Observation of radio frequency emissions from electrochemical loading experiments

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Palladium foil cathodes were electrochemically loaded with deuterium from alkaline solutions of heavy water in specially designed closed calorimeter cells. Here, one cell is described that showed low levels of constant heat (1–7 mW) and radio frequency (RF) emanations, but the RF was not correlated with the heat production. This cell is compared with $Pd_{90}Rh_{10}$ alloy cathodes that showed excess energy bursts of 2.4–44.3 kJ. In these cells, RF coincident with the bursts was observed peaking at different frequencies from about 450 kHz and extending into the MHz range. Some of the excess energy production in LENR may be in the MHz RF range, which has no conventional explanation in electrochemistry.

Keywords: Calorimetry, deuterium, excess energy, palladium, radio frequency.

Introduction

SINCE the early publications by Fleischmann and Pons[1–5], numerous accounts of excess energy production in palladium cathodes electrochemically loaded with deuterium have been reported[6–11]. In spite of this mounting evidence, criticism has been that the excess energy observed is either due to overlooked chemistry, measurement errors (such as calibration issues), or instrumental artifacts[12,13].

As more fully described in another paper, we observed several large bursts of energy in a few of the more than 370 separate electrolysis experiments that we performed[14]. During two of those electrolysis experiments, we were monitoring radio frequency (RF) coming from the cell and observed intense RF emission coincident with the bursts of energy. Because the energy bursts observed were not reproducible, we assumed that an unknown trigger was needed to cause heat production. We developed protocols to add impurities that should affect the uptake and release of deuterium atoms from the palladium cathode. During two chemical additions to cathode #377, we saw intense RF emissions. However, the excess heat produced was very low (<7 mW).

Although light has been observed originating from electrolysis cells[15,16], and RF has been used to trigger heat production[17], RF emissions had not been reported prior to our preliminary account[18]. Excess heat is the signature most often reported in LENR experiments with only sporadic reports of low-level nuclear products. Heat may arise from unaccounted chemistry, but RF in the kHz to MHz range is unique and may point to unexplained processes occurring. After our preliminary account of RF emissions[18], other researchers have observed emissions of RF coincident with heat[19]. This article summarizes the RF emission in cathode #377 and compares it to other results.

Experimental protocols

The methods and materials for the experimental protocols are documented in our previous paper[14]. Cathodes #54 and #60 in Table 1 were a $Pd_{90}Rh_{10}$ alloy, whereas cathode #377 was 99.9% palladium. Preparation and electrical measurements for cathode #377 will be published in detail separately. A brief experimental set-up for cathode #377 is shown in Figure 1. A complete experimental protocol is in the Supplementary Information, available online.

Results and discussion

In majority of the first 335 electrolysis experiments, our tacit assumption was 'the simpler the better'. The R/Ro was not being measured because of concerns that extra equipment may malfunction and produce extraneous heat. More recently, we focused on factors that affect loading of deuterium into the palladium cathode. There are three mechanisms that pertain to loading (Figure 2)[20]. Both the Volmer and Tafel reactions occur at low loading levels, whereas the Heyrovský reaction mainly occurs at high loading levels and high currents. It was reasonable to assume that the structures on the palladium for the Volmer reaction may be different than those for the Tafel reaction and that impurities may block one reaction over the other. To enhance loading, we focused on selective catalyst poisons that could block the Tafel reaction but leave the Volmer reaction less affected.

Unlike prior cathodes, cathode #377 was intentionally contaminated with engine exhaust to poison the surface with CO and hydrocarbons. Nevertheless, it loaded in a conventional manner to approximately $PdD_{0.8}$ ($R/Ro \approx 2$). After several days, the loading did not improve. Deuterated methanol was added to form CO on the surface and

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Table 1. Summary of the major frequencies (RFs) observed

Cathode number	RF (dBm)	Notes
54 (before burst)	5.6 MHz (–22)	RF very strong and not observed before from VSP. This cathode was a $Pd_{90}Rh_{10}$ alloy.
54 (during burst)	5.8 MHz (–50)	Slight shift in RF to a broader distribution with a closely spaced comb to higher frequencies.
60 (bursts 1 and 2)	450 kHz (–60)	Very broad RF emission at 450 kHz. Regularly spaced frequencies in the 5 MHz region with about 133 kHz spacing. This cathode was a $Pd_{90}Rh_{10}$ alloy.
377 (RF initial)	4.79 MHz (–30), 4.82 MHz (–30)	Very narrow emission of two closely spaced frequencies. First and sometimes second overtone observed. This cathode was 99.9% Pd.
377 (RF restart)	4.82 MHz (–30)	Very narrow emission. Generally one frequency with overtones observed
Prior published results[19]	Comb kHz–MHz (–20) 400 MHz (–40) 450 MHz (–50) 800 MHz (–55) 79–81 GHz band	Signal in the 79–81 GHz band based on an internal down-converter. Comb in the kHz–low mHz range not resolved in published plots. However, published data characteristic of $1/f$ noise. This cathode was a Pd–Pt alloy.

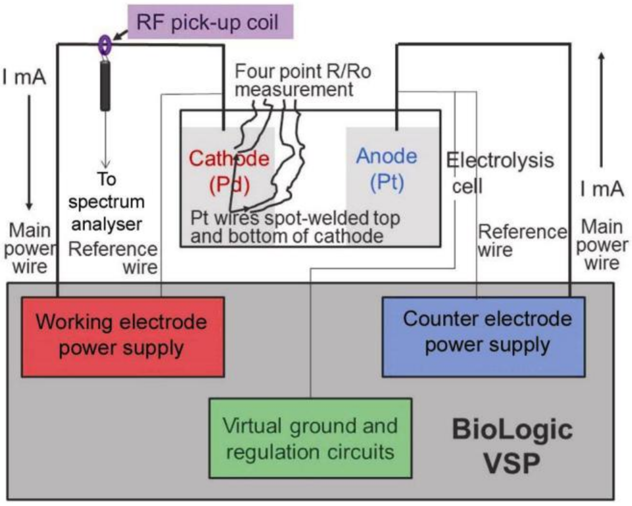

Figure 1. Experimental design for cathode #377. The RF spectrum was taken with a SignalHound SA44B scanned from 5 kHz to 20 MHz using 3000 points. The R/Ro measurements were taken with an Agilent 4362B LCRmeter, transformer isolated on each of the four probe leads. The R/Ro and RF data were collected with LabView – the former in 10 sec intervals and the latter every 30 sec to limit the data bandwidth.

$$H_2O + e^- \rightarrow HO^- + H^0 \qquad \text{Volmer (load)}$$

$$H^0 + H^0 \rightarrow H_2 \qquad \text{Tafel (unload)}$$

$$H_2O + H^0 + e^- \rightarrow HO^- + H_2 \qquad \text{Heyrovský (unload)}$$

Figure 2. Summary of reactions that affect hydrogen loading in metals.

further poison the system[21]. A burst of heat was observed, that could be dismissed as electrochemical oxidation of methanol, but low-level heat persisted for several days (Figure 3). After the addition of methanol, the R/Ro measurement became erratic. Measurement of RF from the cell showed strong emission at 4.8 MHz (Figure 3 *d*). This RF continued even after the low-level heat subsided, until the cell was powered off.

The cell was then restarted and deuterated methanol was again added after a few days. A burst of heat was observed that quickly returned to the baseline with no long-term heat as during the first methanol addition. This heat would be expected from electrochemical oxidation of methanol. After a few hours, pyridine was added. Previous experiments showed that pyridine partially blocked the Tafel reaction and increased loading. A burst of heat was observed that persisted for days at a low level (<5 mW). Throughout this time period, only a weak (–75 dBm) and broad RF signal centred at about 4.3 MHz was present. After a day, strong RF (–30 dBm at 4.79 MHz, a slightly different frequency) spontaneously appeared, coincident with increased oscillations in the R/Ro data, but without change in the measured excess heat. After observing this second RF emission, various components of the experimental set-up were removed to eliminate them as the source of RF without finding the source. Soon thereafter, the RF signal and R/Ro oscillations spontaneously disappeared and did not reappear even after more than a week of further electrolysis.

The source of the RF was either the VSP power supply, or arising inside the cell as other electronics could be removed or powered-off without affecting the signal. The data collected during the restart suggests that the cell is the source, as the low-level heat stayed nearly constant. If the source were external to the cell, then the RF should have added to the heat output of the cell. Subsequent experiments showed that 5 mW of RF injected across the cell (rather than just at the cathode) would be needed to produce a –30 dBm signal on the spectrum analyser. This amount of injected extra energy should be readily observed[22]. Thus, the lack of heat during the RF emission would be consistent with the RF power emanating from the cell and not introduced from an external source.

Another view could be that the VSP potentiostat is the source, but something changes in the cell to initiate a resonance condition for the VSP such that the RF intensity increases dramatically. Potentiostats can cause oscillations under certain conditions[23]. However, several constraints discount that possibility:

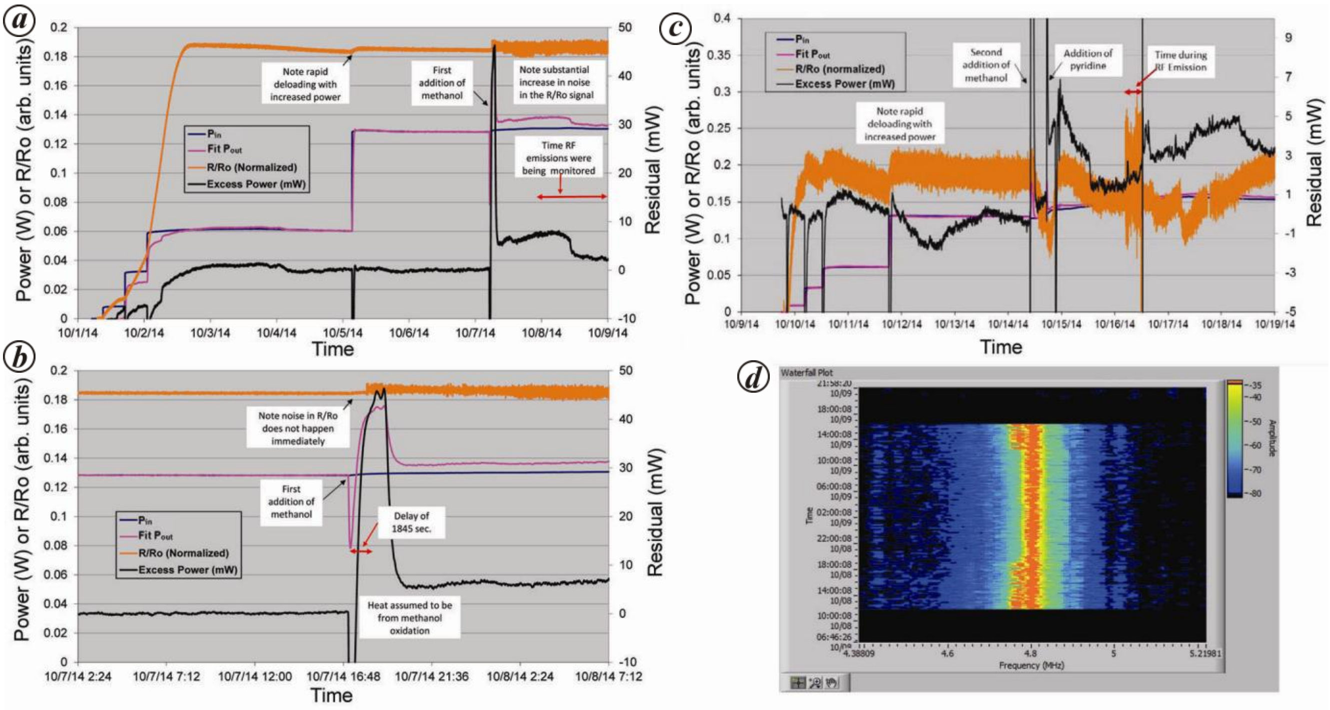

Figure 3. Plots of input power (P_{in}), output power (P_{out}), and R/Ro on left vertical axis and residual power (P_{out}–P_{in}) on the right vertical axis as a function of time. The R/Ro values were normalized to fit on the *Y*-axis. ***a***, Initial start of electrolysis. The RF stopped slightly after the electrolysis was stopped. Note the rapid deloading with increased current (power) that demonstrates the Heyrovský reaction contribution to deloading. ***b***, Expansion of the region in (***a***) during addition of the deuterated methanol. Note that the RF, as indicated by the noise in the R/Ro measurement, started 1845 sec. after the addition. This time may be indicative of formation of oxidation products on the cathode surface or use of oxygen. The heat after addition was assumed to be due to the electrochemical oxidation of methanol. However, the long-term heat was not observed upon the second methanol addition in the restart. ***c***, Restart electrolysis with the arrow indicating time of increased RF emissions. Note the increased noise in the R/Ro measurement during the RF emission. The R/Ro values were amplified and offset to emphasize noise during the RF emission. FFT of the raw data showed no distinct frequency, likely because the acquisition time (10 sec) was too infrequent. ***d***, Waterfall plot of RF emissions during the period marked with a red arrow in (***a***). RF was being monitored and was almost non-existent throughout the restarted run, except where noted. The initial electrolysis had two primary frequencies at 4.79 and 4.82 MHz, whereas the restart showed only 4.79 MHz.

- The VSP was run with a filter set to 4. The manufacture's literature[23] suggests that if oscillations were to occur, they would be at less than 30 KHz.
- Whatever feedback component is present must supply amplification for a RC, LC or RLC circuit to oscillate. The VSP uses a Burr-Brown OPA544 for its output and its gain falls to unity past 2 MHz. Thus, no oscillations should be possible at the observed frequencies near 5 MHz.
- The RF could have arisen from an external source other than the VSP. Why it ceased so soon after the VSP was stopped would be unexplained. Additionally, cathodes #54 and #60 were monitored in a special quiet room shielded from external RF. Yet, they showed RF in this frequency range.
- The cell is inside essentially three nested Faraday cages with RF leakage only possible through the lead wires. Control experiments show that at least 5 mW of RF is needed to affect the R/Ro measurements in the observed manner. How a simple, non-tuned antenna could supply that power into the cell is unexplained.
- Several reviewers have suggested that the equivalent of a Gunn diode or a tunnel diode could be formed electrochemically. These semiconductor devices can oscillate without an external gain loop. How such devices with defined structures would spontaneously form at the electrode surface and produce frequencies in similar ranges is not clear. If they were to form, a mechanism would need to be in place to electrically isolate both terminals of the device from each other, allow electron flow and simultaneously not affect the cell resistance through ionic flux between the anode and cathode. If possible, this may be worthy of study in its own right.

Other cells that had excess energy production were monitored for RF[14]. A summary of those frequencies and intensities is given in Table 1. Besides the noise in the R/Ro, for our systems, RF generation is accompanied by a slight increase in noise on some of the VSP leads (also observed by others)[19], as if the cell were generating a voltage opposing the VSP. This increase in noise can be mimicked by externally feeding RF power into a running cell.

For an electrochemical cell to generate or respond to a 5 MHz signal, it must be something besides electrochemistry as ions in solution do not move that fast. One possible explanation is the motion of deuterium atoms inside the cathode. However, conventional analysis suggests a frequency in the range of 500 kHz that depends on deuterium loading[24,25]. Perhaps, the 450 kHz frequency observed for cathode #60 (Table 1) originates from such a process. A possible explanation for the 5 MHz signal could be the formation of superabundant vacancies due to high deuterium loading, creating deuterium clusters in the vacancies, and the clusters offering easier pathways for diffusion (similar to Cooper pairs in superconductivity). Such a structure could facilitate 5 MHz oscillations within the lattice near the surface, enabling detectable RF emissions to be observed.

Conclusions

RF was sometimes observed in cells undergoing electrochemical loading of deuterium into palladium, with the spectrum dependent upon operating conditions and the presence of excess heat production. A common signal near 5 MHz could be frequency-shifted and its intensity increased (#60) or decreased (#54) by excess heat production. We must emphasize that RF generation of these frequencies is unusual with an unknown cause. The source of the RF may arise from inside the cell, but the origin from the cathode or anode is unknown. The RF frequency is too high to originate from electrochemistry, but may be due to deuterium hopping between lattice sites in highly loaded Pd.

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