

Title

“HIGH RATE AND HIGH EFFICIENCY ORGANIC DIGESTION VIA CATALYZED BY NANO POWDERS.”©¹

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ABSTRACT

Organic molecules are often very strongly assembled. The need to break them down is necessary for many applications including cellulosic fermentation for ethanol production, the destruction of laboratory pathogens and the liberation of lipids from algae for alternative fuels among others. Thermal degradation is well known and the method of choice today, where an aqueous slurry is prepared of the organic material and the temperature is raised above 350 degrees centigrade in a sealed vessel where the organics spontaneously disassemble. This method is reliable and the mechanisms well understood. Raising the temperature of the water, however, is energy consuming, taking 1500 BTU's to raise one liter of water from room temperature to 360 C. Work at DoppStein Enterprises has been studying the use of a 3D porous electrode to degrade organics electrochemically. These electrodes were originally developed for alkaline water electrolysis³ and the process modified to increase the nano catalyst loading. The metallic reticulate electrode is coated on all surfaces with a mixture of nano catalysts adhered by a unique electrochemical process that produces excellent electrical contact with the nano-powders while allowing them to interact with the electrochemical boundary layer. The result is a very high rate, solid-state, three-dimensional (3D) electrode. Our nano recipe includes no noble metals. It is hypothesized that the mechanism may involve the singlet oxygen produced during water electrolysis, attacking oxygen and/or carbon atoms within the organic molecule.

This work is patent pending⁴.

¹ This work was funded and the IP owned By Thom Robinson

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³ “High Rate And High Efficiency Hydrogen Generation Via Water Electrolysis Catalyzed By Nano Powders.” (www.doppstein.com/white_papers)

⁴ Published application “Electrochemical Digestion of Organic Molecules” WO 2013/052374 A1

3D Electrochemical Organic Digestion

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1. Principles of Electrolysis

Water electrolysis to produce hydrogen and oxygen is an old technology originating just weeks after Volta introduced his Pile in 1800 by William Nicholson and Anthony Carlisle. The principle chemical equations are shown below, where the electrochemical flow is shown for alkaline environments, which is the condition used in this research.

Alkaline Water Electrolysis forming diatomic Hydrogen and Oxygen singlets

Anode (“+” Terminal): $2OH^- \rightarrow 1/2O_2 + H_2O + 2e^-$

Cathode (“-” Terminal): $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

Total Reaction: $H_2O \rightarrow H_2 + 1/2O_2$

For organic digestion, we used 1% KOH in water, which has a pH of about 13. The anode produces one water molecule, but the cathode consumes two, resulting in a net loss of one water and the production of one mole of hydrogen and half a mole of oxygen. The hydrogen is diatomic from the moment it is assembled, but the oxygen starts as a singlet (also called “nascent”). It then combines with another singlet producing a diatomic molecule, or in our case, with organic molecules that are available. In the case of a cellulosic, the intra-glucose oxygen is a likely target, but the many carbons may also be attacked.

1.2. Nano-particle Surface Area Effect

As a material is divided into smaller and smaller particles, the three-dimensional surface area per gram increases logarithmically. For example, a one-gram pellet of nickel is 0.6 cm in diameter and has a surface area of 1.12 cm². One gram of 10 nm particles has a total surface area of 67 m² or 27 feet on a side - a 60 million-fold increase. This surface area increase improves electrochemical reactions due to the increase in the ratio of surface atoms. Bulk atoms have 12 neighbors and are unattainable to the liquid boundary layer. Surface atoms have 6 to 9 neighbors and are able to interact with their electron clouds in the reactive boundary layer. As **Figure 1** illustrates, this gives nano-coated surfaces more exposure for a higher electrochemical activity. The powders used in this work are all common transition metals including nano sized Tin, Iron, Nickel and Cobalt. The ratio was important to balance.

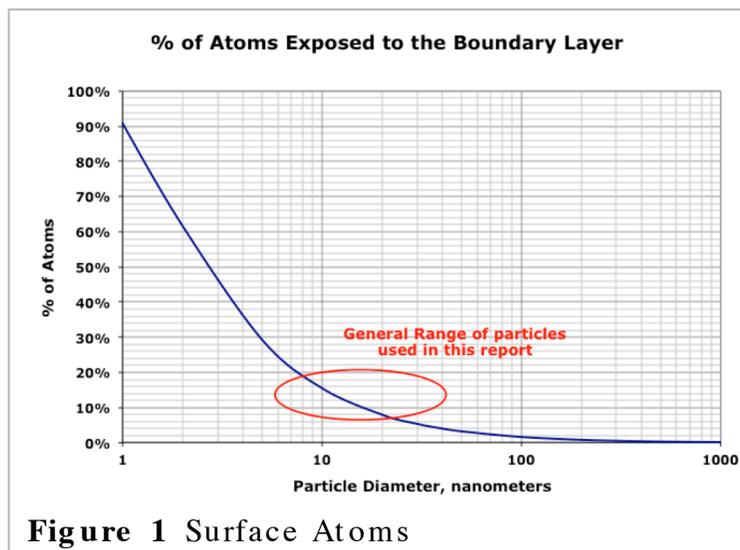


Figure 1 Surface Atoms

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1.3. Coating a Metallic Surface with Nano-catalyst

We used the basic recipe developed in the water electrolysis project⁵ with some changes to the nano powder loading, the coating program and the specific formulation. We use no Noble metals in our work (i.e. no platinum). Our unique method to attach the nano catalysts to a metallic surface in a way that has very low impedance to the reaction sites, covers all surfaces of a porous structure and leaves the particles well exposed to the boundary layer. The coating is uniform on all internal and external surfaces of the current collector, which is a foam nickel made by INCO. **Figure 2** is a comparison of an uncoated and coated porous surface. The coating extends into all internal intricacies of the porous metal substrate greatly extending the reactive surface area.

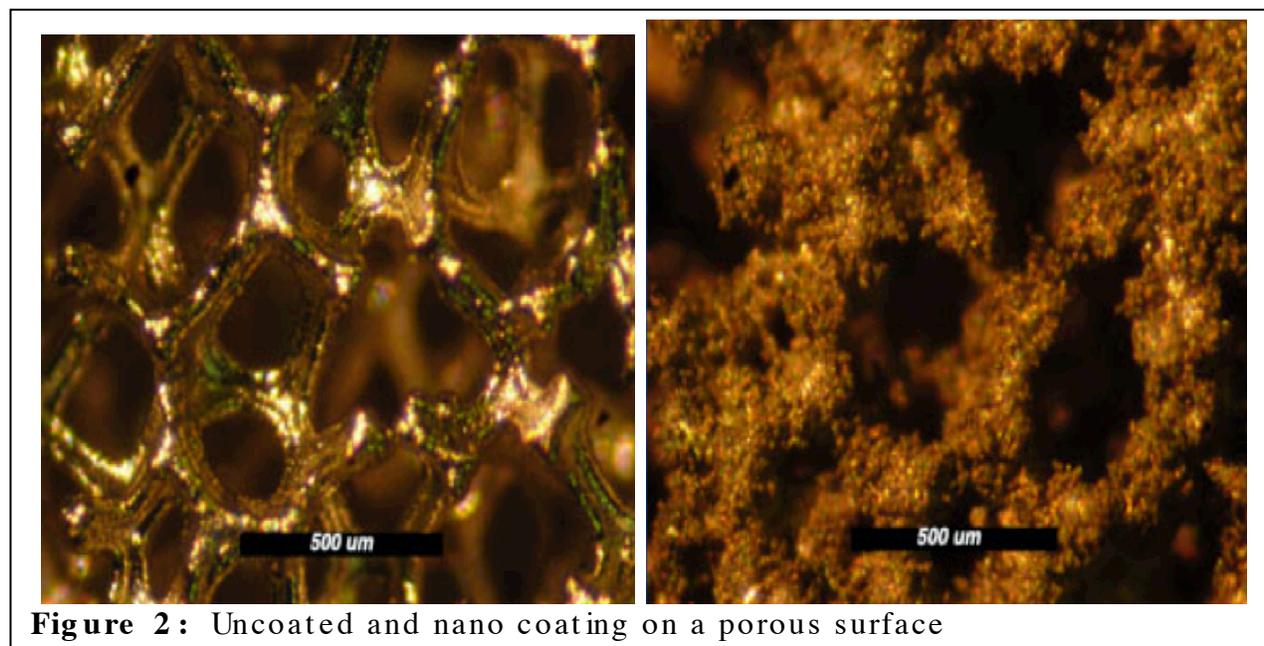


Figure 2: Uncoated and nano coating on a porous surface

The coating process is a modified nickel electroplating process using a complex wave-form of both forward and reverse current pulses. The short forward pulses attaches the powders to all internal surfaces and the reverse pulses strips the nickel off of the nano powders, leaving them exposed to the boundary layer. The exact wave-shape was developed during the water electrolysis project, however, the ratio of nano powders, the total Coulombs delivered during coating and the loading of the powders in the electrolyte are were considerably modified for this application. The coating process method is covered in the published patent application US 2011 0114496⁶, which is in final examination at the time of this writing.

As a side note: These images (and Figures 13 & 14) were taken using my Gr-Grandfather's lovely brass Spencer Lens Co. microscope made in 1905 with a CCD camera added for computer communication. He would smile knowing it is still in use in this laboratory.

⁵ "High Rate And High Efficiency Hydrogen Generation Via Water Electrolysis Catalyzed By Nano Powders." (www.doppstein.com/white_papers)

⁶ <http://www.google.com/patents/US20110114496>

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1.4. Coating effect on Impedance

Electrochemical Impedance Spectroscopy (EIS) is a very useful technique to evaluate the activity of electrodes. **Figure 3** shows the Bode plot for three electrodes in 33% KOH: Smooth Stainless Steel 316 (the base plate of our electrodes), uncoated nickel foam and the foam coated with a trio of nano powders. An impedance scan is a measurement of the total AC impedance (the rms of Ohmic and reactive impedances) as a function of the frequency applied. The lower the impedance, the higher the activity of the electrode. The advantage of the coating is unambiguous.

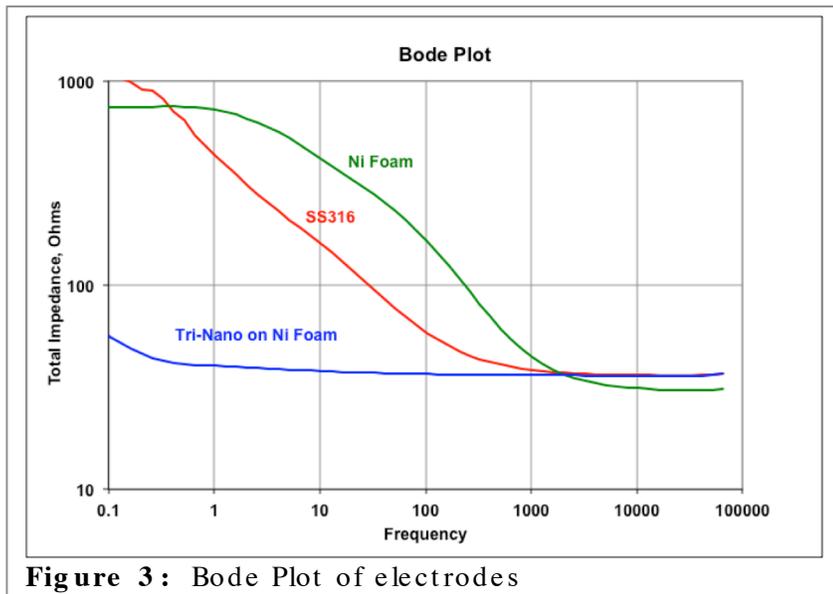


Figure 3: Bode Plot of electrodes

1.4. Coating effect on Electrochemical Activity

Figure 4 shows the Voltammogram curve for the same three electrodes discussed in **Figure 3** for both a cathodic (downward slope and hydrogen producing) and Anodic (upward slope and oxygen producing) directions. In this type of scan, the voltage is very slowly driven from equilibrium to some endpoint while the current is allowed to float. The exposed surface area was 1 cm² and the electrolyte in this case was 33% KOH. The reference electrode is a pure zinc wire. The higher the current density; the better. Notice that the horizontal axis is logarithmic, so the cathodic current density is two decades (100 x) higher with the nano coating.

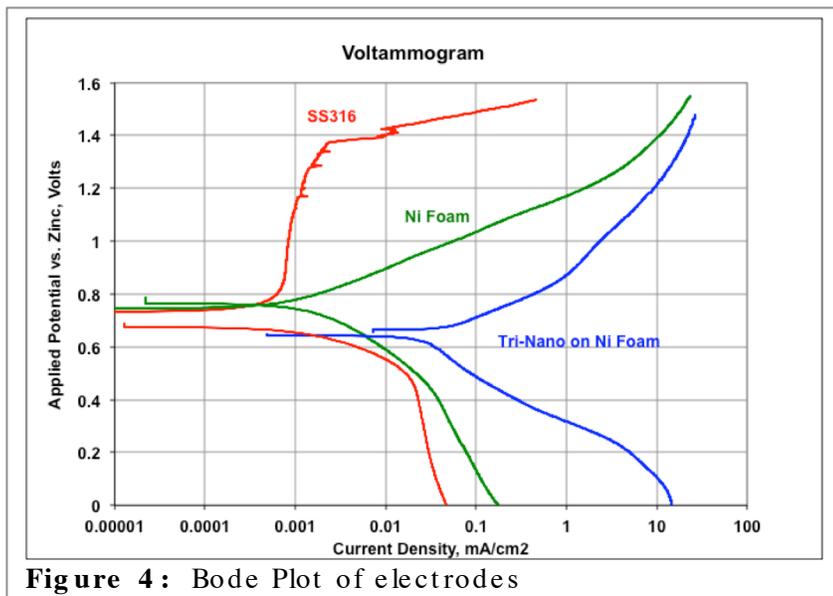


Figure 4: Bode Plot of electrodes

The lower the voltage for any current, the higher the electrochemical energy efficiency. The coated electrode is much more energy efficient than the others.

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2. 4-Cell Bipolar Electrolyzer

2.1 General Design

Bipolar electrolyzers are used for producing mixed gasses or pure gasses depending on design. **Figure 5** shows a block diagram of a bipolar stack with no separator; so producing mixed gases. The end plates are necessarily monopolar, but the inner plates are bipolar, which means the electrodes function as both an anode and a cathode depending on which side of the electrode we are viewing. It is a cathode on one side of a solid metallic surface liberating hydrogen diatomic molecules and hydroxyl ions, then the electrons pass through the body of the electrode to the anodic surface of the same electrode liberating nascent oxygen atoms, and a water molecule. The oxygen singlets soon combine to form diatomic oxygen or in our case, attacking organic molecules in the fluid while consuming hydroxyls. We used a 4-cell arrangement with no separator. **Figures 6 and 7** shows the actual test apparatus. Below the stack is a centrifugal pump and a reservoir for the fluids to pass through. The entire

system uses 500 cc of fluid with the flow from the bottom to the top. Gasses produced are free to escape in the three-neck beaker reservoir. The stack is powered by a DC power supply that passes through a reverse rectifier to switch polarity as programmed. Frequencies studied ranged from 1 kHz to as slow as 0.0001 Hz (1.4 Hrs in each direction). It was found that lower frequencies were best.

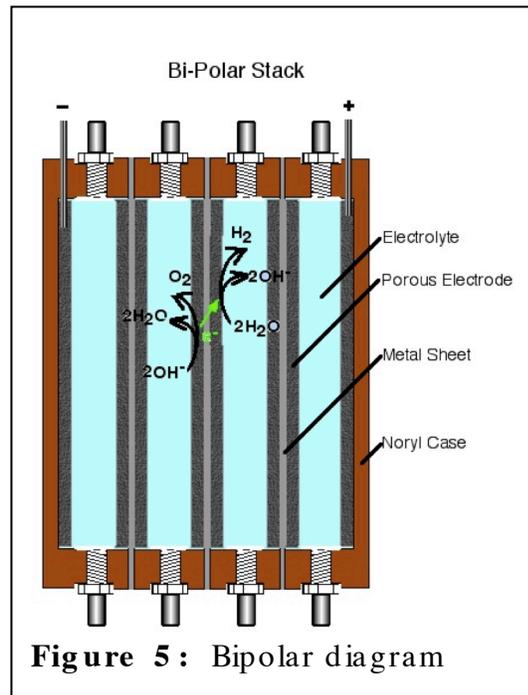


Figure 5: Bipolar diagram

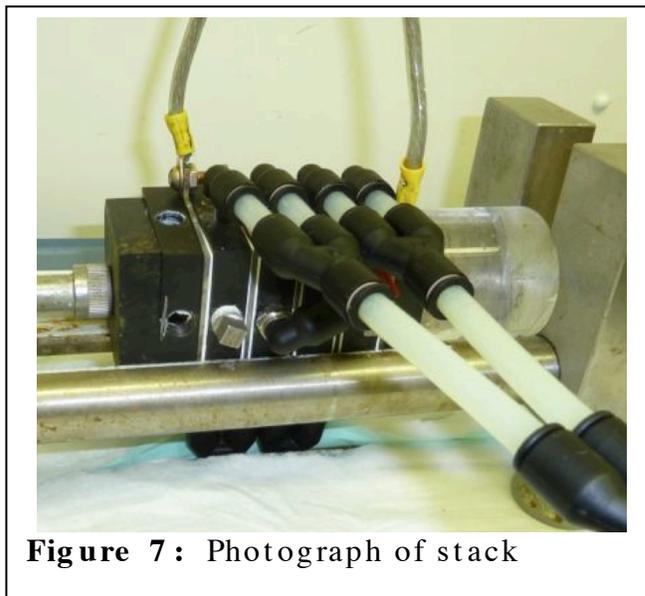


Figure 7: Photograph of stack



Figure 6: Photograph of stack

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2.2 Electrodes

Several electrode designs were studied including Stainless Steel 316 (SS316), Coated SS316, Nickel foam (INCO), Coated Nickel foam, and corrugated coated Dexmet

(<http://www.dexmet.com>).

The corrugated Dexmet would be the most cost effective current collector, and works nearly as well as the expensive nickel foam. All used the SS316 as a backing support. **Figure 8**

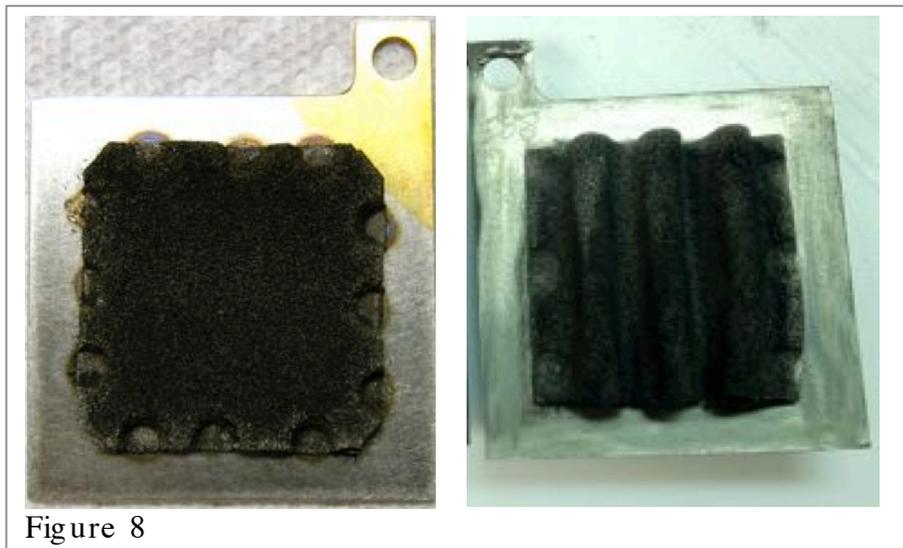


Figure 8

shows two of the designs; flat and corrugated INCO foam for the current collector.

2.3 Electrolyte

The project started using 1% NaCl electrolyte, however, corrosion was a constant problem with the chlorine attacking both the iron and nickel components, forming their chlorides. So we changed to 1% KOH electrolyte, which worked very well. We first demonstrated that at a pH of 13, cellulose such as starch and cellulose do not spontaneously degrade. The loading of test organics was always held at 1% for the initial number. Higher concentrations is almost certainly possible and probably desirable.

2.4 Separator

No separator was used, so the hydrogen simply escapes. If fats (i.e.: lipids) are in the mixture, however, hydrogenation is likely to occur, increasing the energy content of the fat. This may be significant if we move to the liberation of lipids from some bio-mass (e.g.: algae, kelp, wastewater, etc.) through the degradation of the cell and vacuole walls using this process.

2.5 Detection methods

2.5.1 Starches

The amylase portion of starch reacts with iodine, producing a convenient colorimetric method to detect the starch concentration in the circulating fluid. A 1% corn-starch sample was prepared in 1% KOH and a mixture of iodine and potassium iodide was diluted until the proper loading was determined to produced a medium pale blue color when a small amount was added to the starch solution. This was used to find the highest absorption for the Iodine colorant with starch (620 nm). Then we prepared a series of known starch concentrations and used dilutions to develop a calibration curve. Using this curve, only a very small sample (1.0 cc) was needed to be taken from the circulating electrolyte to gain periodic starch concentration readings. Unit conversion then gave values of mg/hr consumed or normalize to AHrs or WHrs.

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2.5.2 Cellulosics

The most reliable method of detection of cellulosics was by filtering through a 0.1 μm Millipore nitro-cellulose filter and weighing of the filter papers and dried filtrates. This did not lend itself to continuous measurements due to the volume needed (50 cc per test), but rather end of test results where a reasonable aliquot of flowing electrolyte was sampled and passed through a Buchner funnel holding the very fine Millipore filter. From this, the solids and the dissolved solids could be found using drying and weighing techniques borrowed from water treatment standard procedures. Analysis of the filtrate to identify what molecules are present after digestion is possible.

2.6 Pulse Shape and Frequency

We tested the effect of duty cycle using 1% corn-starch. First we investigated duty cycle from 100% to 50% and found the optimum. Next we looked at wave-shape (sine or square) and found that which worked best. Then we concentrated on the frequency, studying from DC to 1 mHz, finding low frequencies are best and identified the optimum. Once the electrical driving pattern was determined, all tests reported here were done under this "best" condition.

3. Materials Tested

The diagram to the right is a simplified comparison of the three common polymers of glucose: Starch, Cellulose and Glycogen. The first is mostly soluble, the second is totally insoluble and the last is called "animal starch" and is similar to amylose pectin.

3.1 Starch Digestion

The project started using cornstarch as the organic to be tested. This was a very convenient choice since the content of the remaining starch could be detected using the well

known iodine method (see section 2.5.1). Starch consists of two types of molecules, amylose (normally 20-30%) and amylopectin. The iodine method detects only the amylose portion, but it is logical to assume both are consumed at comparable rates. Much of the early work in establishing the best coatings, the best frequency and wave-form were done using corn starch in 1% KOH electrolyte.

Figure 9 is an example of the digestion rate observed in these experiments. Also included is a reference line made to roughly parallel the digestion rate of 142 grams per hour at this charge level. This

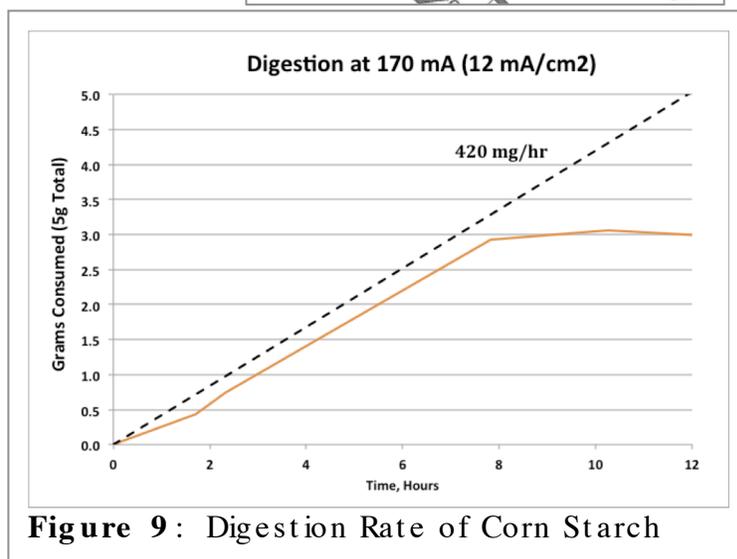
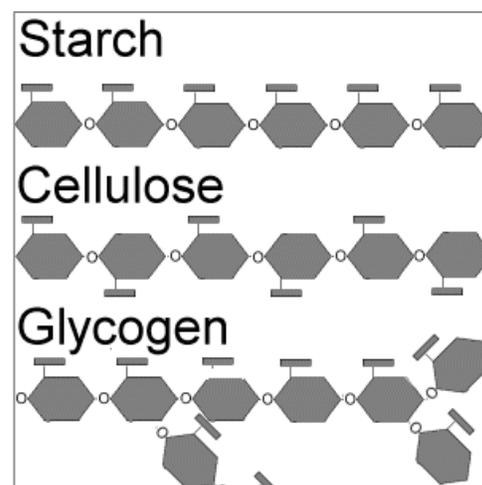


Figure 9: Digestion Rate of Corn Starch

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example used 170 mA galvanostatic power at slow +/- pulse condition. The total amount of starch present was 5 grams and the digestion always seemed to stop near the 3 gram level. But the color of the iodine test changed from the 620 nm maximum absorption to 370 nm maximum absorption brown color. What this means is unclear to this researcher, but loss of amylose is certain.

Figure 10 is a visual comparison of the initial state and the final state with iodine addition.

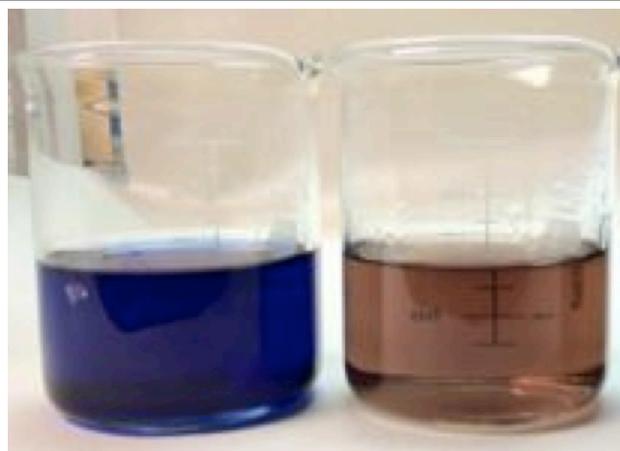


Figure 10: Color Comparison

3.2 Cellulose Digestion

Then the project moved onto the mostly insoluble form of polysaccharides: cellulose. We chose three of them: Pine wood flour, Oak wood flour and micro-crystalline cellulose (MCC). To be consistent with the starch work, we also used 1% KOH and a 1% loading of the cellulose for this work, so there was 5000 mg available.

Figure 11 shows the weight of cellulose that was digested. Essentially all of the initially available dissolved solids were digested, and a considerable

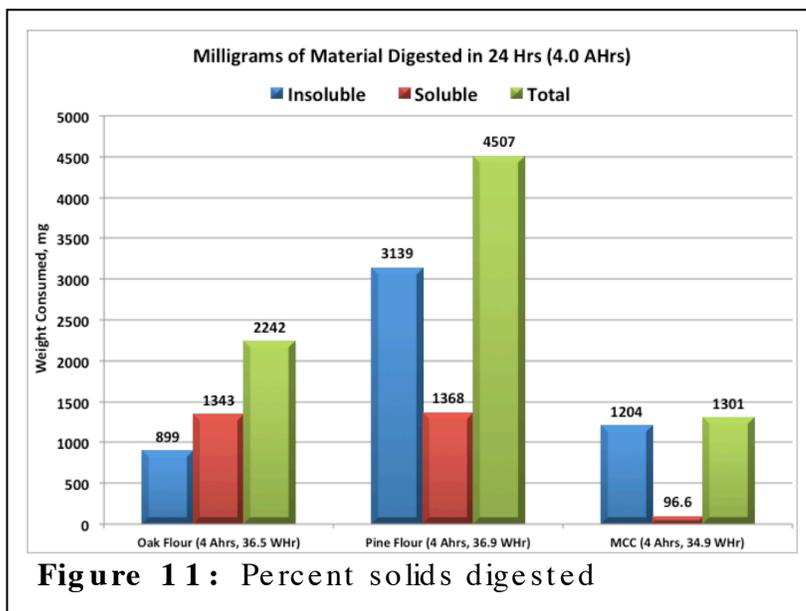


Figure 11: Percent solids digested

amount of the pine flour solids was also digested, resulting in a total of 90% of the solids destroyed. Pine wood contains the highest percentage of lignite, which apparently is easily attacked by the singlet oxygen. There was little soluble material in the initial state (as would be expected), but essentially all that was there, was digested.

Figure 12 shows the pine flour before and after digestion. Clearly the material has been altered by the process. All of the soluble colorant is gone and the solids are altered.



Figure 12: Pre and Post visual

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Below are **Figures 13 and 14** showing the pre-digested and post digested filaments under 50X magnification (1574 um across entire field) with the light filtered through a polarizing lens. Clearly, they are not being chopped up in the middle, but rather on the ends of the strands with the finer particles being totally consumed.

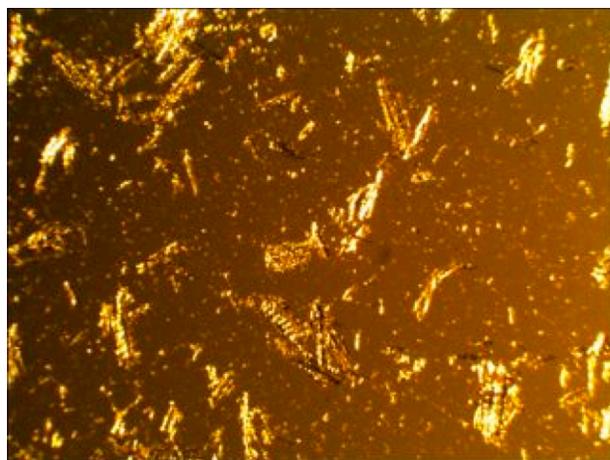


Figure 13: Pine Flour early initial

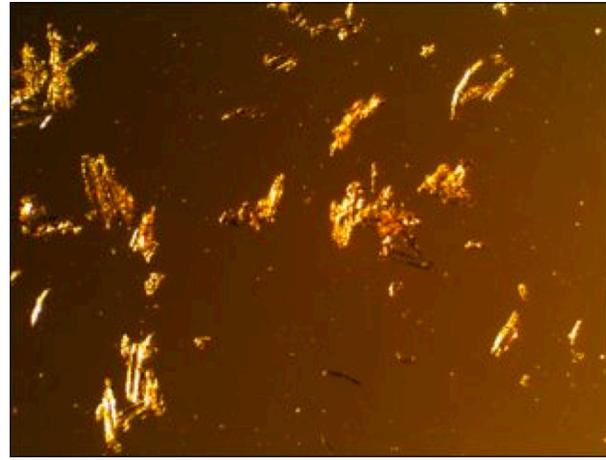


Figure 14: Pine Flour after 24 Hrs

4. Summary Results

The most widely used method to digest organics is to prepare a water slurry of the material to be digested and raising the temperature to about 350° C in a sealed SS container. At this temperature and pressure, water enters a fourth state of matter called the “supercritical state”, where it exhibits both acidic & basic properties and diffusion properties are similar to gasses. Organic molecules spontaneously disassemble under these conditions. We use 500 cc of fluid in our apparatus. If we were to assume that all of the organics disassemble (5 grams), we find a number that gives the thermal method its ideal comparison (25 mg/WHr) using the definition of BTU’s and unit converting to WHrs.

Table 2 is a comparison of the digestion rates for the several organics tested. All but one are ambient. It is clear that dissolved species digests (e.g.: starches) most readily, but insoluble solids are also digested. In this first generation feasibility assembly, the electrochemical digestion yielded from 16 to 9 times more power efficiency than the thermal process for soluble organics and nearly 5 times higher efficiency for insoluble solids. This number would improve even more with design changes such as added turbulence within the cell and optimization of flow rates and temperature.

Table 2	Rate	Per Charge	Per Power	Compared w/ Thermal
	mg/hr	mg/AHr	mg/WHr	R
Corn Starch	316	1859	224	9
Corn St @75 C	413	2430	341	14
Potato Starch	536	3037	391	16
Oak Flour	93	550	61	2.5
Pine Flour	188	1105	122	4.9
MCC	54	319	37	1.5
Thermal	N/A	N/A	25	1

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4.1 Hypothesis

The objective of this work was to demonstrate if the electrodes could break down organic molecules, not to study the mechanism if degradation was observed. However, the mechanism might improve the design in later phases of this work. That non-soluble organics such as cellulose can be oxidized suggests that the singlet oxygen exists long enough to escape the boundary layer and enter the bulk fluid where insoluble species resided.

We propose the following hypothesis: As the singlet oxygen emerges from the boundary layer, it attacks an available oxygen as rapidly as it can, with many combining with another singlet forming diatomic oxygen, but some finding the oxygen's within the organic molecule, forming a diatomic oxygen molecule which bubbles off. The resulting solids then have a lower oxygen content and higher energy density. The singlet oxygen may also attack carbons in the molecules. In future work, the outgassing could be analyzed for CO, CO₂ and O₂ content to better understand the mechanism. Being alkaline, the CO₂ may well go to potassium carbonate, which could also be detected.

5. Conclusions

- Our coating method covers all surfaces inside and outside of a complex porous electrode greatly increasing the catalytic surface area.
- One percent KOH is an effective electrolyte for this application
- Duty cycle and frequency are well understood.
- Digestion of organics includes both soluble and insoluble molecules therefore the singlet has a stable lifetime in the realm of at least hundreds of milliseconds and perhaps even a few seconds long.

6. Next Directions

There are several next directions for this technology:

- 1) Further optimize the physical design to optimize flow characteristics to enhance turbulence and efficiency of insoluble molecules.
- 2) Study the filtrates from the cellulose experiments for small molecules to better understand if the cellulosic is disassembling, or simply being oxidized from the ends.
- 3) Algae or kelp lipid liberation could be studied.
- 4) Biological extermination such as bacterial or viral decontamination.
- 5) Possible wastewater treatment or extraction.

7. Acknowledgements

- We thank Thom Robinson for funding this research.
- Senior Laboratory Assistant Crawford McCarty worked tirelessly in the laboratory and contributed greatly to the success of this project. His many insights and imagination proved invaluable to our progress.

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8. Profile of Robert Dopp

Robert Dopp, President, DoppStein Enterprises, Inc.

Mr. Dopp is one of the foremost authorities on zinc-air fuel cells and air electrode technologies⁷ and a leading expert in the field of water electrolysis and alkaline fuel cells. During his 18-year career as an engineer at Rayovac Corporation, he was a principal developer of the zinc-air hearing aid battery and lead engineer in the development of the air-cathode component. He then served as the Director of Research for Electric Fuel Corporation of Beit Shemesh Israel for five years, developing a high rate and high capacity prismatic zinc air cell.

Mr. Dopp has significant expertise in a wide range and depth of knowledge in battery, fuel cell, and hydrogen generation systems. Forming his own R&D consulting firm and laboratory in 2002 (DoppStein Enterprises Inc., DSE), where as CEO, he consults to battery, fuel cell, and hydrogen generation related industries. He has developed components and designs resulting in longer-life batteries with over four times the energy density of alkaline cylindrical cells, and many tens of times higher energy than many rechargeable batteries. His work in water electrolysis is paradigm changing. His onsite laboratory in Marietta, Georgia provides him considerable flexibility, consulting on the electrochemistry and design of gas electrodes and building cathode machines among other development projects. Mr. Dopp has 41 issued patents⁸ and many pending patents as of Jan '13. Mr. Dopp has been a guest lecturer on university campuses and at technical associations including the National Hydrogen Association and Sandia National Laboratories.

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⁷ "DSE Carbon-Based Air Electrodes." (www.doppstein.com/white_papers)

⁸ Patent List at http://www.doppstein.com/about_dse/docs/Patent%20List.pdf