

Solubility and Diffusivity of Oxygen in molten lead –bismuth eutectic alloy (44.5 % Pb – 55.5% Bi)

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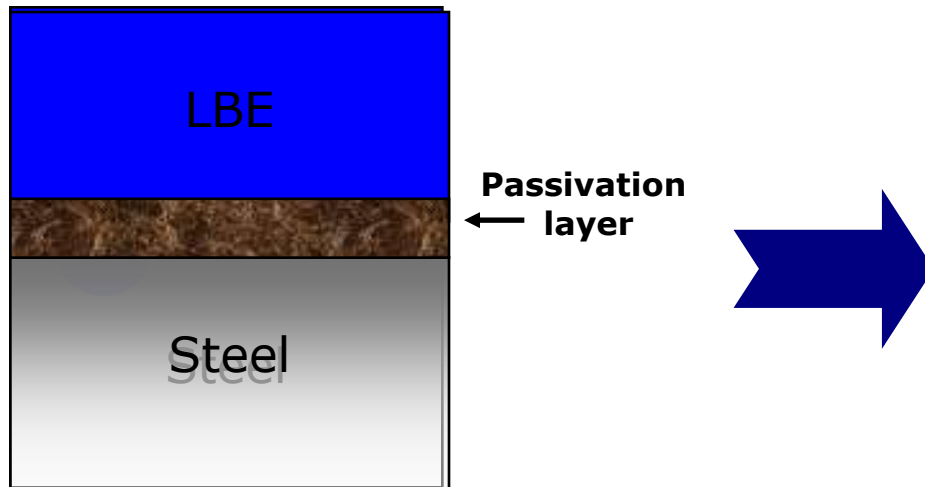
OUTLINE

- ◆ Introduction
- ◆ Experimental
- ◆ Results
 - Oxygen solubility
 - Oxygen diffusivity
- ◆ Conclusions

ADS reactors proposed coolant:

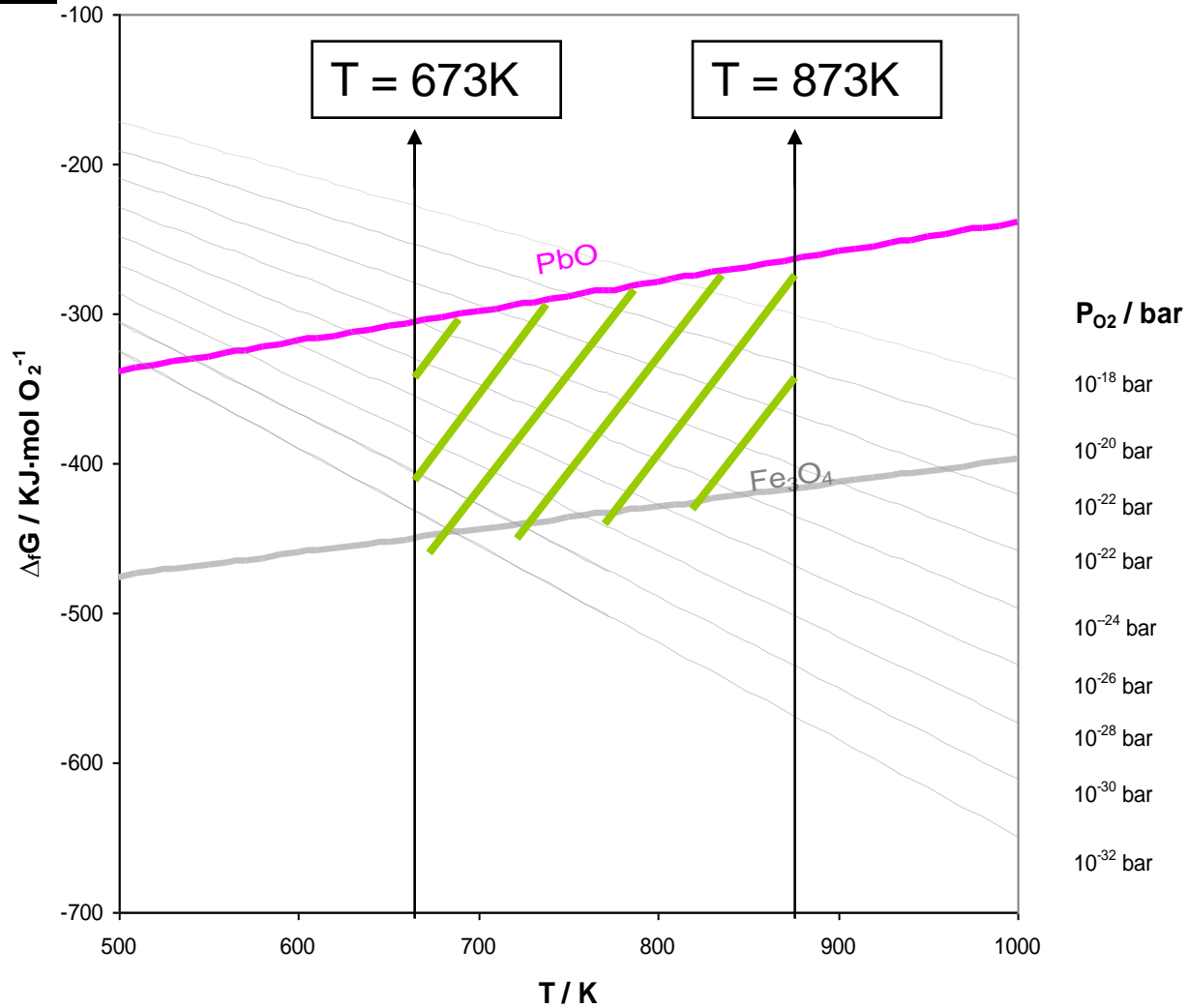
Lead –bismuth eutectic alloy (44.5 % Pb – 55.5% Bi)

Corrosion of steels in systems using molten LBE



Control and monitoring
 of oxygen content in LBE

Oxygen control



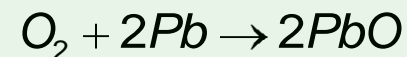
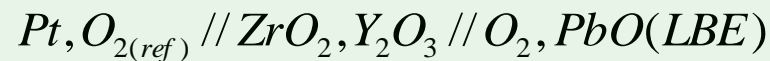
Theoretical

- ▶ Electrochemical cell of the sensor:



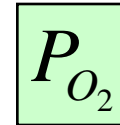
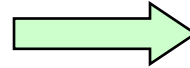
$$\Delta E_{SENSOR} = \frac{RT}{4F} \ln \frac{P_{O_2,RE}}{P_{O_2,SE}}$$

Oxygen saturation conditions

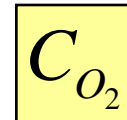
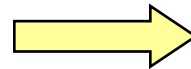


$$\Delta E = \frac{RT}{4F} \ln \frac{P_{O_2,RE}}{P_{O_2,SE} a_{Pb}^2}$$

Electrochemical data



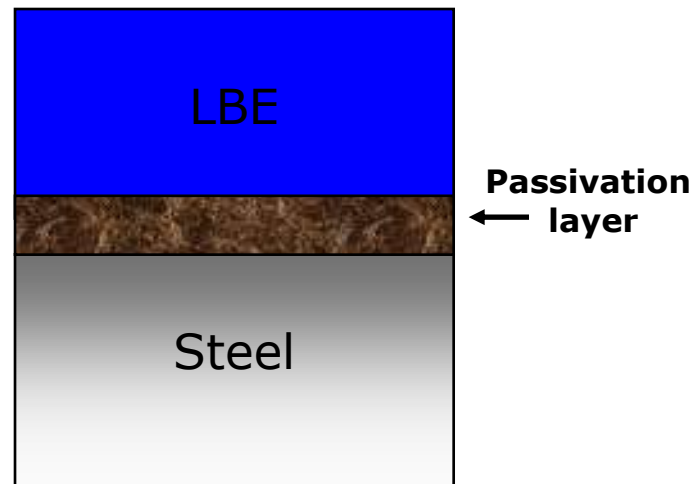
Concentration results



**Oxygen dosification system:
O₂ coulometric pump**

Oxygen diffusion

- ▶ The time scale of the oxygen control process is determined among other factors by the diffusivity of oxygen in liquid metal





Goals

- ◆ Determination of oxygen solubility in LBE from 460°C, to 540°C
- ◆ Determination of oxygen diffusivity in LBE from 460°C, to 540°C

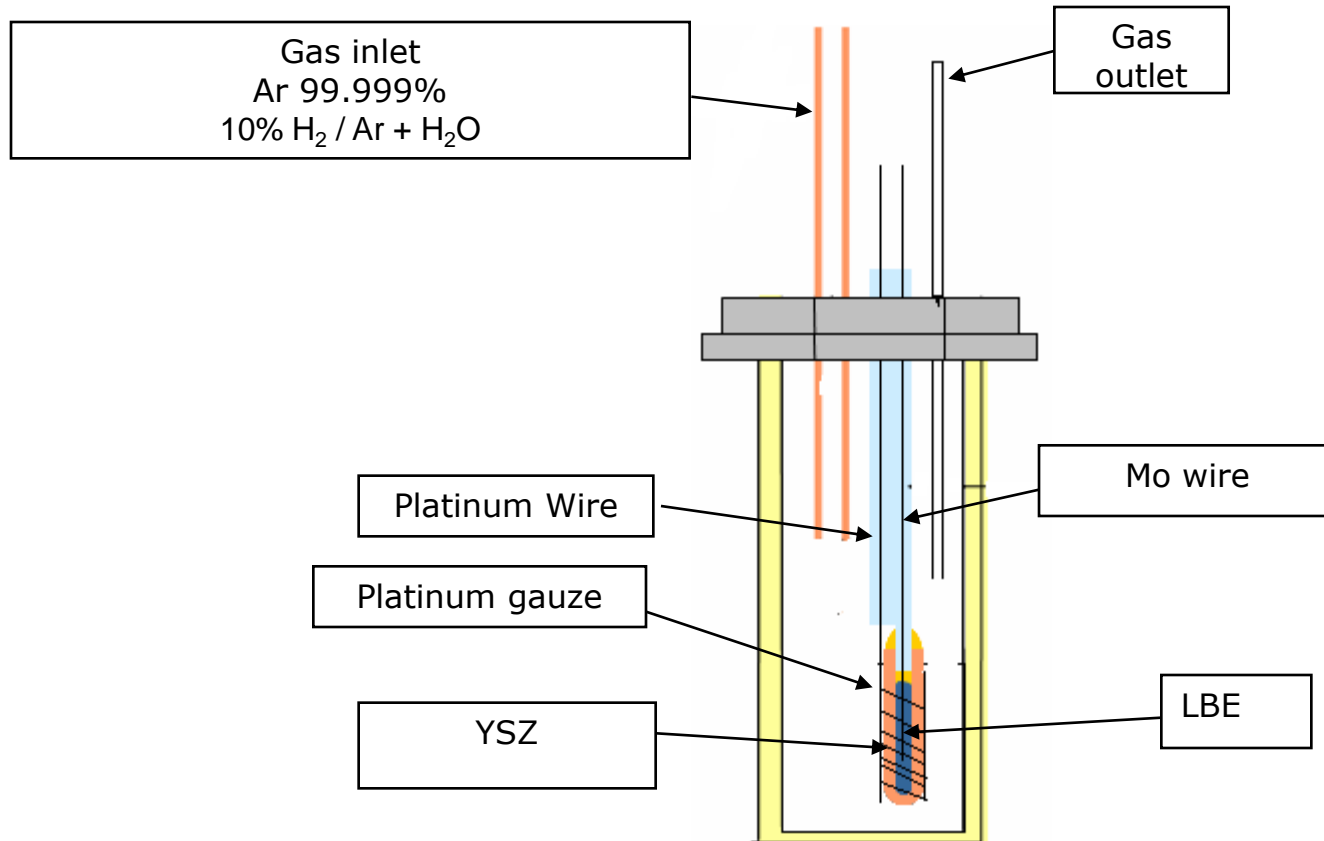


Goals

- ◆ Determination of oxygen solubility in LBE from 460°C, to 540°C
- ◆ Determination of oxygen diffusivity in LBE from 460°C, to 540°C

Experimental setup: Coulometric Oxygen Pump

- Based on Pt / gas sensor





Where:

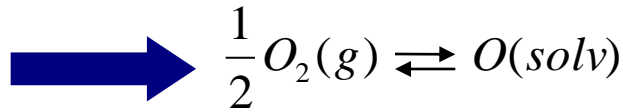
γ_O^0 = activity coefficient of oxygen in LBE

x_O = molar fraction of oxygen in LBE

n_O^i = initial number of oxygen moles

n_O^f = final number of oxygen moles

$$n_O^f - n_O^i = \frac{Q_{ion}}{2 \cdot F}$$



$$E = -\frac{R \cdot T}{2 \cdot F} \ln \left(\frac{a_O}{P_{O_2,ref}^{1/2}} \right) = -\frac{R \cdot T}{2 \cdot F} \ln \left(\frac{\gamma_O^0 \cdot x_O}{P_{O_2,ref}^{1/2}} \right)$$

$$a_O = \gamma_O^0 \cdot x_O$$

$$Q_{ion} = \int_0^t I_{ion} dt$$

E sen

Where:

F = Faraday constant

T = temperature (K)

R = 8.31 (J/mol·K)

a_O = oxygen activity

$P_{O_2,ref}$ = oxygen pressure in the reference electrode (bar)

Where

$$n_O^f - n_O^i = \frac{1}{\gamma_O^0} \frac{M_{atomic}}{W_m} \left(e^{\frac{-2 \cdot F \cdot E_f}{R \cdot T}} - e^{\frac{-2 \cdot F \cdot E}{R \cdot T}} \right) \cdot P_{O_2,ref}^{-1/2}$$

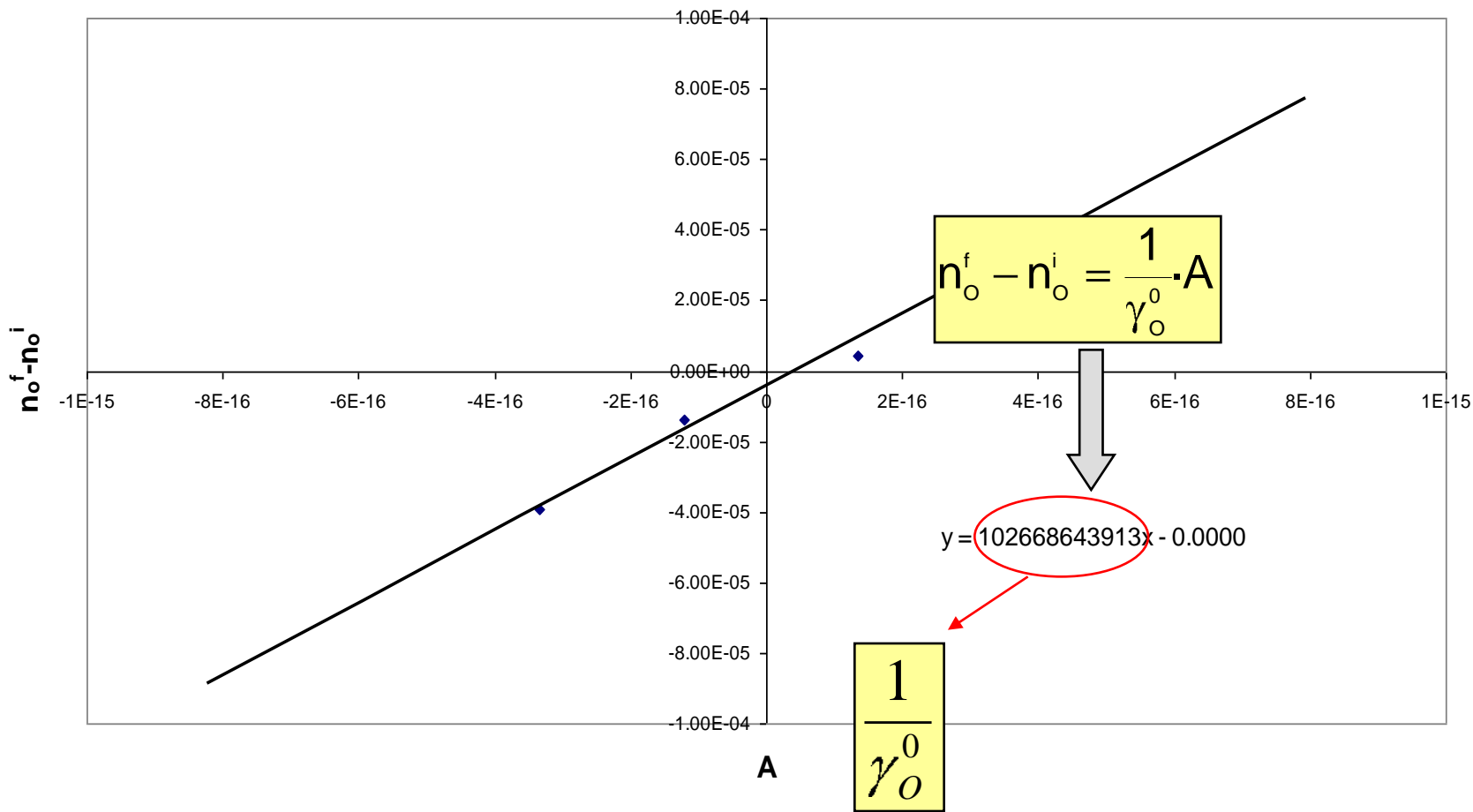
A

$$x_O = \frac{1}{\gamma_O^0} \cdot P_{O_2,ref}^{-1/2} \cdot \left(e^{\frac{-2 \cdot F \cdot E}{R \cdot T}} - e^{\frac{-2 \cdot F \cdot E_f}{R \cdot T}} \right)$$

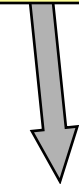
Experimental conditions

- T = 460 °C, 500°C and 540°C
- 8 g LBE
- Reference system Pt / Ar 99.999%
 Pt /10% H₂ / Ar + H₂O
- Oxygen removal / entrance by electrochemical current between Pt and LBE.

T = 460°C



$$\frac{1}{\gamma_O^0} = 1.03 \cdot 10^{11}$$



$$x_{sat} \equiv \frac{1}{\gamma_O^0} \cdot p_{O_2,ref} \cdot \frac{T}{2} \cdot \left(e^{\frac{-2 \cdot F \cdot E_{sat}}{RT}} \right)$$

$$E_{sat} = -0.085V$$



$$x_{sat} = 1.2 \cdot 10^{-6}$$

Oxygen solubility in LBE at 460°C is $1.2 \cdot 10^{-4}$ atomic %.



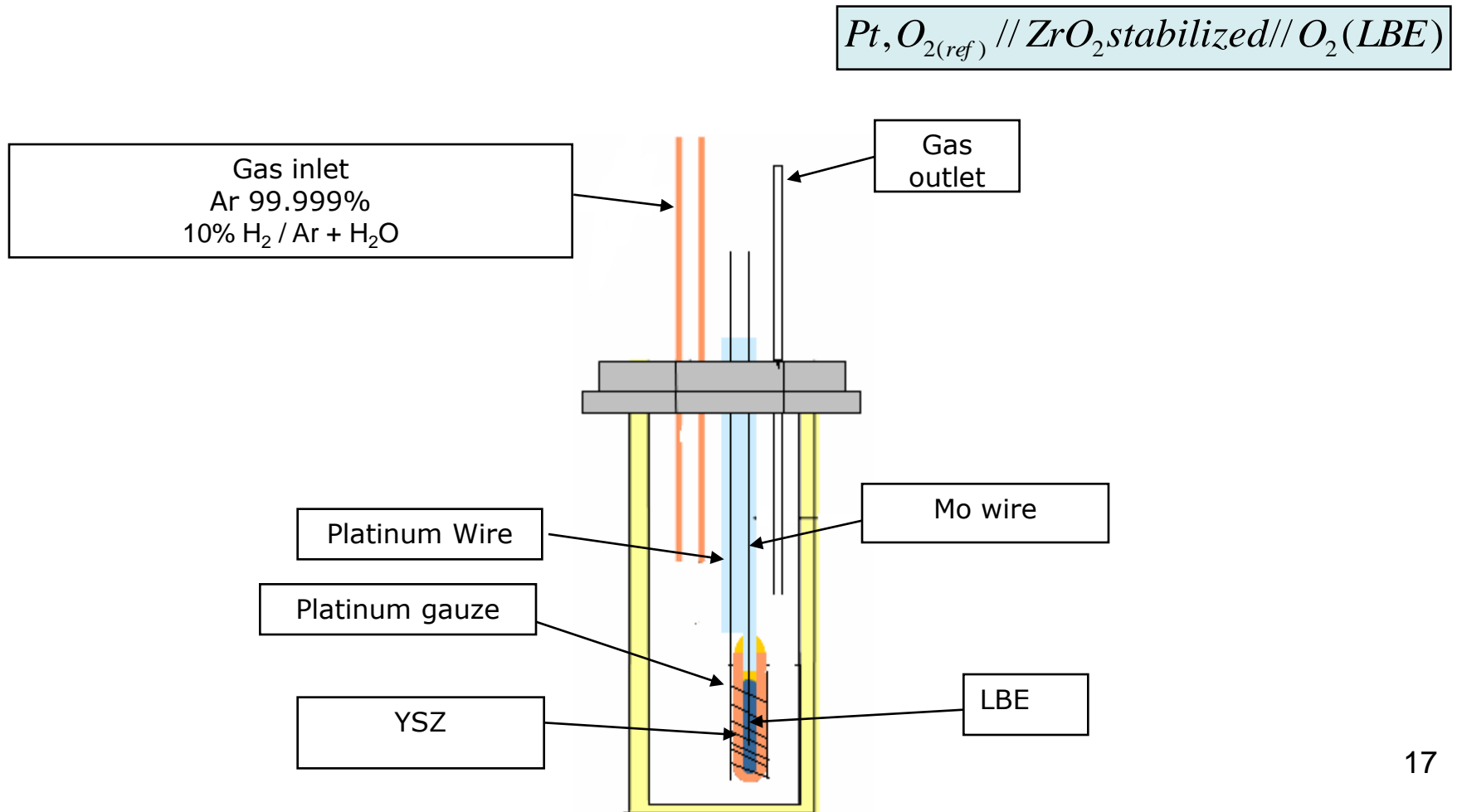
Temperature /°C	X_o	Atomic %
460	$1.2 \cdot 10^{-6}$	$1.2 \cdot 10^{-4}$
500	$1.6 \cdot 10^{-6}$	$1.6 \cdot 10^{-4}$
540	$2.1 \cdot 10^{-6}$	$2.1 \cdot 10^{-4}$



Goals

- ◆ Determination of oxygen solubility in LBE from 460°C, to 540°C
- ◆ Determination of oxygen diffusivity in LBE from 460°C, to 540°C

■ Experimental set-up for oxygen diffusivity studies in LBE



Fick's second law
 (cylindrical electrode)

$$\frac{dC_o}{dt} = \frac{1}{r} \frac{d}{dr} \left(r D_o \frac{dC_o}{dr} \right)$$

Where:

D_o = Diffusion coefficient of oxygen (cm²/s)

C_o = Oxygen concentration (mol/cm³)

r = radius of zirconia tube (cm)

Boundary conditions:

At $t = 0$ and $0 < r < a$ $C_o(r, 0) = C_o$ (1)

At $t > 0$ and $r = a$ $C_o(a, t) = C_o$ (2)

Where:

D_o = Diffusion coefficient of oxygen (cm²/s)

C_o = Oxygen concentration (mol/cm³)

r = radius of zirconia tube (cm)

λ_n = Bessel function root of zero order

Solution:

$$\frac{n_o^f - n_o^i}{V}$$

$$\frac{C_o(1) - C_o(r, t)}{C_o(1) - C_o(2)} = 1 - \sum_{n=1}^{\infty} \frac{4}{\lambda_n^2} e^{-\frac{D_o \cdot \lambda_n^2 \cdot t}{a^2}}$$

$$n_o^f - n_o^i = \frac{Q_{ion}}{2 \cdot F}$$

$$V = \pi a^2 h$$

Where:

Q_{ion} = Electrical charge produced by I_{ion}

F = Faraday constant

n_o^i = initial number of oxygen moles

n_o^f = final number of oxygen moles

Where:

V = Volume (cm³)

a = radius of zirconia tube (cm)

h = height of the liquid LBE in the zirconia tube (cm)

Where:

D_o = Diffusion coefficient of oxygen (cm²/s)

F = Faraday constant

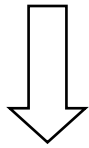
C_o = Oxygen concentration (mol/cm³)

r = radius of zirconia tube (cm)

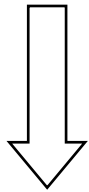
h = height of liquid LBE in the zirconia tube (cm)

λ_n = Bessel function root of zero order

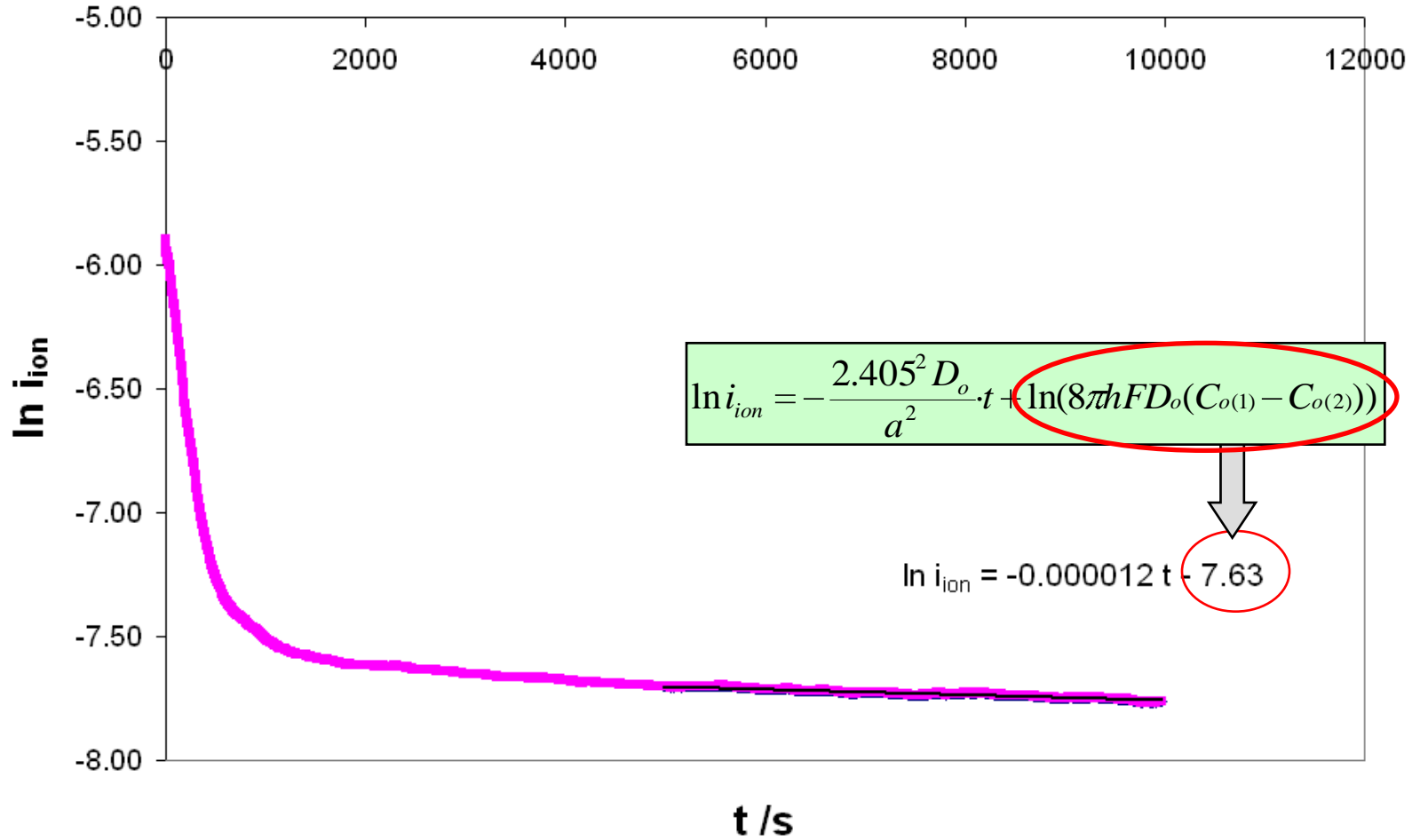
$$\frac{(1/2F) \int_0^1 i_{ion} dt}{\pi a^2 h \cdot (C_o(1) - C_o(2))} = 1 - \sum_{n=1}^{\infty} \frac{4}{\lambda_n^2} e^{-\frac{D_o \cdot \lambda_n^2 \cdot t}{a^2}}$$



$$i_{ion} = 8\pi h D_o (C_o(1) - C_o(2)) e^{-\frac{2.405^2 D_o \cdot t}{a^2}}$$



$$\ln i_{ion} = -\frac{2.405^2 D_o}{a^2} t + \ln(8\pi h F D_o (C_o(1) - C_o(2)))$$





Temperature /°C	$D_o / \text{cm}^2 \cdot \text{s}^{-1}$
460	$1.2 \cdot 10^{-6}$
500	$1.7 \cdot 10^{-6}$
540	$1.2 \cdot 10^{-6}$

CONCLUSIONS

- ◆ A coulometric oxygen pump capable of removing or adding oxygen to LBE has been developed, and it is a key device for determining oxygen solubility and diffusivity in LBE
- ◆ Oxygen solubility in LBE at temperature range studied change from $1.2 \cdot 10^{-4}$ to $2.1 \cdot 10^{-4}$ atomic %.
- ◆ Oxygen diffusivity results are around $1.5 \cdot 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$. It can be seen that oxygen diffusivity doesn't change significantly at this range of temperatures.



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ACKNOWLEDGMENTS

This work was supported by:

-European Union under contracts:

FI6W-CT-2004-516520 (IPEUROTRANS VIth Framework Program)

036469 VELLA Project

- Spanish Ministry of Education and Science (MEC) under contract ENE 2005-08611-CO2-O2, and fellowship BES – 2006-14034

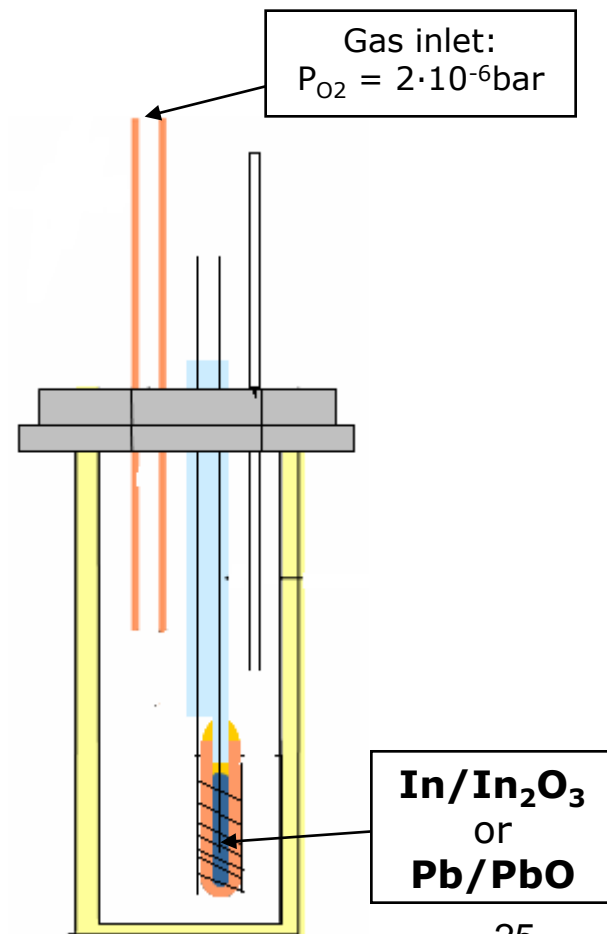
■ Calibration of the experimental design:

- ✓ In / In₂O₃
- ✓ Pb / PbO

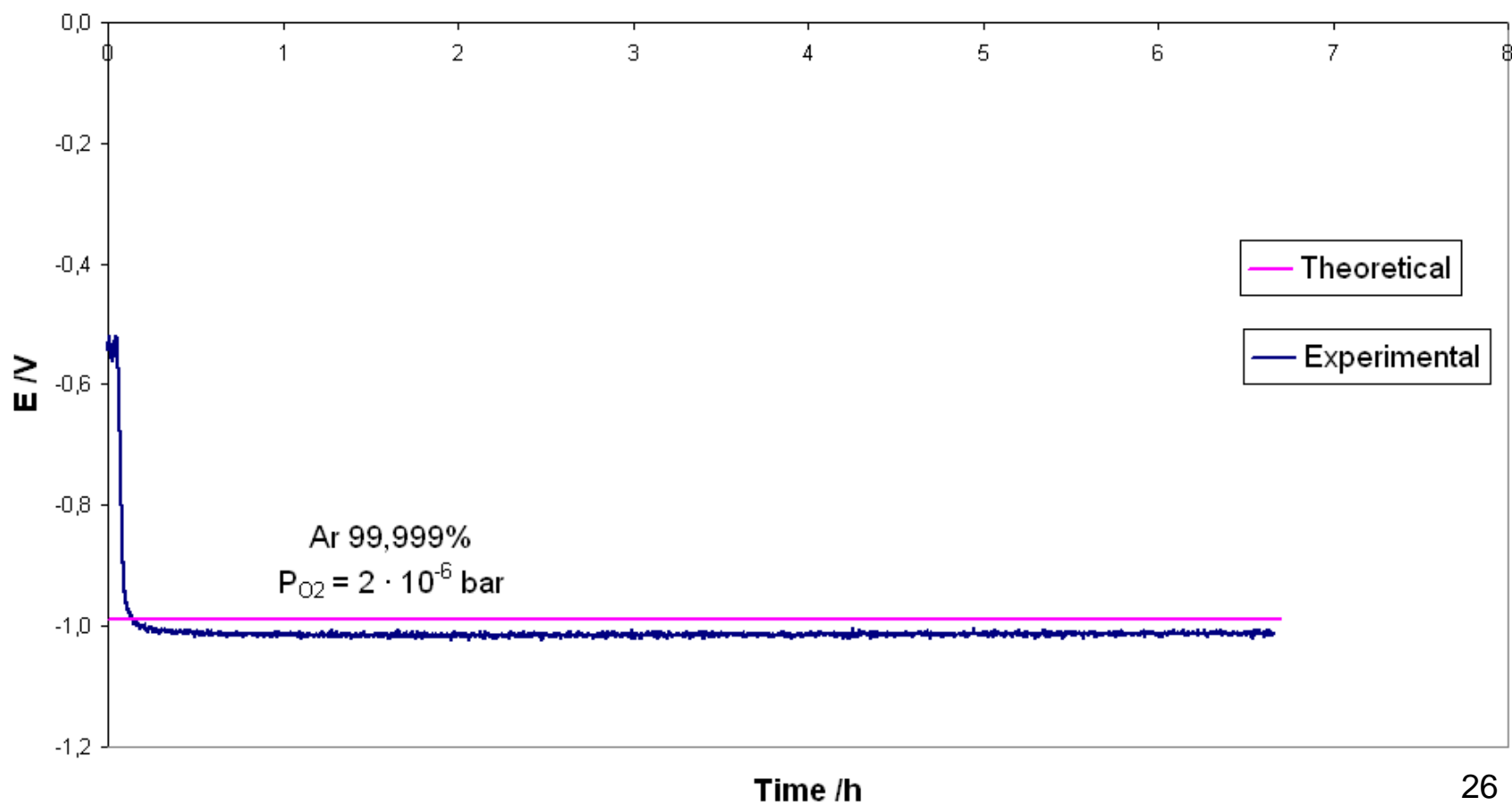
$$\Delta E_{SENSOR} = \frac{RT}{4F} \ln \frac{P_{O_2, Me/MeO}}{P_{O_2, Pt}}$$



**Good agreement between
 $\Delta E_{\text{experimental}}$ and $\Delta E_{\text{calculated}}$**



In/In₂O₃ sensor



Pb/PbO sensor

