Some Thoughts on the Nature of the Nuclear-Active Regions in Palladium

Edmund Storms

ENECO
270 Hyde Park Estates
Santa Fe, NM 87501, USA

ABSTRACT
A large collection of palladium samples, supplied by IMRA Materials (Japan), were studied to determine the relationship between energy production and various properties including the amount of excess volume, the open-circuit-voltage, and the maximum D/Pd ratio. The following conclusions result from the work:

1. Palladium, no matter how well prepared, is very inhomogeneous with respect to the properties relevant to cold fusion. Therefore, most general conclusions can not be based on the behavior of one or a few samples.

2. The bulk properties do not represent the properties of the nuclear-active-regions. Theoreticians need to take special note of this observation.

3. Energy active palladium will continue to produce excess energy even after being subjected to acid treatment or physical removal of the surface. Therefore, "good" palladium is difficult to ruin.

4. A pretest method has been developed to identify "good" palladium.

1. INTRODUCTION

The ability to provide a large amount of nuclear-active-palladium to researchers is essential to the eventual acceptance and commercialization of the Pons-Fleischmann Effect. At the present time, active palladium is discovered largely by accident when energy generation is observed using a calorimeter. This process is slow. A better method involves rapid measurement of properties that influence energy production. In this manner, large batches of palladium can be rapidly sorted into active and inactive material for use in a variety of studies.

Three properties were chosen to be examined: the tendency to produce cracks during loading with deuterium, the maximum average D/Pd ratio that can be achieved, and the chemical activity of deuterium at the surface. A few samples were also studied to determine the deloading rate in air and to locate those regions on the surface from which deuterium loss was occurring. The relationship of these properties to heat production was determined in a few cases.

Additional experimental results are described in several papers published in Infinite Energy[1; 2]. Future results will be published in the same journal.

2. METHODS
2.1 Composition

The composition was measured in two ways; by weighing the cathode and by determining the amount of oxygen released when deuterium dissolved in the cathode. Because loading was done in a sealed cell, containing a recombiner, the amount of oxygen could be measured by displacing oil onto a balance. The oil-constant was approximately 7300 g of oil per 1 mol of dissolved deuterium. At the end of the loading process, the cathode was weighed (± 0.00005 g) and the value used to determine the oil constant for the study. The steady composition achieved after

24 hours was used as the limiting composition. The effects of temperature and current were studied. Typical behavior is shown in Fig. 1. Bubbles on the cathode become visible when the D/Pd deviates from the ideal value.
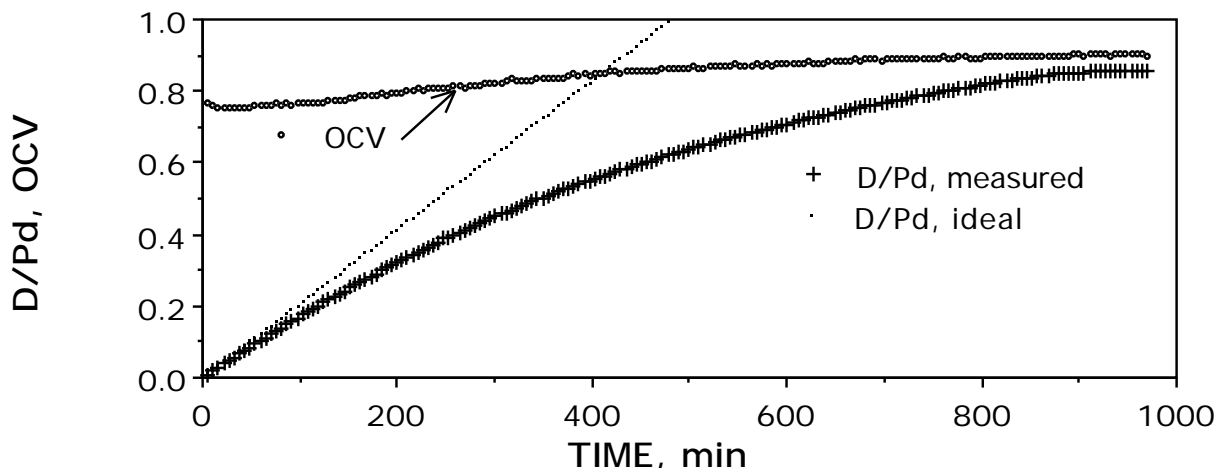

FIGURE 1. Typical loading behavior of palladium is compared to the ideal value based on the applied current. The open circuit voltage is also shown using the same scale.

2.2. Crack Formation

Palladium expands by more than 12% when it is loaded with hydrogen. However, the amount of expansion is frequently greater than that predicted from the published relationship between X-ray lattice parameter and composition. This excess volume is found to fall between 1 and 25% of the initial volume. The excess volume is proposed to result from the formation of cracks, blisters, and dislocations. When these features penetrate the surface, they accelerate loss of deuterium and prevent regions near these structures from achieving a high deuterium content. Because the average crack volume is a mixture of structures that do not contact the surface and those that exit at the surface, the overall effect is highly variable and permits only general conclusions.

The physical volume was measured using a micrometer (± 20 μm for early samples, ± 2 μm later) before and after loading. The following formula was used to calculate the excess volume:

Excess Volume (EV) = [(Final Volume)-(Initial Volume)]/(Initial Volume) - (0.0172+0.14125*D/Pd)

2.3. Chemical Activity of the Surface

The voltage generated between the surface and a reference electrode is proportional to the chemical activity of deuterium in the surface. A Luggin capillary was used to provide a conducting bridge between the cathode and a piece of platinum gauze located outside of the cell. The applied voltage to the cell was interrupted for a short time (5-10 sec.) while the voltage (± 0.001 V) was measured between the cathode and the gauze. Pure palladium produced a voltage of 0.02 ± 0.05 V relative to platinum before loading started. Samples returned to this value after all deuterium had been removed.

2.4 General Deloading

The weight loss was monitored as a function of time after the sample was removed from the cell. When the D/Pd ratio is plotted as a function of time, a straight line results which can be extrapolated back to zero time. In this manner, a determination is made of the composition existing in the cell immediately before the current was stopped. The slope of the resulting line was recorded for many samples. Values between 1×10^{-3} and 22×10^{-3} (D/Pd)/ min were observed. This prop-

erty was very sensitive to how the sample had been treated.

2.5 Localized Deloading

Some samples were examined while deloading under methanol or acetone. The bubble pattern revealed those regions experiencing rapid loss of deuterium. A variety of structures were seen by this technique. The concentration of deloading sites was very nonuniform.

2.6. Power Production

A glass, isoperibolic calorimeter was used. The cell was sealed, contained an internal recombiner, and was stirred at a constant rate. The internal temperature was measured at two positions within the electrolyte and at the cathode. A water-cooled jacket provided a constant reference temperature. Power production was measured relative to the electrolyte power applied during the first few hours of electrolysis, before excess power production started. Figure 2 shows a typical calibration. The standard deviation in excess power of a typical data set was ±0.15 watt. A drawing of the calorimeter can be found in reference[1].
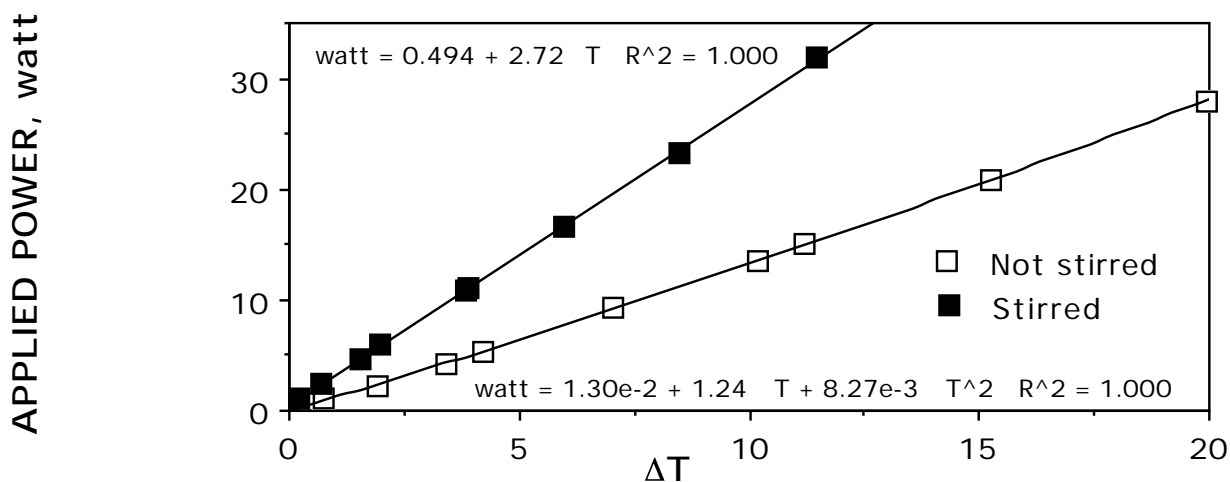

FIGURE 2. Typical relationship between applied electrolytic power and the temperature across the cell wall. Stirring produces a more linear relationship and a steeper slope.

3. RESULTS

Eighty samples which fell into eight sets were examined. One half of the sets contained 500 ppm boron while the remainder were nominally pure palladium. The samples had been subjected to various annealing and surface treatments by IMRA. Each sample was approximately 10 mm wide, 20 mm long and 1 mm thick.

All properties showed a wide distribution around a mean value. It is, therefore, impossible to arrive at a general conclusion based on the behavior of a single or a few samples. Unfortunately, some of the sets contained an insufficient number of samples to make statistical analysis meaningful. Consequently, only a few general conclusions will be presented. These will address the effect of adding boron and the effect of etching the surface with Aqua Regia.

3.1 Composition

Figure 3 shows a histogram that compares samples with and without added boron. The presence of 500 ppm boron both improves the limiting composition as well as making it worse. Clearly some pure samples are better in this regard than are some samples containing boron. The reverse is also true. In addition, samples containing boron lost about 0.00015 g as a result of the electrolytic process. This loss indicates that the surface region is depleted of boron during the loading process.

An Aqua Regia treatment tends to make the property more uniform but does not lead to especially high values.
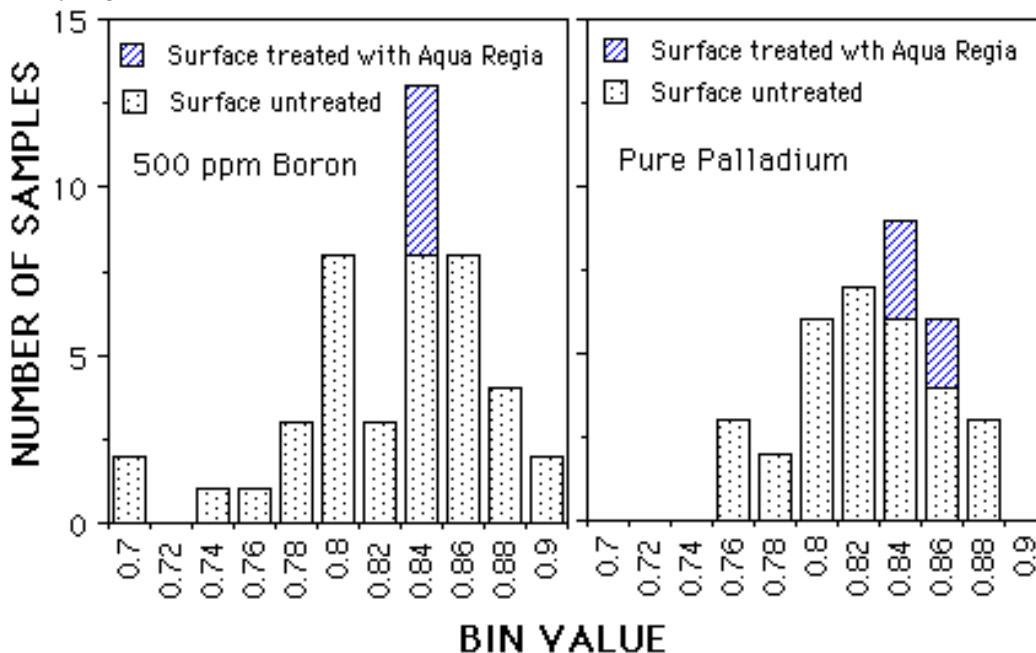

FIGURE 3. The histograms compare the limiting composition of samples containing 500 ppm boron with those that are untreated. The effect of Aqua Regia treatment using 5 samples from each set is superimposed. The bin value for 0.90, for example, shows the number samples having a value between 0.88 and 0.90. Because of edge effects, the values have only a relative meaning.

3.2 Crack Concentration

Shown in Fig. 4 is the excess volume (EV) for "pure" palladium and for samples containing 500 ppm boron. The values are corrected to D/Pd=0.85 because the amount of excess volume tends to increase as the composition within the -phase is increased. The presence of boron increases the average excess volume from 4.3% for pure palladium to 5.6%. In addition, the boron produces a significant number of values over 10%. An Aqua Regia surface treatment appears to have no significant effect on this property.

Samples having a EV near 1% do not form additional EV even after they are deloaded and reloaded. However, the presence of a larger initial EV produces additional EV each time the sample is reloaded. The amount of additional EV is variable between samples.

3.3 Chemical Activity of the Surface

The open-circuit-voltage (OCV), measured during loading, is compared to the average D/Pd in Fig. 1. The initial rapid increased was always followed by slight drop. Those samples that eventually produced excess power usually continued to increase to values above 1.0 V.

Figures 5 and 6 compare the OCV of two samples during deloading. The sample shown in Fig. 5 is a piece of palladium foil that did not make excess power. Thicker samples show the same behavior but naturally take much longer to return to the -phase. The sample shown in Fig. 6 made excess power immediately before the current was interrupted. Indications of a new phase having a OCV above that of − PdD were occasionally seen in other active samples. However, this sample (#42) gave the highest OCV measured thus far.
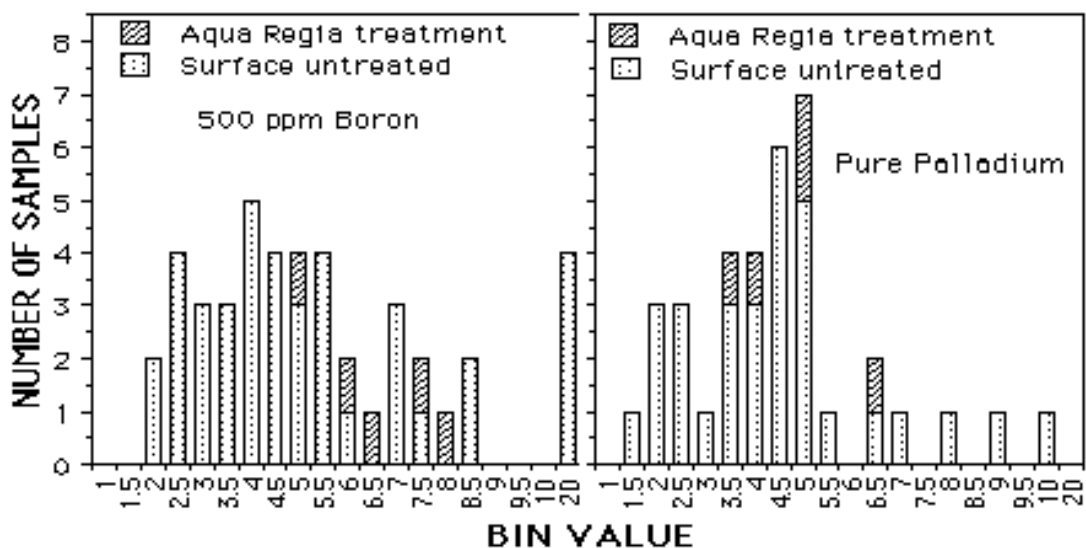
FIGURE 4. The histograms compare the percent excess volume of samples containing boron with those to which boron was not added. The effect of Aqua Regia treatment using 5 samples from each set is superimposed. The bin value for 8.0, for example, shows the number samples having a value between 7.5 and 8.0 percent. Values are extrapolated to D/Pd=0.85.

3.4 Excess Energy

Excess power (EP) production is compared to the measured properties in Table 1. The listed properties were measured after the power measurements. Only general conclusions can be drawn from these few examples because other important variables were not measured and because each sample was very nonuniform with respect to those variables that were studied.

After sample #42 made excess power, a study was undertaken to determine how much abuse to the sample would be required to stop energy production. After the sample had been fully loaded to D/Pd=0.86, EP was sought by increasing the applied current in steps to 3 A. Each current was held for 10 min. while the calorimeter came to equilibrium. Figure 7A shows the EP at 3A. Brief current interruptions had little effect on EP production even when the sample was removed from the cell for a short time. Longer interruptions reduced EP production and required additional time before the previous EP was restored. Between figures 7A and 7B, the sample was washed with Aqua Regia, the surface was polished with 400-600 mesh SiC paper, and all deuterium was removed at 110°C. The OCV was 0.01±0.01V before loading was started. After being fully loaded, the sample produced the behavior shown in 7B. Regular bursts of EP every 2 hr were seen while the current was constant at 2A. These bursts were sensitive to applied current and cell temperature. EP continued to increase after 5 g of Li_2SO_4 was added to 40 ml of electrolyte.

Before the data shown in Fig. 8 was taken, the calorimeter was enlarged and improved. The Pt mesh anode was replaced by a spiral of palladium wire and fresh 0.4 M LiOD electrolyte was used. In addition, 40 μm was removed from the sample surfaces by diamond polishing followed by an Aqua Regia etch and heating in air at 325°C. After reloading, the composition was D/Pd=0.816 with 2.8% EV. Calibration was done on day 0. Thereafter, EP at 3A increased as shown in Fig 8. A current reverse at day 8 produced a minor reduction on day 9. An attempt to determine the composition on day 9 caused the sample to self-heat in air resulting in loss of most contained deuterium. Upon being returned to the cell, energy production resumed after 1 day and continued to increase until the sample was removed and sent for measurement of -emission. No

-emission was detected.

TABLE 1
Comparison between measured properties and excess power production

Sample Number	Designation	Excess Volume, %	Composition D/Pd	OVC	Excess Power, W (at 3 A)
Tanaka 1*		1.7	0.82		7.5
IMRA #38	A1-B3	2.0	0.875	1.25	2-4
Tanaka 4*		2	0.84		2
IMRA #42	A1-B4	1 to 2	0.891	1.35	4.6
IMRA #84**	A2-B2	6.9	0.83	1.00	1.6
IMRA #39	A1-B3	4.1	0.87	1.08	1.1
IMRA #57	A2-B1	6.0	0.83	1.05	0.0
IMRA #10	A1-B1	6.6	0.82	1.00	0.0
IMRA #27	A1-B1	1.0	0.85	0.96	0.0
IMRA #58	A2-B1	4.1	0.79	0.70	0.0
IMRA #62	A2-B1	2.3	0.83	0.66	0.0
IMRA #44	A1-B4	16.1	0.78	0.60	0.0
Tanaka 2*		13.5	0.75		0.0

* Tanaka samples from Refs. [3; 4]
**Surface layer containing O and Si of sufficient thickness to partially flake off during loading.
A1-B3 = pure Pd+ basic process + annealed in vacuum at 750°
A1-B4 = + treatment with Aqua Regia
A2-B1 = 500 ppm B added + basic process
A2-B2 = + annealed in air at 750°

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4. CONCLUSION

The properties of palladium relevant to "cold fusion" are very nonuniform even when samples are treated in an apparently identical manner. To achieve excess energy production, material should have a low excess volume, be able to acquire a D/Pd ratio above 0.85 and have an open-circuit-voltage in excess of 1.0 V referenced to platinum. Because of edge effects, the limiting composition applies only to the sample shape used in this study. Occasionally, a sample will fail to meet one or more of these requirements and still make excess power. Apparently, additional variables are important beyond the ones reported here.

Samples that are found to produce excess power can be reactivated even after being completely deloaded and after the surface is removed. Apparently, the required surface can be reestablished if the properties of the base material are suitable. This discovery means that active samples can be identified and used in other studies without losing the ability to produce heat during transfer.

The bubble pattern seen when a sample is allowed to deload in acetone is an effective method to study the concentration of microcracks and other imperfections that cause local reduction in composition at the surface. Three types of sites are seen; isolated bubbles, lines of bubbles associated with scratches and cracks, and active loss from blisters. Some samples have large regions from which no bubbles are seen to leave.

The behavior of the OCV suggest the presence of a phase having a much larger deuterium activity than pure -PdD when excess energy is produced. Very large OCV values obtained for samples having a bulk composition consistent with -PdD, in the absence of EP, suggest that the surface activity is being modified by the presence of deposited impurities.
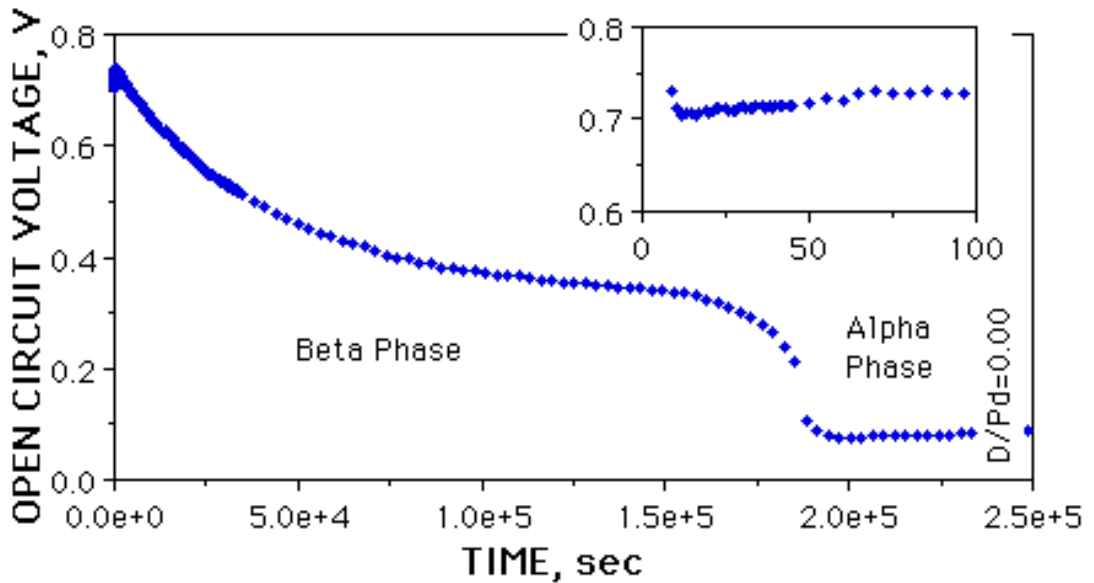
FIGURE 5. Open-Circuit-Voltage of a 50 μm thick Pd foil during deloading in the cell at 30°C. This material did not produce excess power before deloading. The insert shows a characteristic initial increase.
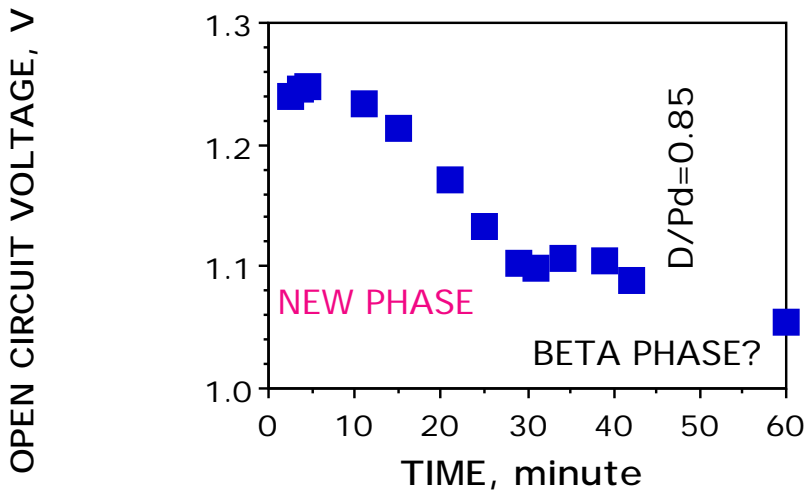
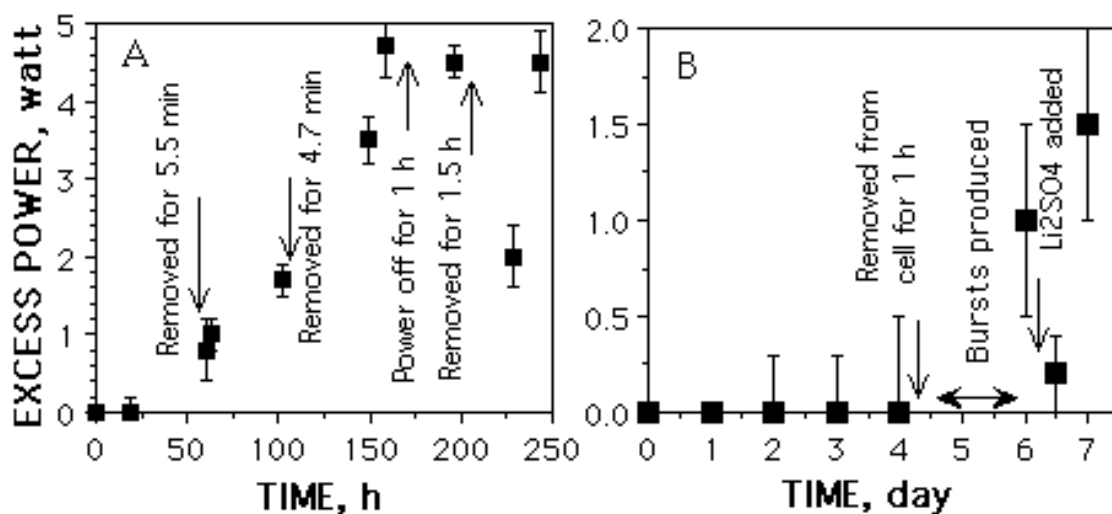FIGURE 6. OCV of Sample #42 deloaded in a cell at 9°C. This sample produced excess power before deloading

FIGURE 7A. Initial onset of power production.
FIGURE 7B. Onset of power production after surface was removed.
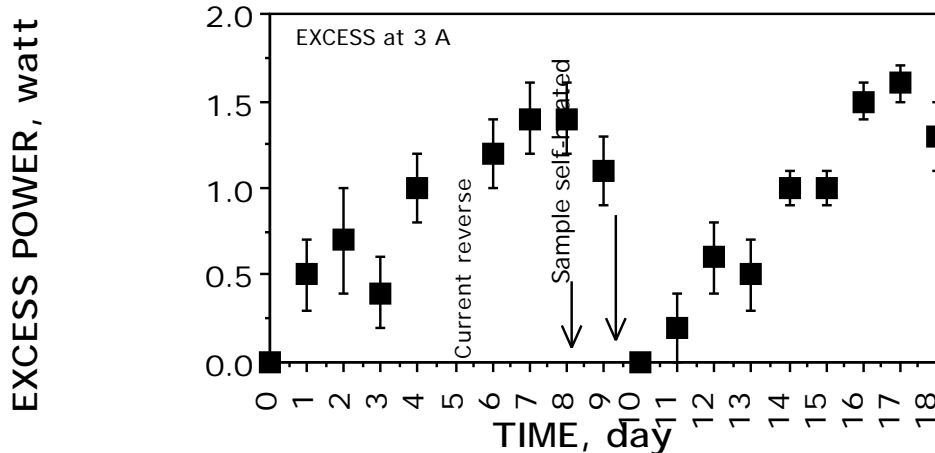

FIGURE 8. Onset of power production after at least 0.080 mm was removed and the sample was washed with Aqua Regia. Self heating occurred when the sample was exposed to air because of a rapid D_2+O_2 reaction.

References

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