BEHAVIOUR AND MONITORING OF NON-METALLIC IMPURITIES IN LIQUID SODIUM

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Outline

- **Hydrogen sensor**

  In-sodium

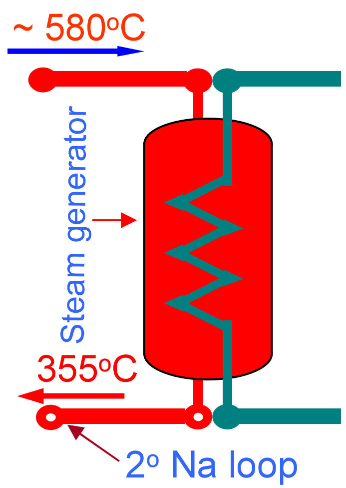
  Argon cover gas

- **Carbon sensor**

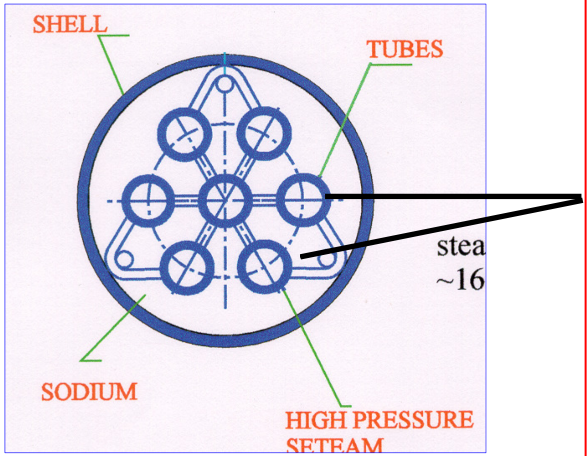
- **Oxygen sensor**

Electrochemical Hydrogen Sensor for in-sodium applications

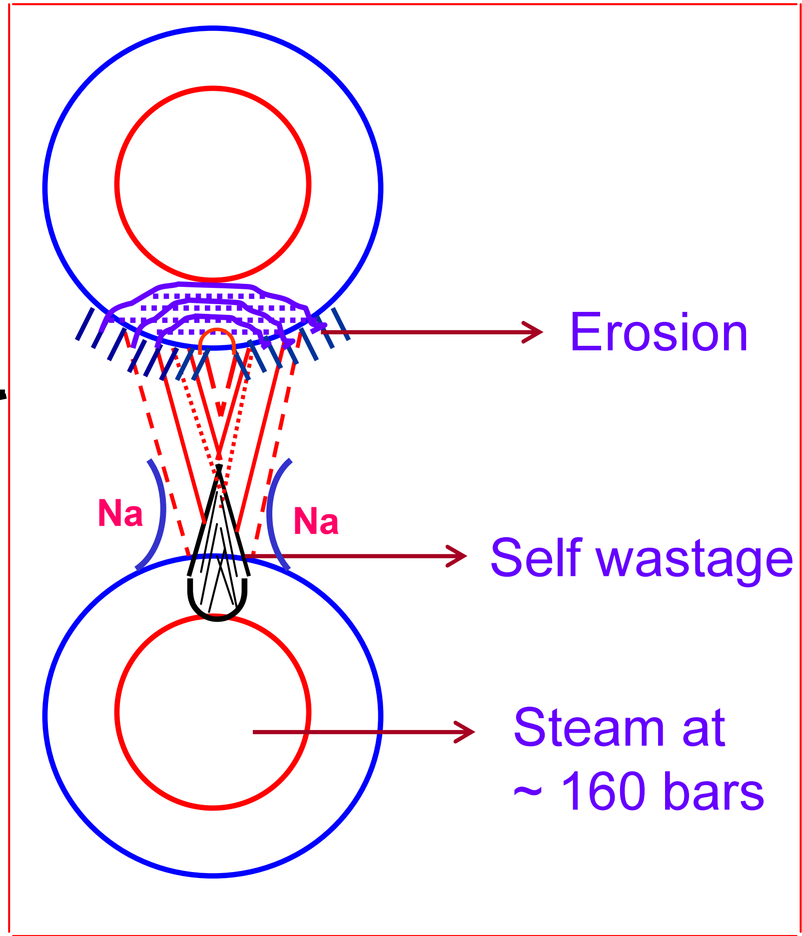
Source of hydrogen



Steam Generator



CS view of SG in FBTR



Steam leak

$Na + H_2O \rightarrow NaOH + \frac{1}{2} H_2$

Requirement

$[H]_{Na} \rightarrow$ leak at its inception

$[H]_{Na} \uparrow$ ~ 10s ppb $\rightarrow$ resolution

Conventional Sensors

- ⌘ Sputter-ion based
- ⌘ QMS based

- ❖ Expensive
- ❖ Bulky
- ❖ Frequent calibration

Development of electrochemical hydrogen sensors

$[H]_{Na}$ // Electrolyte// $(p_{H2})^{ref}$

$$E = RT/2F \ln (p_{H_2}(\text{sample})/ p_{H_2}(\text{ref}))$$

Electrolyte system conforming to

σ_{H-} & stability $P_{H_2} = 0.05 – 5$ Pa $\rightarrow$ 723K

Search for new electrolytes with high σ_i , t_i

Wittingham and co-workers reported (early 70s) use of $CaCl_2$ and CaHCl for this application

⇒ **Only alkaline earth hydrides and halide systems expected to be stable under operating conditions ⇒ (Ca,Sr,Ba)HX hydride ion conducting**

⇒ **Alkaline earth bromides and lithium halides have low melting points**

Systems studied - DSC, σ and t_i

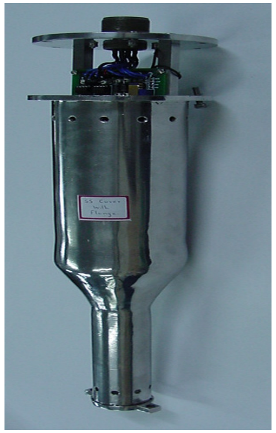
$LiCl-CaCl_2$, $LiBr-SrBr_2$, **$CaBr_2-CaHBr$**, $SrBr_2-SrH_2$, $CaCl_2-CaHCl-LiCl$

A mixture of CaO, CaH_2, MgO & Mg → **First time used as reference electrode**

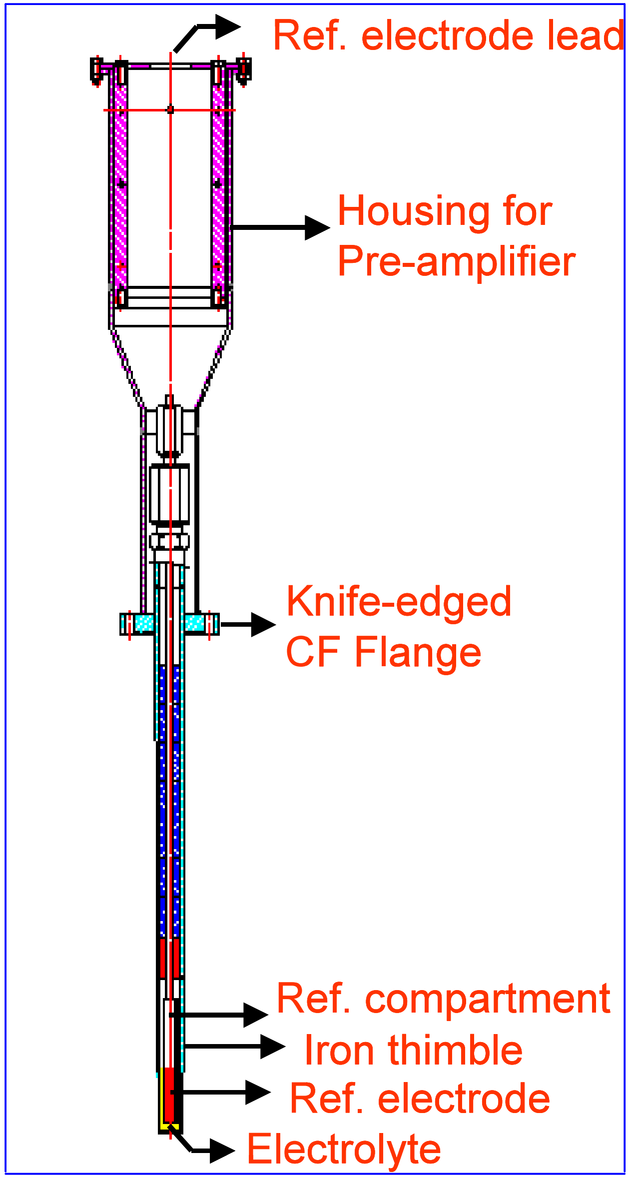
- **facilitates casting electrolyte at high temperature**

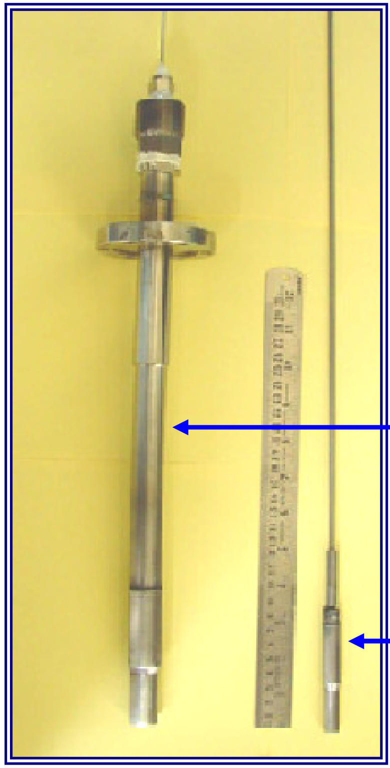
(R.Sridharan, K.H.Mahendran, S.Nagaraj, T.Gnanasekaran & G.Periaswami, J. Nucl. Mater. 312 (2003) 10)

Schematic diagram of ECHM sensor with the pre-amplifier



Housing for
Pre-amplifier



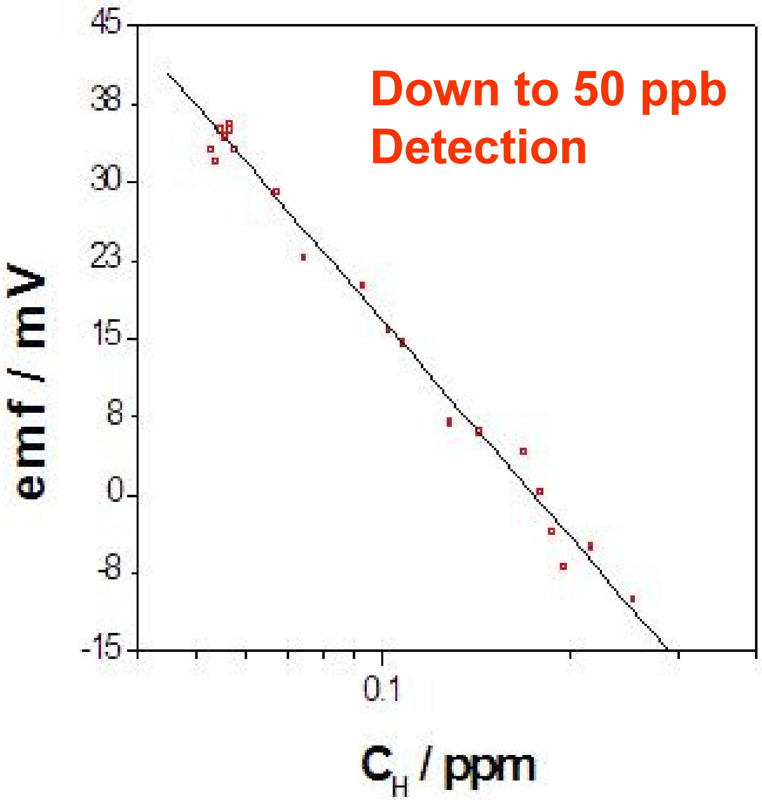


Electrochemical
sensor

Reference
electrode

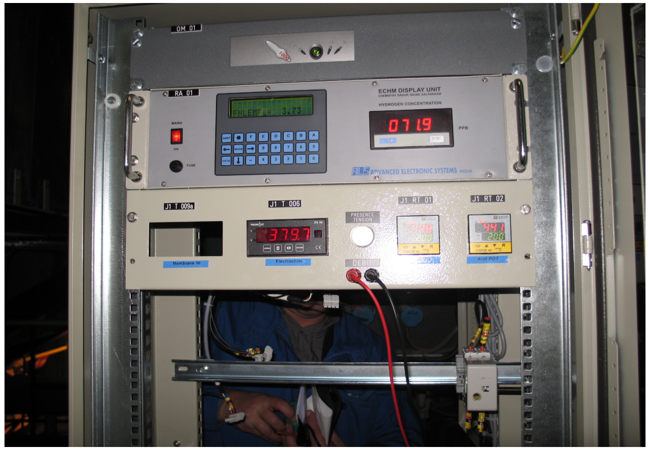
(Kitheri Joseph, K. Sujatha, S. Nagaraj, K.H. Mahendran, R. Sridharan, G.Periaswami, T. Gnanasekaran, J. Nucl. Mater. 344 (2005) 285)

Performance evaluation in lab



10 ppb ↑ bg 50 ppb

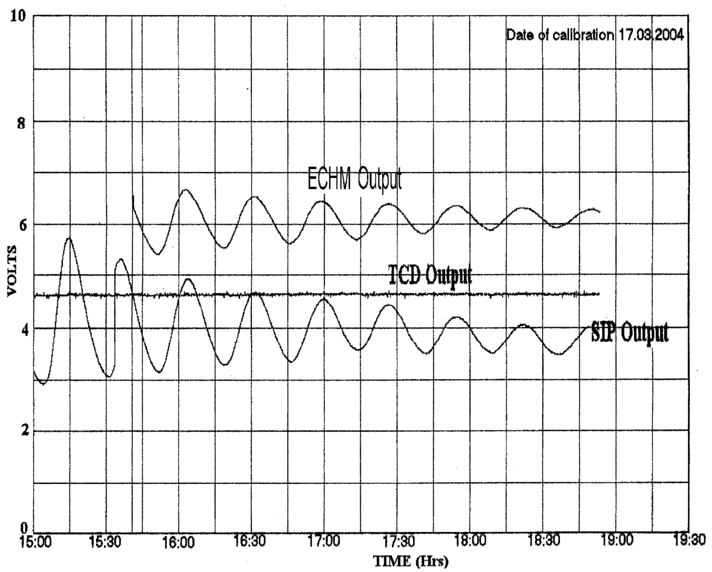
No drift < 50 ppb



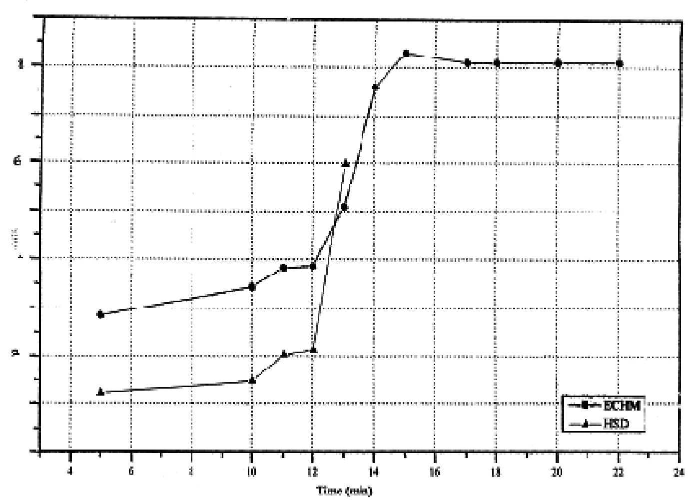
Output of electrochemical hydrogen meter as a function of hydrogen concentration in liquid sodium

ECHM display unit

Response of ECHM to hydrogen and steam injections in large sodium facilities

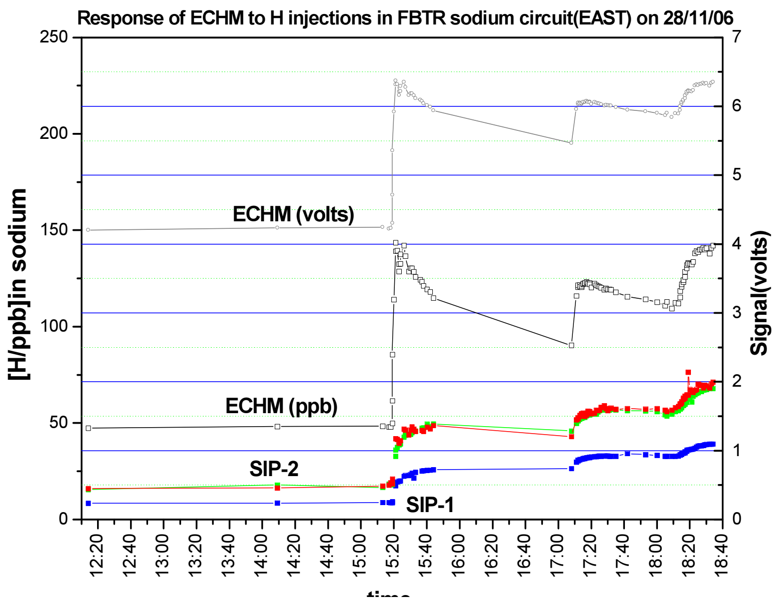


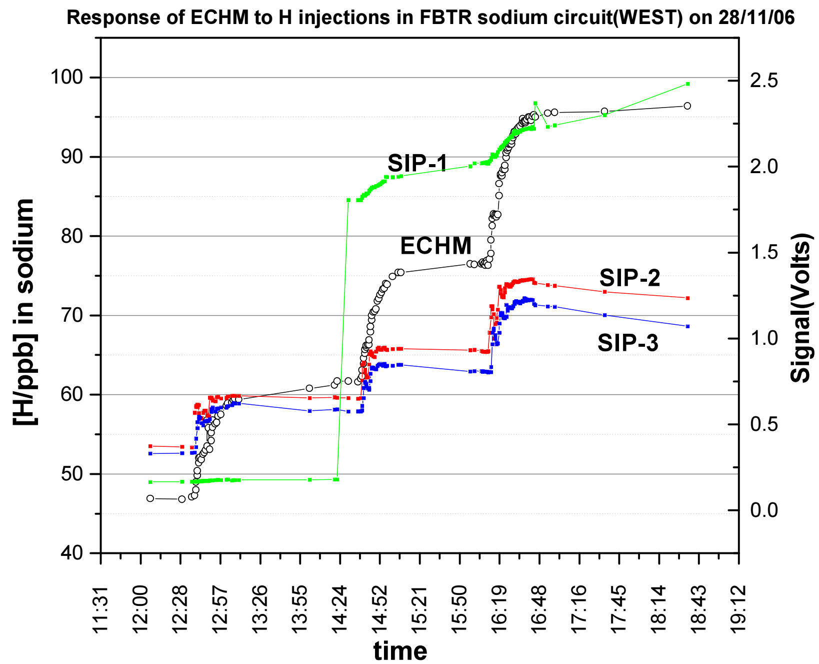
Response (volt) of the sensor to hydrogen injection in Steam Generator Test Facility



Sensor response to steam injection in Sodium Water Reaction Test Facility

Response of ECHM to hydrogen in FBTR



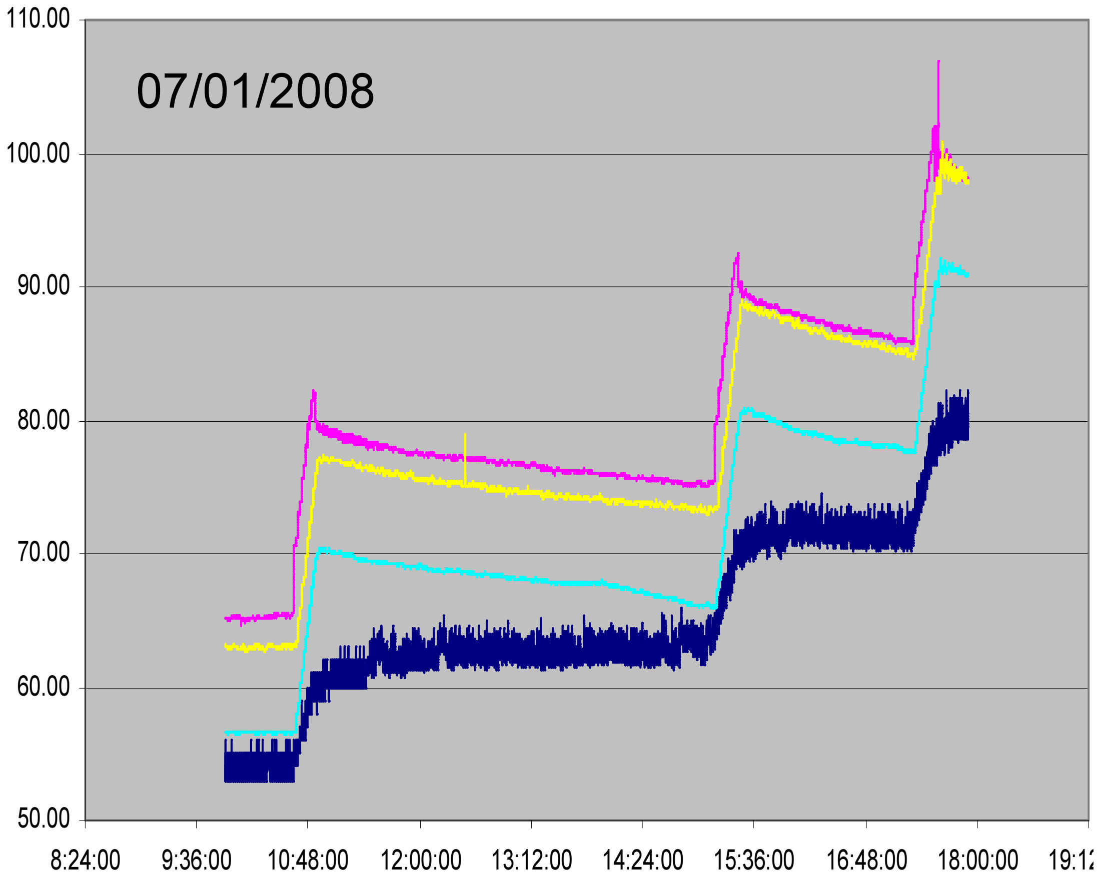


Several years of successful operation

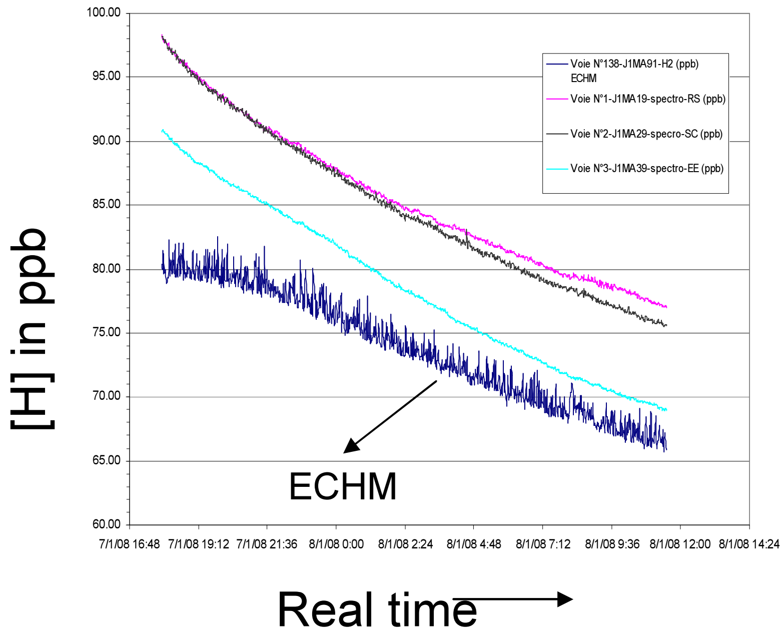
- ECHM response to changes in hydrogen level is instantaneous & reproducible
- Noise in ECHM signal is ±1 ppb at 50 ppb (±2% of background level)

Incorporation in PFBR

ECHM installed in Phenix Reactor, France in October 2007



Response to three hydrogen injections into sodium



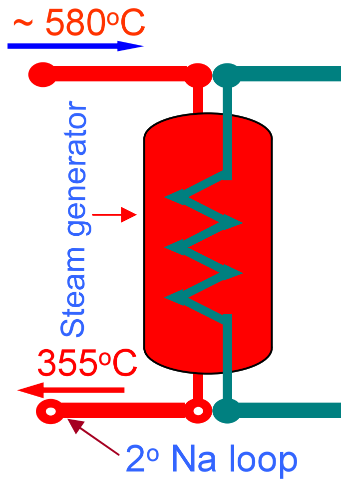
- Unlike the conventional sensors which require frequent calibration at the plant, this electrochemical sensor needs one time calibration in the laboratory before installing in sodium circuits.

- These are quite inexpensive, compact and maintenance free compared to the classical sensors

(JPh. Jeannot, T. Gnanasekaran, C. Latge, R. Sridharan, L. Martin, R. Ganesan, JM. Augem, JL. Courouau, G. Gobillot ANIMMA International conference,7-10 June (2009) Marseille, France)

Hydrogen sensor for argon cover gas

Source of hydrogen



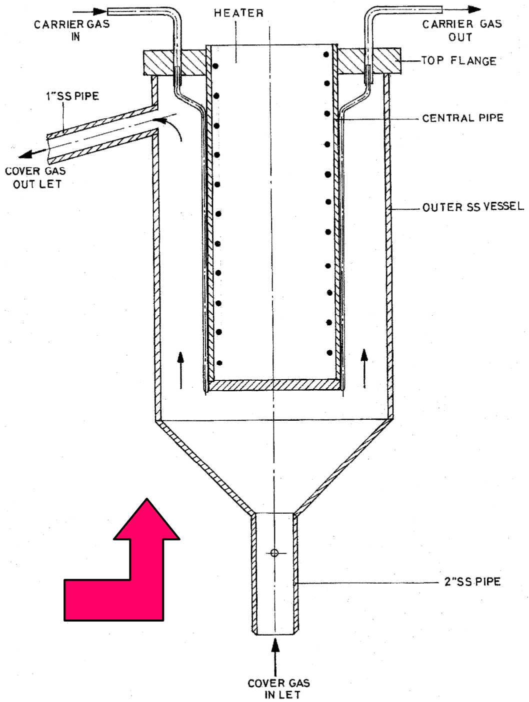
$Na + H_2O \rightarrow NaOH + \frac{1}{2} H_2$

Start-up of reactor (T_{Na} ~ 250°C)
Low power operation

H_2 escapes to cover gas → steam leak detection

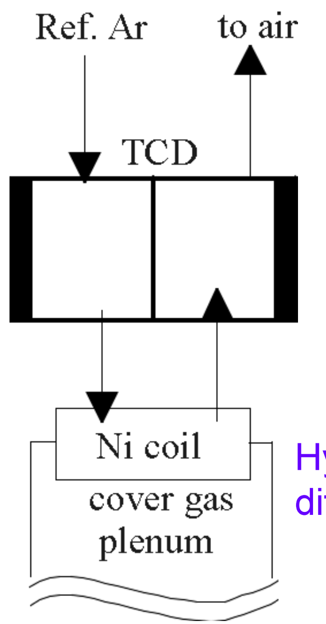
Steam Generator

Nickel Coil Assembly



Schematics of nickel coil assembly after incorporation in cover gas stream (FBTR)

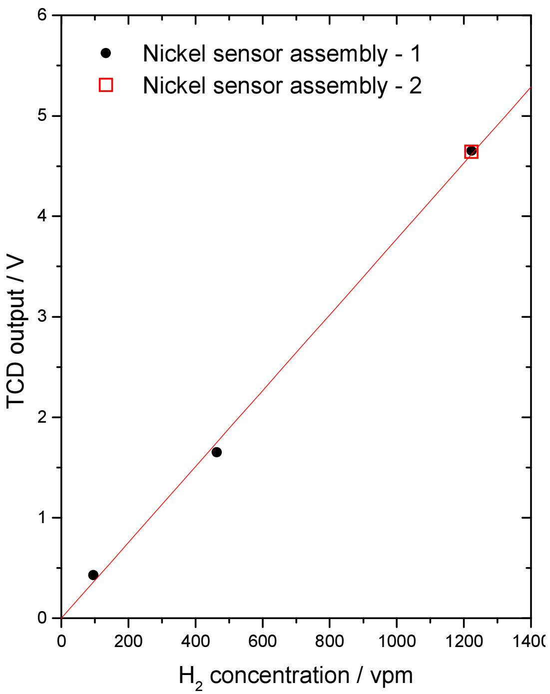
Scheme Ni coil - TCD

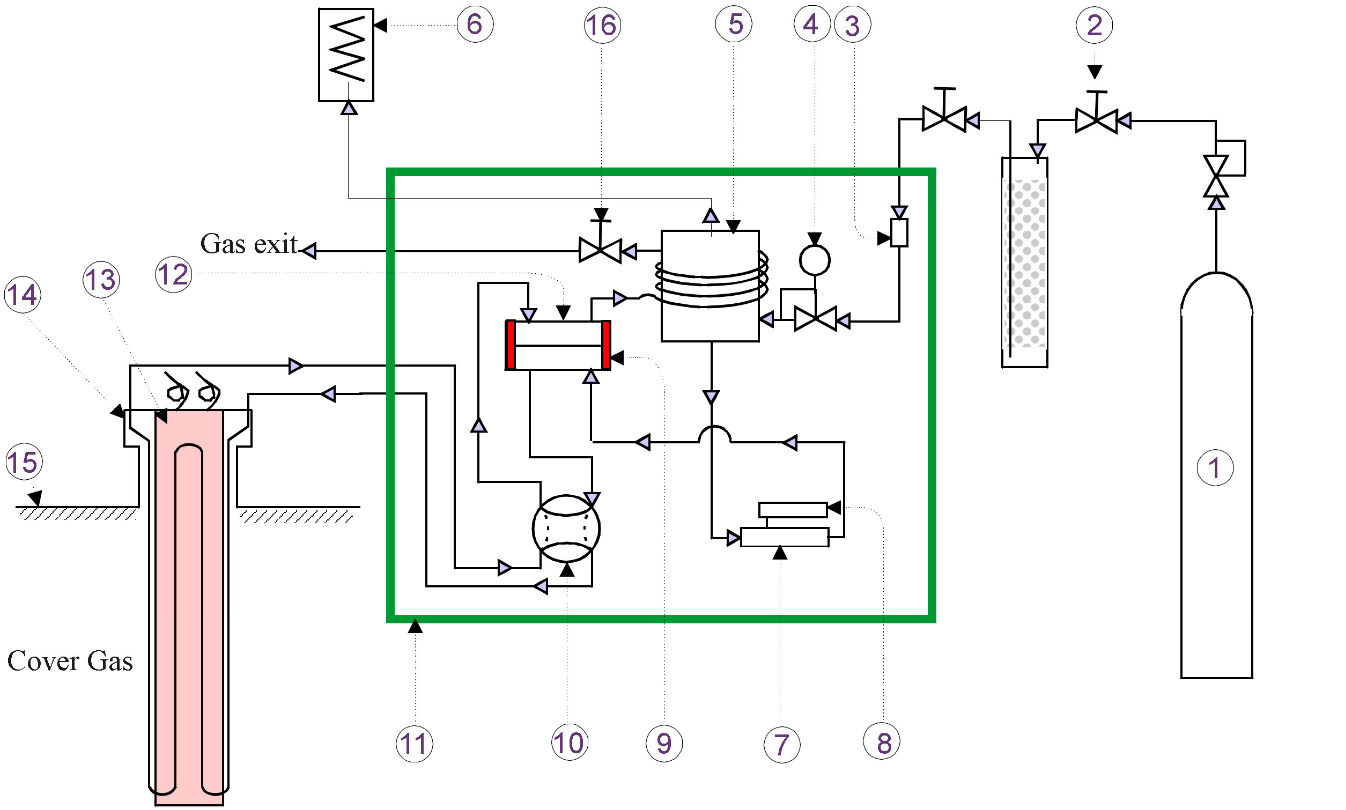


Argon sweeps

Hydrogen diffuses in

Schematics of hydrogen detection system for argon cover gas





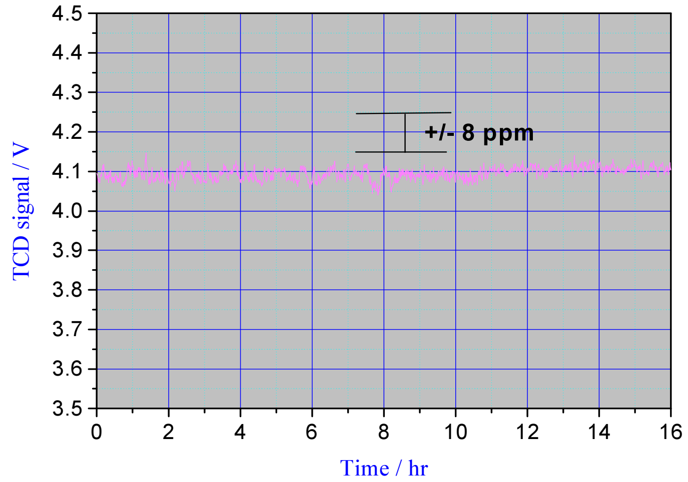
1. Argon gas cylinder
2. Inlet control valve (V2)
3. 15µ filter
4. Line regulator
5. Buffer tank
6. Pressure sensor
7. Mass flow controller (MFC)
8. Power supply to MFC
9. TCD block heater
10. Two way sample- bypass valve
11. Argon Gas Manifold cum TCD unit
12. Thermal Conductivity Detector (TCD)
13. Nickel Coil heater
14. Nickel Coil Assembly (NCA)
15. Expansion tank
16. Needle valve (V3)

Calibration of nickel coil assemblies (T = 773 K) for different concentrations of H_2

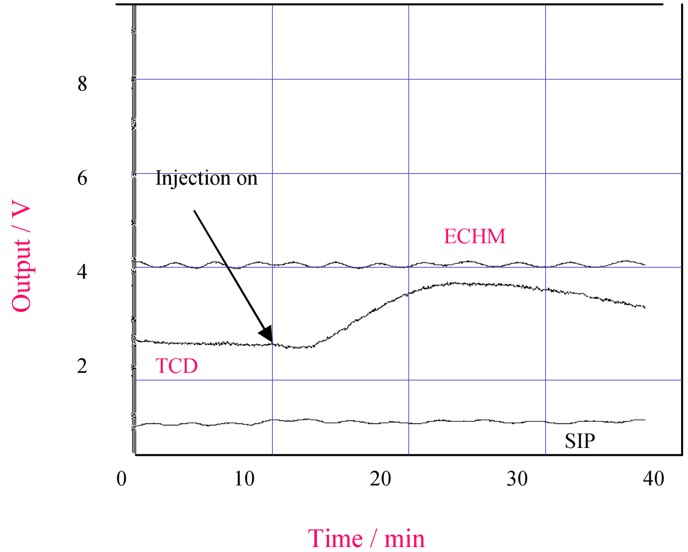
(K.H. Mahendran, R. Sridharan, T. Gnanasekaran & G. Periaswami, Ind. Eng. Chem. Res. 37(1998) 1398)

Performance in FBTR and other facilities

Functional – FBTR (13 years), SGTF (7 years) & SOWART (7 years)



Baseline stability of TCD response



Response of CGHM to H_2 injection at SGTF

Modifications made to improve its performance

- Elimination of mass flow controller   Fine metering valve
- Micro controller based control unit designed and fabricated

temperature dependency of the signal
voltage to vppm output
frequency transmission

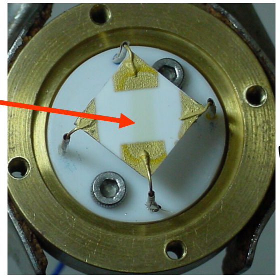
Noise = +/- 2 vppm   **MDL = 12 vppm**

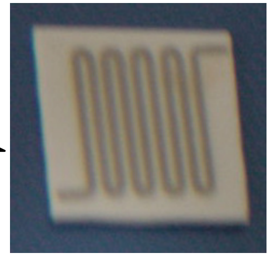
Integration in PFBR

Hydrogen Sensor for cover gas monitoring (1- 80 vppm)

Semiconducting metal oxides → Change in surface conductivity

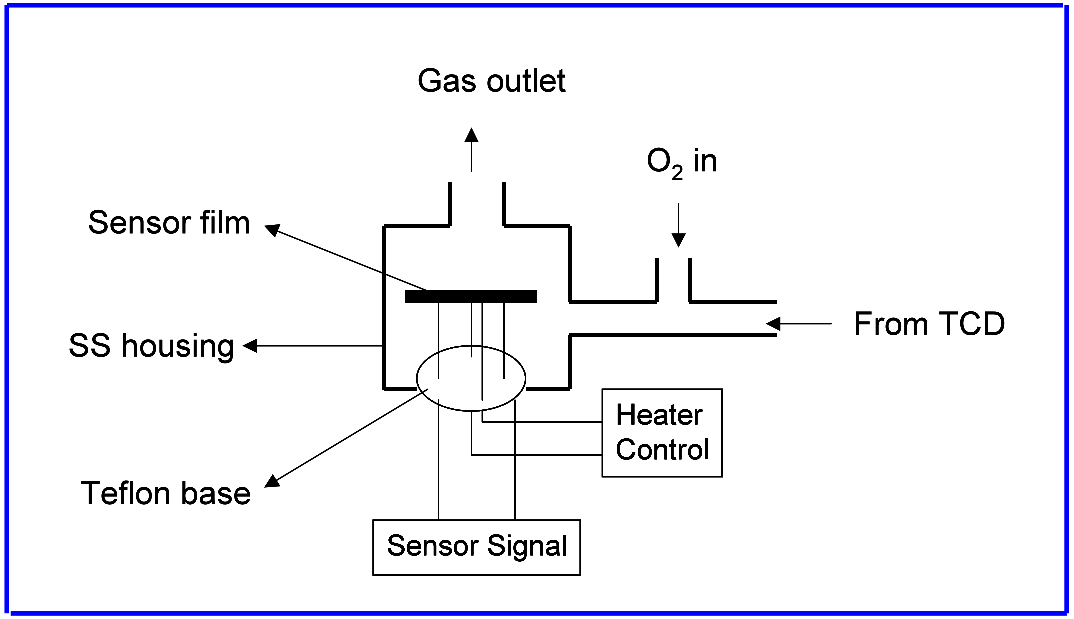
$Pd\text{-}SnO_2$ thin film form

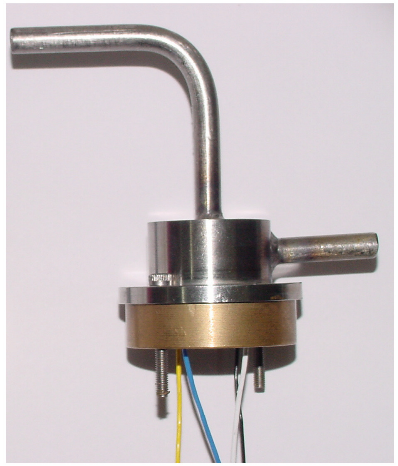




Heater

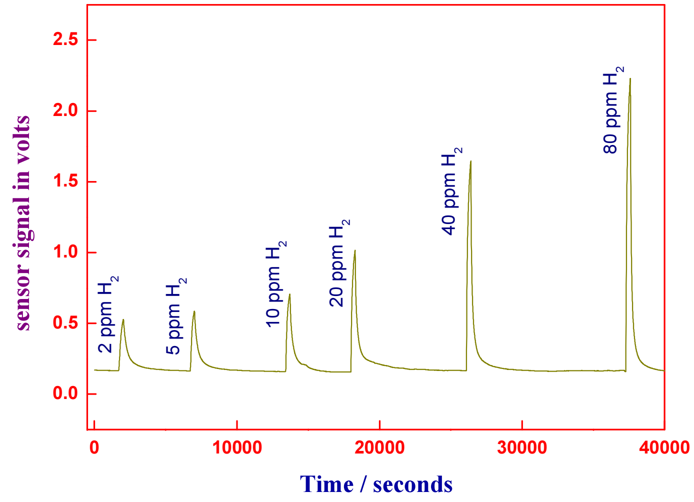
Scheme for integration with TCD based system



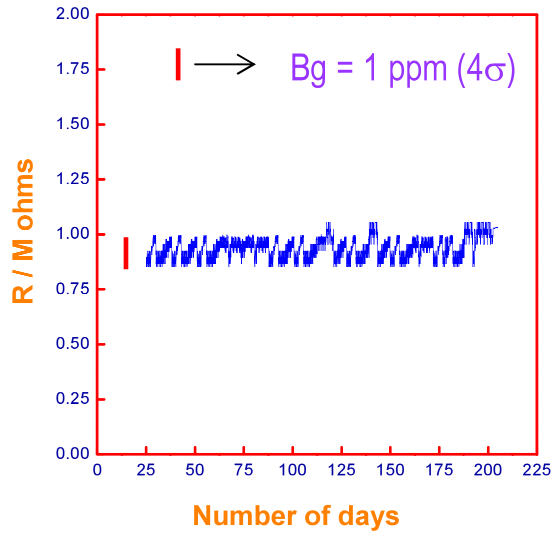


Compact Sensor

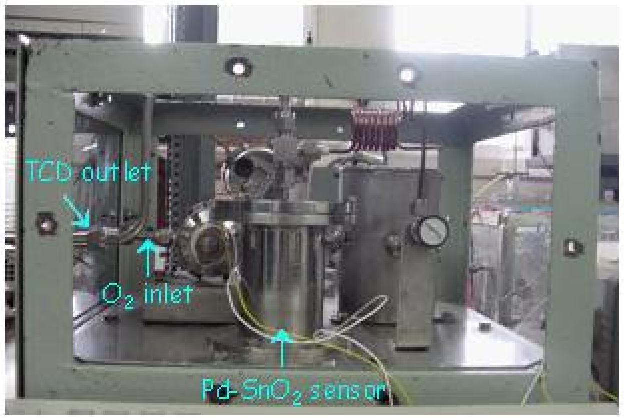
Sensors tested in-tandem with TCD based system



Sensor's response to 2 to 80 ppm of H_2

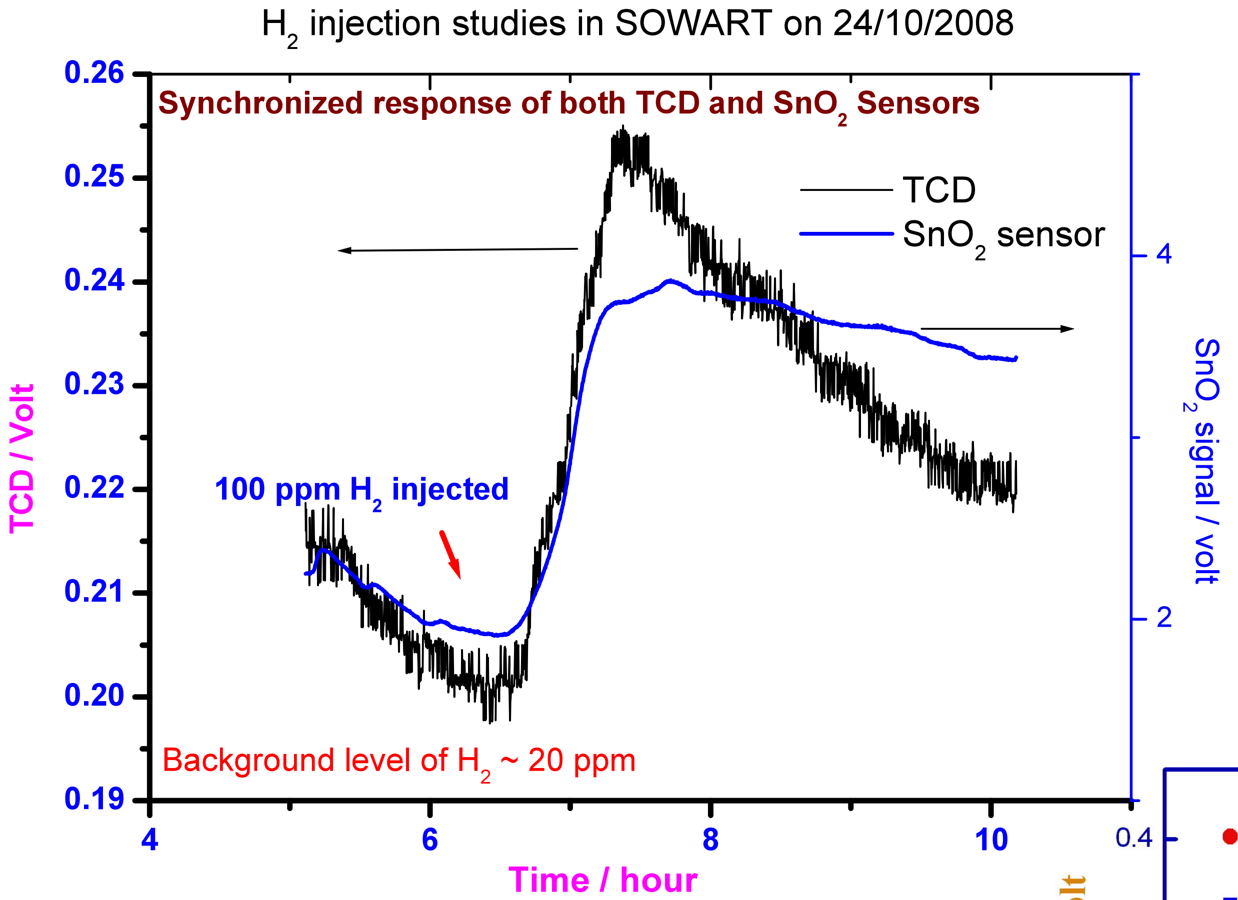


Baseline stability for 6 months

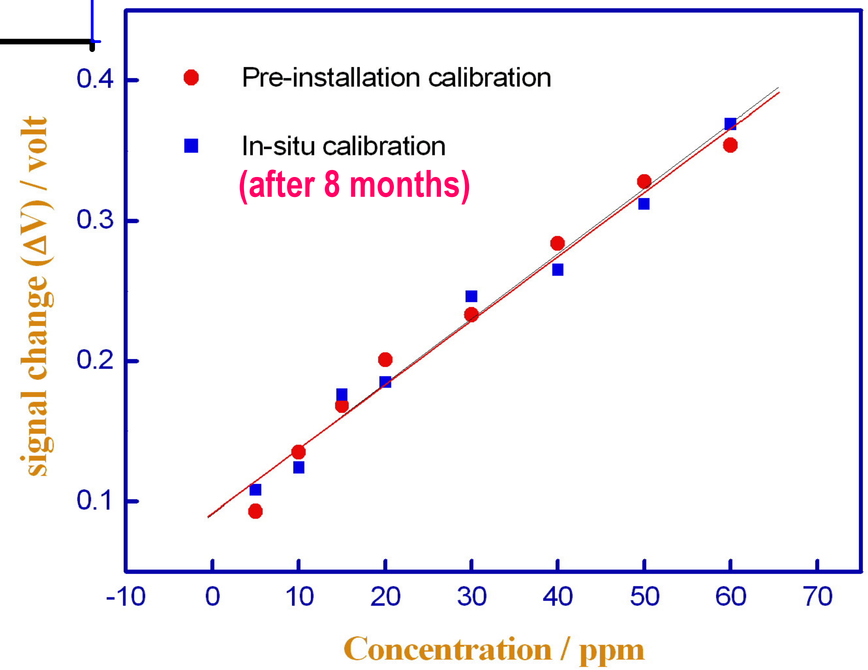


Sensor module with gas manifold and built-in pre-amplifier

(E. Prabhu, K.I. Gnanasekar, V. Jayaraman, T. Gnanasekaran & G. Periaswami, A.J.Phys. 14 (2005) 33)



Performance in SOWART



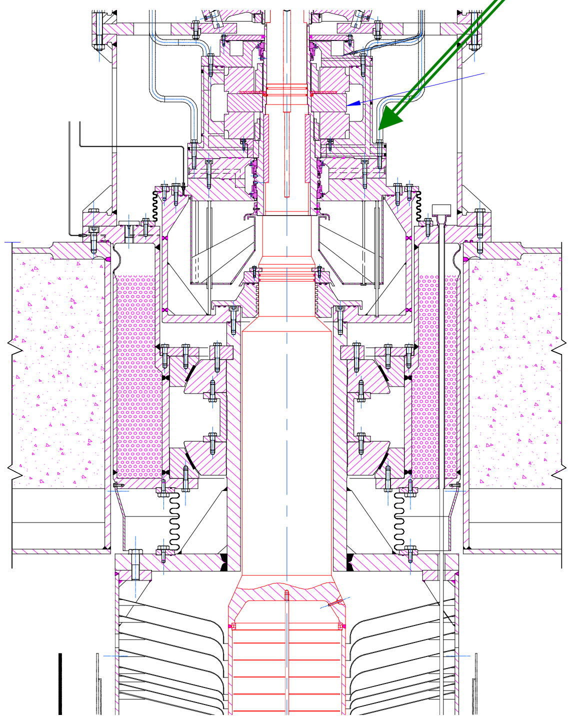
Functional - SOWART (3 years)
SGTF (1 year)

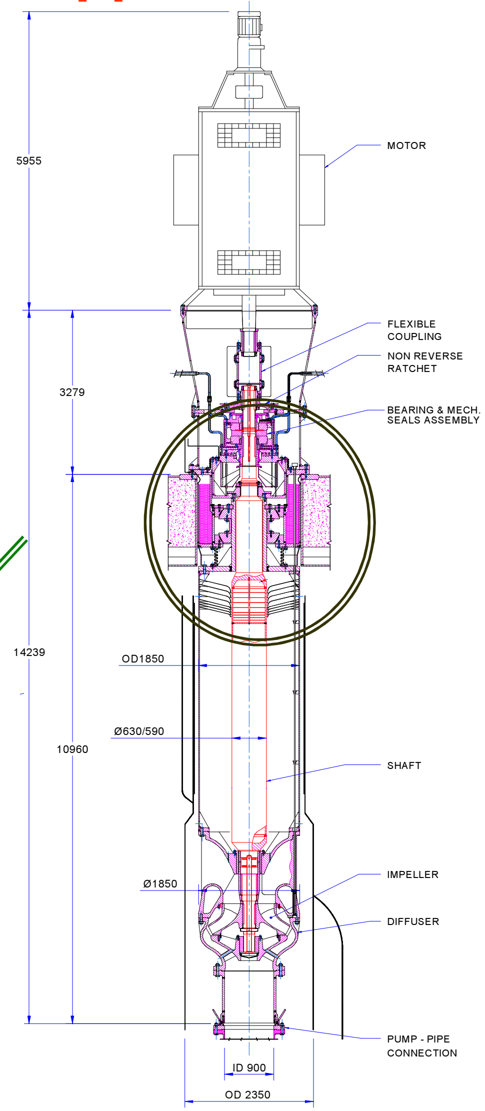
Electrochemical Carbon Sensor for in-sodium applications

Source of Carbon

- ❖ **Shaft cooling by hydrocarbon oils**
- ❖ **Oil leak can lead to cracking and increase of carbon activity in sodium**

Sodium circulated by centrifugal pumps





Cell Configuration

$$C / Li_2CO_3\text{-}Na_2CO_3 / Fe / C_{Na}$$

$$E = -(RT/4F) \ln (a_c)^{Na}$$

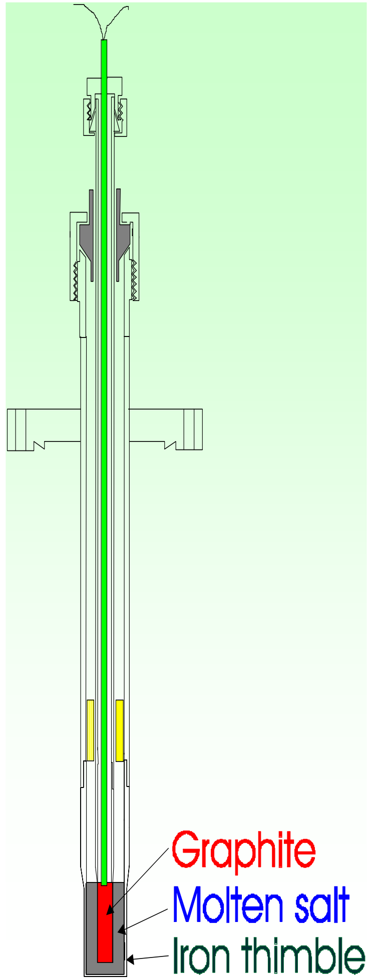
Hobdell et al reported (1971)

Earlier Problems

1. *Reverse polarity*
2. *Poor reproducibility and stability*

↓

Thermodynamic analysis & electrochemical investigation carried out ⇒ cell assembling procedure standardised



Application

Carbon potential of sodium measured in dynamic system. Speciation of carbon in sodium done.

Electrochemical Reactions in molten carbonate melt

Electrochemical reaction at ref. electrode	$C + 3\,O^{2-}$	$\Leftrightarrow$	$CO_3^{2-} + 4\,e^-$
Electrochemical reaction at sodium electrode	$CO_3^{2-} + 4\,e^-$	$\Leftrightarrow$	$C + 3\,O^{2-}$
Net reaction	C_{ref}	$\Rightarrow$	C_{sple}

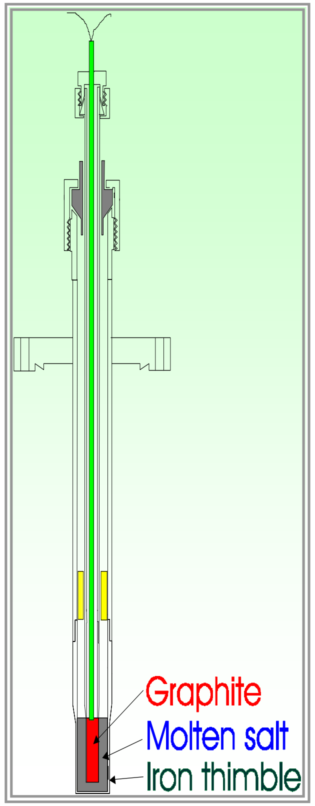
Cell emf = - [RT / 4F] ln $(a_C)^{Na}$

Interfering reactions

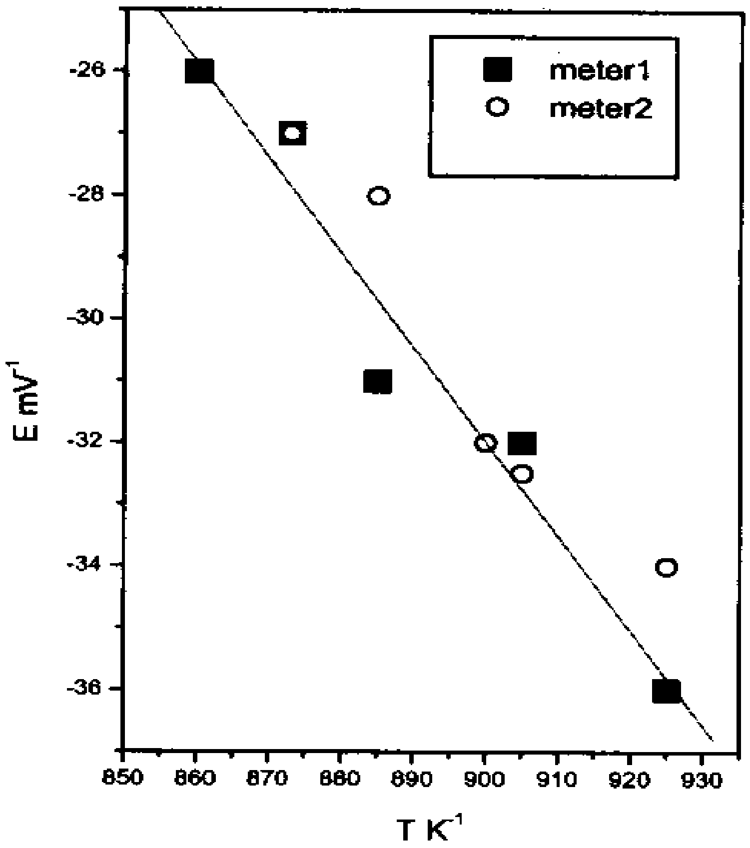
With super oxides and peroxides

CO_2	+	$1/2\ O_2$	+	$2e^-$	$\Leftrightarrow$	CO_3^{2-}			(A)
CO	+	$2O^{2-}$			$\Leftrightarrow$	CO_3^{2-}	+	$2e^-$	(B)
C	+	$3/2O_2$	+	$2e^-$	$\Leftrightarrow$	CO_3^{2-}			(C)
2C	+	$3O_2^-$	+	e^-	$\Leftrightarrow$	$2CO_3^{2-}$			(D)
C	+	$3/2\ O_2^{2-}$			$\Leftrightarrow$	CO_3^{2-}	+	e^-	(E)

Dependent on oxygen partial pressures ⇒ Can lead to reversed polarity. Change in magnitudes



➢ Modified procedure for sensor assembly evolved and implemented



Response of ECCM to temperature

- Carbon potential measurement by ECCM corroborated by Ni foil equilibration studies
- Foil used Nickel 100µm
- Equilibration temperature 650°C
- Equilibration period – 360 h

Functional

FBTR - 12 Years
BIM - 1 Year

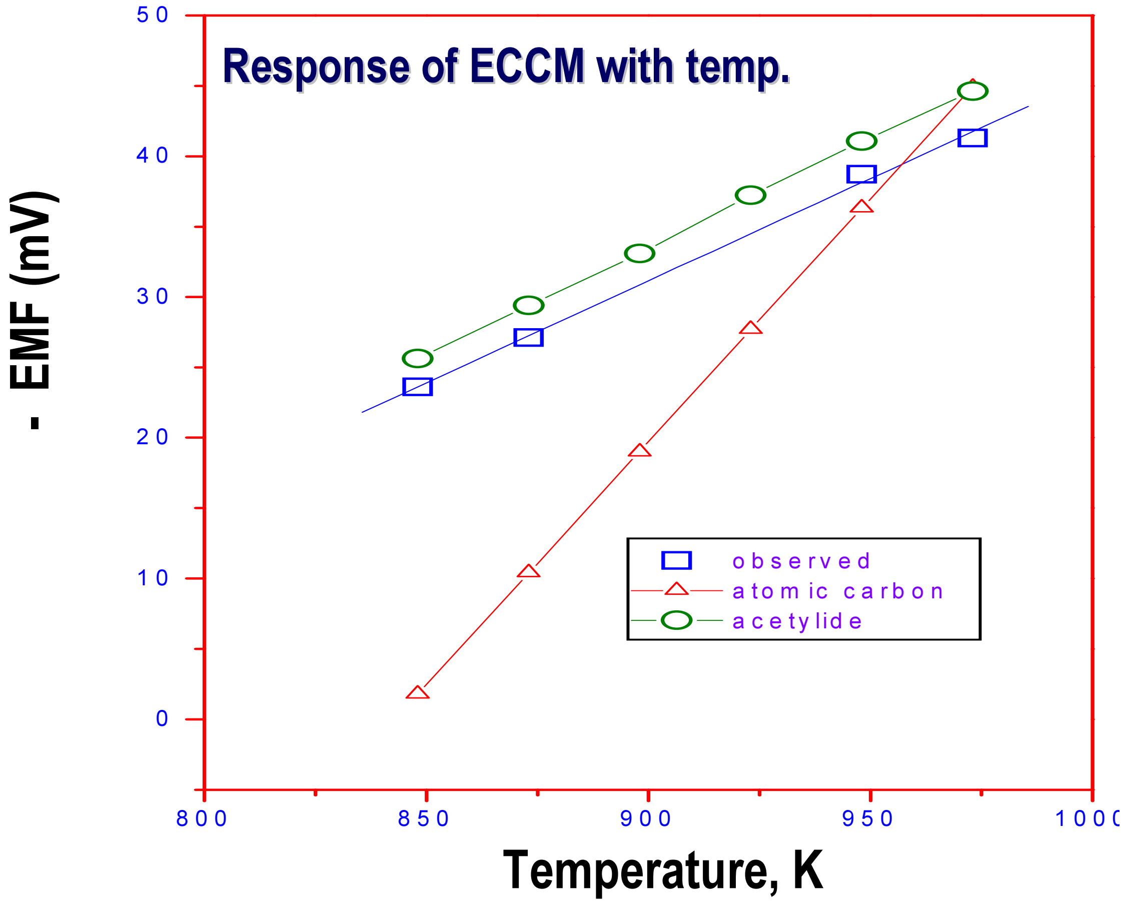
(S.Rajan Babu, R.Ranganathan, P.R.Reshmi, T. Gnanasekaran & G. Periaswami, Unpublished results)

Correlation of emf output with the species present in sodium

$$C + 3O^{2-} \Leftrightarrow CO_3^{2-} + 4e^-$$

$$CO_3^{2-} + 4e^- \Leftrightarrow C + 3O^{2-}$$

$$C_{ref} \Rightarrow C_{sple}$$



$$2Na + 2C \Leftrightarrow Na_2C_2$$

$$K = [a_{acet}] / [a_c]^2$$

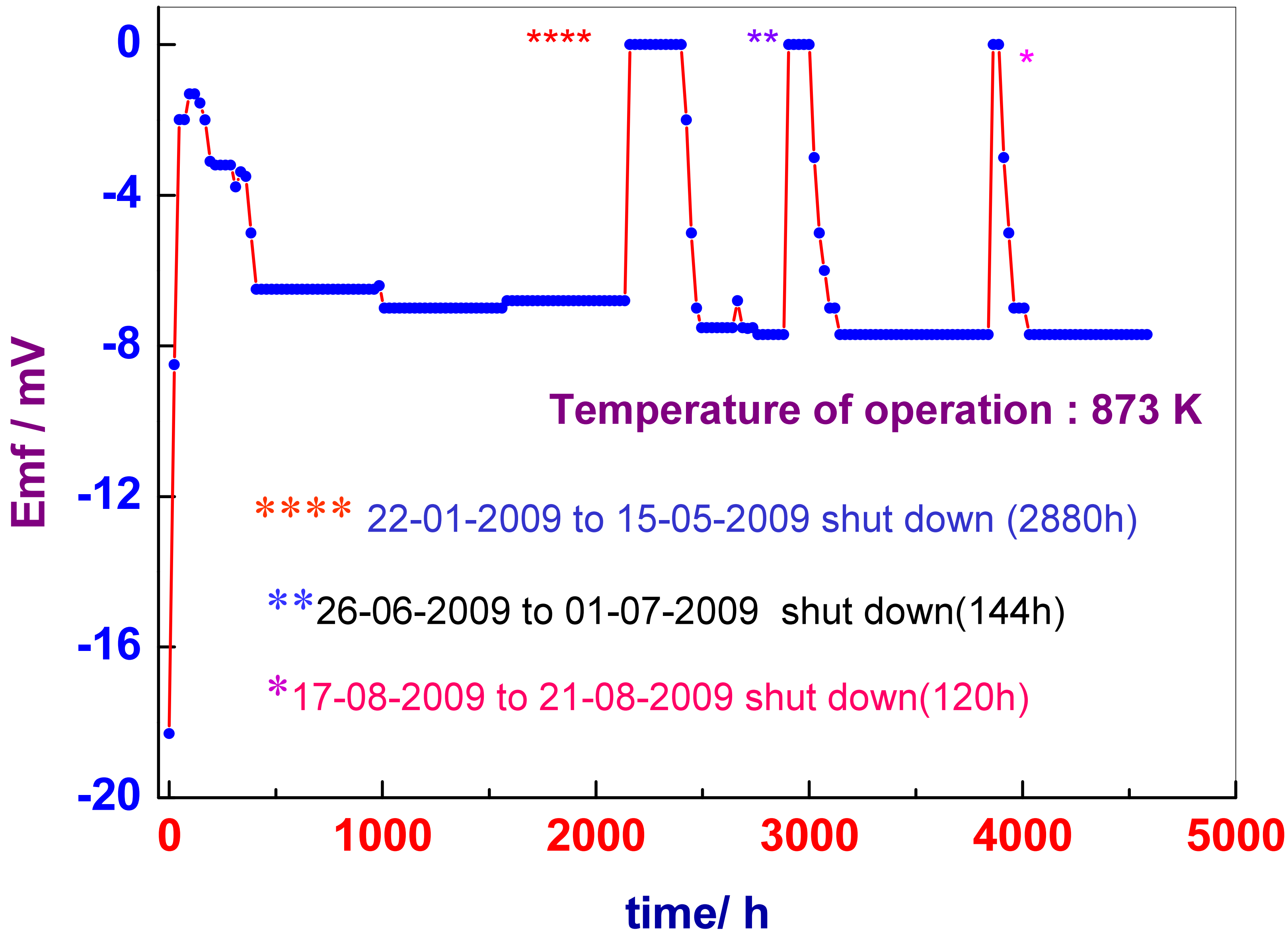
$$a_C \; \alpha \; \sqrt{[a_{acet}]}$$

$$\alpha \; \sqrt{[C/2] / [C_2^{2-}]^{sol}}$$

$$E = -[RT/2F] \ln a_c$$

Indicates the presence of carbon as acetylide in molten sodium

Chronoamperometric studies → Diffusion of carbon through iron dictates the response



Response of electrochemical carbon sensor
during operations in BiMetallic (BIM) loop

Yttria Doped Thoria (YDT) based Oxygen Sensor for liquid sodium

Source of oxygen

Steam leak
Sorbed moisture

Electrochemical concentration cell

W, In/In_2O_3 | YDT | $[O]_{Na}$

Requirements (for use in liquid sodium)

High density YDT bodies
Better mechanical strength
Helium leak rate $\leq 10^{-9}$ std. l / s

Conventional Method high sintering temperatures

Poor mechanical strengths
(Unpredictable life-time)

Novel Combustion Synthesis

Mixing of fuel and aqueous metal nitrates (clear solution)
↓
Evaporation at 90-95°C
↓
Transparent colourless gel
↓
Drying at 140-150°C
↓
Polymer precursor
↓
Combustion below Ignition temperature, T_g (about 20-30°C < T_g)
↓
Calcination in air 700°C / 2 h
↓
YDT powders
← Sintering
Products

Features

Simple and fast
Economic and a low temperature process
Scale-up

Advantage !!

(Rajesh Ganesan, S.Vivekanandhan, T.Gnanasekaran, G.Periaswami & Raman S.Srinivasa, J. Nucl. Mater 325 (2004) 134)

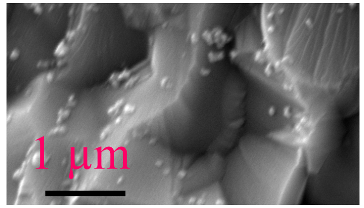
Scaled-up operation for device fabrication

~ 3 kg of electrolytic grade nanocrystalline YDT powders prepared

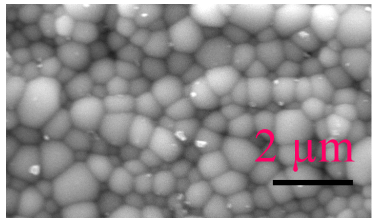
Sintering Studies

Condition	Sintering Temp. (K)	Theoretical density (%TD)	Helium leak rate (std.l/s)
YDT (no binder& sintering aid)	1798, 1873 & 1923	< 90	$>10^{-6}$
YDT (PVA binder)	1798, 1873 & 1923	<90	$>10^{-6}$
YDT (ZnO as sintering aid)	1798 & 1873	<90	$>10^{-6}$
YDT (ZnO as sintering aid)	1923	94 – 98	$\sim10^{-9}$ - 10^{-10}

Fractured

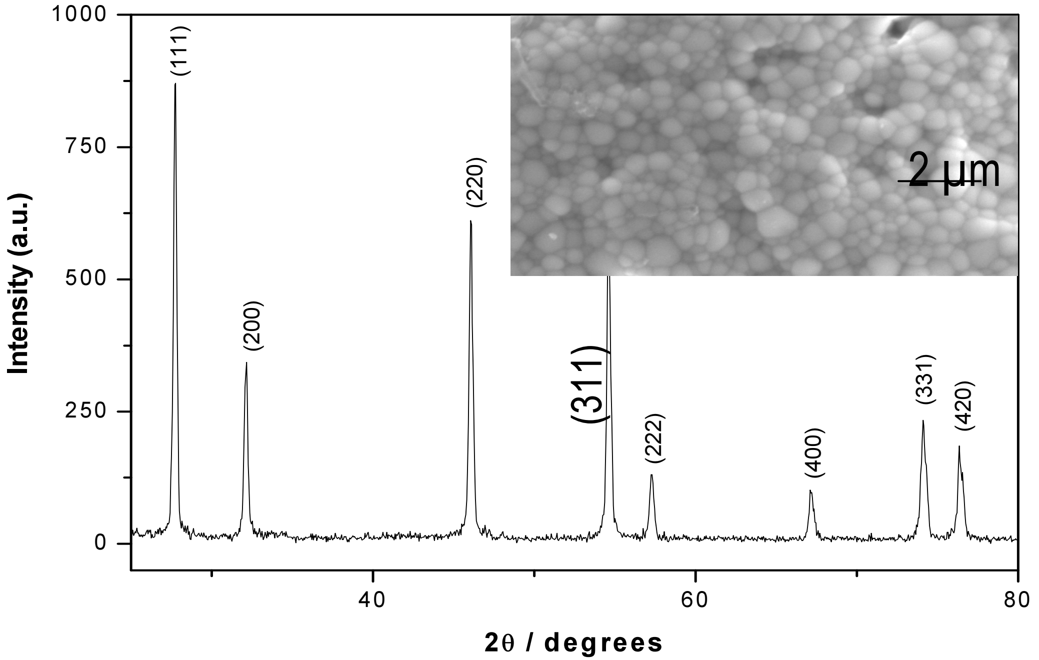


Surface



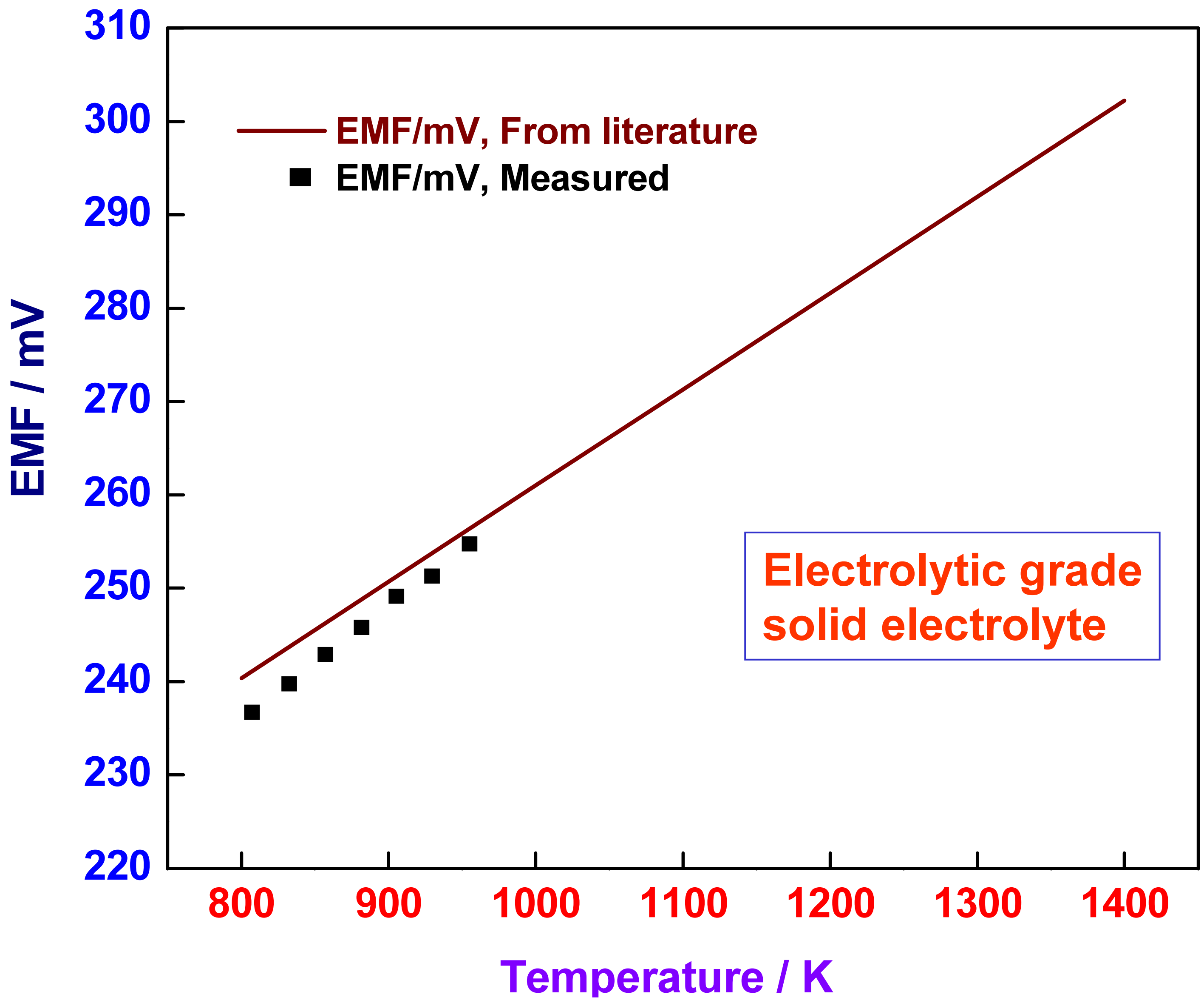
(V. Jayaraman, D. Krishnamurthy, Rajesh Ganesan, A. Thiruvengadasami, R. Sudha, M.V.R. Prasad and T. Gnanasekaran, Ionics 13 (2007) 299 – 303)

Compatibility Studies in Sodium



YDT sample (sintered at 1923 K) retrieved after equilibration in liquid sodium for 1000 h at 773 K

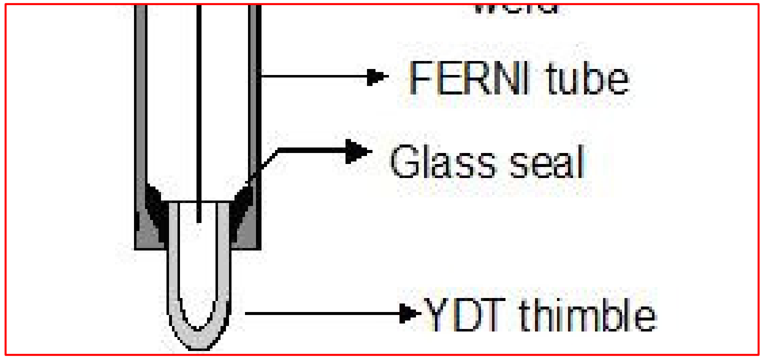
compatible in liquid sodium !!



EMF output from cell of configuration Pt, Ni/NiO|YDT|Fe/FeO, Pt as a function of temperature and its comparison with theoretical output

Fabrication of Sensor

Proposed Scheme



Small thimbles instead of longer tubes

Thermal gradient across

- ❖ **Optimization of machining thimbles and sintering to high density #**
- ❖ **Preparation of suitable glass solder and FERNI alloy**
- ❖ **Optimization of soldering FERNI alloy with YDT thimbles #**

in collaboration with Central Glass & Ceramics Research Institute, Kolkata

Assembly of Sensor

FERNI portion after welding with SS pipe

Glass-soldered YDT thimble with FERNI

A view of complete sensor assembly

Sensor assembled and under testing in liquid sodium
W, In/In_2O_3 | YDT | $[O]_{Na}$, SS

Conclusions

In-sodium applications

- *Electrochemical hydrogen sensor*

  Tested in large sodium facilities & FBTR
  Implementation in PFBR

- *Electrochemical carbon sensor*

  Tested in large sodium facilities & FBTR

- *Electrochemical oxygen sensor*

  Tests in lab in progress
  Tests in large sodium facilities planned

Argon cover gas applications

- *TCD based sensor system*

  Tested in large sodium facilities & FBTR
  Implementation in PFBR

- *Semiconducting oxide based sensor system*

  Tested in large sodium facilities

Contributors

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