

## EXCESS HEAT AND TRITIUM MEASUREMENTS IN Ni-H<sub>2</sub>O ELECTROLYTIC CELLS

M. Srinivasan<sup>@</sup>, P. Adi Babu<sup>†</sup>, M. B. Bajpai<sup>\*</sup>, D. S. Gupta<sup>\*</sup>,  
U. K. Mukherjee<sup>†</sup>, H. Ramamurthy<sup>†</sup>, T. K. Sankarnarainan<sup>\*</sup>,  
A. Sinha<sup>@</sup>, A. Shyam<sup>@</sup>

<sup>@</sup>Neutron Physics Division, <sup>\*</sup>Chemical Engineering Division,  
<sup>†</sup>Process Instrumentation Systems Division  
Bhabha Atomic Research Centre  
Trombay, Bombay 400085, India

### 1. BRIEF DESCRIPTION OF THE CELLS AND CALORIMETRIC TECHNIQUE

A large number of open cell electrolysis experiments of the Mills and Kneizys<sup>(1)</sup> type have been carried out in light water solutions of 0.6M K<sub>2</sub>CO<sub>3</sub>, 0.1M Li<sub>2</sub>CO<sub>3</sub> (natural and enriched in Li<sup>6</sup>) and 0.6M Na<sub>2</sub>CO<sub>3</sub> using Ni as cathode and Pt as anode, at the Bhabha Atomic Research Centre in Bombay. The cells were fabricated of double walled glass dewars with either vacuum or air between the inner and outer glass vessels. In the more recent experiments there was no silver coating in the dewar, rendering the cells transparent. A variety of nickel samples were tested as cathodes: some were solid nickel foils; others were in the form of porous sheets sintered from fine nickel powder; some cathodes were produced by electrodepositing nickel onto a stainless steel rod and later peeling it off; yet others were in the form of a mesh made of Ni fibres (procured from National-Standard Co., USA). While most of the experiments deployed planar geometry for the electrode assembly, a few cells used cylindrical geometry. In some cells a mixture of H<sub>2</sub>O and D<sub>2</sub>O was used. No external stirrer was employed. However during the electrolysis runs, the vigorous bubbling caused by the escaping H<sub>2</sub> and O<sub>2</sub> gases served to mix the solution well and reduce temperature gradients. Typically a bank of five operating cells and one dummy cell was run at a time. Experiments with a given bank lasted for two to six weeks each. Two type-T copper-constantan thermocouples, either bare or encased in a stainless steel or glass tubing were deployed in each cell for temperature measurements. The difference ( $\Delta T$ ) in average temperature at steady state between the operating cell ( $T_c$ ) and that of the reference cell ( $T_{ref}$ ) was taken as a measure of the heat generation in the cell. The accuracy of the differential temperature measurements is estimated to be better than  $\pm 0.5^\circ\text{C}$ . The cells were calibrated using resistance heaters. For each cell  $\Delta T$  was measured at steady state for different input joule powers. The maximum input joule power  $[(V-1.482) * I]$  varied from 1.0 to 6.5W depending on the cell design and calibration constant. Cell currents varied from  $\sim 0.1\text{A}$  to  $\sim 1.5\text{A}$ .

Calorimetric measurements have so far been carried out in over 70 cells, since January '92. Results as of October '92 were reported<sup>(2)</sup> at ICCF-3 in Nagoya and those of the further studies (up to August '93) were presented<sup>(3)</sup> at ICCF-4 in Maui. A few similar open cell measurements have also been carried out by one of the authors (MS) at SRI International in Menlo Park,<sup>(4)</sup> California, during the winter of 93-94 employing very sensitive RTDs for the temperature measurements.

As a general observation it was noted that for the results to be reliable, the ambient air and reference cell temperature variations/fluctuations should be much smaller than the  $\Delta T$  given by  $(T_c - T_{ref})$  being measured. Likewise, the difference in reading between the two temperature sensors of a cell, which is a measure of temperature gradients in the cell, should be  $\ll \Delta T$  being measured. It was observed that even minor changes in electrode assembly design, or the height-

to-diameter ratio of the solution region of the cell (this influences the pattern of convection currents), the presence of structural components, if any, which may impede convection induced mixing, etc. can result in unacceptably large ( $T_1 - T_2$ ) values, giving rise to poor reliability of the  $\Delta T$  measurements. This aspect was given due attention in cell design as there was no separate mechanical stirrer in our cells.

## **2. SUMMARY OF CALORIMETRIC RESULTS**

A summary of the main findings of the calorimetric studies is given below:

(1) Of the 70 or so cells investigated to date roughly half have shown "detectable" amounts of "excess power", typically  $\leq 1.0W$  with respect to the quantity  $(V - 1.482) * I$ . However, the fact that there were indeed many cells which did not indicate any "excess power" and wherein the electrolysis points fell neatly on the calibration line gives us confidence in the validity of the calorimetric technique employed. In the BARC measurements the lower limit of detectable excess power was  $\sim 0.2W$ , whereas in the experiments conducted by MS at SRI International, apparent excess power values down to 30mW could be measured because of the use of very sensitive RTDs for temperature measurements. On the other hand the maximum excess power observed at SRI was only  $\sim 0.2W$ ; possible reasons for this are being examined.

(2) The "excess power" expressed as a fraction of the input joule power varied between 10% and 110%. In most cases the percent "excess power" diminished with increasing input power.

(3) In majority of the cells investigated, the absolute "excess power" was almost constant above a threshold value of input power which varied from 0.15W to  $\sim 0.6W$ . In the more recent desilvered flask experiments at BARC the electrolysis runs did not scan the region below about 1.0 to 1.5W; hence we do not know where the threshold for "excess power" was in these runs. In these new cells the electrolysis data points fell on a line nearly parallel to the calibration line.

(4) Neither a Ni-Ni cell nor a Pt-Pt cell has ever indicated any "excess power" in our experiments so far.

(5) In most cases, if any "excess power" was present, it was detectable on the very first day of commencement of electrolysis. If the electrolysis was interrupted for a day or two for a heater calibration run and resumed subsequently, the "excess power" reappeared once again. The "excess power" episodes (with interruptions for heater calibration runs) have been observed for up to 6 weeks.

(6) In some cells if no "excess power" was observable within the first few days, subjecting the Ni electrode to high current anodic stripping (electrolysis with reversed voltage at a current of 1 ~ 2 amps for a period of 10 to 24 hours) resulted in appearance of some "excess power", lasting for days to weeks thereafter.

(7) Likewise in other cells not showing "excess power", taking the electrode assembly out and having it cleaned for a few hours in an ultrasonic cleaning bath (under distilled water) had a similar beneficial effect. However, unfortunately for us, these procedures did not always succeed in switching on a "dead" cell.

(8) One of the remarkable observations was the role of certain additives on the "excess heat" phenomenon. For example when the PVC sheathed copper-constantan thermocouples with bare junction exposed to the electrolyte which were used for temperature

measurements were replaced by similar thermocouples encased in stainless steel tubes, none of the cells showed "excess heat". But the moment we went back to the bare copper-constantan thermocouples or used glass encapsulated TCs, the "excess heat" reappeared. We conclude that stainless steel is a "poison" (or inhibitor) and copper a promoter for the "excess heat" phenomenon, whatever its nature may be.

In this context it is significant to point out that the "success rate" of observing "excess heat" which was over 90% in our Nagoya paper<sup>(2)</sup> dropped to ~ 50% in the results reported at Maui.<sup>(3)</sup> The former cells used copper-constantan thermocouples with their bare hot junction dipping directly into the electrolytic solution while the latter cells employed glass encapsulated TCs. (It was verified by using mercury in glass thermometers that the temperature measurements of the bare thermocouples was genuine and not due to some electrochemical artifact).

The beneficial effect of adding small quantities of copper was pointed out by R. Bush of the California State Polytechnic University, Pomona at the Maui meeting. Addition of trace amounts of copper in the form of cupric nitrate crystals into his electrolyte, significantly improved the excess heat margin in their Ni-H<sub>2</sub>O cells. After the Maui meeting Bush's suggestion of adding copper directly into the electrolyte was tested during January '94 in two K<sub>2</sub>CO<sub>3</sub> cells at BARC. In both these cells there was a dramatic increase in the "excess power" margin from about 10% level to ~ 50% level after copper was added in the form of cut wire pieces. One of these cells (with fibrex Ni cathode) has shown an excess power margin of 2W at an input electrolytic joule power of 4W. Similar copper addition tests in several cells carried out by MS at SRI however did not show any improvement in raising "excess power" levels.

(9) Some cells which showed "excess power" in the BARC experiments used a parallel plate electrode arrangement with a Pt foil anode on one side of the Ni foil cathode (interelectrode gap ~ 8 mm) instead of the normal Pt wire anode wound around a central Ni cathode. Similarly "sandwich" type electrode assemblies wherein a planar Ni electrode is sandwiched between a pair of perforated teflon plates and bound tightly by means of a Pt wire anode coil have also shown "excess heat" in several cells.

(10) Finally, a remark may be in order regarding the use of anodic operation of the nickel electrode for purposes of cell calibration. We find that often time, the  $\Delta T$  points in such runs fall below the heater calibration curve. However in several other runs these "reverse electrolysis" points fall close to or on the heater calibration line. The reason for this behavior has not yet been understood.

### **3. TRITIUM MEASUREMENTS**

At the Nagoya meeting we reported<sup>(2)</sup> that more than 50% of the cells analyzed showed tritium at levels of  $\geq 10$  Bq/ml. Observation of tritium even when the electrolyte did not contain any D<sub>2</sub>O (other than natural abundance) was a surprising new finding which has been met with considerable skepticism. We ourselves would have had less faith in these results were it not for the fact that at least one cell [Cell # OM-3 with enriched (54% Li<sup>6</sup>) Li<sub>2</sub>CO<sub>3</sub> solution in H<sub>2</sub>O] which was sampled, distilled and counted every few days showed a steadily increasing tritium activity reaching a maximum value of 225 Bq/ml, at the end of about a month (See Figure 8 of our Nagoya paper<sup>(2)</sup>). The tritium results reported at Nagoya were from the analysis carried out at the Isotope Division of BARC which handles tritium samples of varying strengths received from other research groups of BARC also. There is therefore scope for suspicion that cross contamination could have occurred during distillation/counting of samples there. This is one of the reasons why we reported tritium results only above a rather high value of 10 Bq/ml, at that time. The background count rate in the scintillation counting set up used therein was ~ 48 cpm which corresponds to ~ 3 Bq/ml, since counting efficiency was ~28%.

In order to avoid any likelihood of cross contamination, we acquired (in May '93) a new low noise liquid scintillation counting set up, exclusively for the analysis of our electrolysis samples only. This has been installed in a laboratory where no other tritium or radioactivity is handled. This unit has a background count rate of ~ 27 cpm equivalent to a tritium activity of ~ 2 Bq/ml (or 120 dpm/ml). This new set up is found to be capable of detecting tritium levels in the electrolyte down to 0.5 Bq/ml (~ 30 dpm/ml). The tritium results reported<sup>(3)</sup> at ICCF-4 in December '93 were obtained using this new set up. Prior to loading any cell with electrolyte it was ensured, to begin with, that the electrolytic solution does not contain any tritium contamination. The main findings (during May-August, '93) regarding tritium production in Ni-H<sub>2</sub>O cells, as reported at the Maui meeting are as follows:

- (a) 10 out of 23 (roughly 40%) of the Ni-H<sub>2</sub>O cells analyzed showed tritium.
- (b) No preference is seen for T-production, with respect to electrolyte type, H<sub>2</sub>O vs. D<sub>2</sub>O, natural vs. enriched Li, or type of Ni cathode material.
- (c) The maximum amount of tritium measured in the post Nagoya experiments is only ~ 200 dpm/ml (~ 3.5 Bq/ml).
- (d) Electrolytic enrichment of the tritium isotope cannot account for the tritium observed by us, since the currents were < 1.5 amp, temperatures of cell operation above ambient, and addition of make up water was carried out frequently.
- (e) Surprisingly the tritium activity of the electrolyte in several cells was found to vary in a sawtooth fashion. Close scrutiny of the sampling/distilling and counting techniques, in conjunction with several auxiliary measurements, strongly suggests that the tritium level in the electrolytic solution actually increased and decreased, and that it was not a measurement artifact or experimental error. While a sudden sharp increase of tritium activity can be understood as a production (or burst) phase, the decreasing phase lasting for tens of days at times, cannot be accounted for easily. We are thus forced to conclude that there is a strong as yet unidentified mechanism cleansing the electrolyte of tritium periodically. It could be an electrochemical adsorption/desorption phenomenon on the nickel cathode surface.

#### 4. DISCUSSION AND CONCLUSIONS

Excess power measurements in open Ni-H<sub>2</sub>O cells have also been carried out by at least five other groups so far, namely Noninski,<sup>(5)</sup> Notoya,<sup>(6,7)</sup> Ohmori and Enyo,<sup>(8,9)</sup> Criddle<sup>(10,11)</sup> and Bazhutov et al.,<sup>(12)</sup> besides the originators of this concept namely Mills et al.<sup>(1,13)</sup> There has however been persistent criticism/suspicion that the "excess heat" in open cells could be due to recombination effects. At BARC, early on, we did carry out Faraday efficiency measurements in some cells by measuring the volume of electrolytic gases evolved and found it to be > 95% but since our excess heat margins were up to 70% or even 100% at times, we concluded that recombination effects cannot account for the excess power reported by us. Until now we have not carried out any Faraday efficiency measurements simultaneously with calorimetry to confirm that Faraday efficiency is close to 100% in a heat producing cell. Also the fact that we have never measured excess power over and above V\*I in any of our open cells has led to suggestions that recombination/leakage current effects need to be addressed by us.

Recently J. E. Jones et. al.,<sup>(14)</sup> of Brigham Young University, Provo, Utah and Veranth et. al.,<sup>(15)</sup> of Bose Corporation, Massachusetts, have reported measuring Faraday efficiency simultaneously with calorimetry and claim that the apparent excess power in their open Ni-H<sub>2</sub>O cells can be accounted for by recombination effects. Of these, the Jones experiment was carried out at such low currents (0.96 mA to 8.08 mA) and power levels (< 11 mW) that they are not

perhaps particularly relevant to the higher current regimes ( $> 100$  mA) of most other open cell experiments. At very low currents there are competing electrochemical phenomena which come into play and which need to be considered to interpret Faraday efficiency measurements. However the Bose experiments were at a current of 0.35 amps (cell voltage  $\sim 3$  V). They measured the mass of water reformed in a separate test tube containing Pt catalyst, into which the electrolytic gases were directed. Since the amount of water reformed was less (by  $\sim 30\%$  to  $40\%$ ) than that expected on the basis of coulombs passed ( $\sim 1$  ml of water is expected from 3 Ah of charge passed), by precisely the quantity that could account for the excess power ( $30\%$  to  $40\%$ ) measured in their open cells, they conclude that the apparent excess power in their cells could be accounted for by recombination or leakage current effects within the cells. However, it is instructive to note at this point, that Mills et al., find that in their Ni-H<sub>2</sub>O cells with K<sub>2</sub>CO<sub>3</sub> solution which generate excess power, while the Faraday efficiency measured from gas production was close to 100% (see Table III of Ref. 13), "The combustion of the gases . . . . was incomplete" (see p. 118 of Ref. 13), supposedly due to formation of "dihydrino molecules", which do not combine with oxygen.

The crucial test in open cells therefore appears to be to perform simultaneously calorimetry, measurement of masses of water lost due to electrolysis and water reformed catalytically in an adjacent vessel. There are three possible outcomes: If recombination were the source of excess power, mass of water lost would be equal to the mass of water reformed but both will be lesser than the Faraday value. On the other hand if the excess power were of nuclear origin, mass of water lost from cell will be equal to that reformed and both will correspond to the Faraday value. In contrast if Mill's dihydrino molecule formation theory were valid, mass of water lost will correspond to the Faraday value but mass of water reformed will be much lesser in the case of a heat producing cell. It would be advantageous to also measure the rate of evolution of electrolytic gases in order to have an independent check on the Faraday efficiency. Such experiments are currently underway at SRI International with a view to resolving some of these issues.

The other approach is to carry out closed cell experiments, although Mills et. al., seem to indicate that according to their theory of compact hydrogen atom formation, excess heat will not be observable in closed cells. On the other hand if the excess heat is nuclear in origin as Robert Bush has suggested, closed cell experiments should indicate excess heat unambiguously. Further the excess heat should probably not depend on whether carbonate or hydroxide is used or whether the alkali salt is of Na, K, Rb or Cs. Bush and Eagleton<sup>(16)</sup> are perhaps the only group to date to have carried out extensive calorimetric studies in Ni-H<sub>2</sub>O systems using closed cells. They have experimented with over 30 cells during the period August '91 to February '94<sup>(17)</sup>. Bush was the first to propose and present experimental evidence to suggest that the light water excess heat effect is of nuclear origin. An elegant overview of the Cal Poly work<sup>(18)</sup> traces the historical evolution of Bush's concept that the excess heat in these light water cells is due to nuclear transmutation reactions involving a proton (from H<sub>2</sub>O) and an alkali metal atom of the electrolyte such as K, Rb or Cs. So far Notoya and Enyo<sup>(6)</sup> are the only other group who have provided experimental support to Bush's theory that in a K<sub>2</sub>CO<sub>3</sub> cell Ca is being formed from potassium.

The other evidence indicating that some nuclear phenomenon is indeed occurring in these cells is the detection of tritium in the electrolyte by the BARC group. As discussed earlier in this paper, Notoya<sup>(7)</sup> has since also presented evidence that tritium is formed in some of their Ni-H<sub>2</sub>O cells. Interestingly however neither Bush and Eagleton<sup>(17)</sup> nor Bazhutov et al.,<sup>(12)</sup> detected any tritium in their cells inspite of careful analysis of the electrolyte samples. The open cell experiments conducted by MS at SRI have also not shown any tritium to date.

In conclusion it thus appears that further carefully planned experiments are warranted in both open and closed cells to definitively settle the issue of the origin of the apparent excess power in Ni-H<sub>2</sub>O cells. The question of tritium production also needs to be independently verified.

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