Progress towards understanding anomalous heat effect in metal deuterides

O. Azizi[1], A. El-Boher[1,*], J. H. He[1], G. K. Hubler[1], D. Pease[1], W. Isaacson[1], V. Violante[2] and S. Gangopadhyay[3]

[1]The Sydney Kimmel Institute for Nuclear Renaissance, Department of Physics and Astronomy, University of Missouri, Columbia, Missouri 65211, USA
[2]ENEA Research Center, Frascati, Italy
[3]Department of Electrical and Computer Engineering, University of Missouri, Columbia, Missouri 65211, USA

The present article summarizes anomalous heat events which were observed in a large number of electrolysis experiments using heavy water and palladium-based cathodes. The amount of excess heat produced by some of these experiments is too large to be accounted for by any known chemical processes. It was found that events of the anomalous heat effect (AHE) are accompanied by increased cell voltage during electrolysis and that there are characteristic cathode surface morphologies which are associated with excess heat events. AHE has been observed during electrolysis following dynamic stimulation of the cell by time-dependent electrolytic currents (SuperWaves) and ultrasonic excitation. Past experiments have increased our understanding of the anomalous heat effect in the palladium–deuterium systems, but there is much left to be learned.

Keywords: Anomalous heat, dynamic stimulation, electrolysis, palladium deuterides, surface morphology.

IN 1989, Fleischmann and Pons reported on an anomalous heat effect (AHE) that they observed when performing electrolysis of heavy water with a palladium cathode[1]. This discovery attracted worldwide attention due to its obvious potential to become a cheap and abundant source of energy. Many researchers rushed to replicate Fleischmann and Pons' electrolytic experiments, but very few were initially successful. This irreproducibility soon made AHE a quite controversial topic and even its existence was discounted by most scientists. Despite this early stigma, however, small groups of scientists around the world have continued to do AHE experiments for the last 25 years. Many of these independent groups confirmed occasional production of excess heat when using electrochemical or gas diffusion techniques to load deuterium into palladium-based materials. The persistently sporadic nature of AHE experiments has suggested that the production of excess heat must depend on many diverse experimental and material parameters. Most of the conditions needed to produce excess heat remain under investigation and contention. One condition which has been generally agreed upon is that the higher the cathode loading ratio the more likely a test cell is to produce excess heat. More specifically, it has been found that when the average deuterium atomic loading ratio within a palladium cathode exceeds 0.88, it increases not only the probability for excess heat but also the total amount of excess heat produced[2]. In addition, experiments have shown that the excess heat is related to the structures of cathode materials. For instance, palladium cathodes having the [100] preferred crystal orientation have a higher probability of yielding excess heat bursts[3,4]. However, good reproducibility of AHE remains the major issue.

The Sydney Kimmel Institute for Nuclear Renaissance (SKINR), established in 2012, is currently the only research entity in the US university system dedicated to understanding the AHE[5]. SKINR originated from a private company, Energetics LTD/LLC, which was created in 2002 to do research on AHE. The charter mission of SKINR was defined by Robert Duncan in 2012: 'to find the origin of the Anomalous Heat Effect (AHE) with a sound materials science approach and with no preconceptions as to the origin of the phenomenon. To publish findings in the open literature and to openly collaborate worldwide with researchers in the field and in cross disciplines.' In keeping with this mission, SKINR has expanded upon several collaborative AHE research relationships which were first started under Energetics LTD/LLC. SKINR's current research partners include several internationally recognized institutions such as NRL, ENEA, Coolescence and ReResearch.

Since 2002, SKINR (Energetic LTD/LLC) and its collaborators have made steady progress toward understanding AHE through the use of shared samples, ideas and more than a thousand individual and joint experiments. Many excess heat (EH) events involving electrochemical loading of deuterium in palladium-based alloys have been observed. Table 1 summarizes most of the electrolysis experiments and EH events which were recorded from 2002 to 2009. Many of these experiments showed excess heat events that had a coefficient of performance (COP) ranging from 5% to 30% and a few particularly notable experiments had COP exceeding 1500%. Total energy

*For correspondence. (e-mail: elbohera@missouri.edu)

Table 1. Statistics of excess heat in electrolysis experiments performed during 2002–2009

				2002			2003			2004			2005			2006			2007			2008			2009		
	Total	EH	Repr. (%)	Total	EH	Repr. (%)	Total	EH	Repr. (%)	Total	EH	Repr. (%)	Total	EH	Repr. (%)	Total	EH	Repr. (%)	Total	EH	Repr. (%)	Total	EH	Repr. (%)	Total	EH	Repr. (%)
Alloys	36	9	25.0	2	0	0										3	2	66.7	24	6	25.0	2	0	0.0	5	1	20.0
Coating vapour deposition	5	1	20.0	1	0	0	4	1	25																		
Coating RF	17	4	23.5																			10	3	30.0	7	1	14.3
Storms	4	4	100.0				2	2	100				2	2	100.0												
Pd–V	8	2	25.0																2	1	50.0	6	1	16.7			
Pd–Ca	6	1	16.7																			6	1	16.7			
Annealings	20	3	15.0																			8	2	25.0	12	1	8.3
Pd–ZrO	2	1	50.0																			2	1	50.0			
Pd–Fe	8	3	37.5																8	3	37.5						
Pd–NT–Re	14	5	35.7																6	4	66.7				8	1	12.5
Nanowires	1	1	100.0																1	1	100.0						
Pd–La	7	4	57.1																3	2	66.7	4	2	50.0			
GD etching	64	19	29.7							7	1	14.3	18	4	22.2	6	5	83.3	17	2	11.8	16	7	43.8			
Pd–PdO	18	4	22.2										2	0	0.0	5	2	40.0							11	2	18.2
SWCNT	90	17	18.9													40	11	27.5	39	4	10.3	11	2	18.2			
Pd–Re	17	7	41.2													3	2	66.7	12	4	33.3	2	1	50.0			
Commercial	50	2	4.0				8	0	0	6	0	0	13	0	0	15	1	6.7				8	1	12.5			
Vittorio	180	22	12.2	4	1	25	10	2	20	26	3	11.5	57	2	3.5	44	12	27.3	17	0	0.0	19	2	10.5	3	0	0.0
ET	110	6	5.5							18	1	5.6	50	0	0	5	0	0.0	12	2	16.7	12	0	0	13	3	23.1
Rejected	199			7			2			43			30			41	0	0	32			33			11		
Total	856			14			26			100			172			162	0	0.0	173			139			70		
Relevant exp.	657	116	17.7	7	1	14.3	24	5	20.8	57	5	8.8	142	8	5.6	121	35	28.9	141	29	20.6	106	23	21.7	59	9	15.3

Repr., Reproducibility; EH, Excess heat.

analysis of experiments that had the highest amount of excess heat proves that the source of energy exceeds that of any known chemical process. The sporadic nature of excess heat events, however, has not yet allowed SKINR to identify the basic physical processes responsible for the observed excess energy. Our studies have therefore concentrated more on characterizing the surface morphology and composition of various cathode materials and accurately quantifying the excess heat produced when these different cathodes are used in electrochemical systems.

Examples of SKINR experimental data will be presented in this article, that show the existence of AHE events yielding hundreds of kilo Joule of energy and having average COP greater than 1500%. All of the experiments used electrolysis in heavy water (D_2O) with pure palladium (Pd), palladium alloys or composite Pd cathodes coated with carbon nanotubes. Also common to all of the SKINR experiments was the inclusion of some form of real-time calorimetry that allowed accurate measurement of any excess heat events. Experimental data will be provided that dynamic electric currents (SuperWaves) and ultrasonic cavitation of cathode surfaces can significantly enhance the probability of obtaining AHE in electrochemical cells. Finally, a brief outline of the current and near-term research objectives of SKINR and the approach to understanding AHE and its physical origin(s) will be presented.

First, the results of Energetics LTD/LLC experiment #64 will be presented. This experiment used electrolysis of a pure palladium cathode in 0.1 M $LiOD/D_2O$. The palladium cathode material for this experiment was first cold-rolled to 50 μm thickness, then annealed in vacuum at 850°C for 60 min, and then given a final chemical etch in 50% aqua regia for 1 min. An Energetics LTD proprietary approach called 'SuperWaves' was used to apply the electric energy utilized for electrolysis. SuperWaves consist of a superposition of time-dependent regulated currents having several different amplitudes and frequencies. SuperWaves are designed to dynamically modify the interface between the electrodes and electrolyte so as to increase the flux of deuterium in and out of a Pd cathode. The SuperWaves approach has been tried and refined in many different electrolytic experiments with the final result that it improves the probability of obtaining a high loading fraction of deuterium and increases the probability of having an AHE. During experiment #64, heat from the electrochemical cell was measured using an isoperibolic calorimeter with spatially distributed temperature sensors, as seen in Figures 1 and 2. Three independently operated cells were put in a stable water controlled temperature heat sink bath with an accuracy of ± 0.01°C. Heat mainly flows radially out from the cell to the heat sink. Figure 3 *a* shows the large excess energy release event that lasted for 17 h with a measured maximum output power of 34 W and an average output power of 21 W. Throughout the above event the average electrolytic input power, calculated from 50 kHz sampling rate of applied voltage and current, was only 0.81 W and yielded a calculated average COP of 2500%. The start of the AHE was accompanied by a gradual increase in the electrochemical cell voltage. As shown in Figure 3 *b*, the cell voltage gradually increased from a stable value near 3 V up to about 15 V. Throughout the excess heat event the cell voltage remained elevated and it also exhibited rapid fluctuations which were about 20% of the new average level. The end of the AHE was marked by a relatively sudden halt in the voltage fluctuations and a continuous drop in the cell voltage back to 3 V. The cause of the above voltage increase and voltage fluctuations during the onset and the process of an AHE remains uncertain. It is expected, however, to be related to changes in the cathode electrical property and surface morphology of the cathode that in turn modulates the impedance of the electric double layer. It should be noted that the AHE

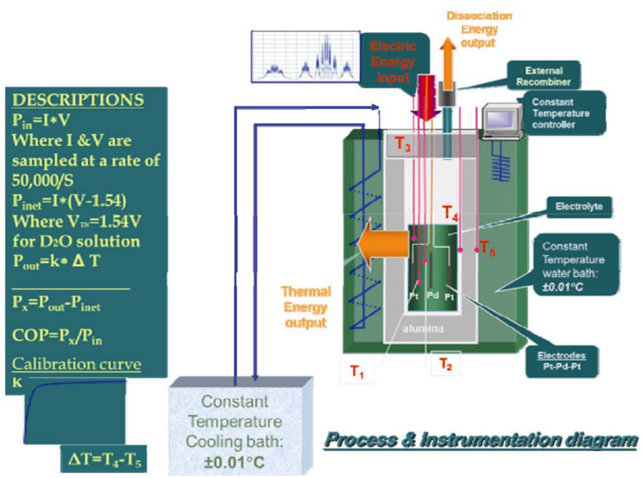

Figure 1. Electrolytic cell with isoperibolic calorimeter.

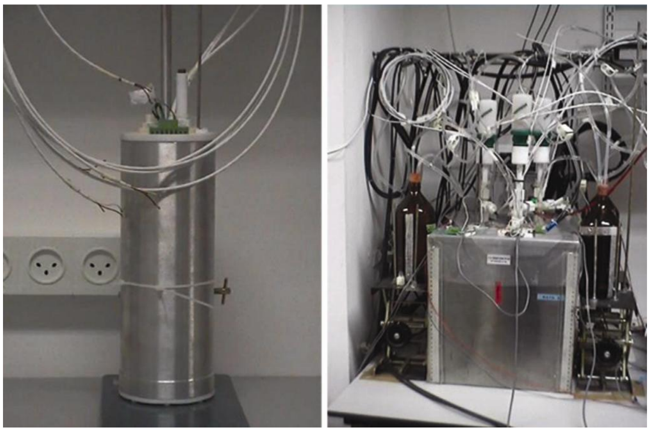

Figure 2. (Left) Electrolytic cell and (right) experimental set-up with three cells in the constant temperature controlled bath.

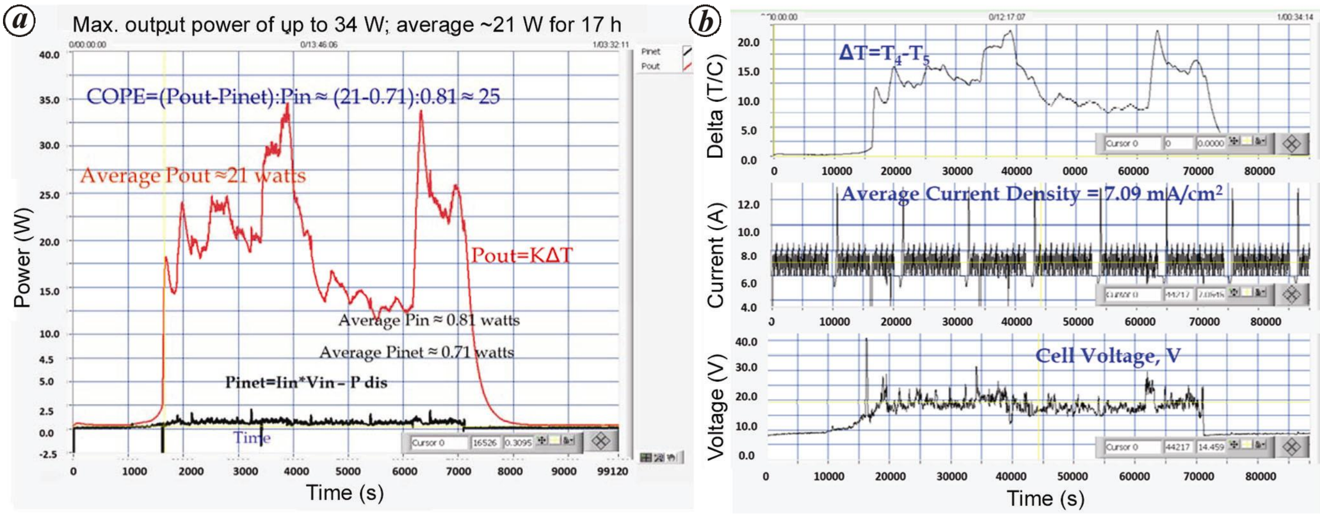

Figure 3. Calorimeter results and electrochemical parameters in electrolysis of 0.1 M $LiOD/D_2O$. ***a***, Excess power (red) versus input power (black). ***b***, Currents and voltages of the electrochemical cell.

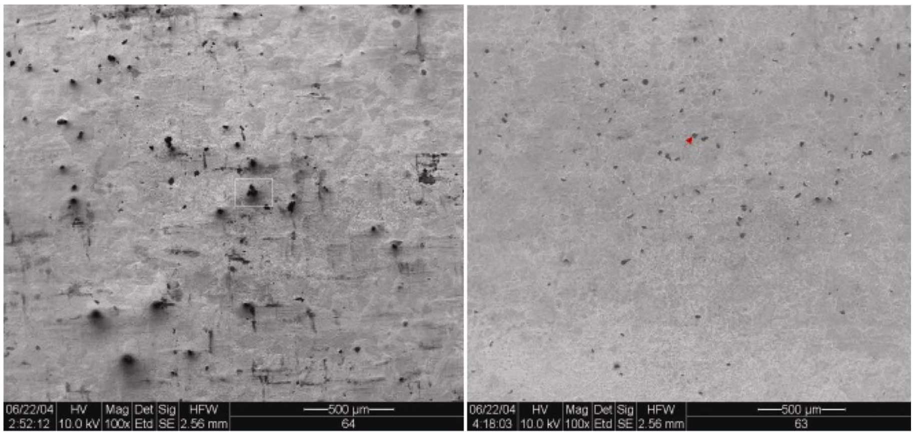

Figure 4. Post-electrolysis SEM analysis of foil #63 with no excess heat, and foil #64 (left) with excess heat; both cut from the same rolled strip after rolling and annealing.

occurred less than 5 h after the electrolysis began, leaving no possibility that chemical energy was somehow stored in the system and then released.

After the excess heat event in experiment #64, the Pd cathode was examined using a scanning electron microscope (SEM). Many black spots were observed on sample #64 cathode surface, as shown in Figure 4 *a*. The figure also shows another cathode surface, sample #63, obtained from a prior experiment. Experiment #63 started with a cathode cut from exactly the same rolled Pd strip as used for #64. For this cathode, however, no excess heat events were observed and there are fewer and smaller black spots compared to #64. Energy dispersive X-ray spectroscopy (EDX) indicates that the black spots are composed mainly of non-metallic elements (e.g. C and O). Figure 5 shows the grain size distribution of the cathode from sample #64 compared to many other Pd cathode samples. The mean grain size of sample #64 was 63.6 μm. Palladium cathodes from electrolysis experiments with and without AHE were all found to have similar grain size distribution, which indicated that there is no obvious correlation between excess heat bursts and palladium grain size. More detailed examination of cathodes using SEM images reveals interesting surface features that may be correlated to AHE. Figure 6 *a* shows the typical surface morphology of sample #64 after electrolysis, which yielded large amounts of excess heat. The palladium cathode exhibits rough surfaces and has a distinctive labyrinth-like surface structure. The power spectral density (PSD) function was used to characterize the rough surface structures. The double peaks at positions 1.0 and 1.8 μm^{-1} were identified in the PSD (see Figure 6 *b*), suggesting that two periodicities co-exist for the surface structures. The presence of double peaks in the PSD appears to be a characteristic structure for excess heat events. Similar double peaks were also observed

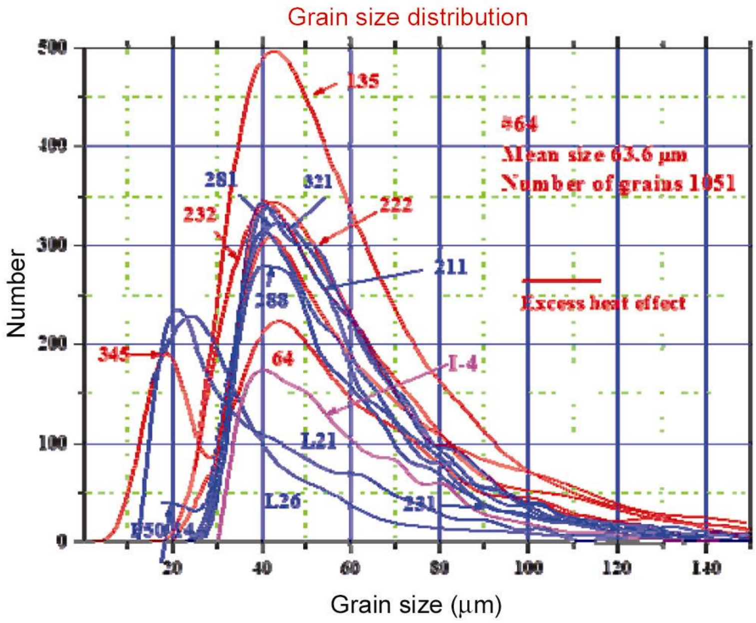

Figure 5. Grain size distribution of the cathode from sample #64 compared to other cathodes which either exhibited excess heat (red lines) or did not (blue lines).

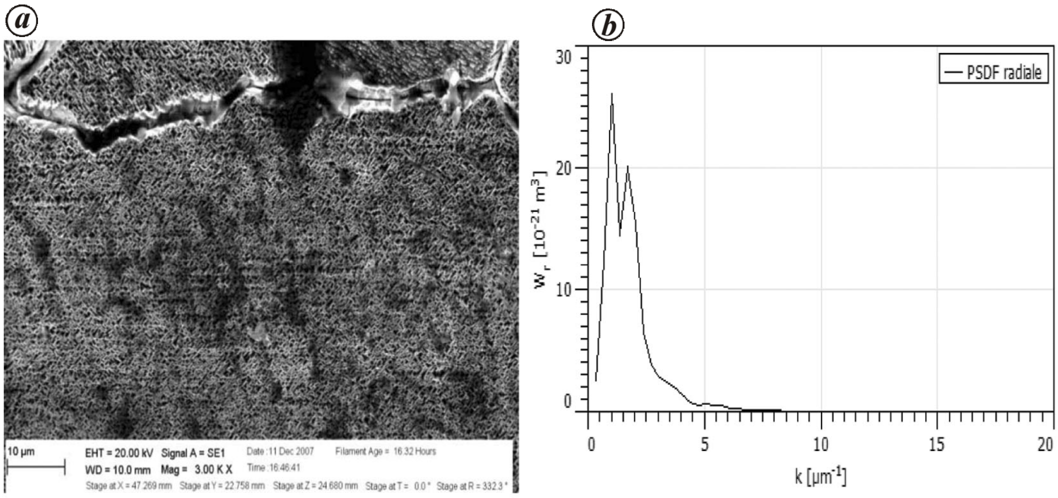

Figure 6. Post-electrolysis cathode sample from experiment #64 which had a very large AHE. ***a***, SEM image of the cathode. ***b***, PSD of the cathode surface structure.

in the L66 sample that had 25–30% excess heat in electrolysis[6].

It has been previously shown that external stimulation by lasers[7] and magnetic field[8] can promote AHE. During 2007–2008 Energetics LTD investigated electrolysis in open cells using ultrasonic (US) waves to generate cavitation in the vicinity of cathodes followed by SuperWaves as a possible technique to stimulate an AHE. Nineteen different experiments followed the above recipe and 14 of these produced observable amounts of excess heat. Applying ultrasonic cavitation during electrolysis was done using four ultrasonic piezoelectric transducers in a specifically designed electrochemical cell. Heat from the electrochemical cell with US excitation was measured using water mass flow calorimetry, as shown in Figures 7 and 8. Figure 9 shows the excess heat measured in two typical electrolysis experiments using pure Pd cathodes in $LiOD/D_2O$ with periodic application of US and SuperWaves. The first example (Figure 9 *a*) shows an excess heat event which lasted for 18 days, released 1.32 MJ of excess heat and had a maximum COP of 525%. The second example of US excited excess heat (Figure 9 *b*), lasted 23 days, released 185 kJ of excess heat and had a maximum COP of 140%.

Ultrasonic waves are expected to excite cathodes through mechano-chemical cleaning of cathode surfaces and by causing surface pits which are created by shockwave-generated cavitation jets. US-induced pits are expected to be especially significant relative to promoting AHE because they cause dynamic mechanical deformation of the near-surface layer of the cathode resulting in defects (e.g. dislocations and vacancies) that can potentially trap deuterium. Figure 10 *a* shows the strongly pitted surface structures resulting from US cavitation of a Pd cathode compared to another cathode (#64) surface shown in Figure 10 *b*, which did not have any US exposure. Unique characteristics of ultrasonic excited cathode experiments include:

- Very high deuterium loading with D/Pd > 0.95 using low current densities of 6–10 mA/cm^2.
- The deuterium stays in β-phase in the Pd for a very long time (>100 days) following current shutdown.
- There is a high density of pits on the surface of the Pd cathode.
- Micro-size craters with signs of melting occur on the surface of Pd cathodes.

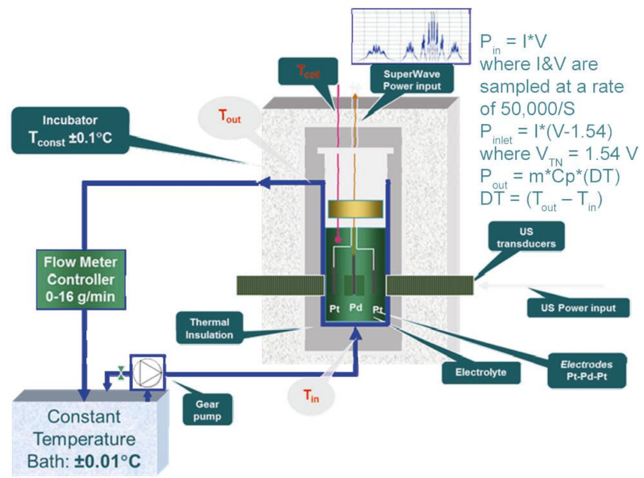

Figure 7. Electrolytic cell with ultra sound excitation and mass flow calorimetry.

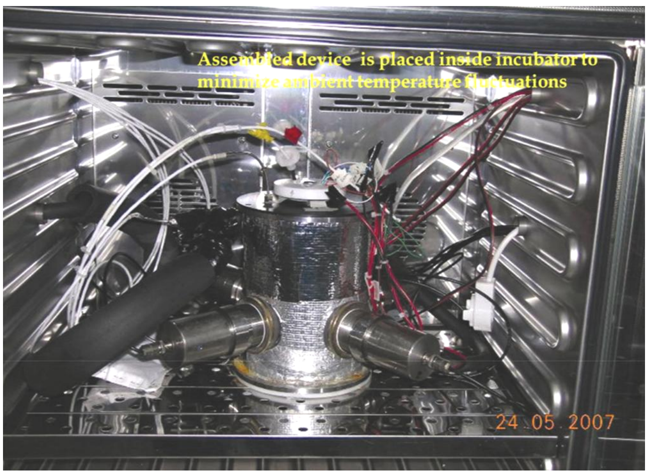

Figure 8. Experimental set-up of ultrasound stimulated electrolytic cell (#3) with mass flow calorimetry.

Finally, a recent AHE result is presented which used a composite cathode made from Pd coated with carbon nanotubes. Single-walled carbon nanotubes (SWCNTs) have emerged as a promising material for a variety of applications due to their unique electrical and physical properties. Russian scientist A. Lipson was the first to apply carbon nanotubes to AHE research in 2007 in collaboration with Energetics Technologies Ltd[9]. Similar Pd–SWCNT composite cathodes were prepared in 2013 by S. Gangopadhyay's group at the University of Missouri in Columbia via drop casting of an aqueous dispersion of SWCNT onto pre-treated palladium foils at a relatively low density of 0.1 mg/cm^2. The foils were then electrodeposited in 0.1 M $PdCl_2$ at a current of 2.5 mA. Finally, the finished Pd–SWCNT cathode was subjected to electrolysis in 0.1 M $LiOD/D_2O$ solution by applying a constant current in an open isoperibolic calorimeter. The measured input and output powers remained nearly equal and quite stable for 17 days. This quiescent period ended abruptly when two consecutive excess heat bursts occurred, as shown in Figure 11 *a*. The first burst started on 18 November 2013 and lasted for about 3 h, when it spontaneously stopped. During this time the event released 75 kJ of excess heat with a peak COP of 5500% and an average COP of 3500%. The second burst occurred about a day and a half later. This event lasted for about 1 h and 30 min and released 13 kJ of excess heat with a peak COP of 2700% and an average COP of 1660%. Immediately following these two events it was verified that the power supply voltage output was being correctly recorded and that all of the signal carrying connections were intact. During the following weeks a similar power supply was repeatedly 'stress tested' to see if it might be possible to induce some sort of high-frequency oscillations or to create any other type of power supply fault that might create excess heat. All of these tests yielded null results and instilled additional confidence in that previous power measurements were correct.

The excess heat bursts created by the Pd–SWCNT electrolysis described above were accompanied by variations in the electrolytic cell voltage which were quite similar to those recorded in prior excess heat events using Pd alloy cathodes. The start of the AHE was first indicated by slight dips in the nominally constant cell current of 50–51 mA and closely followed by the measured cell voltage changing from a steady value near 2.5 V up to a rapidly fluctuating value around 7–10 V, as shown in Figure 11 *b*. During the excess heat bursts, the Pd–SWCNT cathode had a resistance which was about 2.1 times its initial unloaded value. Presuming the usual relationship of resistance ratio versus loading ratio for pure palladium would indicate an average D/Pd atomic loading ratio of only 0.75. It is expected, however, that the actual atomic loading ratio within localized portions of the Pd–SWCNT cathode would be much higher. These bursts are similar to those reported by the Naval Research Laboratory[10].

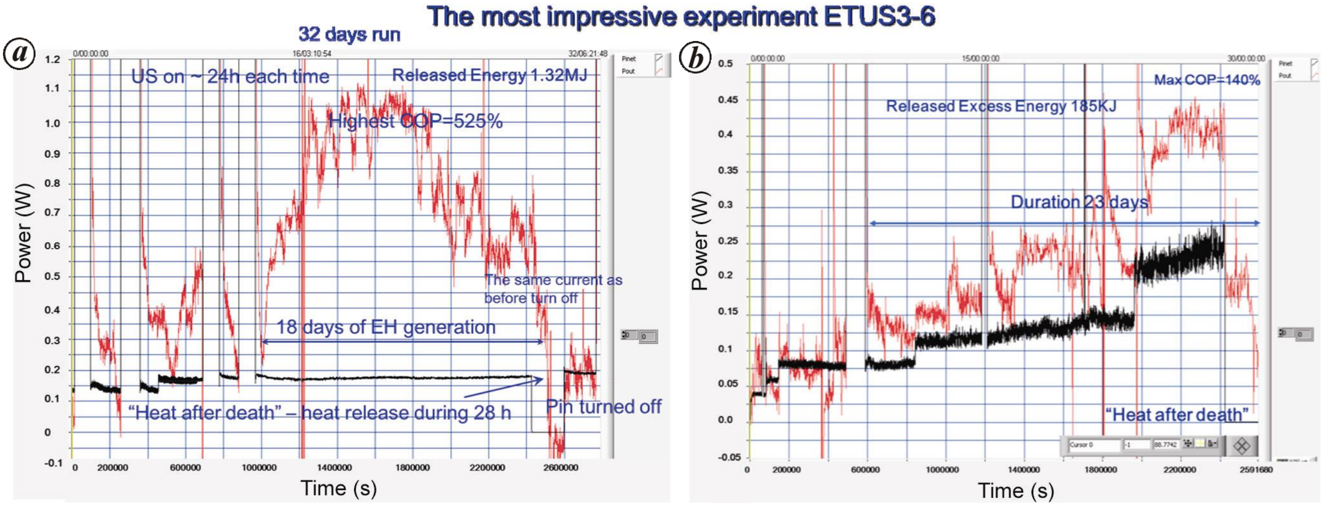

Figure 9. Two examples of excess energy releases resulting from periodic application of ultrasonic waves and SuperWave electrolytic currents. (***a***) US3-6 and (***b***) US2-11 experiments.

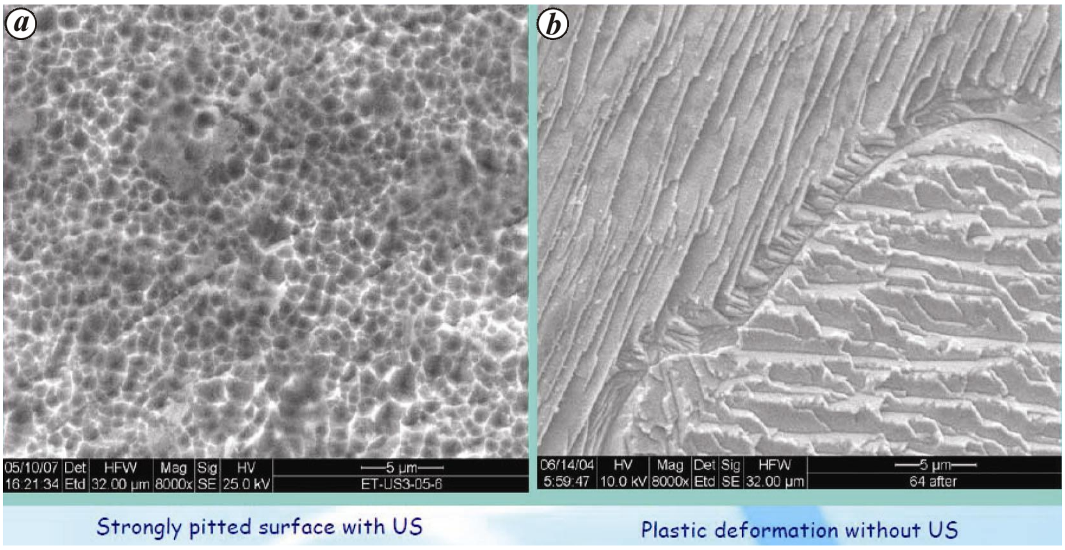

Figure 10. SEM images of two palladium cathodes (***a***) with and (***b***) without periodic application of ultrasonic waves.

Figure 12 *a* presents a SEM image of 'cauliflower-like' surface texture of the Pd–SWCNT cathode which showed excess heat bursts. The heights of these distinctive surface features were measured by atomic force microscopy (AFM) and a PSD plot derived from these heights is given in Figure 12 *b*. Two peaks can be seen in this plot, one at 3 μm^{-1} and the other near 12 μm^{-1}. The post-AHE 'cauliflower-like' surface of the Pd–SWCNT cathode is quite different, in both appearance and characteristic feature sizes, from the labyrinth structures seen on the excess heat-producing pure Pd cathode from experiment #64. Despite the above quantitative differences, there appear to be some common cathode characteristics, such as complex surface structures and the ability to absorb large amounts of deuterium, which are generally accepted as enhancing the probability of an AHE. SKINR experiments suggest a promising distinctive feature of highly reproducible excess heat-producing cathodes having a double peak morphology which appears in PSD surface analysis of cathodes.

The excess heat experiments described above show that electrolysis of heavy water using palladium-based cathodes is a complex, nonlinear and time-dependent electrochemical process. This process loads deuterium into the cathode and modifies the cathode surface so as to occasionally yield an AHE. SKINR and other AHE researchers have demonstrated that adding many different kinds of dynamic stimulation to the usual electrolytic process increases the probability of having an AHE. The considerable diversity and complexity found in just the three different AHE experiments discussed above provide some clue as to why excess heat events have proven to be

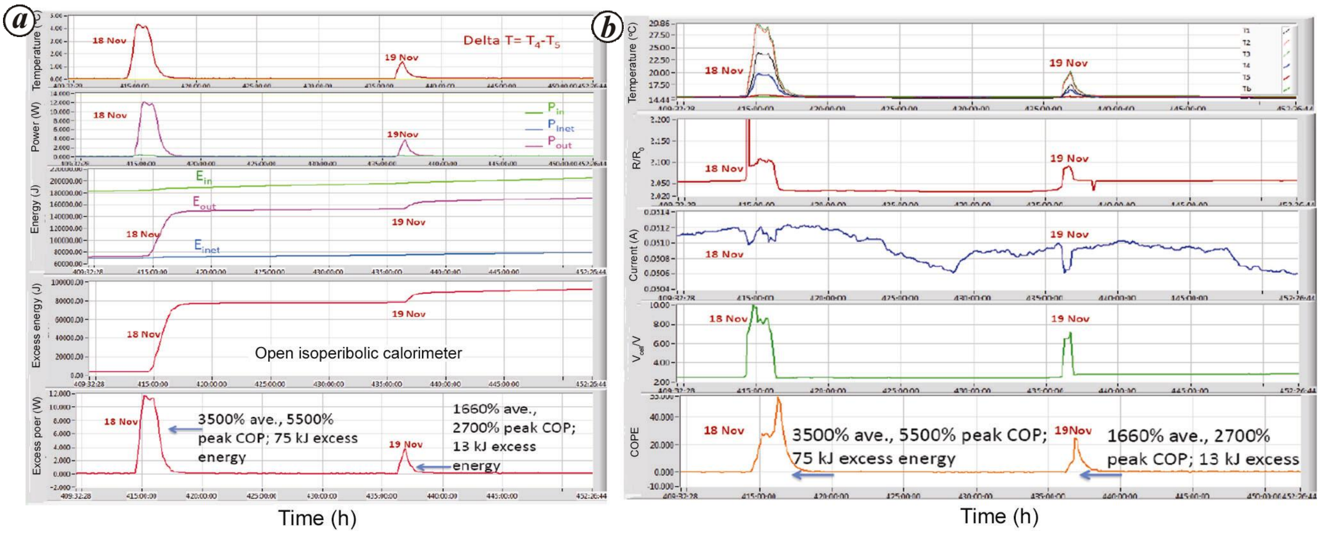

Figure 11. Two consecutive excess heat bursts observed during electrolysis of heavy water using a Pd–SWCNT composite cathode. ***a***, The measured input and output energies and power, and the calculated excess energy and power. ***b***, The electrolytic cell voltages and currents along with various measured temperatures, the resistance ratio of the cathode and COPE.

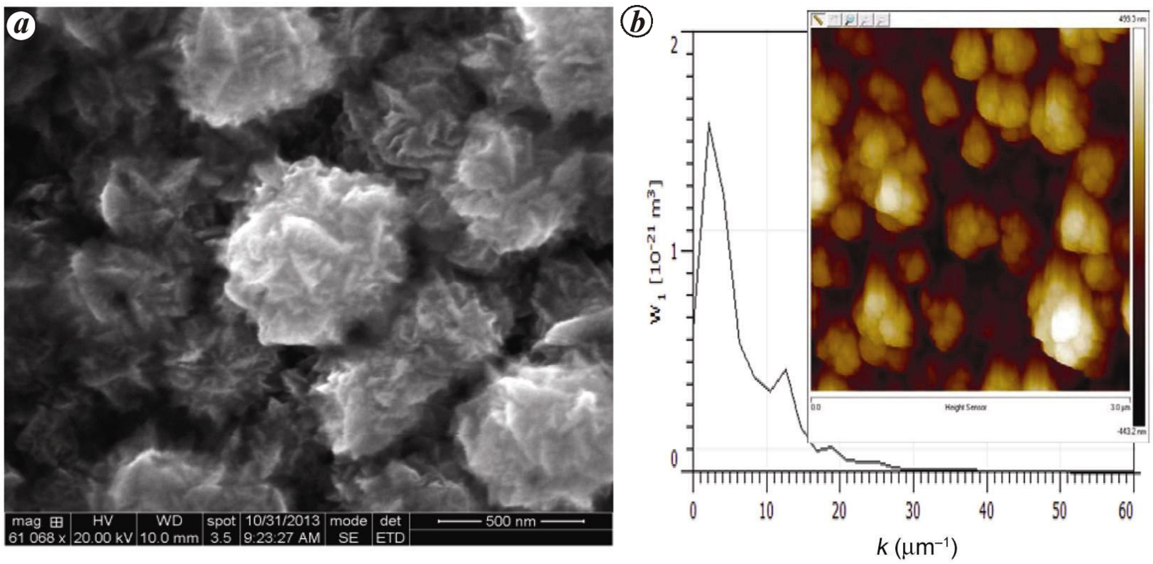

Figure 12. Post-electrolysis images of a Pd–SWCNT cathode which yielded excess heat bursts. ***a***, SEM image showing the surface morphology. ***b***, PSD plot of AFM-measured feature heights across the surface. (inset) Original AFM image.

difficult to reproduce and elusive to understand. Anomalous heat effect seems to have a profound sensitivity to many different material and electrochemical parameters and most of these are continuously changing throughout the course of any electrolytic experiment.

Despite the obvious complexity of electrolytic experiments and the tendency for AHE to be irreproducible, SKINR's intent is to improve the understanding of this unique and interesting phenomenon by leveraging off the following characteristics:

- When an excess heat event is activated, there are typically many subsequent heat bursts which last for several hours providing the opportunity to add additional diagnostics.
- The time persistent nature of AHE bursts suggests that 'just right' conditions are typically self-perpetuated by the electrolytic system and that they might therefore be subject to external modulation.
- The probability of having an AHE in an electrolytic cell has been demonstrated to increase when dynamic electrolytic currents are applied and/or when cathode surfaces have been subjected to ultrasonic cavitation. SKINR is currently working towards extending these sorts of stimulations to higher frequencies as well as exploring different types of stimuli.

- Cell voltages increase during excess heat events. This implies that there are dynamic conditions associated with electrode materials, cell impedance and electrochemical reactions which SKINR intends to further study and characterize.
- The composition, internal structure and surface morphology of the cathode (such as double peaks which appear in PSD surface analysis), obviously affect both deuterium loading and the probability of having an AHE. SKINR and its collaborators plan to increase the understanding through improved control of cathode metallurgy, creating tailored surface morphologies, and comprehensive pre- and post-characterization of cathodes.

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