Synthesis and characterization of an Iron pico-hydride. A permanent electric dipole with high enthalpy of formation

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Synthesis of an Iron Pico-hydride. Strategy

- The synthesis of an Iron pico-hydride is a very slow reaction: the conversion is some thousand ppm/day. Experiments are shut down after some 10 days corresponding to a conversion of some 20,000 to 30,000 ppm.
- The conversion from thermal results was evaluated against the maximum enthalpy of formation (680 MJ/mole Fe or 7.1 keV).
- The conversion was then evaluated against the converted products yielding a conversion corresponding to an enthalpy of formation of 390 MJ/mole Fe or 4.5 keV)
- These last values are the true values and are accounted for by the model.

Synthesis and characterization of an Iron pico-hydride. A permanent electric dipole with high enthalpy of formation

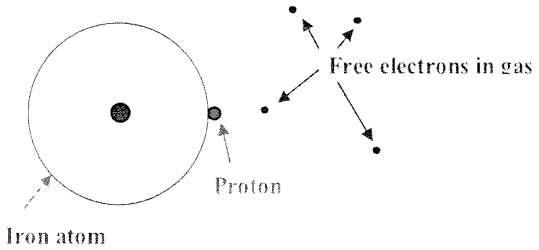
- The synthesis of an Iron pico-hydride occurs under very specific conditions.
- The enthalphy of formation is very high (1000 time higher than usual chemical reactions).
- The pico-hydride formed is a permanent electric dipole of atomic size.

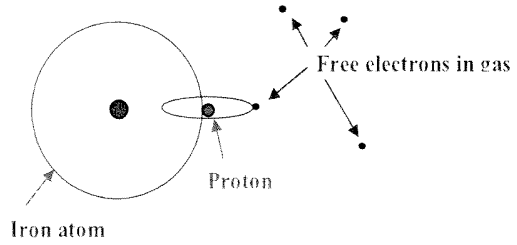
Synthesis of an Iron Pico-hydride.

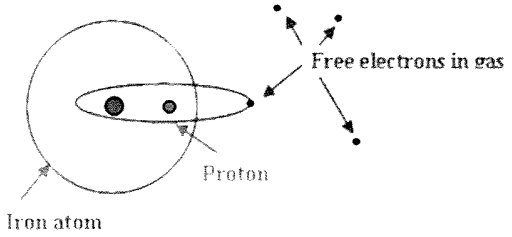
- For an Iron pico-hydride to be formed, 3 ingredients must be present in the reacting medium: **Iron** in the solid state in contact with **Hydrogen** in the gas phase and free electrons in this gas phase. The free electrons are provided by the presence of **Sodium** in the gas phase: the reaction proceeds at high temperature (1100°C)
- In the experiments reported here Iron is in the form of a powder (<40 μ) and the Sodium is in the form of a lump, that generates ionized sodium vapour when rising the temperature. An hydrogen cylinder delivers hydrogen at a regulated pressure.

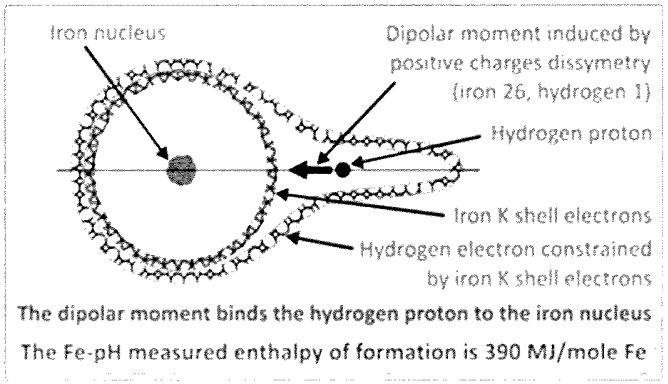
Synthesis of an Iron Pico-hydride.

- Overcoming the Lenhard-Johnes and Coulomb barriers









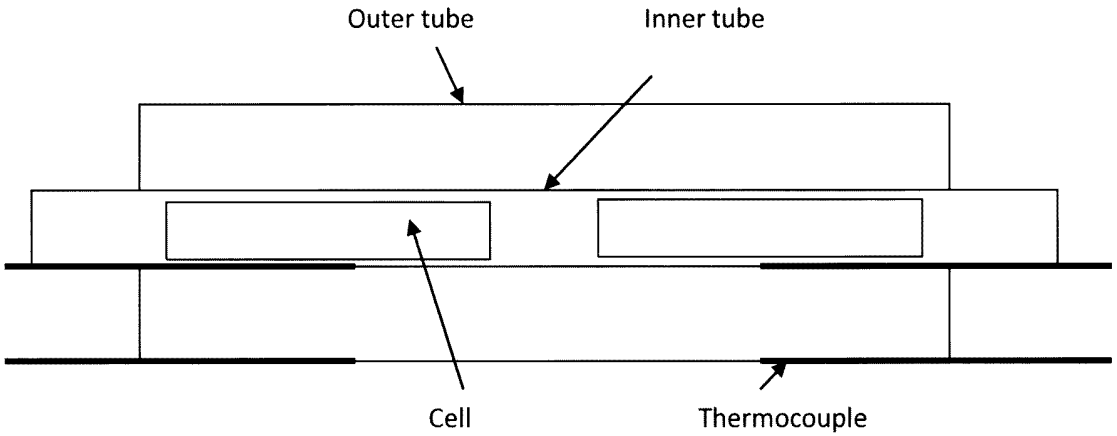
Enthalpy of formation of an Iron Pico-hydride and main properties

- A crude quantum mechanical treatment of the synthesis of a pico hydride has been presented at NEW-3SC-9 (J.J Dufour, X.JC. Dufour and J.D Vinko "*Pico-Chemistry: the possibility of new phases in some Hydrogen/Metals Systems*" IJMP-B Vol **27** N° 15 (2013) 1362038)
- This treatment points to the enthalpy of formation of an Iron pico-hydride to be in the order of magnitude of the energy of the Iron K layer (7.1 keV/atomFe or 681 MJ/moleFe)
- The analysis of the reaction product by HR ICP MS can be interpreted by the pico-hydride formed being an atomic size permanent electric dipole.
- From HR ICP-MS results the enthalpy of formation is 4.5 keV/atomFe or 390 MJ/Mole Fe. This that can be explained by tuning the parameters of the quantum mechanical treatment.

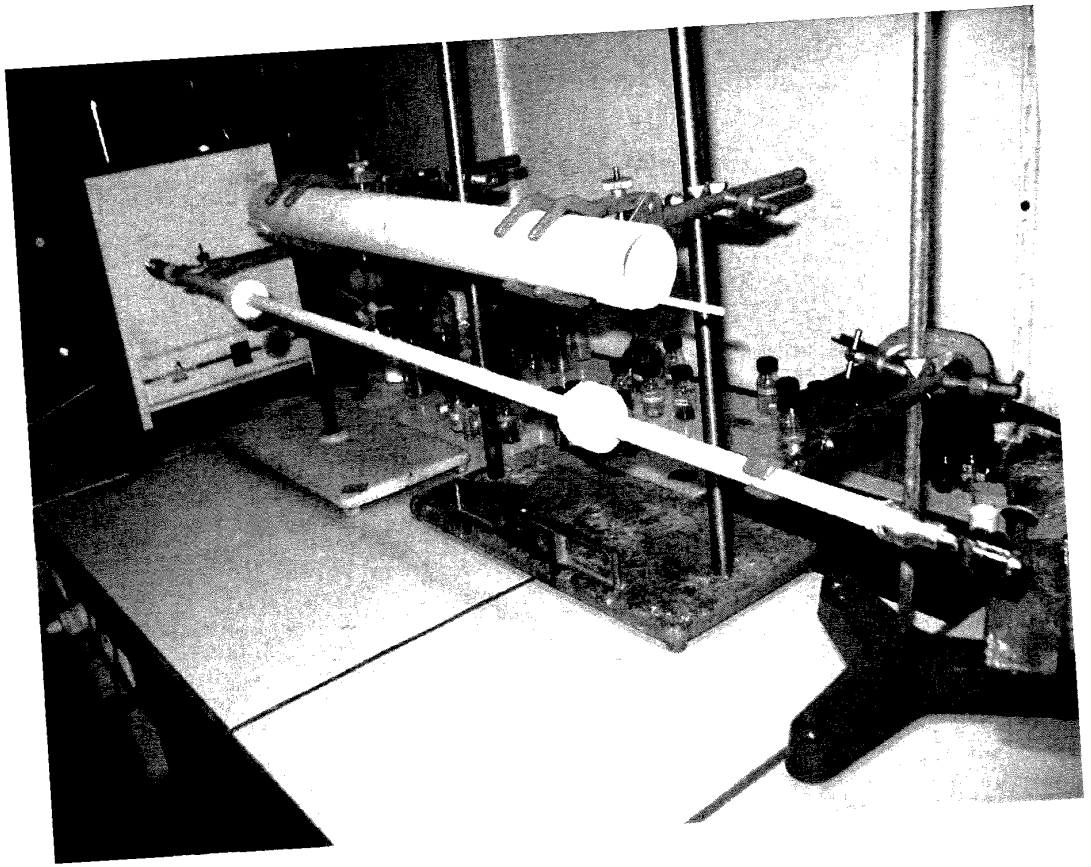
Enthalpy of formation of an Iron Pico-hydride. Calorimetry

- A differential calorimeter, able to operate up to 1200°C was used.
- Two alumina co-axial tubes (inner tube 8x12 mm outer tube 38x45 mm) are placed in a cylindrical heater with heating tube 50 mm inner diameter)
- In the smaller alumina tube, 2 cells (7 mm diameter and 85 mm long) are inserted in a position symetrical to the center of this tube: one contains a reference powder and the other the powder to be tested.
- The heat flows from the furnace tube to the outer and then to the inner alumina tubes.
- Four N thermocouples (in 2x4 alumina tubes) measure the surface temperatures of the 2 last tubes allowing calculation of the heat fluxes exchanged between them

Overall scheme of the calorimeter



- The 4 thermocouples are shown in position (the 2x4 mm alumina tubes are not represented). **Heat fluxes are thus calculated from the measurement of 4 potential differences (thermocouples)**



Overview of the calorimeter

N thermocouples are inserted in 2 alumina tubes (2X4 mm) one fixed against the inside of the larger tube (38x45 mm) and the second against the outside of the smaller tube (8x12 mm)

Data processing

- Data are collected using a data logger (AOIP SA 70). The acquisition time was varied from 5 s to 2 mn.

- Calculations are made using a spreadsheet. For each cell, the total power flowing from the 2 cells between the 2 cylinders **(ignoring second order ends effects)** is calculated from the measure of the 4 temperatures as

$$W = W_{COND} + W_{RAD} \quad \textbf{(W)}$$

Data processing

The power flowing from the **active cell** is denoted W_A and from the **reference one** W_R. W_R **is normalized to** W_A**, using a normalization coefficient** D.

The differential power between the 2 cells can thus be detected as $W=W_A-DW_R$

It has been shown experimentaly that D **is constant during the whole experiment.**

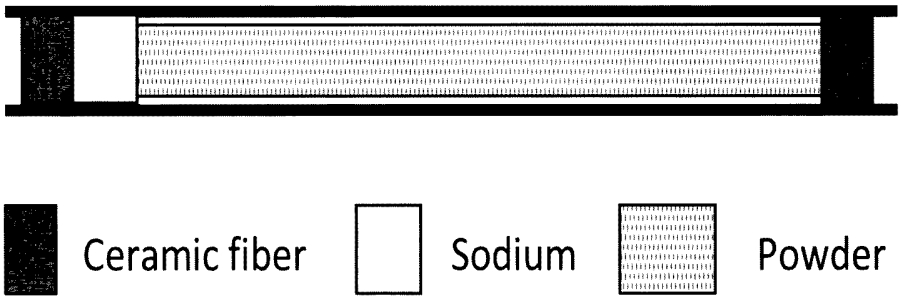
An experiment with Fe and Na

- Active cell: **Na 0.259g Fe 1.087 g SiC 1.087 g**
- Active powder volume 1.36 cm3

- Reference cell: **Na 0.260 g SiC 1.704 g**
- Reference powder volume: 1.37 cm3

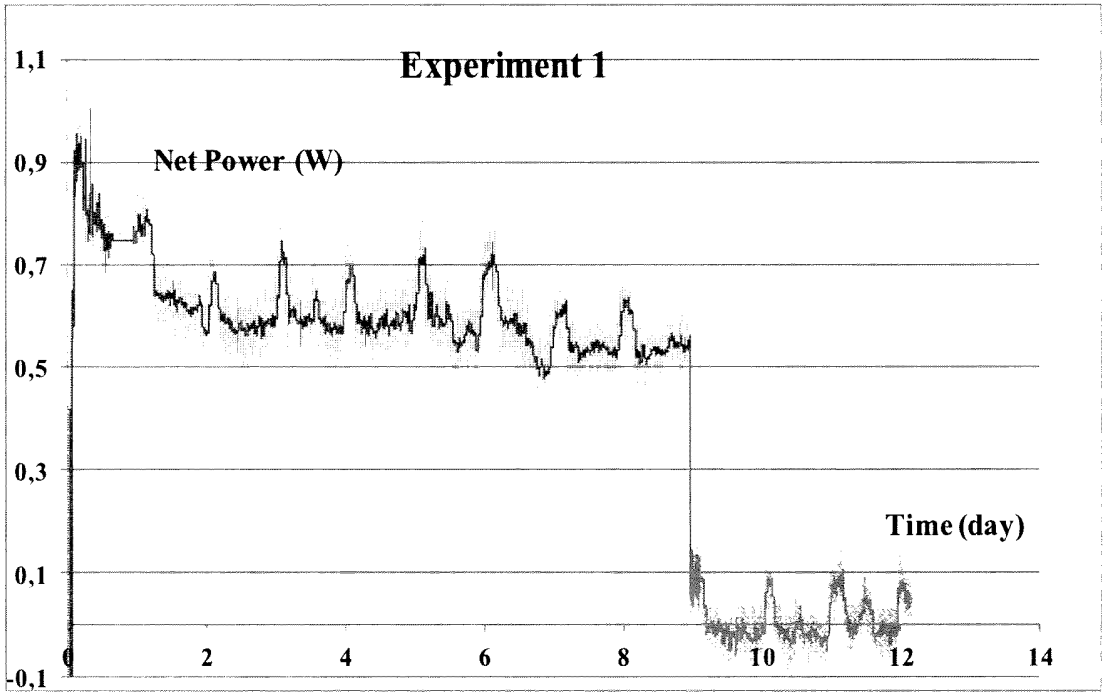
- Heater set point 1075°C. Temperature rise of the system under hydrogen from ambiant to 1075°C

Detail of the active cell



The synthesis during 9 days

- The synthesis was stopped after 9 days by pumping out the hydrogen down to a vacuum of 7 Pa.(Peaks are daily variations of the lab temperature).



Experiments run

- 5 experiments were run to test the influence of the electron source and of the cells material

Experiment number	Active cell	Reference cell	Electron source	Cells material
1	Na + Fe + SiC	Na + SiC	Sodium	304 L steel
2	LiAlH4 + Fe + SiC	LiAlH4 + SiC	Lithium	304 L steel
3	Na + SiC	Na+ SiC	Sodium	Alumina
4	Na + SiC	Na + SiC	Sodium	304 L steel
5	Na + Fe +SiC	Na+ SiC	Sodium	Alumina

- Experiments 1 and 5 were run with the same load composition (Fe and SiC) and the same amount of Sodium.

Comparing Experiments 1 and 5. Corrected conversion in experiment 1

- **Experiment 1** yielded a mean power *W*= 0.590 W during 9.1 days, resulting in a total energy release of 458,784 J. Calculated on the basis of the iron content in the load (1,087 g) the conversion is 34,700 ppm (Reference 681 MJ/mole Fe).
- **Experiment 5** yielded a mean power *W*= 0.450 W during 9.1 days, resulting in a total energy release of 349,920 J. Calculated on the basis of the iron content in the load (1,120 g) the conversion is 26,470 ppm (Reference 681 MJ/mole Fe).
- This can be explained by some 0.330 g of the 304 L steel of the cell used in **Experiment 1** having reacted. The reaction products from the 304 L steel of the cell are in the form of bright golden yellow scales on the cell walls.

Characterization of the Iron pico-hydride

The iron pico-hydride synthetized in **experiment 1** was analysed by ICP MS HR (Thermo ELEMENT 2XR).A resolving power round 10,000 was used (thus resolving Ar-O interferences) and the scan was from mass 23 to mass 68.

A reprentative mineralized sample (12N HNO_3 MS grade) was prepared from the solid sample resulting from the synthesis.

Care was taken when recovering this sample from the cell to minimize introduction of the small golden yellow scales resulting from the reaction of the 304 L steel of the cell.

Characterization of the Iron pico-hydride

- **Iron** is Fe used to prepare the load. Iron is natural Fe
- **Composite** is the representative sample of the treated load.

		^{54}Fe	^{56}Fe	^{57}Fe	^{58}Fe	Total counts
Natural Iron	Mass	53.938812	55.934839	56.935396	57.933277	
	%	5.9	91.72	2.1	0.28	
Iron	Mass (meas.)	53.9456	55.9400	56.9403	57.9386	
	%	5.98	91.51	1.94	0.56	12,275,755
Composite	Mass (meas.)	53.9456	55.9400	56.9403	57.9386	
	%	5.06	92.24	2.32	0.38	11,398,997

- **Composite** shows a significant decrease of ^{54}Fe and a significant increase of ^{57}Fe when compared to **Iron**.

Characterization of the Iron pico-hydride

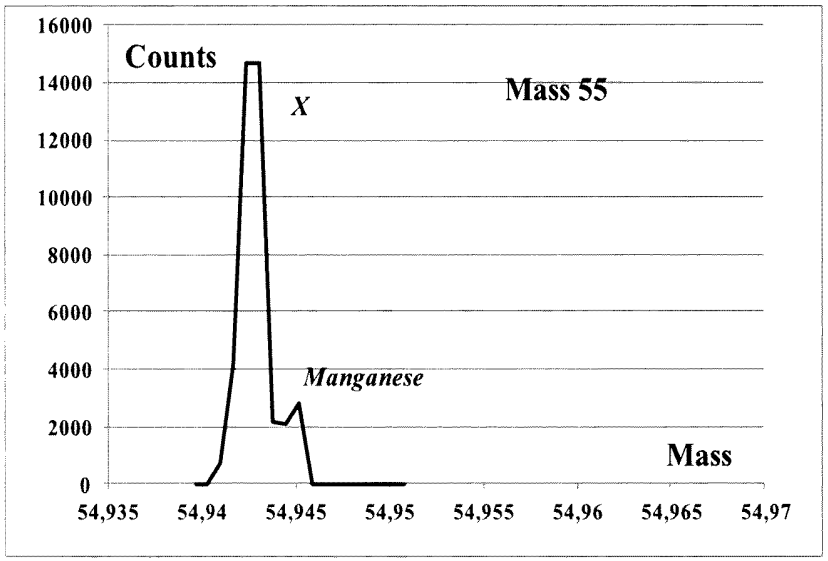
- For further analysis, **Composite** has been normalized to **Iron** (1.0769) and will be refered to as **N.Composite.**

		^{23}Na	^{52}Cr	^{55}Mn from cell	^{55}X
Natural	Mass	22.989767	51.940509	54.938047	
	%	100.0	83.79	100.0	
Iron	Mass (meas.)	22.9929	51.9672		
	Total counts	28,740	46,377		
N.Composite	Mass (meas.)	22.9922	51.9672		
	Total counts	109,080	59,089	1,686	42,205

- At mass 55, **N.Composite** shows a sizeable peak (42,205 counts), which is not in **Iron**.
- At mass 52 the excess of counts in **N.Composite** gives an estimation of the pollution of **N.Composite** by Manganese from the cell: 1,686 counts

Characterization of the Iron pico-hydride

- The spectrum at mass 55, shows a sizeable peak (X) and a small one at its right foot that can attributed to Manganese (see previous slide)



- Normalizing the mass scale with Manganese, the mass of ^{55}X is found to be 54.9352. What is ^{55}X ???

Characterization of the Iron pico-hydride. What is ^{55}X ?

- Among the radioactive species at mass 55 (^{55}Cr, ^{55}Co, ^{55}Ni and ^{55}Fe), ^{55}Fe has the mass closest to that of ^{55}X (54.9383 compared to 54.9352).
- But the measured radioactivity of the solid sample extracted from the cell and from which **Composite** has been obtained is within the background: 8cps (measured by a SAPHYMO CoMo 170 contaminamètre α, β particles and X, γ photons).
- By contrast a 157 Bq ^{55}Fe sealed source returns 57 cps ($<2\pi$).
- Should ^{55}X be ^{55}Fe, the activity of the sample would have been 1.97×10^{11} Bq. Such a level of activity could not have been missed.

Characterization of the Iron pico-hydride. What is ^{55}X ?

- The object ^{54}Fe-pH under consideration is far from being an usual atom.

- Compared to its counterpart (^{55}Co), its positive charge is complex: a positive nucleus with charge 26 and some 10 fm diameter, and a positive charge 1 at a few picometers, bound to the Iron nucleus by an oscillating electron, resulting in ^{54}Fe-pH being a permanent electric dipole.

Characterization of the Iron pico-hydride. What is ^{55}X ?

- It is then conceivable that the single charged $^{54}Fe\text{-}pH^{+}$ permanent electric dipole could behave during its time of flight through the electric and magnetic fields of the MS machine as if its apparent transient effective electric charge is slightly higher than *e*.
- The mass spectrometer sorts atoms according to their *m/e* ratios. If the apparent transient effective charge of $^{54}Fe\text{-}pH^{+}$ is *e* increased by 223 ppm, then the actual mass of ^{55}X is 54.9474, which is the mass of $^{54}Fe\text{-}pH$.

Comparing conversion from thermal measurements and from ICP-MS analysis

- For **Experiment 1** under consideration the overall conversion from thermal results of the load (corrected for steel cell polution) is found to be : 26,500 ppm for 9.1 days (2,910 ppm/day), based on an Enthalpy of formation of 681 MJ/mole Fe (7.1keV/atom Fe)

  For **Experiment 1**, the overall conversion from MS results (calculated at mass 54) is found to be 60,260 ppm, resulting in an enthalpy of formation of 390MJ/mole Fe (4.5 keV/atom Fe), assuming all Fe isotopes have the same reaction rate.

  The difference between the 2 approaches can be explained by adjusting the parameters of the model.

Enthalpy of formation and main property of an Iron pico-Hydride

- The enthalpy of formation of an Iron Pico-hydride is 390 MJ/mole Fe (4.05 keV/atom Fe).

- The picohydride formed is a permanent electric dipole of atomic size.