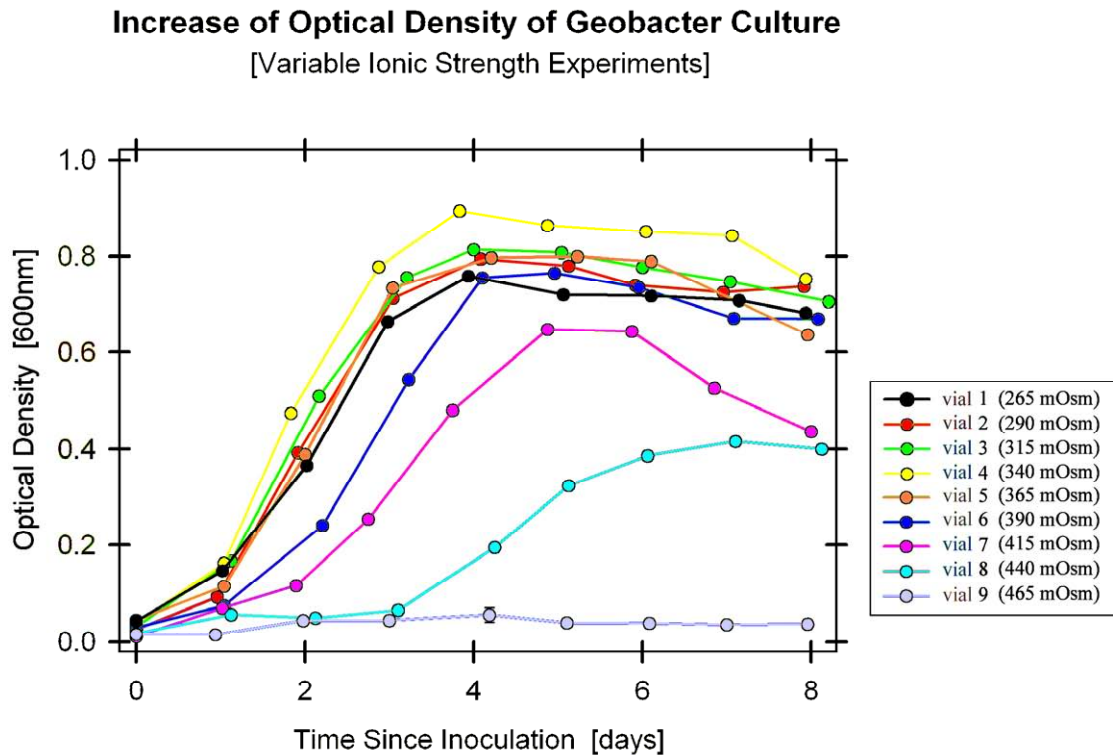
If the total US distributed generation capacity is ~147GW (source: California Distributed Energy Resource Guide, Oct. 2005), or the equivalent of  $\sim 49 \times 10^6$  3kW-sized units, the calculations above extrapolate into  $\sim 2.7 \times 10^{15}$  BTU of stored energy savings in the U.S. per year. However, one must also consider, if the source of fuel (e.g. acetate) for the proposed technology is ultimately via the fermentation of biomass, that upper limits on fuel production are inherently imposed by availability of such source material.

The proposed technology is not intended to explicitly contribute to energy conservation (by the end-consumer), but to increase the use of renewable fuels, with high efficiency. However, the

reduction of energy expended in simply transporting traditional fuels (such as petroleum) large distances would itself be sizeable (since bio-fuels can be produced close to the end-consumer), although, at this time, exceedingly difficult to accurately estimate.

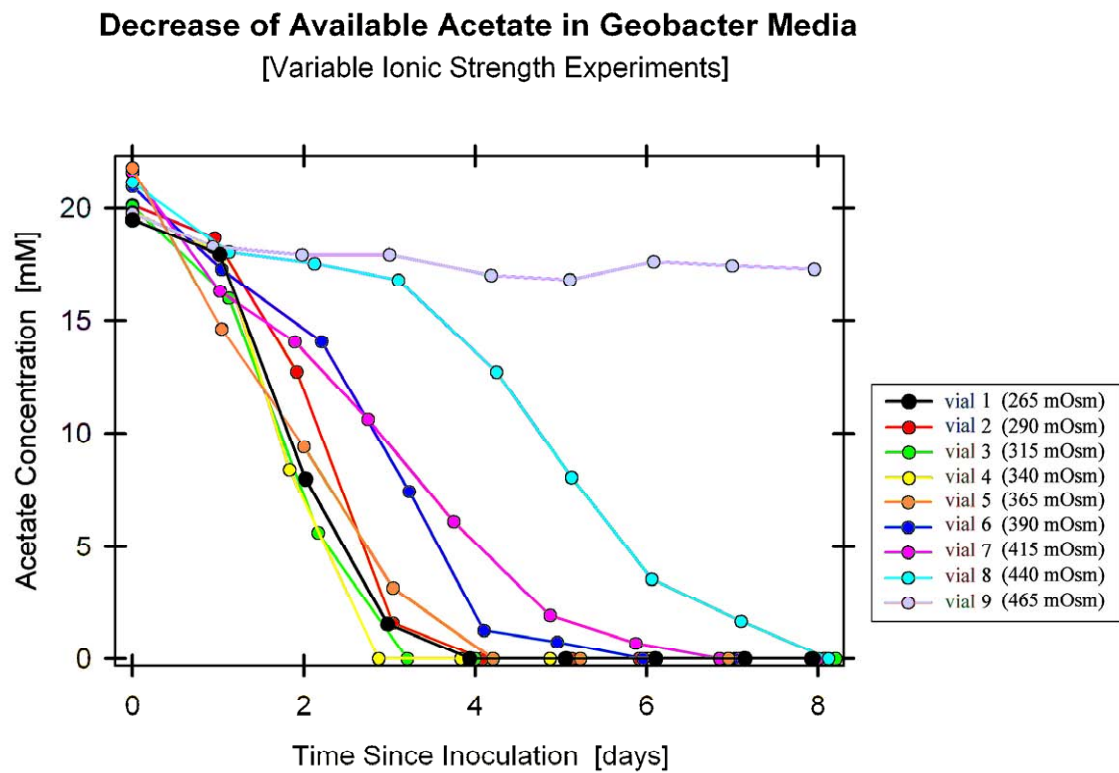
The higher efficiency of the proposed system will result in far less net CO<sub>2</sub> emission as compared to currently available fossil fuel driven products (except for processing and transporting the biofuel, the CO<sub>2</sub> emitted is equivalent to the CO<sub>2</sub> sequestered by the original biomass). Also, there are zero CO, sulfur, NO<sub>x</sub>, or particulate emissions associated with our technology. Thus, if we assume our efficiency to be about twice as high as current technology, total CO<sub>2</sub> emissions would be approximately halved, and all other noxious emissions eliminated, for every consumer adopting our technology.

## 5. SUPPLEMENTAL INFORMATION



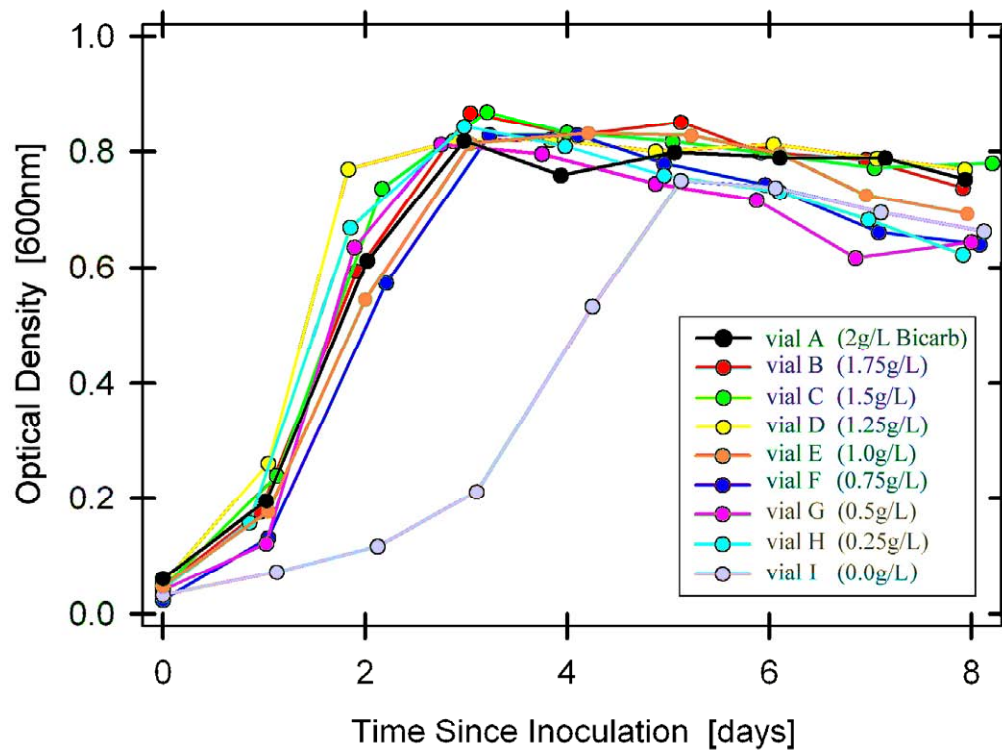
**Figure 1. OD600 Time-course in Incrementally Increasing Ionic Strength Media. [Note: Error bars are present in Figures 1-4, but are generally smaller than the datapoints themselves.]**





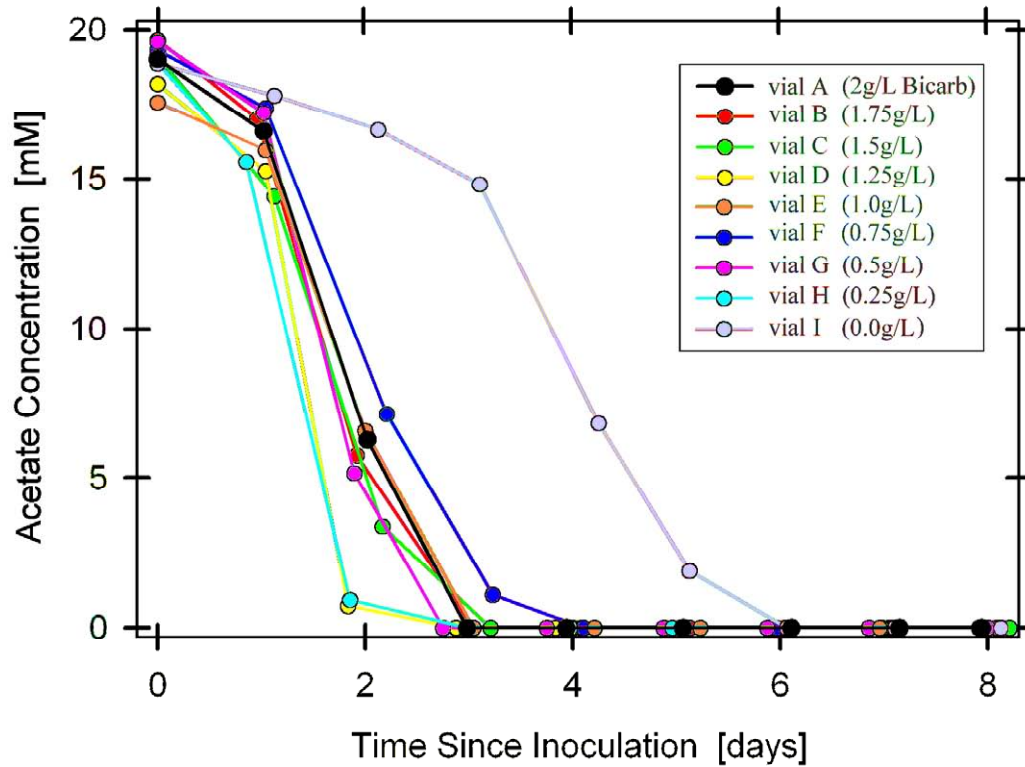
**Figure 2. Acetate Concentration Time-course in Incrementally Increasing Ionic Strength Media.**

### Increase of Optical Density of Geobacter Culture [Variable pH Experiments]



**Figure 3. OD600 Time-course in Incrementally Decreasing pH Media.**

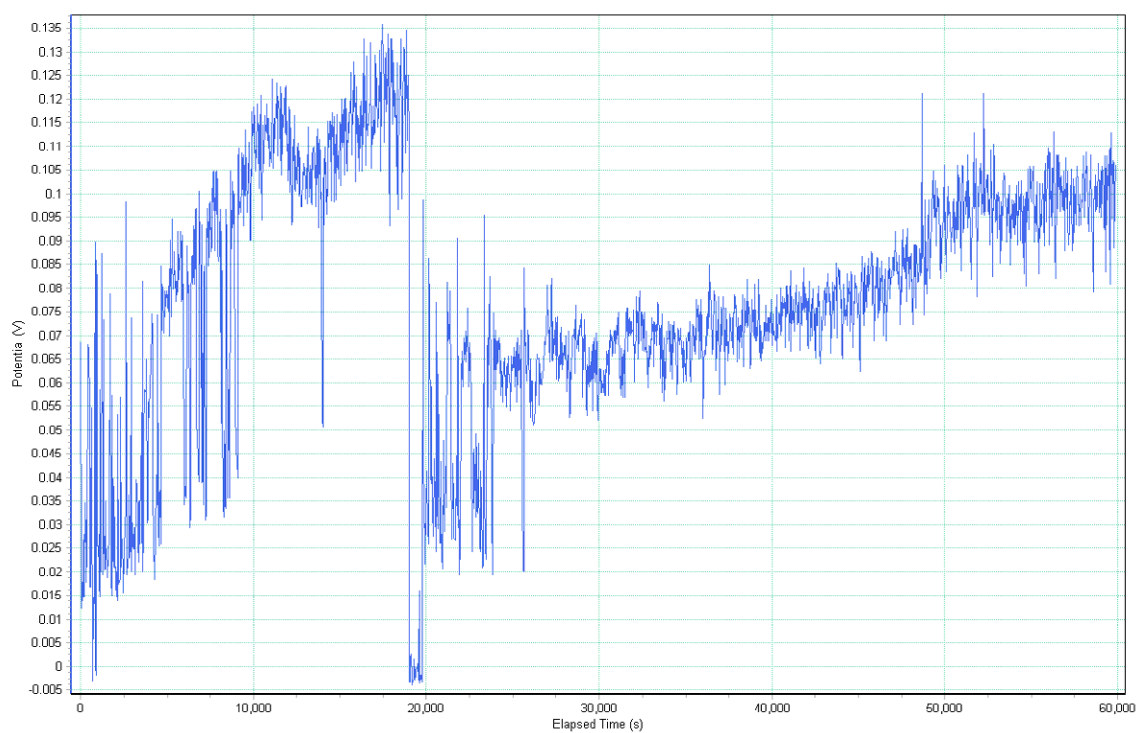
# **Decrease of Available Acetate in Geobacter Media** [Variable pH Experiments]



**Figure 4. Acetate Concentration Time-course in Incrementally Decreasing pH Media.**

Vial	Na-Bicarbonate [g/L]	pH
A	2	6.82
B	1.75	6.78
C	1.5	6.74
D	1.25	6.69
E	1	6.61
F	0.75	6.48
G	0.5	6.39
H	0.25	6.14
I	0	5.89

**Table 1. Sodium Bicarbonate and pH levels for Vials A-I.**



**Figure 5. Representative Plot: Increase in BFC Voltage During First Day of Operation of One BFC Trial (Applied Load: 100 $\Omega$ ).**