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Challenges in the control of metallic didymium production towards reducing greenhouse gas emissions

João Batista Ferreira Neto
Andre Luis Nunis da Silva
Celia Aparecida Lino dos Santos
João Ricardo Filipini da Silveira
Maciel Santos Luz
Fernando José Gomes Landgraf

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Instituto de Pesquisas Tecnológicas do Estado de São Paulo
S/A - IPT
Av. Prof. Almeida Prado, 532 | Cidade Universitária ou
Caixa Postal 0141 | CEP 01064-970
São Paulo | SP | Brasil | CEP 05508-901
Tel 11 3767 4374/4000 | Fax 11 3767-4099

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Challenges in the control of metallic didymium production towards reducing greenhouse gas emissions

J. B. Ferreira Neto[1], A. L. N Silva[1], C. A. L. Santos[1], J. R. F. Silveira[1], M. S. Luz[1] and F. J. G. Landgraf[1]

[1] Institute for Technology Research of Sao Paulo State - IPT, Brazil

OUTLINE

- RE Initiatives in Brazil
- Electrolytic reduction of Neodymium/Didymium oxide
- PFC gas emissions during Nd/Pr reduction
- Controlling of PFC gas emissions
- Conclusions

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China is responsible for almost 90% of the world's REE production

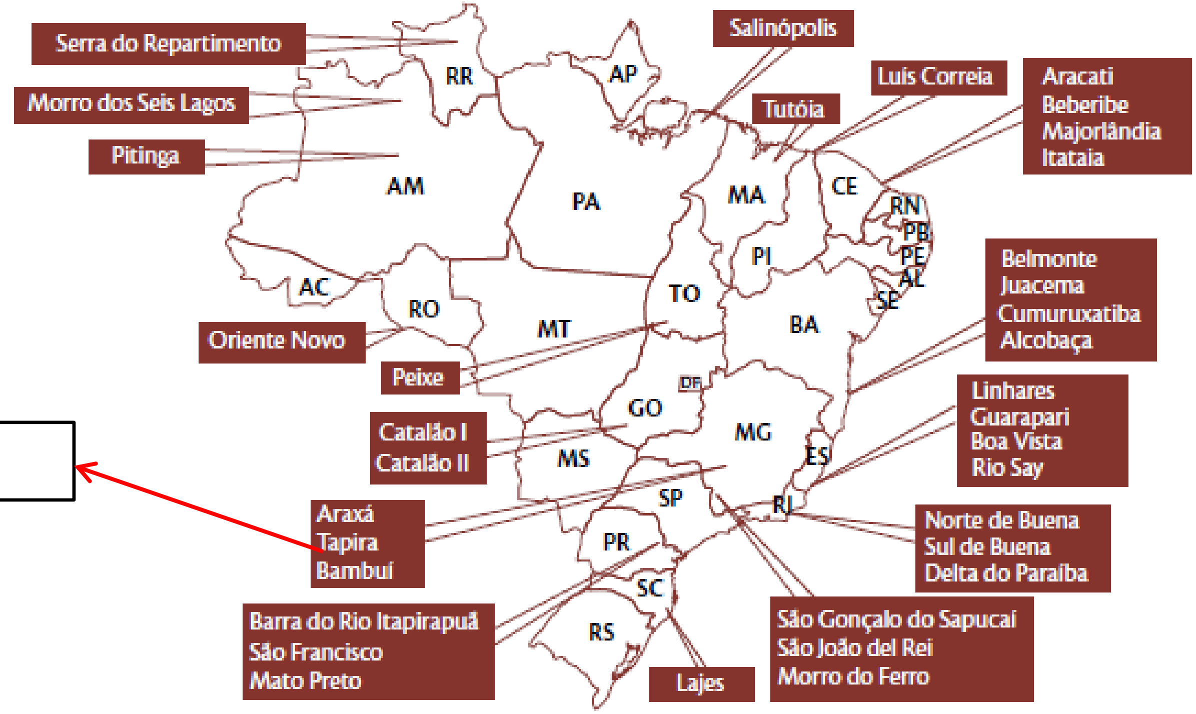
World Reserves of RE

	Mine production[e] 2014	2015	Reserves[5]
United States	5,400	4,100	1,800,000
Australia	8,000	10,000	[6]3,200,000
Brazil	—	—	22,000,000
China[7]	105,000	105,000	55,000,000
India	NA[8]	NA[8]	3,100,000
Malaysia	240	200	30,000
Russia	2,500	2,500	([9])
Thailand[10]	2,100	2,000	NA
Other countries	NA	NA	41,000,000
World total (rounded)	123,000	124,000	130,000,000

Fonte: U.S. Geological Survey, Mineral Commodity Summaries, January 2016

RE Oxide basis

Most important RE ore deposits in Brazil



Fonte: MCTI, apresentação no CT-Mineral (2010).

Tailings of Nb ore extraction - CBMM

Mineral	%
Bariopyrochlore	**4**
Limonite, goethite	36
Barite	20
Magnetite	16
Gorceixite	6
Monazite	**4**
Ilmenite	5
Quartz	4
Others	5
Total	100

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CBMM invested ~US$ 20 million:

- **Concentration plant (3.000 t/y)**
- **Solvent Extraction Plant (~3 t/y)**
  - **Lanthanum Oxide**
  - **Cerium Oxide**
  - **Heavy RE oxides**
  - **Didymium Oxide (Nd, Pr)**

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(Nd,Pr)-Fe-B magnets production

Ore
↓
Concentrate
↓
Oxide

→ CBMM

↓

Metal (Nd,Pr)

→ **CBMM/IPT project**
Electrowinning
$(Nd,Pr)_2O_3$

↓

Alloy
↓
Powder
↓
Sintering/magnet

→ Knowledge at universities and research institutes

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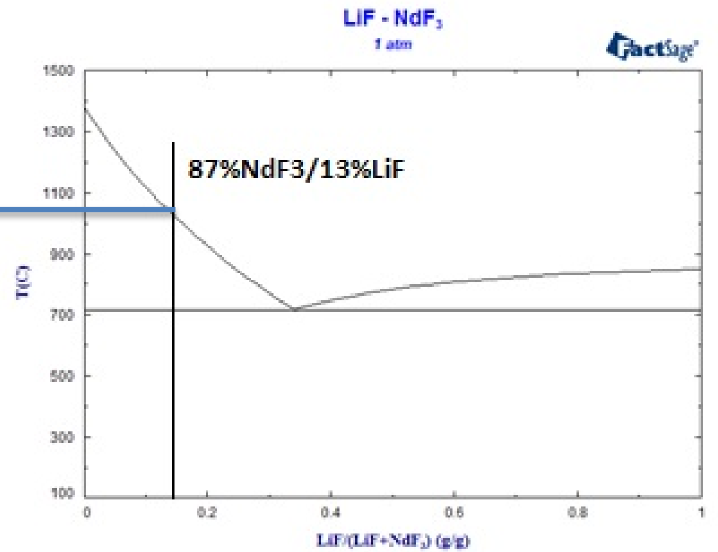
Electrolytic reduction of (Nd,Pr) oxide

- Electrolyte: Fluoride molten salt:
  - low melting temperature (close to the Nd melting point: 1024° C);

1020° C



  - high thermodynamic stability;
  - high ionic conductivity
  - low viscosity
  - low vapour pressure

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Electrolytic reduction of (Nd,Pr) oxide

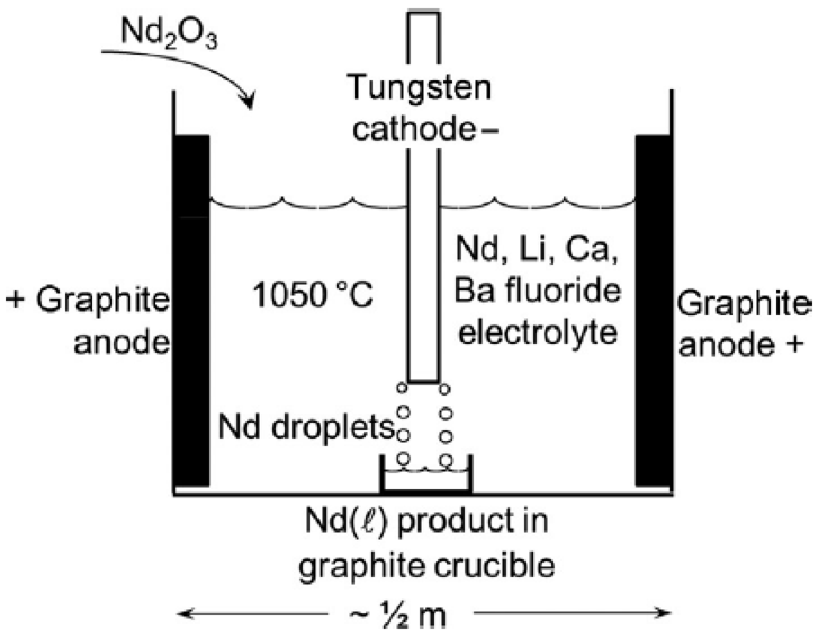
- Electrolyte: Fluoride molten salt:
  - NdF_3 increases the Nd_2O_3 solubility in LiF
    - Limited solubility: max ~4% Nd_2O_3 in 13%LiF-87%NdF_3

X

~8% Al_2O_3 in fluoride molten salt (Hall Heroult)

Narrower operational window

Electrolytic reduction of (Nd,Pr) oxide



Chinese industrial cells (3 kA):

- Cell Voltage: 9 -11 V
- Current efficiency: 65 – 78%
- Anode current density: 1 – 1,25 A/cm^2
- Cathode current density: 5,5 – 6,5 A/cm^2
- Power consumption: 11 – 13 kWh/kg Nd
- Nd yield: 95%
- Nd production: 1,7 – 2,3 t/month

$Nd_2O_3 + 3\ C = 2\ Nd + 3\ CO$

$Nd_2O_3 + 1.5\ C = 2\ Nd + 1.5\ CO_2$

Anodic: $3\ [NdOF_5]^{4-} - 6e^- = 3/2\ O_2 + 3\ Nd^{3+} + 15\ F^-$

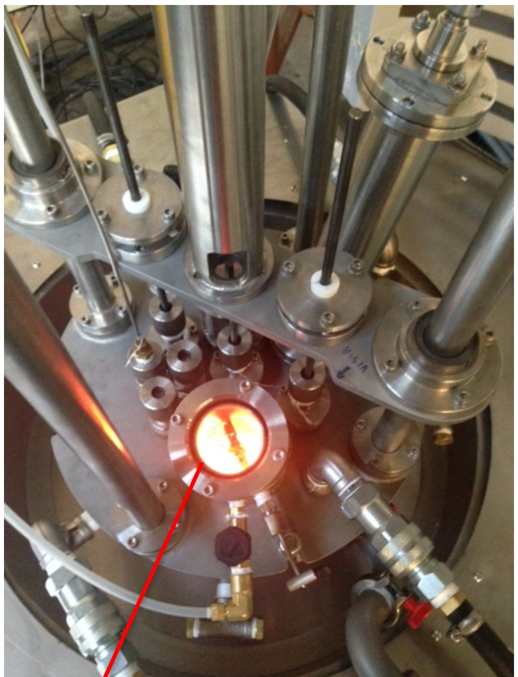
Cathodic: $2\ [NdF_6]^{3-} + 6\ e^- = 2\ Nd + 12\ F^-$

Electrolytic reduction of (Nd,Pr) oxide

Oxide Feeding System

Cathode

TC



Window View

Anode support

Crucible

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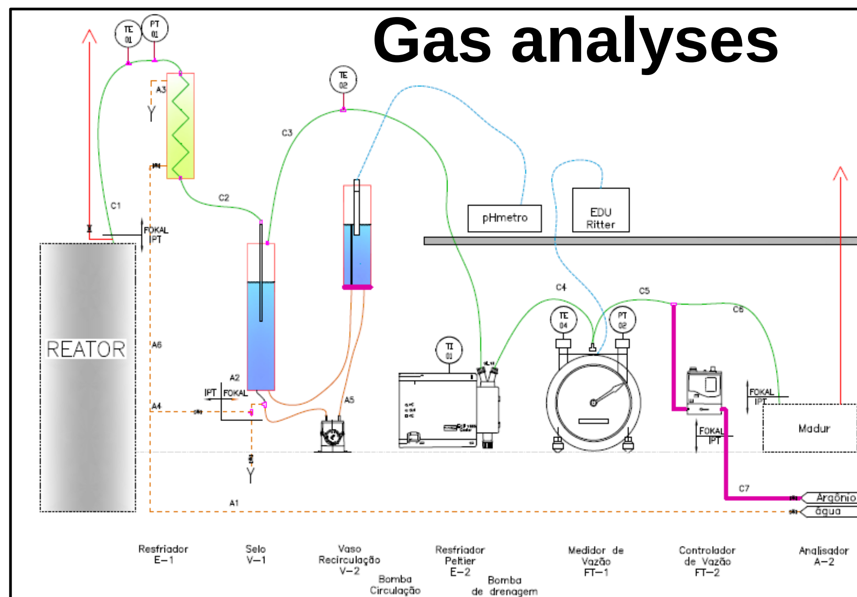
Electrolysis

Experimental conditions:

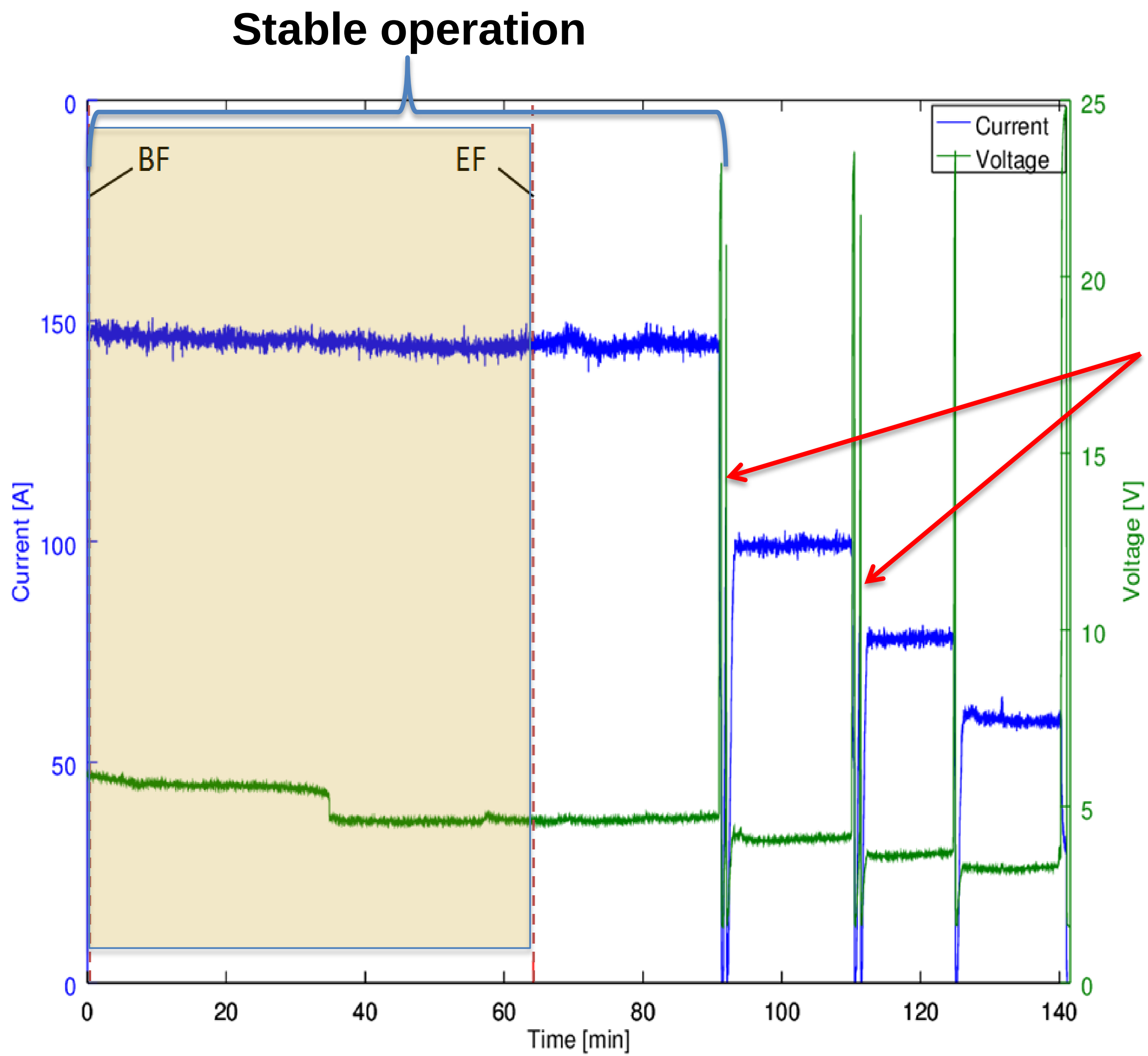
- 14 -19 kg $LiF-REF_3$ (RE=Pr, Nd)
- T = 1020 - 1050 ° C
- Didymium oxide: 400-900 g
- I = 80-150 A; V = 3,5 – 5 V
- Current density:

  - Anode: 0,3-0,5 A/cm^2

  - Cathode: 4-6 A/cm^2



Electrolysis



Feeding rate control = Electrolytic process control

Electrolysis

Didymium

Typical chemical composition of Didymium produced by electrolytic reduction in molten salt determined by ICP-MS

Elements	LiF - REF3 (% w)
Al	<0.001
Mg	<0.001
Ca	<0.001
Si	<0.05
Pr	25-40
Nd	60-75
O	0.002
C	0.05
REE	<0.1

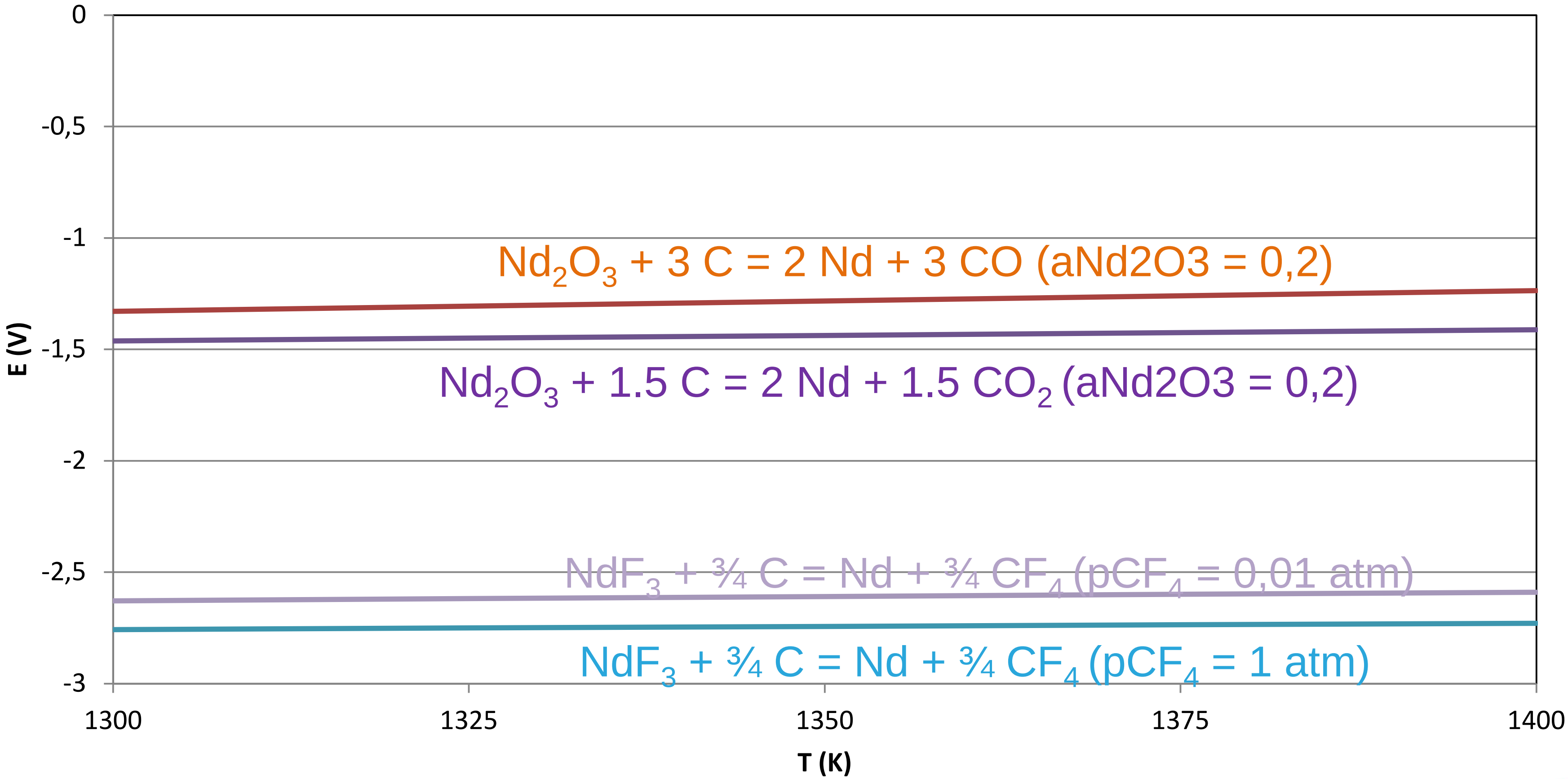
- Gas generated: 0.18 to 0.3 kg of CO_2 (COeq + CO_2)/kg of Didymium
- CO/CO_2 ratio = 3-4
- Current Efficiency up to 70 %

PFC gas emissions during Nd,Pr electrowinning

a A + b B = c C + d D

$E = E° - RT/nF \ln [(aC^c * aD^d)/(aA^a * aB^b)]$

$E° = -\Delta G° /nF$



aNdF3 = 0,38 (87%NdF3-13%LiF); pCO = 0,7 atm and pCO_2 = 0,3 atm

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PFC gas emissions during Nd,Pr electrowinning

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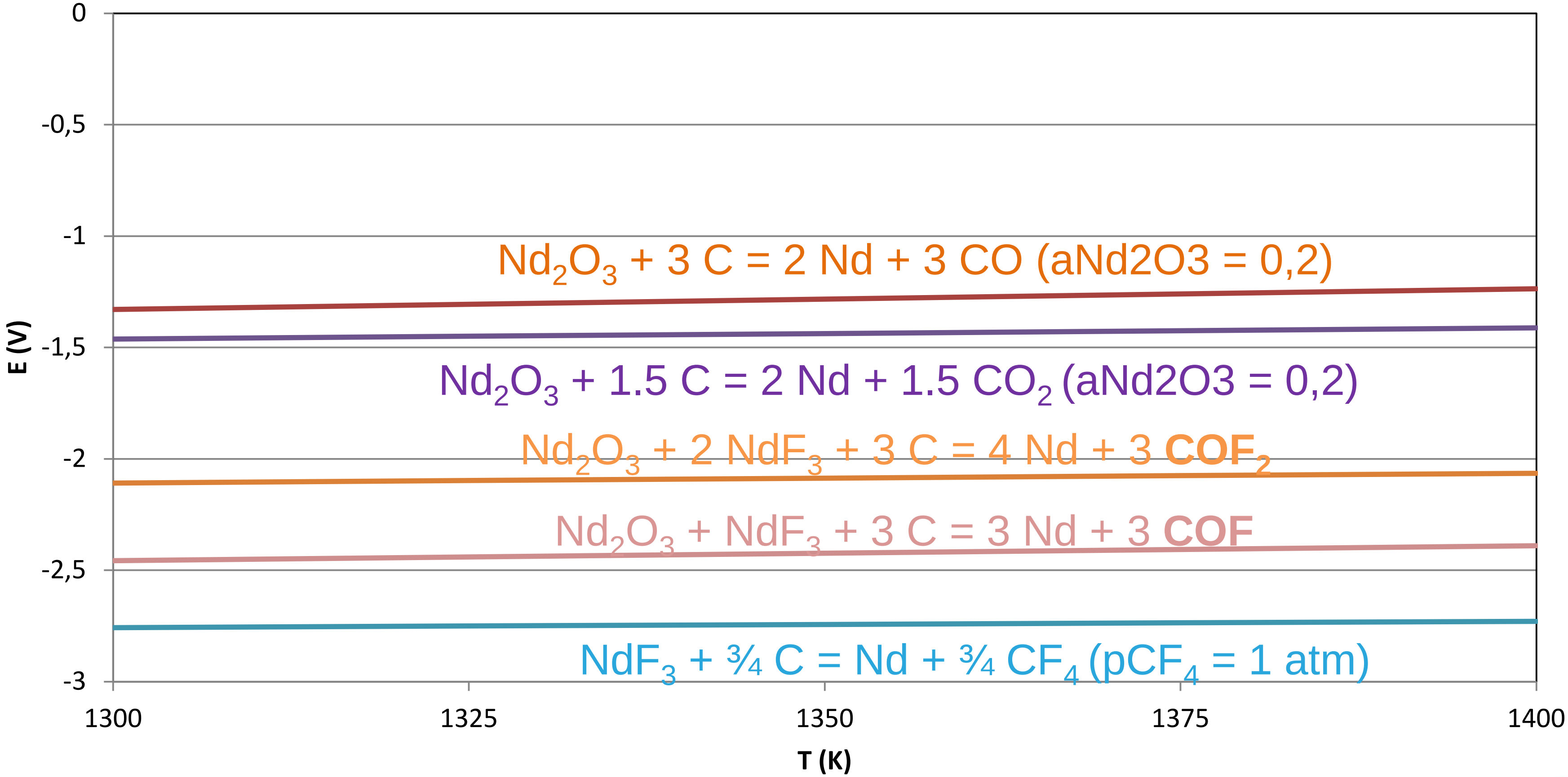
E° = -ΔG° /nF



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PFC gas emissions during Nd,Pr electrowinning

$$a\,A + b\,B = c\,C + d\,D$$

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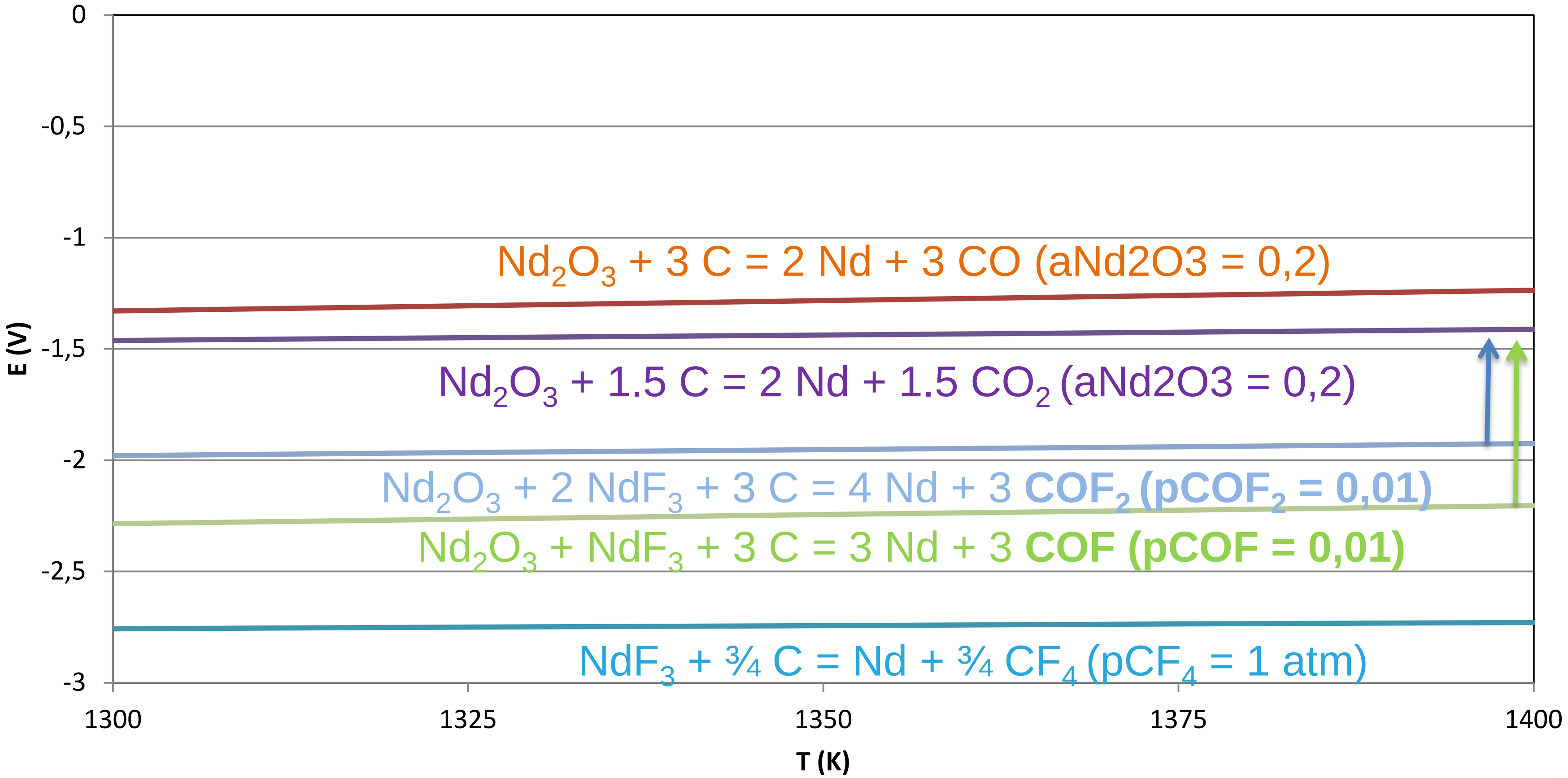

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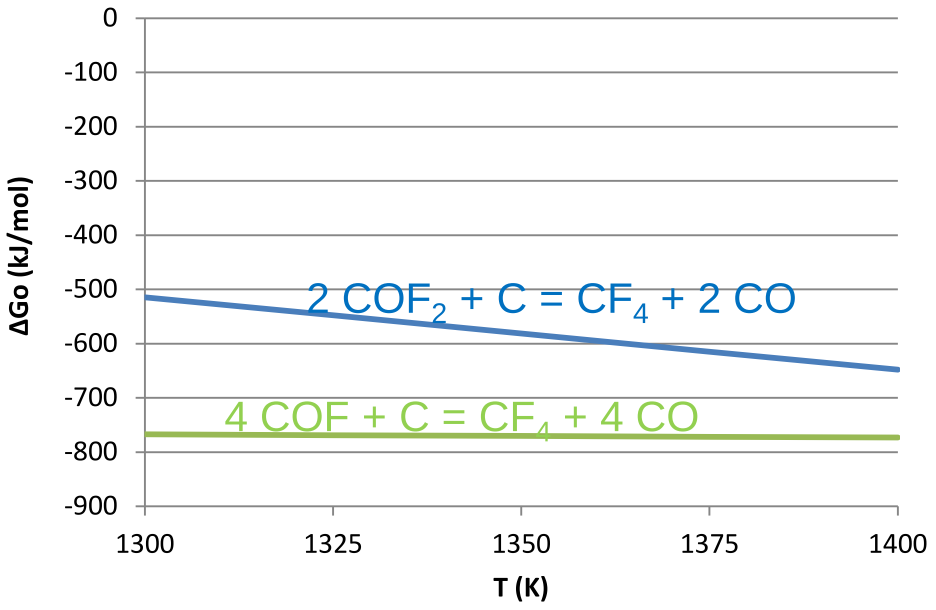
$$E^\circ = -\Delta G^\circ /nF$$

COF_x + C (anode) = CF_4 + CO



E (V) of a specific product at the anode does not only depend on the temperature, but also the anode current density and the activity of dissolved species in the molten salt at the interface with the anode.
The process can move easily from oxide reduction to fluoride oxidation.

PFC gas emissions during Nd,Pr electrowinning

A few papers have discussed PFC gas emissions

Keller at al (1998):

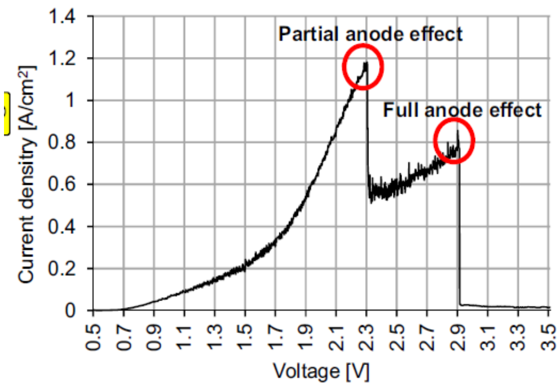
Cells: 20 – 100 A

- Observe CF_4 as high as 20% of off-gas without full anode effect (CD: 0,1 – 0,2 A/cm^2) (voltage, oxide content not reported)

- Operate a 100 A cell without any CF_4 detection with CD: 0,03 A/cm^2

CD: too low to keep T of electrolyte in an industrial cell (~0,5 A/cm^2)

Vogel et alii (2015-2017):



- Partial anode effect

- Up to 7% of CF_4 and 0,7% C_2F_6 in the off-gas only during full anode effect

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PFC gas emissions during Nd,Pr electrowinning

Vogel et alii (2015-2017):

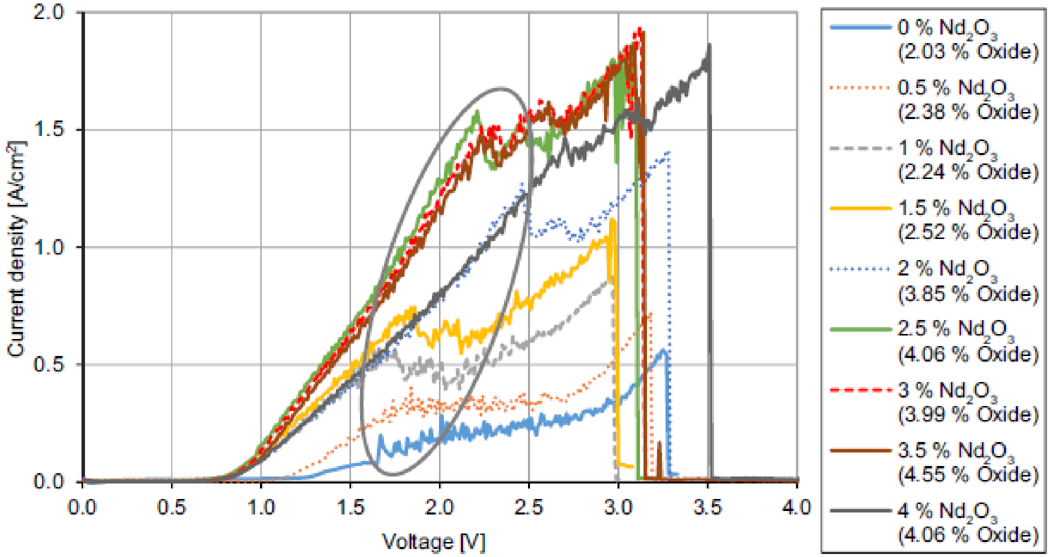

Fig. 8 Linear voltammograms for increasing oxide feeding amounts at 50 mV versus Pt-wire at 1050 °C in 85 % NdF_3–15 % LiF (510.5 g)

Nd_2O_3 dissolved
X
Critical current densities (CCD) which causes partial anode effect

↑ CCD and ↑ V with ↑ dissolved Nd_2O_3

Electrolysis: CD < CCD can prevent PFC

PFC gas emissions during Nd,Pr electrowinning

Vogel et alii (2015-2017): Distinct CF_4 levels not directly related with anode effect

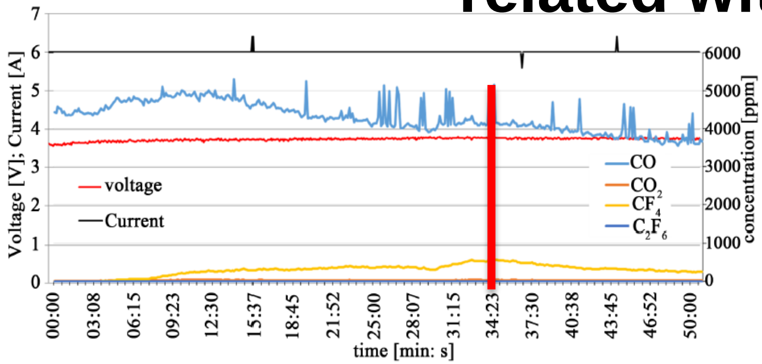

Figure 7. Galvanostatic neodymium electrolysis with slowly evolving CF_4 emission without voltage disturbances.

Nd_2O_3: from 2 to 0,052%

CD: 0,08 A/cm^2

CF_4: up to ~10% off-gas without any anode effect

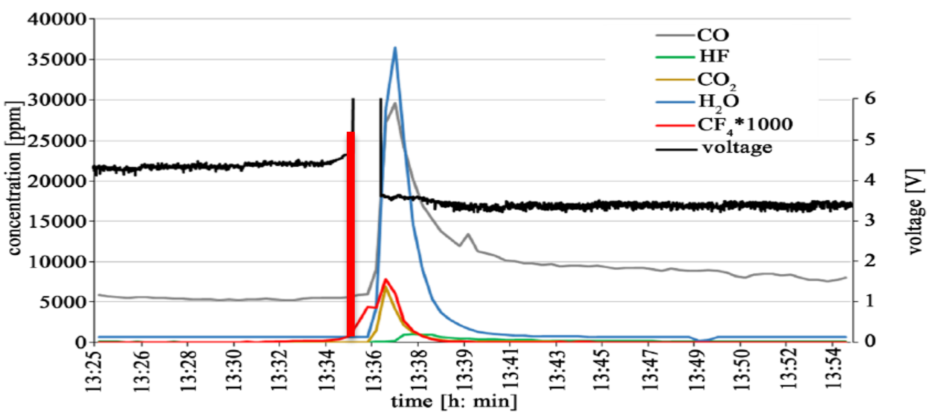

Figure 14. Automatic feeding of 1% neodymium oxide after 1 minute in full anode effect.

Nd_2O_3 : < 1%

CD: 0,4 A/cm^2

CF_4: ~0,2% off-gas only during a full anodic effect

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PFC gas emissions during Nd,Pr electrowinning

Vogel et alii (2015-2017): Distinct CF_4 levels not directly related with anode effect

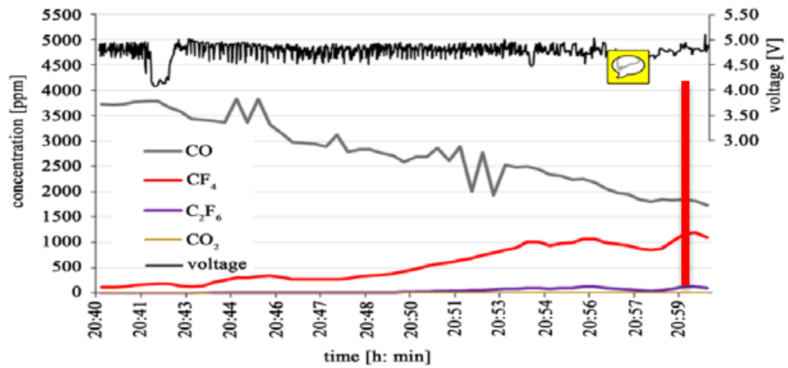


Figure 16. Galvanostatic electrolysis at 50 A without feeding and strong PFC emission.

CD: 0,7 A/cm^2

CF_4: up to ~65% off-gas without any anode effect

Based on the emission 7% of CF_4 and 0,7% C_2F_6 (observed during the full anode effect) extrapolated for the entire operation:

74 g CF_4/kg Nd + 12 g C_2F_6/kg Nd: CO_2eq: 700 kg/kg Nd (X 30.000 t Nd/y ~ 20 M t CO_2 eq/y)

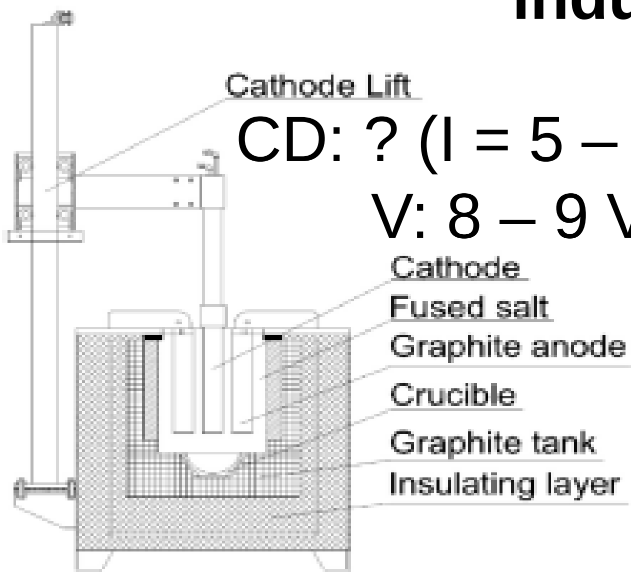
X

0,43 kg CO_2eq/kg Al (X 60 M tAl/y ~26 M tCO2 eq/y)

PFC gas emissions during Nd,Pr electrowinning

Zhang et al (2017): First time PFC determined in an industrial Chinese plant

CD: ? (I = 5 – 6 kA)
V: 8 – 9 V



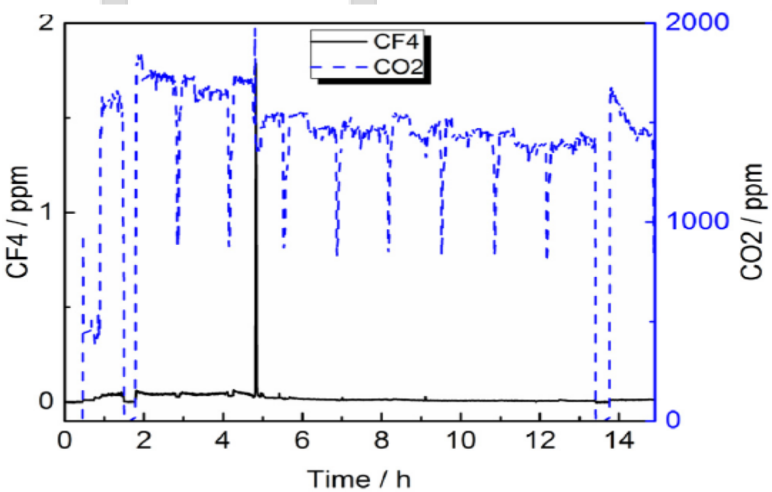


Fig. 2. CF_4 concentration of neodymium metal during regular production.

1 cell: 9,5 g CF_4/t Nd (15 h operation): 0,07 kg CO_2eq/kg Nd

16 cells: 26,9 g CF_4/t Nd (75 h operation): 0,2 kg CO_2eq/kg Nd

X

CO_2eq: 700 kg/kg Nd (Vogel et al)

X

0,43 kg CO_2eq/kg Al

PFC gas emissions during Nd,Pr electrowinning

- Preliminary analyses (chromatography) at IPT cell:
  - during normal operation (without anodic effect) (0,5 A/cm²): CF_4 **Not Detected** (detection limit: 0,1%)
  - during full anodic effect (0,5 A/cm²): ~ **0.5 %** CF_4 (diluted in the electrolytic chamber)

0,7 kg CO_2eq/kg Nd (IPT – preliminary result)

X

0,2 kg CO_2eq/kg Nd (Zhang et al – industrial cell)

X

700 kgCO_2eq/kg Nd (Vogel et al)

X

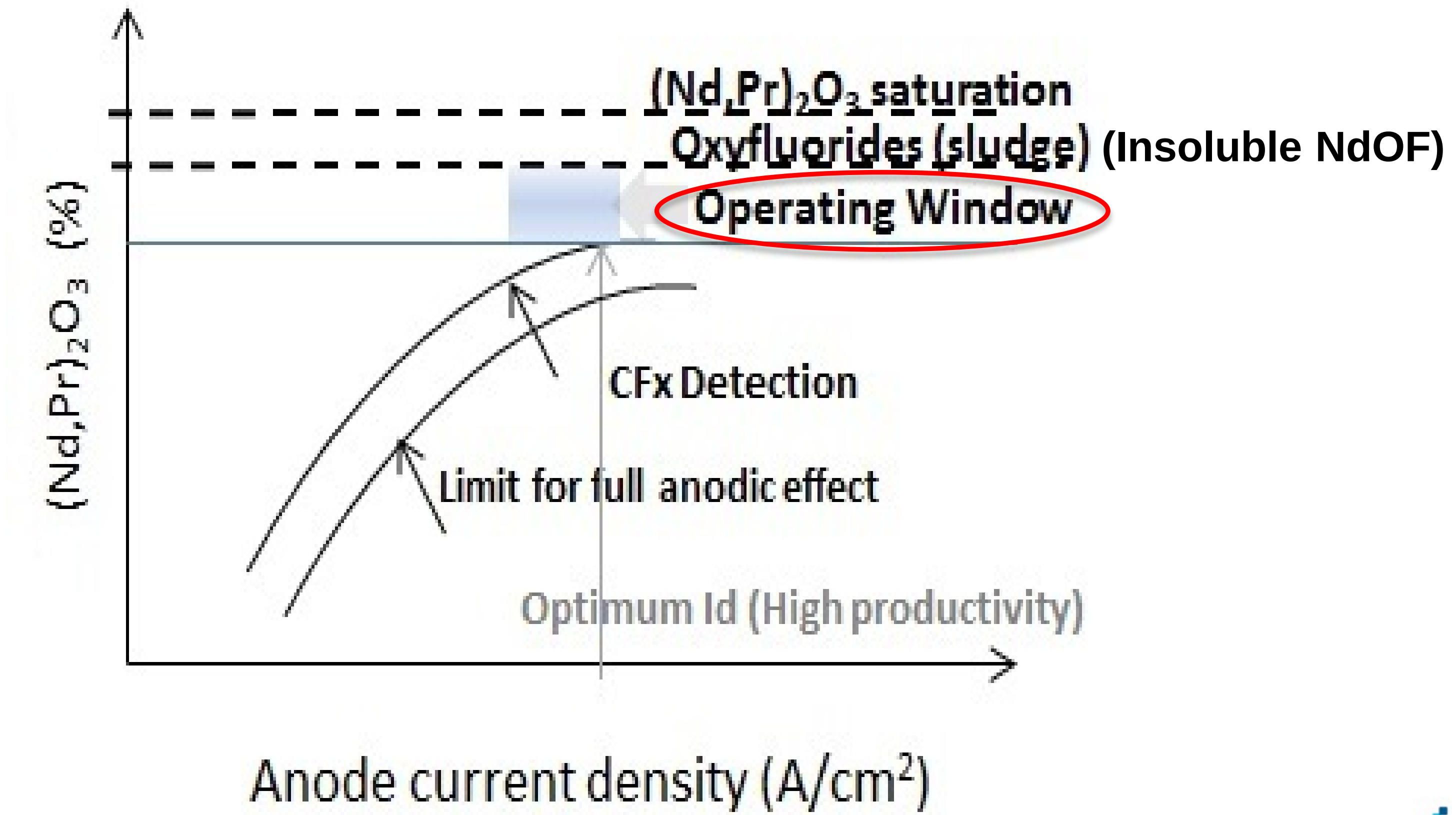
0,43 kg CO_2eq/kg Al

Controlling of PFC gas emissions during the electrolytic reduction of Nd/Pr oxides

How to determine an operation window:

↑ productivity (↑ CD)

↓ PFC gases emissions



Conclusions

- Metallic didymium (>99%) was produced in a laboratory electrochemical cell.

- The electrochemical process is stable if the oxide concentration in molten salt is properly controlled, by controlling the oxide feeding rate and the electric parameters of electrolytic process (voltage and current).

- There is a great discrepancy in the literature concerning the specific quantity of PFC gases emitted per t of Nd/Pr during the electrolysis of neodymium/didymium oxide.

- It is proposed an operational procedure to determine an operation window which might guarantee high productivity with low greenhouse gas emissions

ありがとうございました

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jbfn@ipt.br

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