

Research Article

Codeposition Methods: A Search for Enabling Factors

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Abstract

This paper is a preliminary report on results obtained from a series of experiments conducted April–September 2009. The experiments were designed to test for excess power using the basic methods disclosed in 1991 by Szpak, Mossier-Boss and Smith. A large and repeatable excess power signal was observed and the efforts to test mundane explanations for the signal are described. The design, fabrication and calibration methods of a new type of Seebeck calorimeter used for these experiments are also disclosed.

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PACS: *****

1. Introduction

The field of Condensed Matter Nuclear Science (CMNS) began March 23, 1989 with the controversial name of Cold Fusion; the field quickly gained a negative reputation in the mainstream scientific community because the effects claimed in the original paper by Fleischmann, Pons, Hawkins were not easily reproduced [1]. In this seminal paper, the authors claimed that when a deuterated palladium cathode was electrolyzed in lithium deuterioxide, the cell produced more thermal power than was provided by the DC electrical input power. The observed cathode power densities were commensurate with nuclear power densities, leading to claims of a room temperature nuclear process and a scientific controversy that has persisted for two decades.

Producing the power gain observed in the Fleischmann and Pons experiments required considerable skill and patience. In the early years of 1989–1990, excess power results were sporadic and required many weeks of electrolysis to observe. In 1990–1991 Dr. Stanislaw Szpak, working at the Naval Ocean Systems Center in San Diego, California (SPAWAR-SSC), developed a codeposition method designed to deposit palladium and deuterium concurrently onto a metal substrate, typically copper or gold foil.

Szpak claimed that this method created the conditions to produce the Fleischmann–Pons excess power effect without a long incubation period. It was claimed that codeposition methods provide for a fresh ever-expanding cathode surface

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and non-steady-state conditions. The need to provide a uniform current density for high deuterium loading was also eliminated. Szpak and his co-workers tested mainly for temperature gains, reporting that the cathode remained 2–4°C hotter than the electrolyte. Claims for elevated levels of tritium in the deuterium-based electrolyte were also made [2].

Over the years, several researchers have attempted to reproduce the Szpak methods but success has not been uniform. Dr. Melvin Miles has arguably been the most successful and has reported positive excess power results in several papers such as Ref. [3]. Experiments reported in 1996 by the Naval Research Laboratory (NRL) in Washington, DC did not produce significant excess power results, but their reported calorimetric errors for these codeposition experiments were ± 200 mW [4]. For many years, the SPAWAR-SSC group in San Diego has reported evidence from CR39 studies supporting the claim that nuclear reactions can result from codeposition methods [5].

In 2008 Dr. Michael Melich contacted the author and several other experienced researchers in the field of CMNS with specific codeposition experience and publication histories, inviting them to attempt reproduction of the codeposition heat effect. The project was funded through the Naval Research Laboratory for six months. The project required that each researcher design and build a calorimeter with at least a 3% level of precision and then attempt to produce credible levels of excess power using Szpak's codeposition methods. This paper reports on the author's efforts to meet the goals of this project.

2. The Seebeck Cell Calorimeter

The Seebeck Cell Calorimeter was designed to provide calorimetry at a 1% level of precision. Seebeck calorimeters have been used in the CMNS field for several years. Dr. Edmund Storms has written several papers about building and working with Seebeck calorimeters [6]. Storms' approach has been to build a box lined with thermoelectric converters (TECs) and then to place the cell under test inside the box. As heat flows out through the TECs, a voltage is produced that can be calibrated to scale with power dissipated in the cell. To function properly, the cold side of the TECs must be kept at a constant temperature so the voltage can be calibrated reliably. Storms and others have traditionally used water coupling to keep the cold side of the TECs at a constant temperature. This method, while effective, is not very portable or affordable. Water coupling is a technical challenge and requires expensive bulky equipment. The approach used in this study relies on air coupling to keep the cool side of the TECs at a constant temperature (Fig. 1).

The Seebeck Cell Calorimeter is shown in Fig 1. The laser view port is also visible, providing access for cathode inspection and laser stimulation. The area of the view port is $\sim 4\%$ of the total surface area of the calorimeter. In the center of the laser view port is a detector for an optical spectrometer used for laser tuning. The 4-inch DC brushless fan provides a strong air flow up the axis of the heat sinks. Two thermistors are secured in the aluminum trough to provide feedback for controlling air temperature to within $\pm 0.02^\circ\text{C}$. Highly conductive thermal epoxy (Duralco 128) provides good thermal transfer but is not electrically conductive.

The core of the calorimeter is a square piece of borosilicate glass 15 cm long and 45 mm on each side (Friederich & Dimmock, #BST45-200). Wall thickness is 2 mm. A square Teflon lid provides sealing for the electrochemical cell and support for up to nine electrode holders/thermistor probes. The Teflon lid provides pass through holes for thermistors (Digi-Key, 2250 Ohm, #615-1000-ND), an immersion heater, a gas vent tube, an anode, a main cathode, a calibration cathode, and a siphon tube so that the electrolyte can be changed during operation without loss of precision (Fig. 2).

Two copper plates are epoxied to the outside of the cell wall, the magnets are epoxied to the copper plates and the TECs are epoxied to the magnets. The copper plates provide an optional high voltage electric field; the two magnets provide a 500 G magnetic field at the cathode (United Nuclear, two $2'' \times \frac{1}{4}''$ plate magnets). The copper plates are electrically insulated by the Duralco 128 epoxy. A 25×50 mm viewport provides visual and laser access to the cathode during operation without loss of calorimetric precision. The 50×50 mm TECs (Thermal Enterprises, EBay store, #TEC310117657888) are epoxied directly to the electrochemical cell except the area containing the copper plates and magnets, providing rapid heat transfer properties and thermal equilibration. The thermal epoxy used was Duralco 128



Figure 1. The Seebeck Cell Calorimeter is shown inside a temperature controlled enclosure on top of a rack with a fan to provide vigorous air stirring and a consistent airflow over the heat sinks attached to the TECs and the cell walls. Airflow temperature is controlled to $\pm 0.02^\circ\text{C}$, stability is $\pm 0.01\text{ W}$.

with 10% flexibilizer (Cotronics Corp., # 105RF-1) added to avoid thermal expansion damage (Fig. 3).

The final steps in the calorimeter fabrication process are shown in Figs. 3 and 5. The heat sinks (Custom Thermo-electric, #HS54541401) shown in Fig. 3 provide good thermal coupling to the well-controlled airflow. The heat sinks help maintain the cold side temperature of the TECs at a constant value. The simple calorimeter stand shown in Fig. 5 was made from off-the-shelf parts available at most hardware/electronics stores.

3. Calorimeter Performance and Calibration

The calorimeter was completed and installed in a temperature-controlled enclosure for calibration. The enclosure is an Avanti wine cooler that has been modified by adding a Nichrome wire heater and brushless DC fans to stir the air vigorously. The enclosure temperature was set to 32°C and controlled to within $\pm 0.02^\circ\text{C}$. 100 mL of LIOH electrolyte was mixed to a concentration of 0.15 M and a platinum foil cathode $8 \times 10 \times 0.25\text{ mm}$ was used. The anode was a coil of platinum wire with an inside diameter of 12 mm and five turns over the cathode length. An immersion heater was in the

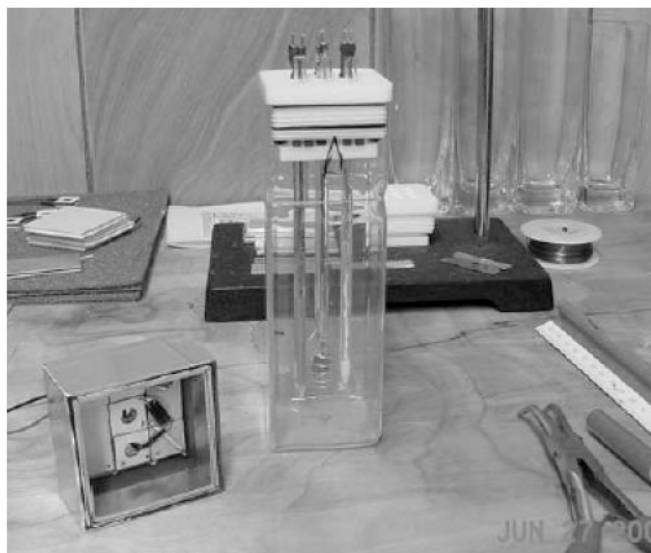


Figure 2. The electrode holders and thermistor probes are 5 mm diameter sealed glass tubes. Hook up wire is 0.5 mm platinum wire spot welded to copper wire sealed inside the glass tubes. The platinum wire is sealed against the soft glass tubing making an airtight seal.

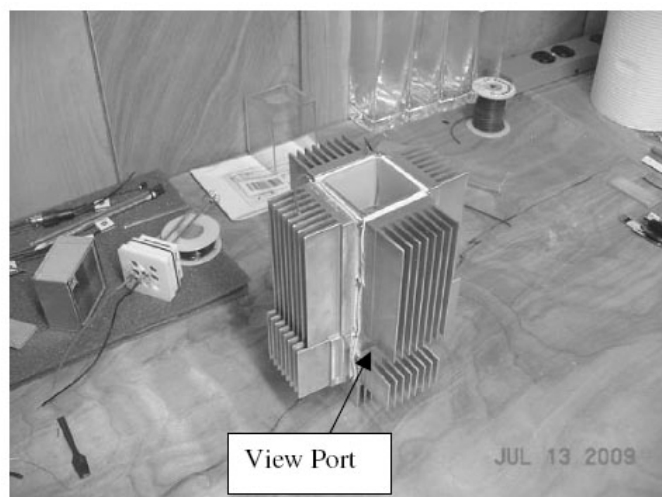


Figure 3. Aluminum heat sinks were epoxied to the TECs for air-coupled temperature control. The heat sinks conduct heat out of the cell so efficiently that the calorimeter can handle high electrical power input. The calorimeter has been tested 0–20 W and demonstrated a 1% level of precision.

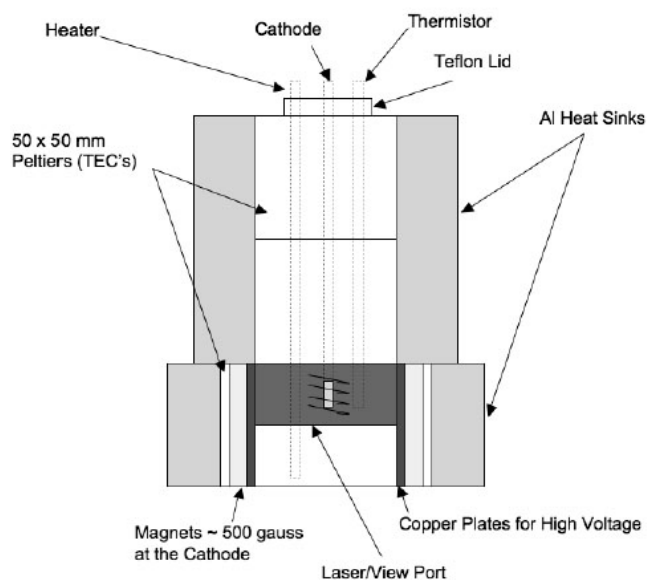


Figure 4. A schematic of the Seebeck cell calorimeter in cut-away view.

cell and provided constant DC power at 11 W to keep the cell temperature about 45°C so the recombiners would work



Figure 5. A rack was constructed from commonly available parts; the aluminum trough was perforated to allow uniform air flow over the heat sinks. Two thermistors were placed in the aluminum trough to provide precise control of the air temperature as it flows over the heat sinks.

properly. A calibration was performed from 0 to 4 W of electrolysis power. The cell was closed and recombination of the gases was provided by alumina pellets coated with 0.5% platinum. The cell was not mechanically stirred, although the external magnetic field provided some degree of stirring. The following calibration plot resulted (Fig. 6).

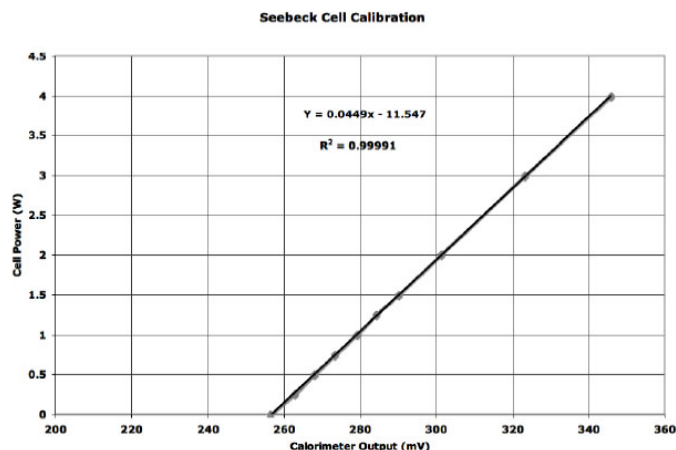


Figure 6. The calorimeter voltage output over 0–4 W is linear and has an R -squared of 0.9999; The presence of the immersion heater at a constant 11 W produces a 256 mV signal when electrolysis power is zero. Calibrations were made with electrolysis power; when resistance power of a few watts was added to electrolysis power, the calorimeter reported a power balance within 1%.

Calibration revealed that this calorimeter requires re-calibration when the cell is opened for maintenance or a new experiment is started; if the cell lid is not opened, then an existing calibration will hold for many weeks, longer than the routine maintenance interval of the calorimeter. The calorimeter has a 10 min time constant, so a thorough calibration can be completed in 30 h. The results of a typical calibration are shown in Fig. 7.

4. Calorimeter Properties

- Precision $\sim 1\%$.
- Time constant ~ 10 min.
- Time to reach equilibrium ~ 6 time constants.
- Sensitivity ~ 5 mW.
- Operational stability during electrolysis ± 0.01 W.
- Stability duration > 72 h at ± 0.01 W.
- Power range tested 0–20 W.
- Calorimeter permits changing cathodes during operation.
- Calorimeter permits removing/replacing electrolyte during operation.
- Calorimeter provides a viewing/laser access port without precision loss.
- Calorimeter provides high voltage capability for electric field application.
- Calorimeter provides a magnetic field of ~ 500 G at the cathode.
- Calorimeter provides nine holes in the cell lid for probes/electrodes.
- Calorimeter provides an in-cell resistance heater for checking calibration.

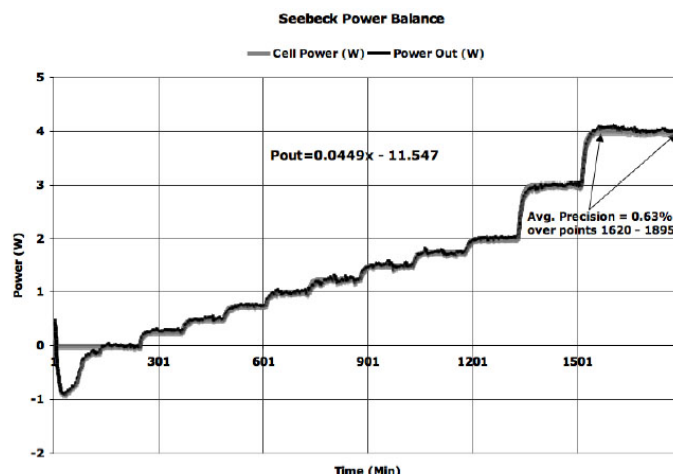


Figure 7. This plot demonstrates that the fitting equation provides for a good input/output power balance over the tested range of 0–4 W; Precision = $(P_{\text{out}} - P_{\text{in}})/P_{\text{in}}$ at $\sim 1\%$.

- Low cost $\sim$ \$2000.
- Portable—weighs a few pounds and occupies less than 1 ft³.

5. Experimental Results

Two experiments will be discussed in this paper, NRL681 and NRL684; both experiments produced an excess power signal, ranging from 175 to 250 mW. Subject to further testing, the origin of the excess power signal appears to be nonchemical.

The schematic shown in Fig. 8 is typical for experiments NRL681 and NRL684d; the key features are external magnets, a second cathode for calibration, an immersion heater and a siphon (not visible) located in the left rear of the cell to allow replacement of the electrolyte during the experiment. All cells were closed and gases recombined using 1/8 inch alumina pellets coated with 0.5% platinum reduced (Alpha Aesar, #89106). The recombiner pellets were placed in a 1/8 inch groove in the Teflon lid as shown in Fig. 8. The recombiners worked well as long as cell temperature was maintained between 45 and 50°C. A bubbler containing spent electrolyte was used to monitor recombiner activity.

Experiment NRL681 cathode was a copper substrate plated with gold for approximately 5 min at 3 V, 0.2 A. The cathode was $8 \times 10 \times 0.6$ mm, the anode was a coil of 0.999 Pt wire with an inside diameter of 12 mm (Fig. 9), and the electrolyte used was 0.15 M LiCl, 0.025 M PdCl₂ in 100 mL of 99.9% D₂O from Aldrich.

These experiments differed slightly from Szpak's original protocol. Codeposition experiments normally use bare copper cathodes, electrolyte with twice the concentration and begin electrolysis using very low currents for about a week. This long low-current period plates the palladium smoothly onto the cathode; current is increased when the electrolyte has become clear, indicating that palladium has plated onto the cathode.

The protocol for NRL681 and NRL684 applied electrolysis of 3 W immediately, reaching 6 V at 0.5 A without a slow ramp up. A magnetic field of 500 G was always present. Experience soon showed that the concentration of the electrolyte needed to be reduced by 50% because the palladium build-up on the cathode was excessive. Szpak's protocol was changed slightly because gold plating was less expensive than gold foil and high voltage/current produces a coarse

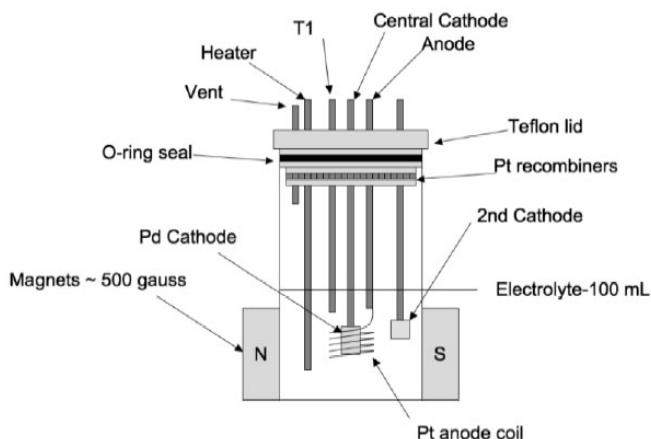


Figure 8. The schematic shown is typical for NRL681 and NRL684. Titanium proved to be a good inert material for the second cathode. It depicts only the cell and magnets for clarity. Details showing the TECs, copper plates and aluminum fins have been suppressed. More details are shown in Fig. 4.

layer of palladium containing many vacancies, which Hagelstein has conjectured might be helpful in the production of excess power. The author was further motivated to use high voltage and gold-plated copper cathodes throughout the entire experiment because Dr. Dennis Cravens followed the low voltage protocol on bare copper cathodes and obtained a null result. Elevated temperature in this series of experiments might also be an enabling factor in the observation of excess power. Temperature was maintained at 45–50°C to improve recombiner function in the closed cells.

Interval 1 of Fig. 10 shows a good zero power balance. Interval 2, resistance heater power to 3 W and power balance to within 1% precision. Interval 3, electrolysis power to 3 W, excess power observed ~175 mW. Interval 4,

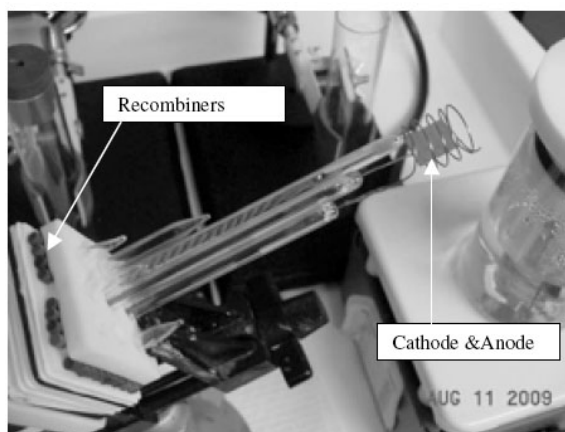


Figure 9. The cell lid, recombiners, sealed glass electrode holders and cathode/anode are shown following the gold plating process, typical for NRL681.

electrolysis power to 1 W, power balance to within 1%. Interval 5, resistance heater at 1 W, power balance to within 1%. Interval 6, zero power balance to within 1%.

Experiment NRL681 was a very clear demonstration that the Seebeck Cell Calorimeter had long-term stability and could show a good power balance. However, NRL681 left open the possibility that the effect was chemical in origin or was due to the presence of an immersion heater used to keep the cell at 40°C.

Experiment NRL684d was designed to permit changing or repositioning of the electrodes and removal/replacement of the electrolyte while the experiment is running. This can be done without changing calorimeter performance or calibration. The cathode used for NRL684d was a $4 \times 10 \times 0.6$ mm Cu substrate plated with Au for 5 min at 3 V, 0.2 A. The anode coil was 0.999 Pt wire with an ID of 12 mm. Electrolyte was 0.15 M LiCl and 0.025 M PdCl₂ in 100 mL of 99.9% D₂O. A 5 mm glass tube 16 cm long was located in the left rear of the cell to remove/replace electrolyte during the experiment. Cathode width was reduced from previous experiments so the cathode can be withdrawn through the 5 mm lid pass-through during the experiment.

This permits testing different cathode materials very quickly without changing calorimeter performance or calibration. Over a 30 h period, NRL684d produced the result shown in Fig. 11:

Interval 1 of Fig. 11, the Ti cathode was electrolyzed in hole No. 5 at 3 W; the gold plated copper cathode was in hole No. 3 without electrolysis power. Power was in balance to within 1%. Interval 2, electrolysis power was switched to the gold plated copper cathode in hole No. 3 outside of the anode coil. After a transient disturbance due to switching cathodes, power came into balance within 1%. Interval 3, exchanged electrodes. The Au plated Cu cathode was put into hole No. 5, inside the Pt anode coil. However, electrolysis power continued to the inert Ti cathode now located in hole No. 3. Again power was in balance to within 1%. Interval 4, electrolysis was diverted to the gold plated copper cathode now located in hole No. 5 inside the Pt anode coil. An excess power signal of 250 mW appeared very quickly and cell temperature increased at the same time by 4–5°C. The excess power signal and cell temperature remained elevated, producing ~5 kJ of excess energy. Interval 5, a pump was activated near point 1210 to remove the deuterium-based electrolyte and replace it with hydrogen-based electrolyte of identical volume and concentration as that used at the start of the experiment. As seen in Fig. 11, the excess power signal declined over a nine-hour period. Normally, equilibrium is re-established in about 1 h. Possible explanations might be the presence of a non-chemical exothermic process or a calorimeter error. Future experiments will attempt to clarify this issue.

NRL684d made some credibility advances over NRL681. For example, the inert Ti cathode was electrolyzed in the

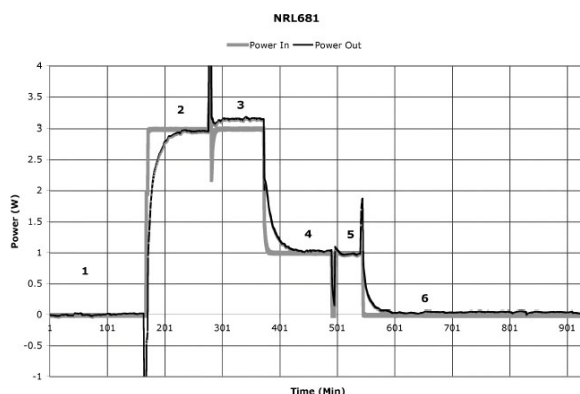


Figure 10. This plot shows that the calorimeter reports a power balance at all intervals except No. 3; during this interval the gold plated copper cathode was electrolyzed at 6 V, 0.5 A and ~175 mW of excess power was observed.

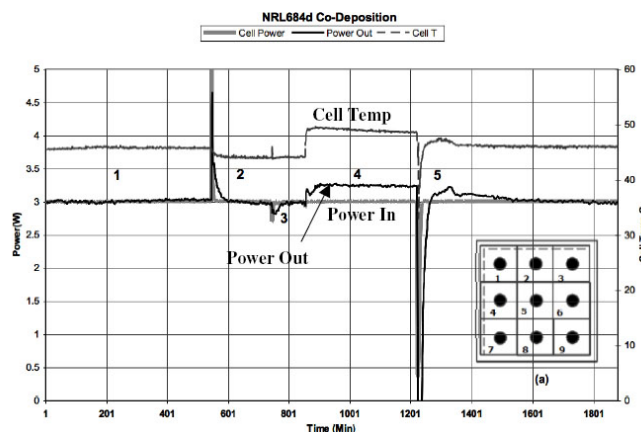


Figure 11. This plot shows a 30 h test consisting of five intervals producing a good power balance at all intervals except No. 4. During this interval the gold plated copper cathode was electrolyzed inside the anode coil and produced a 250 mW excess power signal. The inset (a) shows the lid configuration for this experiment.

same location and manner as the gold plated copper cathode, yet only the gold plated copper cathode produced excess power when electrolyzed inside the Pt anode coil, indicating that the calorimeter was functioning properly. Further, the excess power signal appeared when electrolyzed in a deuterium-based electrolyte but declined slowly to zero when deuterium was replaced with light hydrogen, suggesting the signal might be non-chemical in origin.

6. Discussion

While great care was taken during the experiments to avoid the creation of false positives, the possibility of error was always considered. Colleagues have made several suggestions for sources of effect-producing errors. Most have been tested and shown to be a non factor. One suggestion, made by Dr. Ken Grabowski from NRL, remains open. His concern was that the single immersion heater might create a hot spot within the calorimeter, in turn causing a false positive. This idea was tested briefly by turning off the immersion heater and increasing the enclosure temperature to provide an operating temperature of 45°C. Under these conditions, the excess power signal did not appear. However, the experiment was not conducted with fresh electrolyte and that may have been a factor. The immersion heater was turned back on during the follow-up experiment and the excess power signal returned very slowly, inconsistent with previous experiments. The effect of the immersion heater was tested several times with an inert cathode in an inert electrolyte (LiOH) and the false positive was never observed. If the use of an immersion heater is the source of a false positive, it seems reasonable to expect that the effect would be observed in all types of electrolytes but it is not. The effect is observed only in deuterium-based electrolyte.

Since this calorimeter is a new design, it seemed prudent to study how heat is evolved inside the Seebeck Cell Calorimeter when electrolysis is performed using inert electrodes and electrolyte. Thermistors were placed in holes 1,3,7, and 9 while duplicating the protocol shown in interval 4 of Fig. 11. Two temperature gradient contour maps are shown in Fig. 12a and b.

In Fig. 12a, the immersion heater was off while 3 W of electrolysis was applied to the platinum cathode in hole 5 (center), resulting in a small gradient running from the lower left corner to the upper right corner. Figure 12b shows the gradient when an 11 W resistance heater was turned on in hole 4 plus 3 W of electrolysis power applied to the cathode

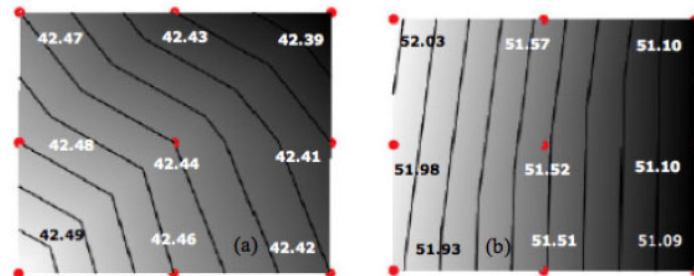


Figure 12. (a and b). The contour plots show temperature gradients produced during electrolysis of a platinum (inert) cathode in LIOH. Thermistors were placed in each of the cell lid corners at holes 1, 3, 7 and 9. The other five temperatures are simply averages from adjacent thermistor probes. The heater is in hole 4, left side center of the cell. Temperatures are in Celsius.

in hole 5. With the resistance heater on, a moderate thermal gradient was produced from left to right across the cell (Fig. 12b). Even with the thermal gradient, the calorimeter produced a power balance at 3 and 14 W (Fig. 13).

7. Enabling Factors

Overall, the claims of Szpak and his co-workers were observed in this series of experiments – codeposition methods produced a significant and repeatable excess power signal that appeared without a long incubation period. The excess power signal appeared only when using deuterium-based electrolyte and was strongest when the cathode was gold plated copper. A new observation was made – the robust excess power signal only appeared when the gold plated copper cathode was electrolyzed inside the anode coil. When electrolyzed outside the anode coil, a null result was normally observed.

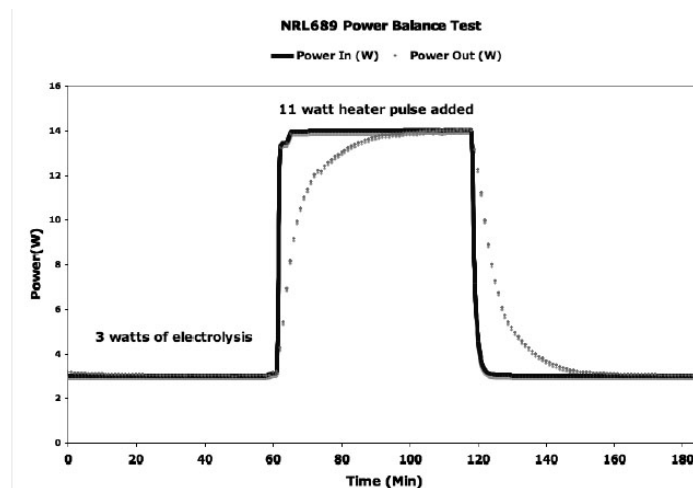


Figure 13. This plot shows the calorimeter is not affected by temperature gradients. The contour map of Fig. 12a relates to the intervals 0–60 and 120–180 min when the immersion heater is off. The interval 60–120 min relates to the contour map shown in Fig. 12b when the heater is on.

Additional experiments are underway using fresh materials and will attempt to clarify the role of various factors in the production of excess power using codeposition methods. The enabling factors under consideration are the gold plated surface, the external magnetic field, the role of the anode, plating palladium at high current/voltage initially, and the role of the immersion heater as a possible source of error.

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