

DESAFIOS TECNOLÓGICOS DA REDUÇÃO ELETROQUÍMICA DE TERRAS-RARAS

LPM / MA

08.11.22

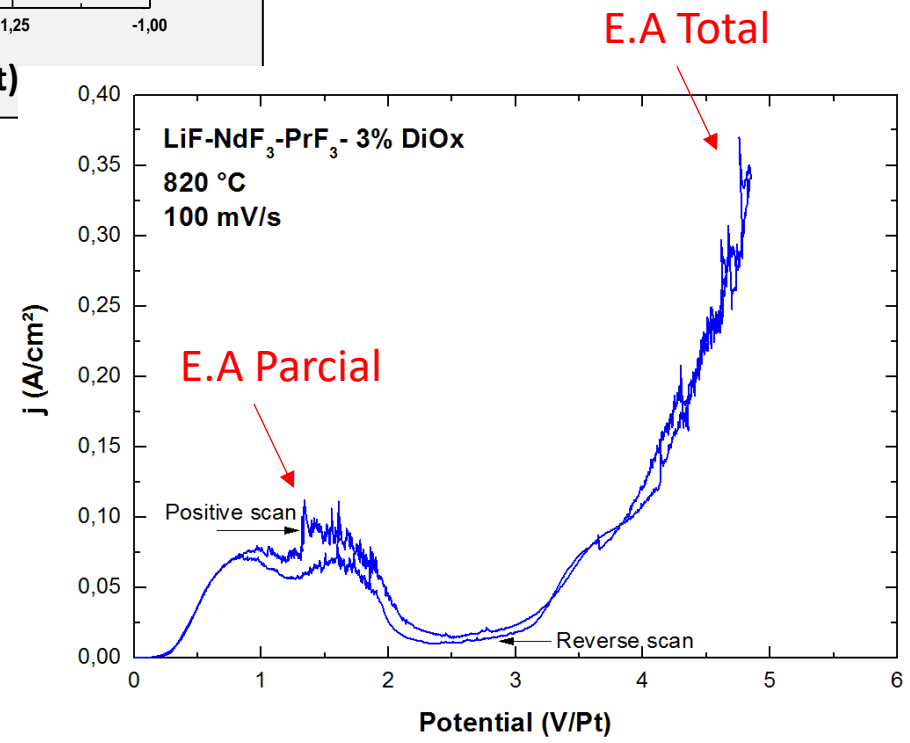
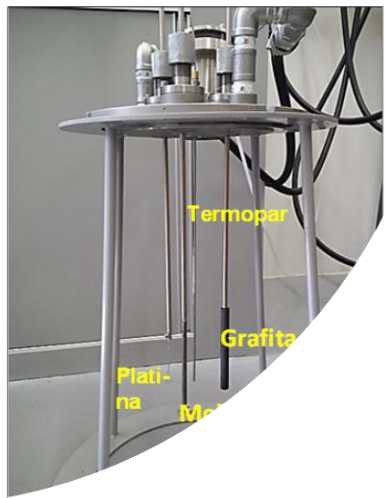
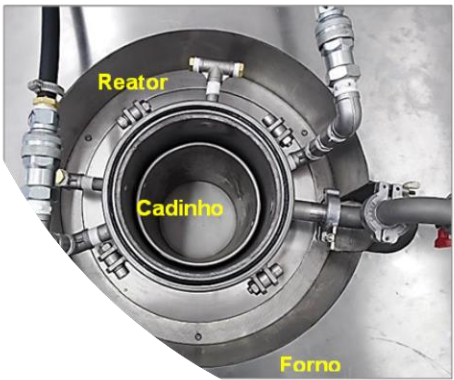
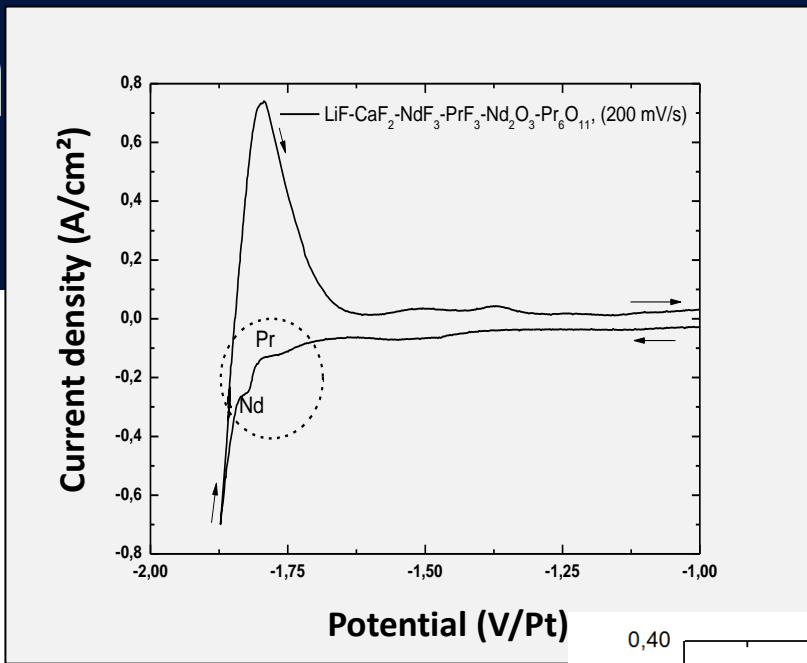
VI Seminário Brasileiro de Terras-Raras – VI SBRTR

SUMÁRIO

- Breve resumo sobre redução de óxido de Terras Raras
- Desafios do desenvolvimento tecnológico
 - Material
 - Operacional
 - Ambiental



Voltametria cíclica



ELETRÓLISE – ESCALA LABORATORIAL



- Capacidade: 150 A
- Produção: 400 – 700 g
- T = 1030 – 1050 °C
- Sais: LiF – NdF₃ – PrF₃



ELETRÓLISE – ESCALA PILOTO

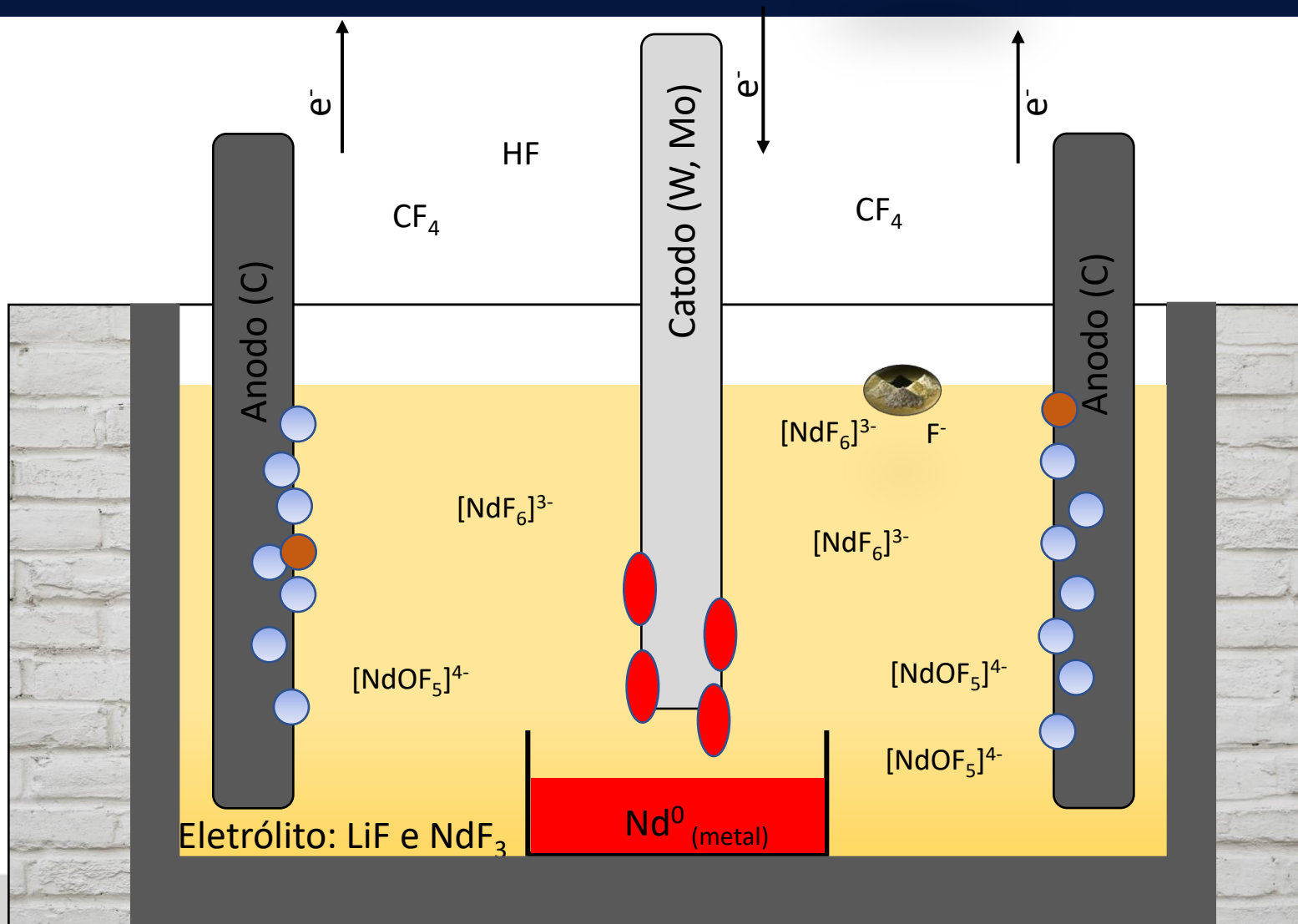


- Capacidade: 1500 A
- Produção: 0,5 – 1,5 kg/h
- T = 1030 – 1050 °C
- Sais: LiF – NdF₃ – PrF₃

Eletrólise em sais fundidos

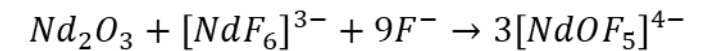


Exemplo: Nd_2O_3

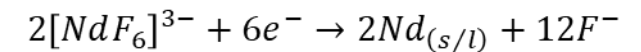


➤ Alimentação de Nd_2O_3

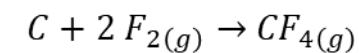
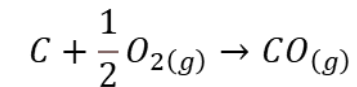
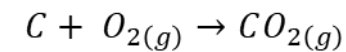
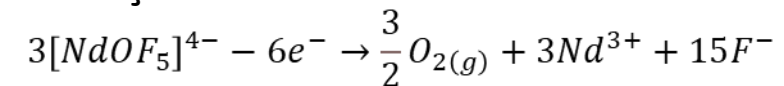
➤ Dissolução



➤ Redução no catodo



➤ Oxidação no anodo

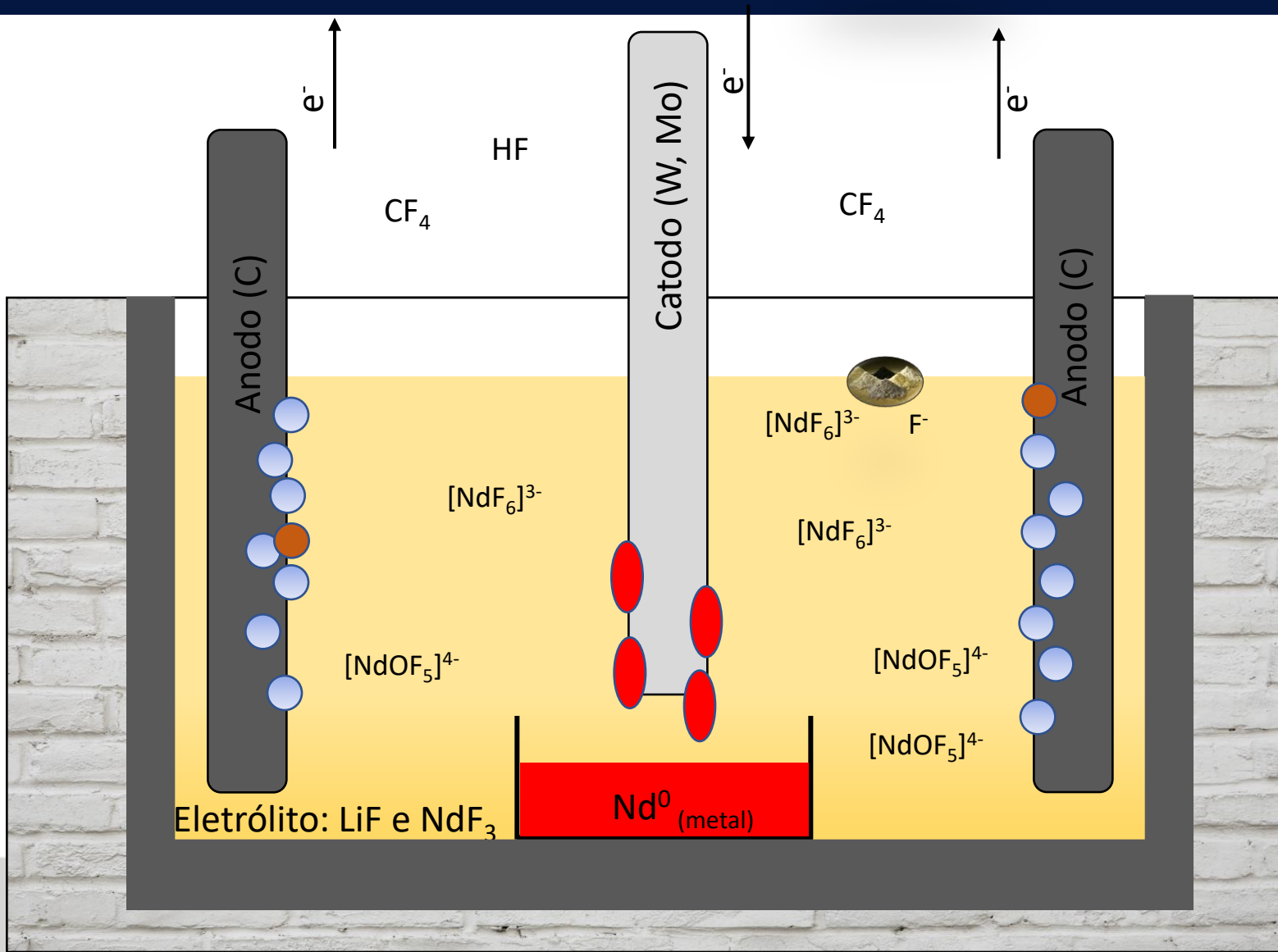


Emissão de PFCs

Eletrólise em sais fundidos



Exemplo: Nd_2O_3

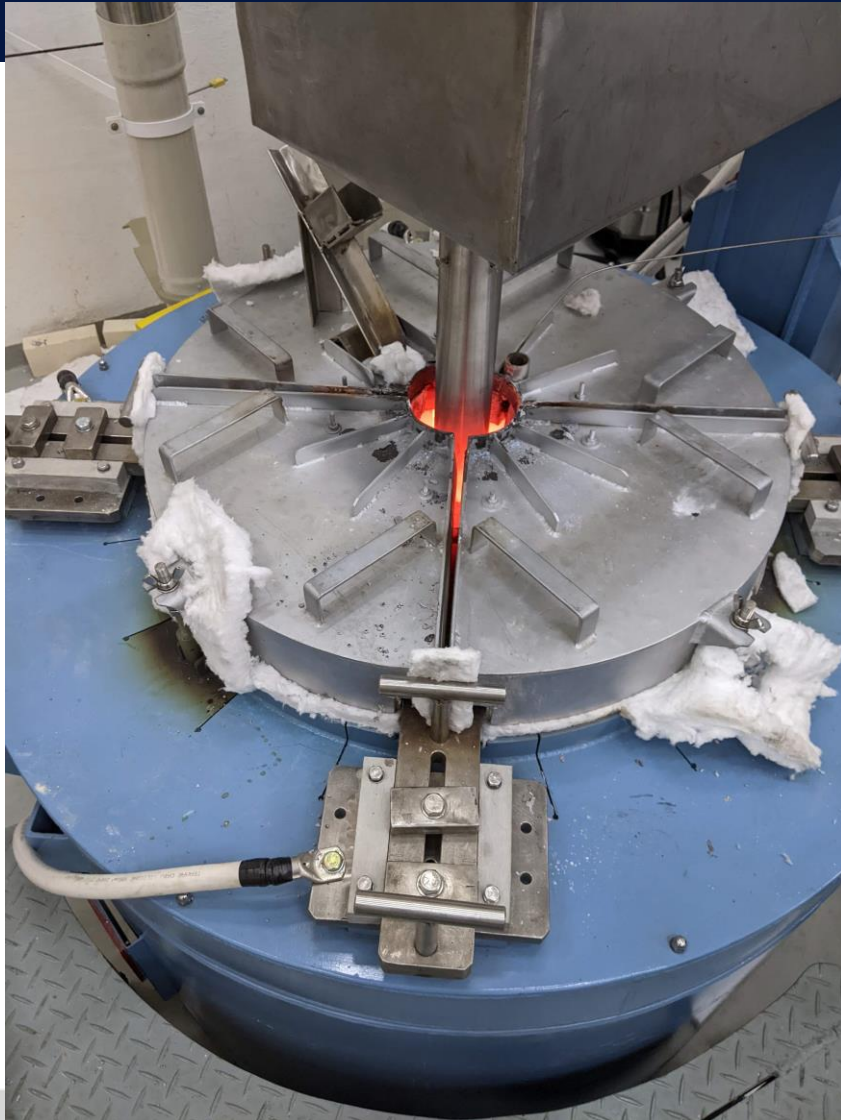


Materiais

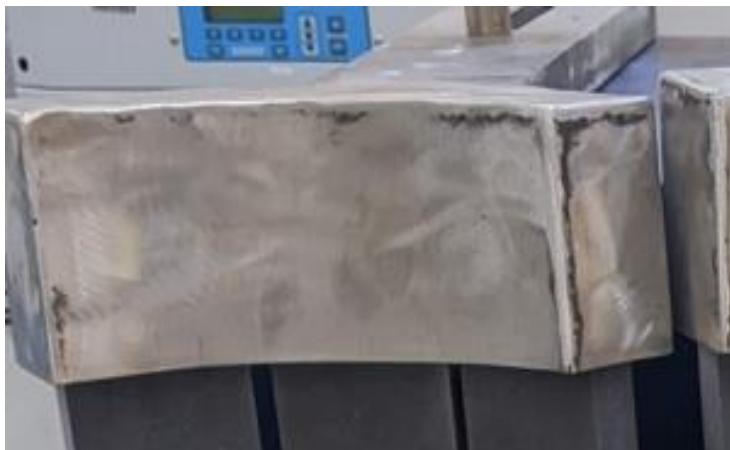
Operacional

Ambiental

MATERIAIS



MATERIAIS

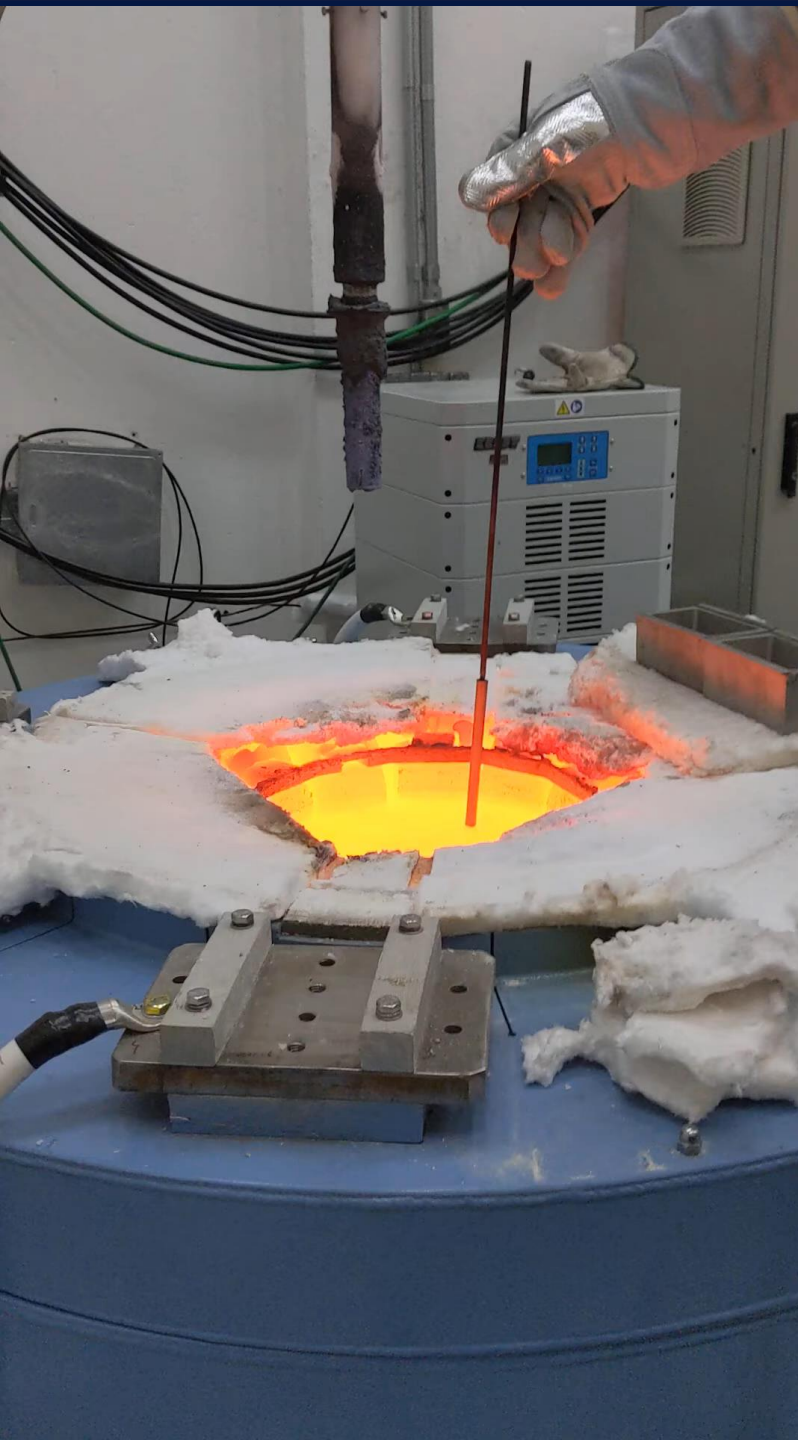


Desgaste

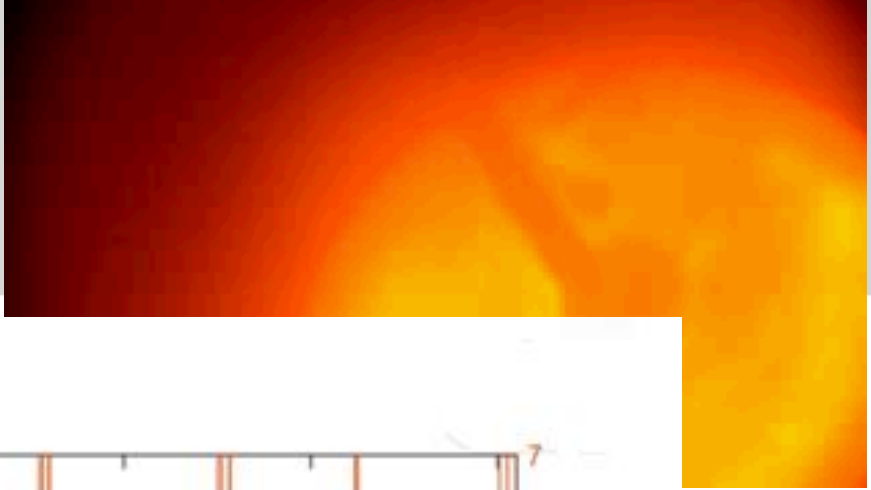
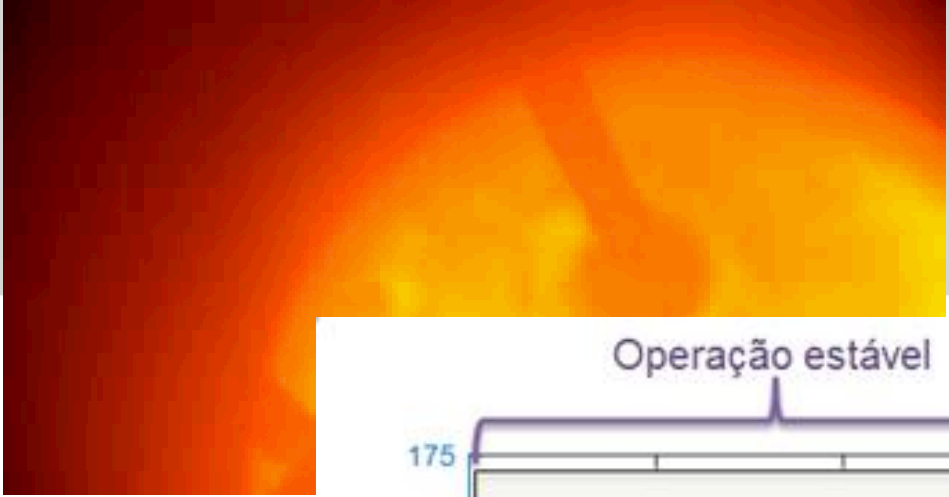
incrustação



OPERAÇÃO

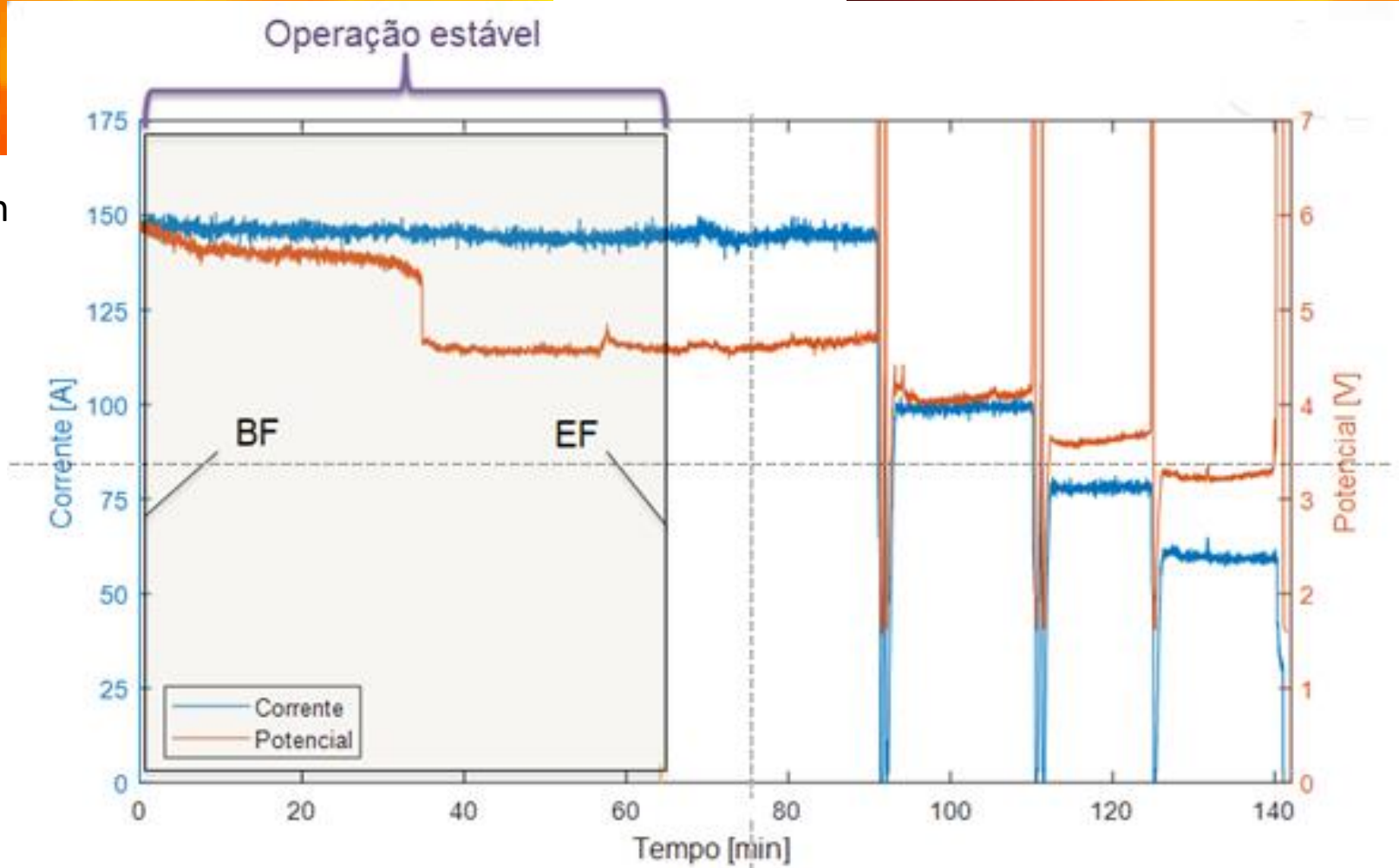


- Alimentação de óxido de didímio
- Evaporação dos sais
- Temperatura
- Recuperação do metal produzido



Alta con

lo



POTENCIAL DA CÉLULA



$$E_{cel} = E + \eta_{c,anodo} + \eta_{diff,anodo} + \Delta\Phi - \eta_{c,catodo} + \Delta\Phi_{anodo} + \Delta\Phi_{catodo}$$

Sobrepotencial anódico devido a transferência de carga

Transferência de massa da espécie eletroativa para $j \gg j_0$ e $j_{lim} \rightarrow C_w = \text{nulo}$ (Vogt e Thonstad, 2002)

$$\eta_c = \frac{RT}{\alpha F} \ln \frac{j/j_0}{(1 - j/j_{lim})}$$

Transferência de massa da espécie eletroativa (Vogt, 2017)

$$\frac{I}{(n/v_{Nd_2O_3})F} = k_{Nd_2O_3} A(1 - \theta)(C_{Nd_2O_3} - C_w)$$

$$\eta_c = \frac{RT}{\alpha F} \left[\ln \left(\frac{I}{A(1 - \theta)j_0} \right) - \ln \left(1 - \frac{v_{Nd_2O_3}}{n} \frac{I}{Fk_b A C_{Nd_2O_3}} \right) \right]$$

POTENCIAL DA CÉLULA

$$E_{cel} = E + \eta_{c,anodo} + \eta_{diff,anodo} + \Delta\Phi - \eta_{c,catodo} + \Delta\Phi_{anodo} + \Delta\Phi_{catodo}$$

Sobrepotencial anódico devido a difusão de gás

$$E = E^0 + \frac{RT}{nF} \ln C^s$$

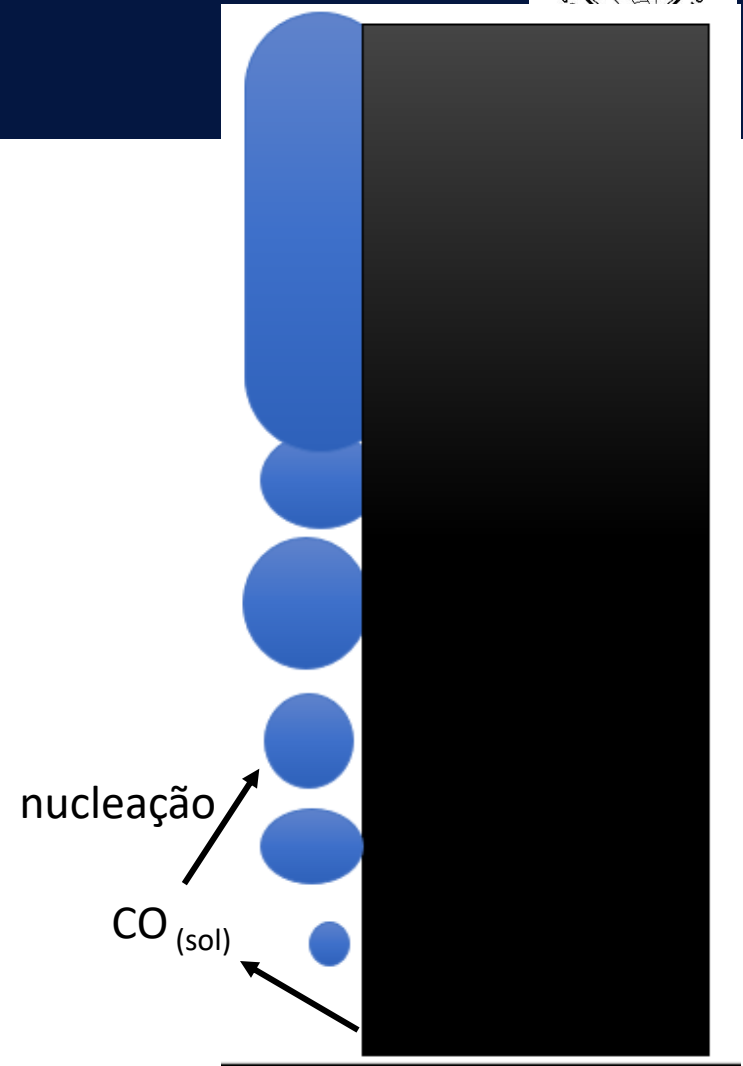
$$\eta_{diff} = E - E_e$$

$$\eta_{diff} = \frac{RT}{nF} \ln \frac{C^s}{C^0}$$

$$\frac{I(1-f_I)}{(n/\nu)F} = kA(1 - \theta)(c_\infty - c_w)$$

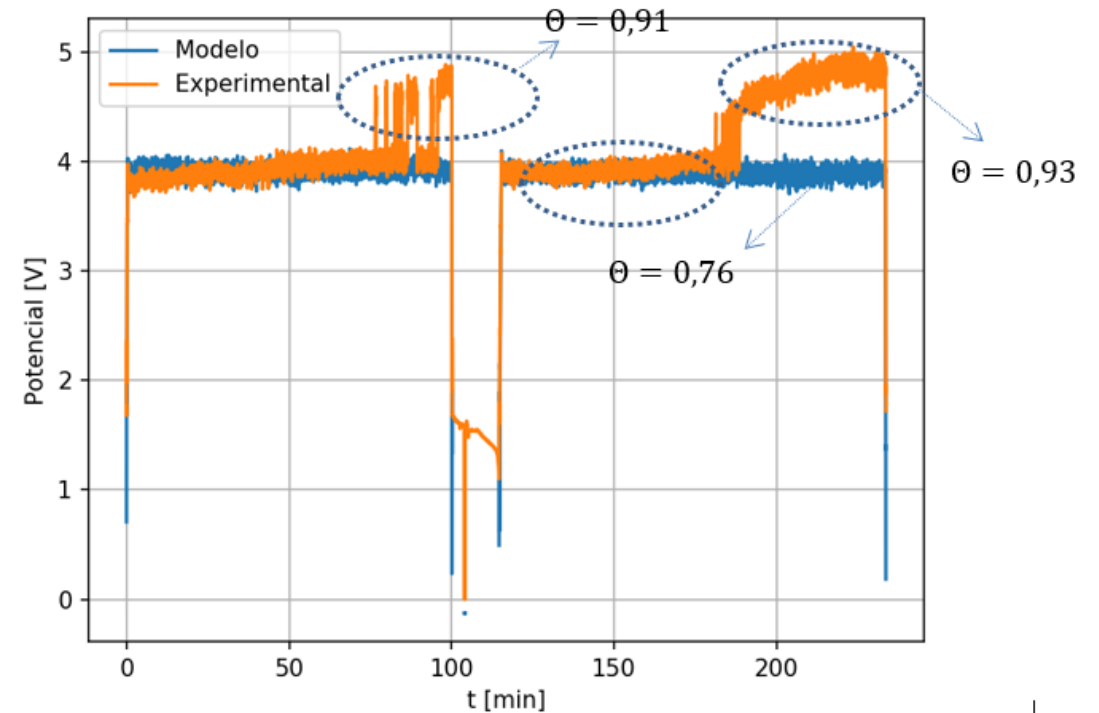
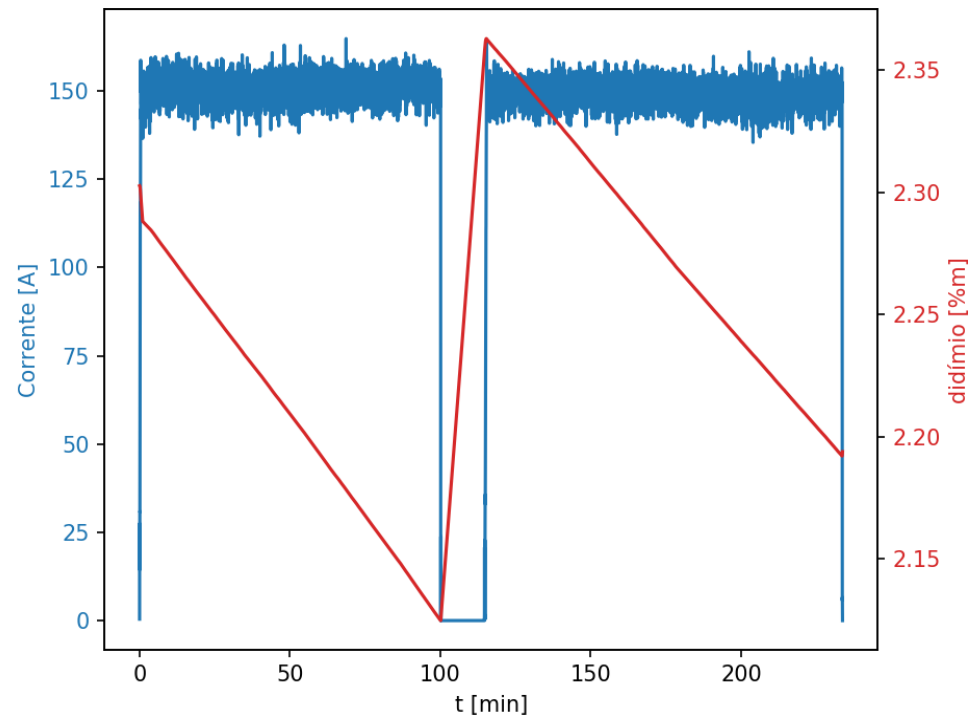
$$k_b = 1,65D_s Re_b^{0,5} \left(\frac{\mu_L}{\rho_L D_s} \right)^{0,5} \Theta^{0,5} (1 - \Theta) / (2R)$$

$$\eta_{diff} = \frac{RT}{nF} \ln \left[1 + \frac{I}{AFk_b C_{sat}} \right]$$



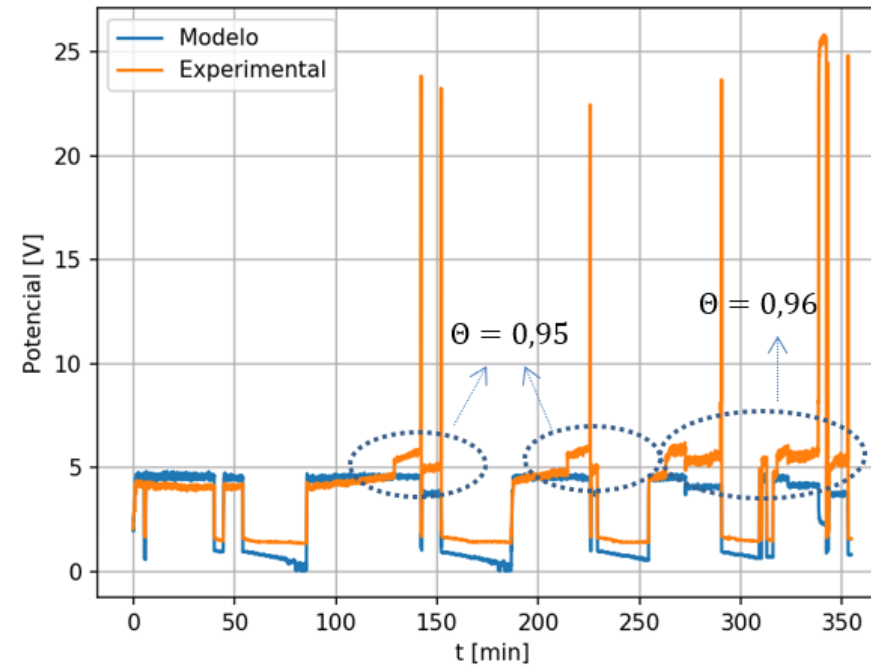
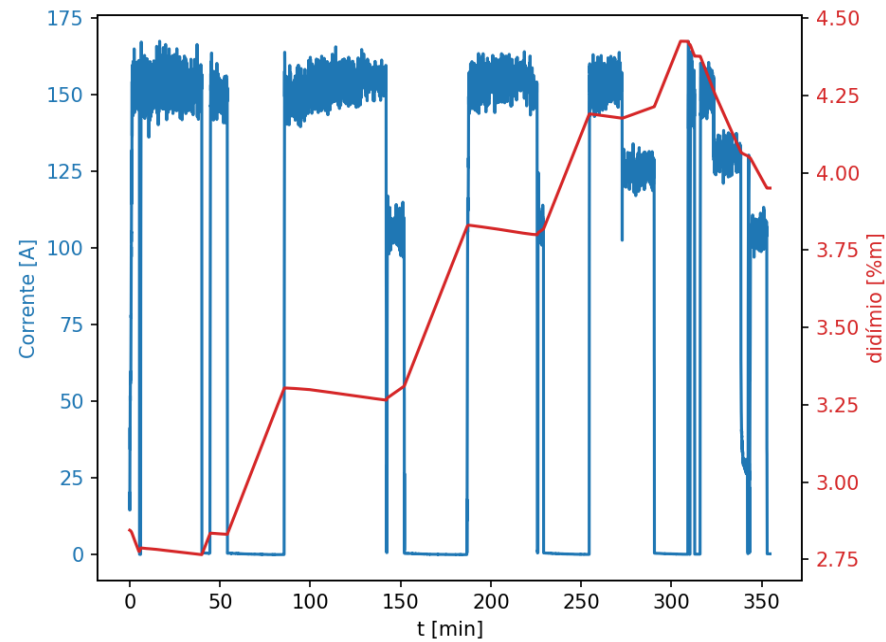
COMPARAÇÃO DO MODELO COM RESULTADOS EXPERIMENTAIS

Ensaio Estável



COMPARAÇÃO DO MODELO COM RESULTADOS EXPERIMENTAIS

Ensaio Instável



I. MECANISMOS DE FORMAÇÃO DAS BOLHAS

Qual é o mecanismo para célula eletroquímica?

Perda de molhabilidade do eletrólito sobre o anodo na polarização (células Hall-Heroult, Thonstad, 2001)

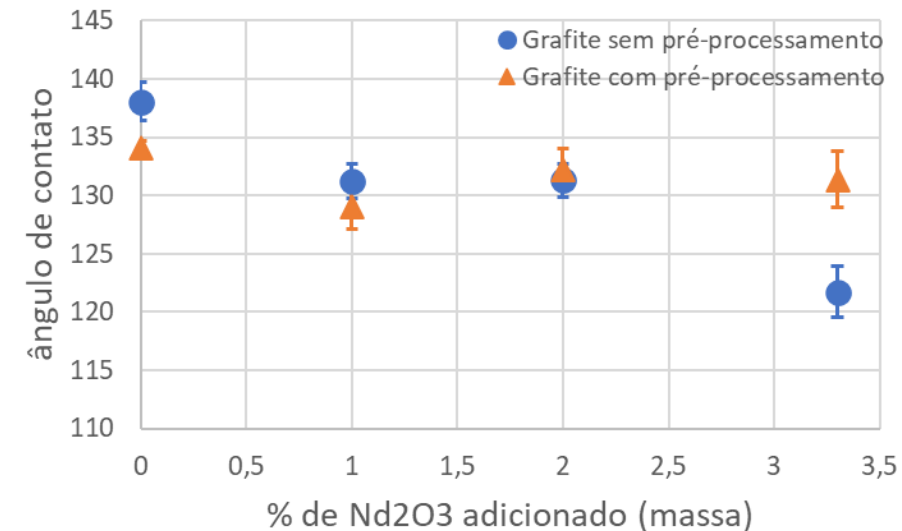
Baixa molhabilidade leva a nucleação por mecanismos clássicos (Vachaparambil e Einarsrud, 2018)

Teoria clássica de nucleação

$$J = C \exp\left(\frac{-16\pi\gamma^3\Phi(\vartheta)}{3kT(SP)^2}\right)$$

Lubetkin (2003)

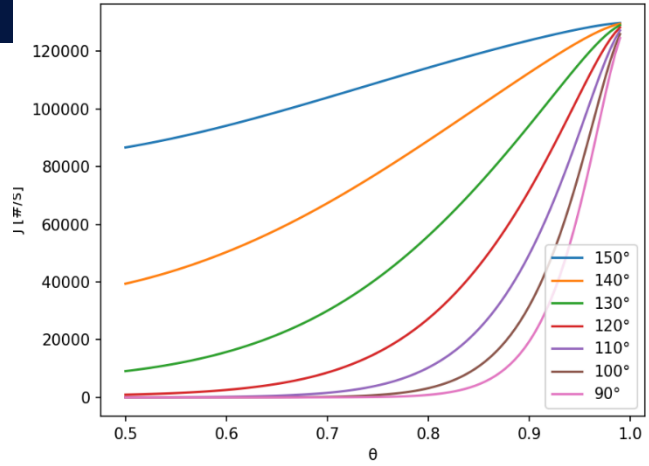
$$\Phi(\vartheta) = \frac{1}{4}(1 + \cos\vartheta)^2(2 - \cos\vartheta)$$



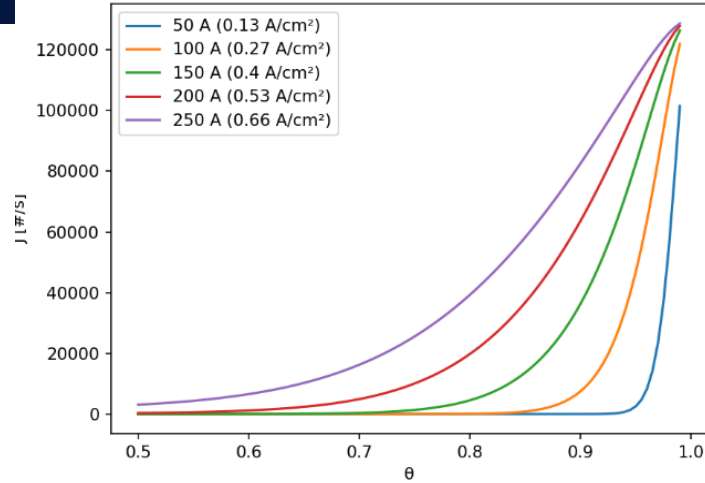
I. MECANISMOS DE FORMAÇÃO DAS BOLHAS

$$J = C \exp\left(\frac{-16\pi\gamma^3\Phi(\vartheta)}{3kT(SP)^2}\right)$$

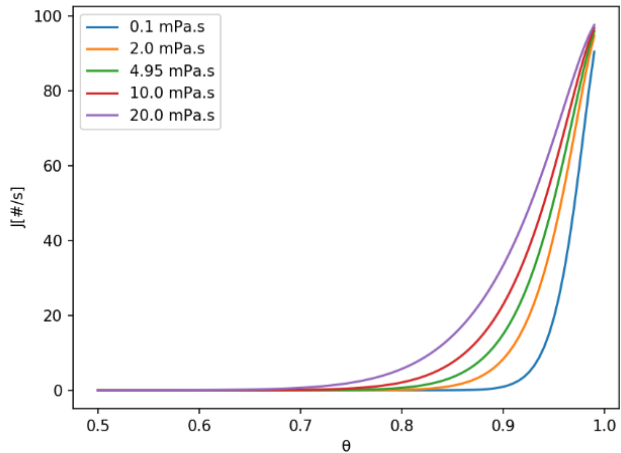
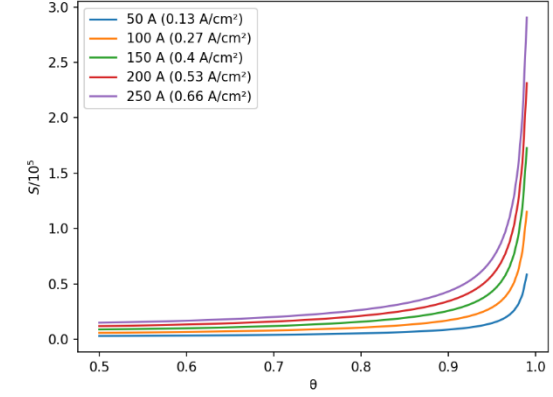
$$\eta \frac{I/A}{(u_{Nd} n / u_{gas}) F} \left(1 - \frac{2}{3} f_g\right) = k_b (C_o - C_{sat})$$



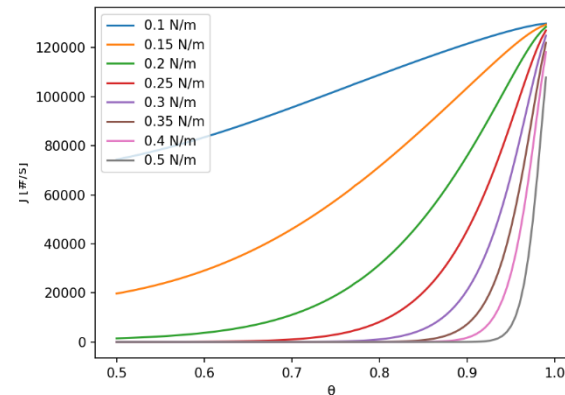
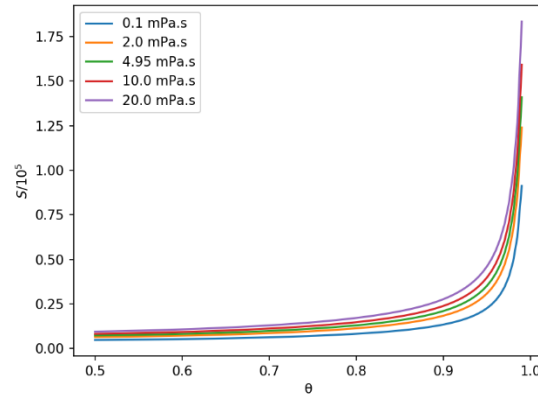
molhabilidade



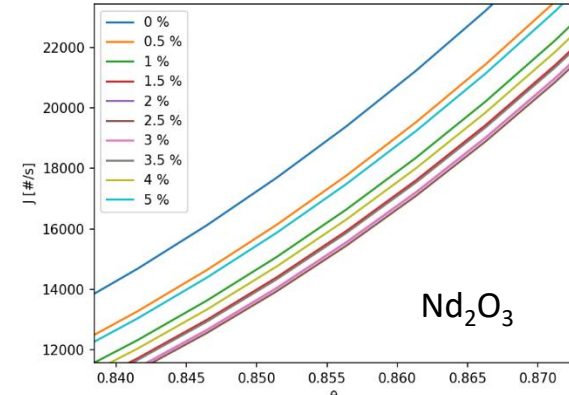
Densidade de corrente



Viscosidade



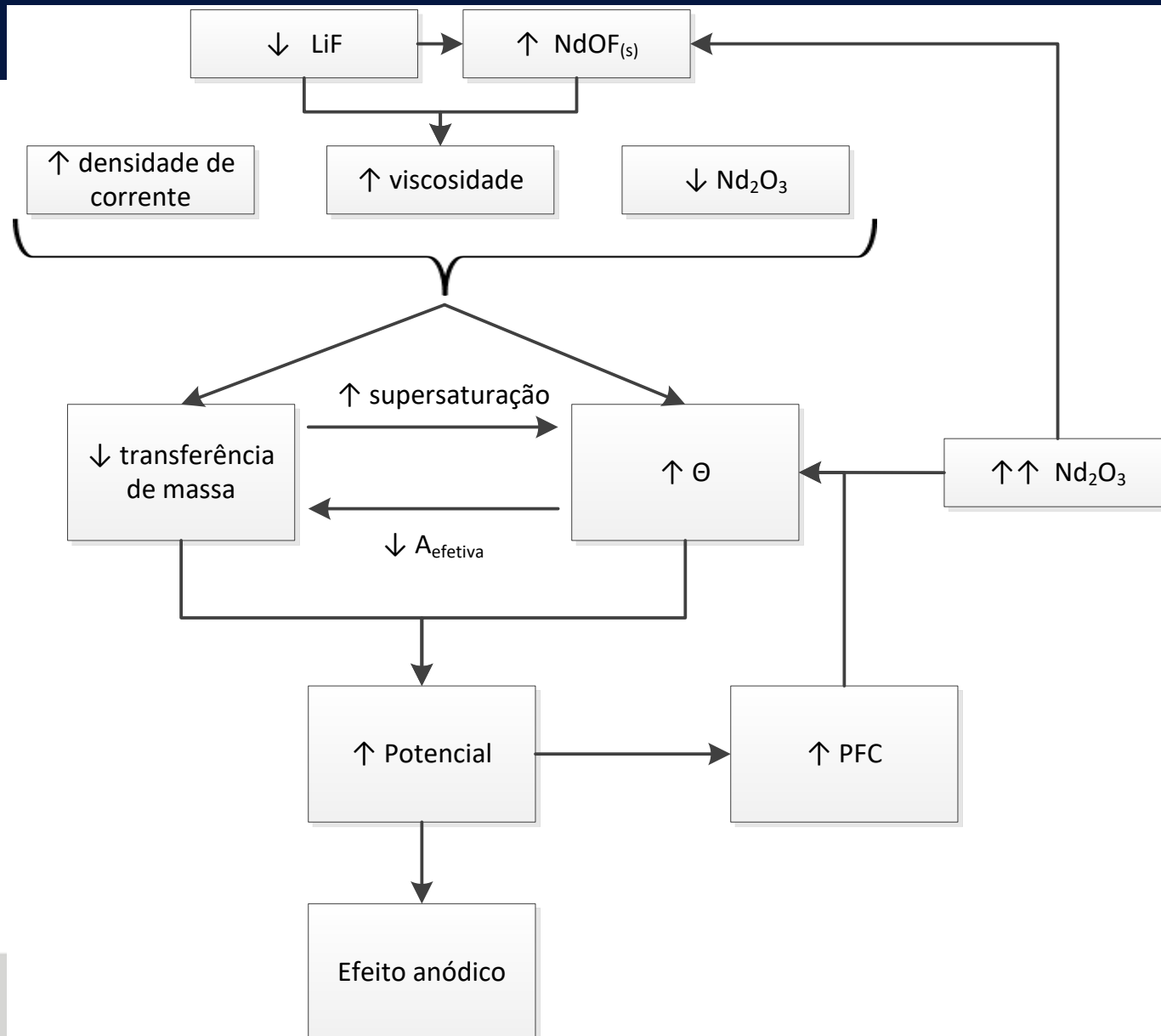
Tensão superficial



Nd_2O_3



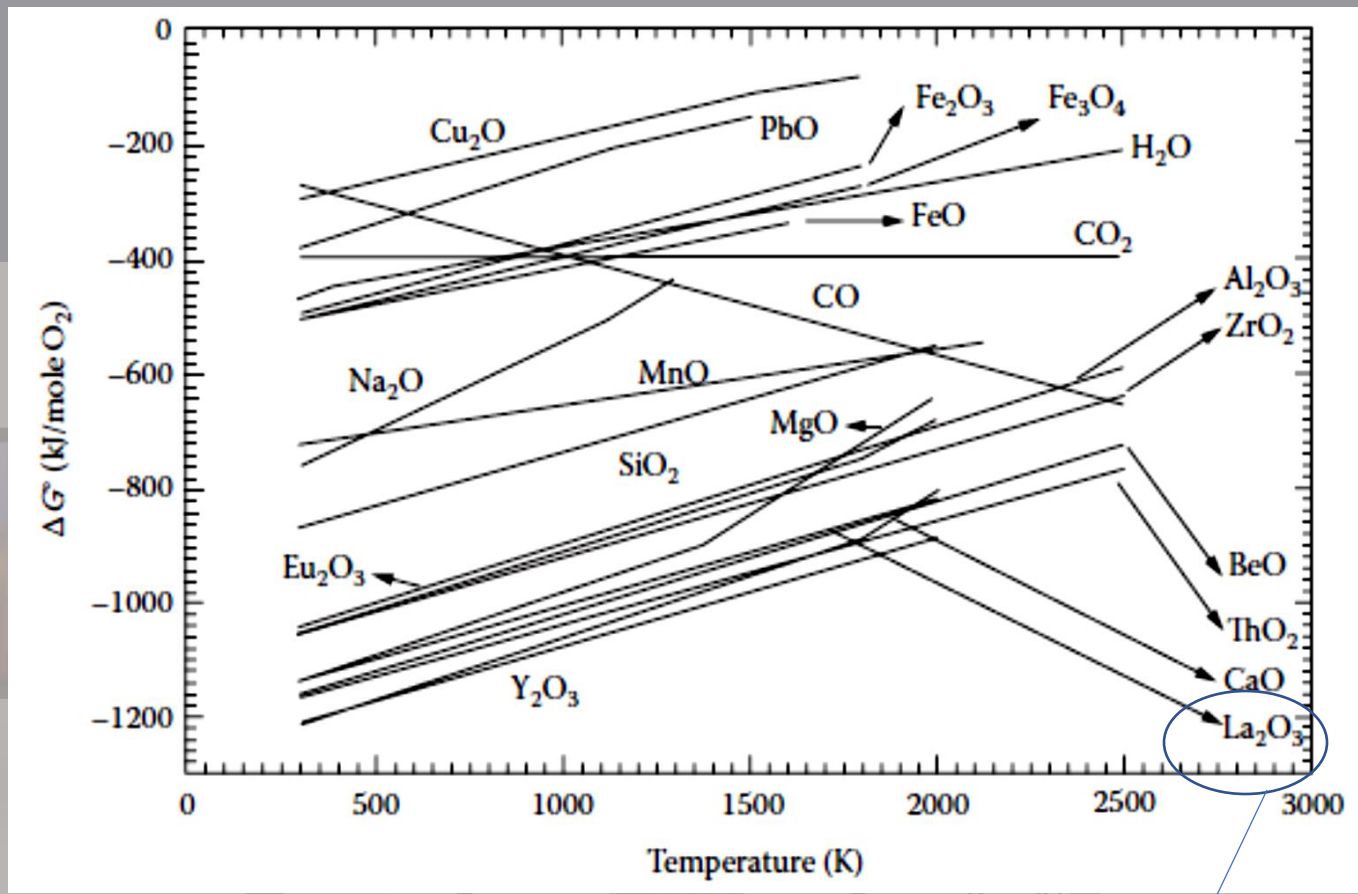
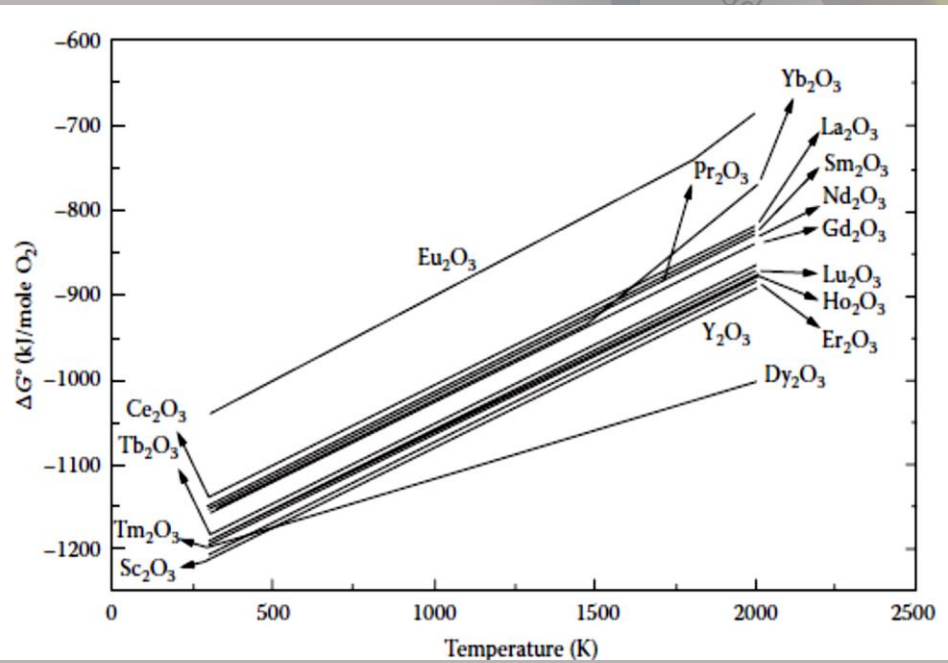
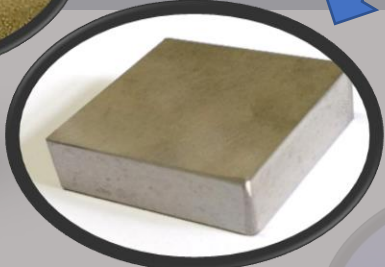
PROPOSTA DE MECANISMO DE EFEITO ANÓDICO



MINA



Redução



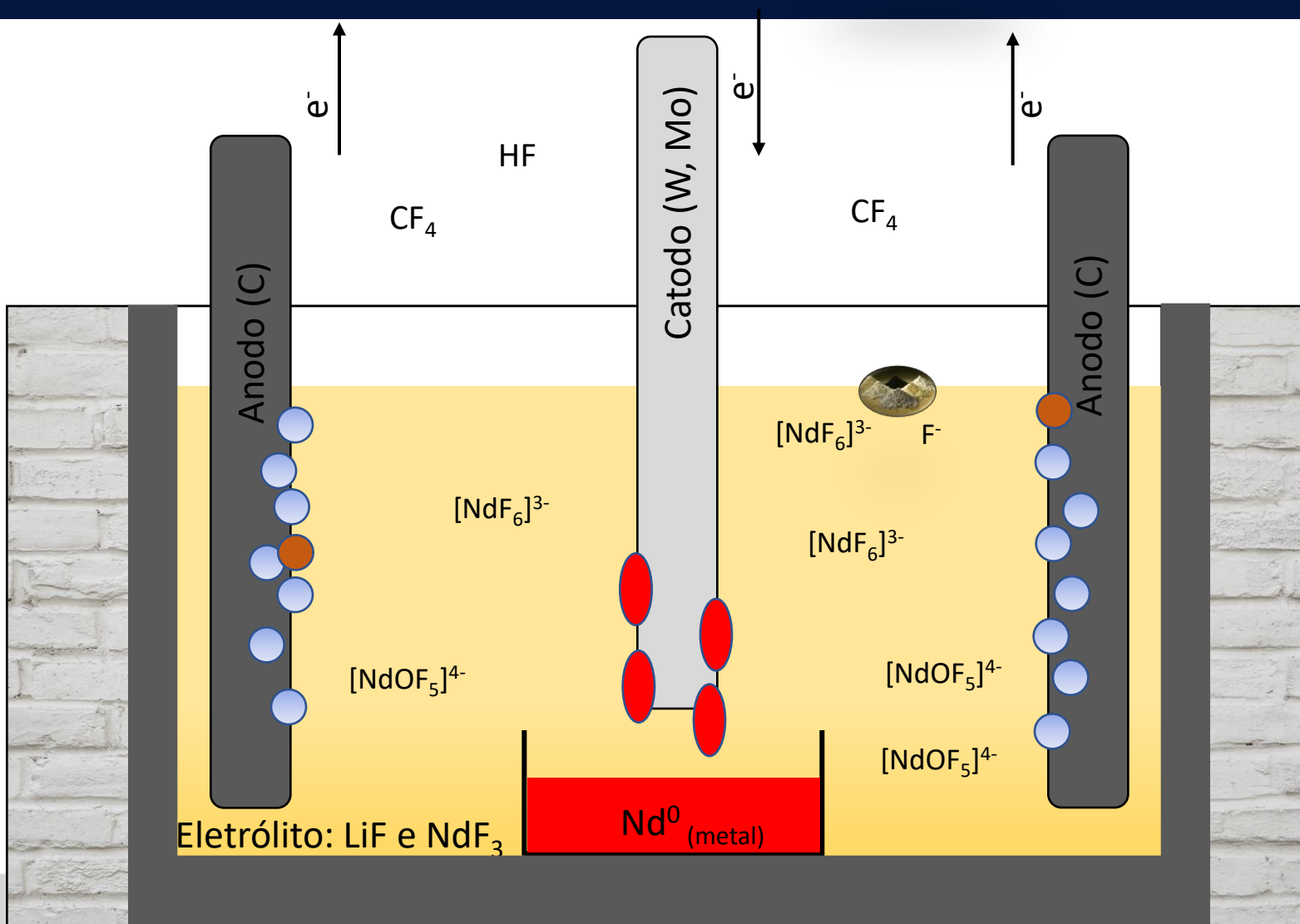
(KRISHNAMURTHY; GUPTA, 2015).

Se houver contaminação na célula → contaminação do metal

Próximo:
Nd₂O₃,
La₂O₃,
Pr₂O₃

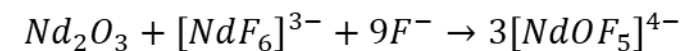


Exemplo: Nd_2O_3

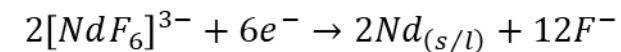


➤ Alimentação de Nd_2O_3

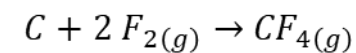
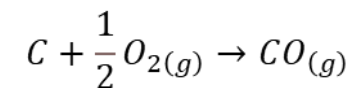
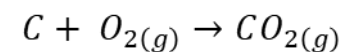
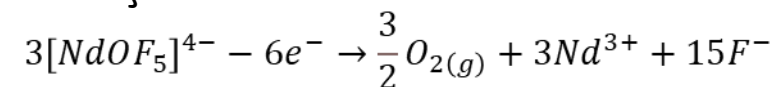
➤ Dissolução



➤ Redução no catodo



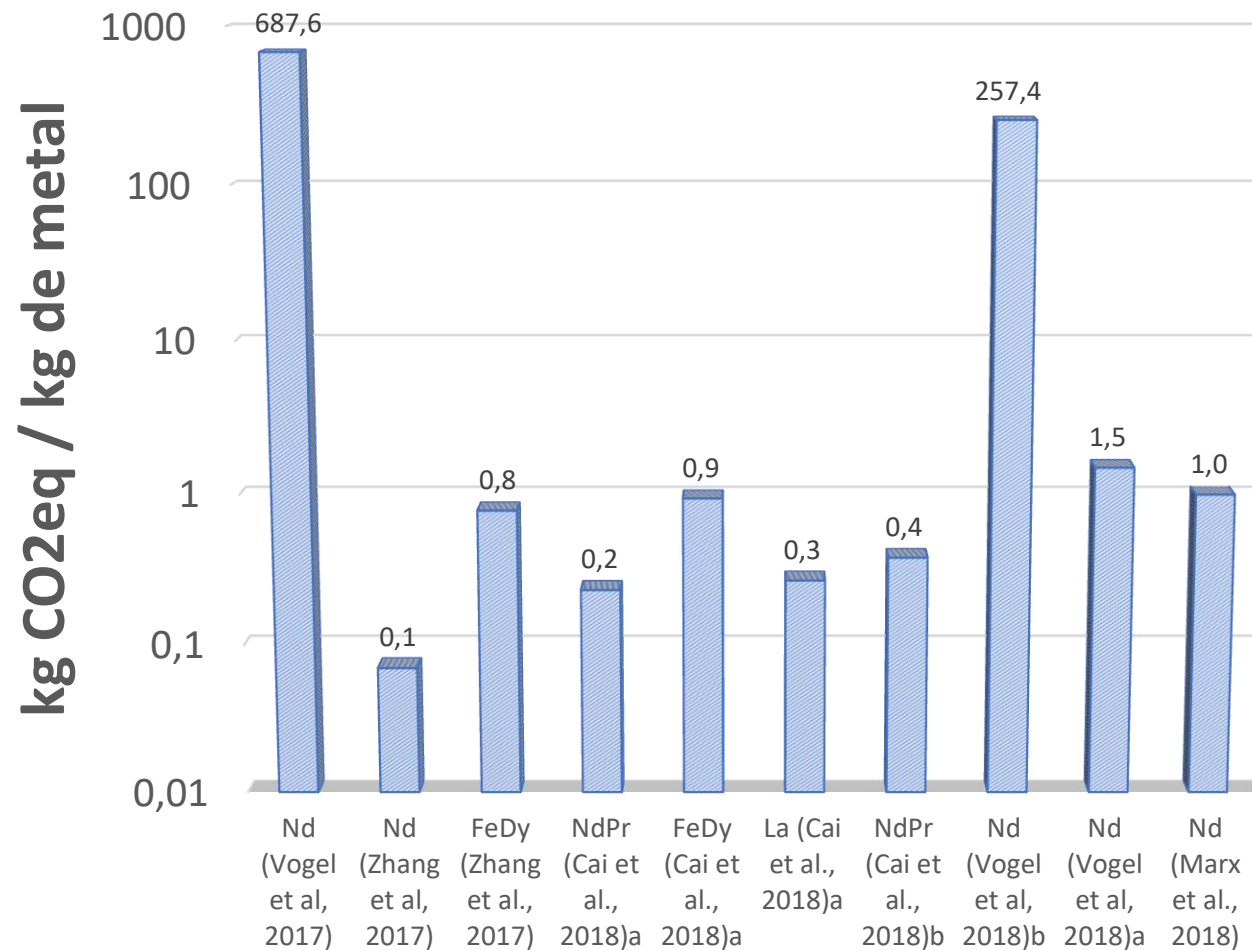
➤ Oxidação no anodo



Emissão de PFCs

Comparação entre publicações

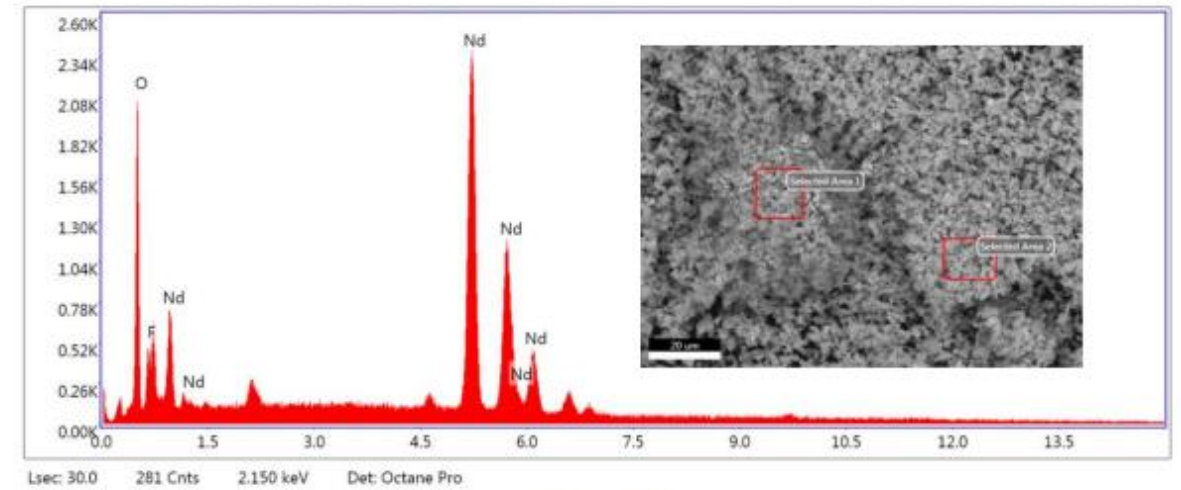
- (1) Fatores de emissão de PFCs mensurados com base na operação de uma célula eletrolítica em escala laboratorial e emissões equivalentes a operação contínua em condição de efeito anódico (Vogel and Friedrich, 2017);
- (2) Estudo conduzido na unidade produtiva da Qiandong RE Group (Zhang et al, 2017);
- (3) (a) Novo estudo conduzido na unidade produtiva da Qiandong RE Group após automação da alimentação (b) Estudo conduzido na unidade produtiva de National Ionic RE Center. (Cai et. al., 2018);
- (4) Estimativas de produção de PFCs para um cenário de (a) média emissão e para um cenário de (b) baixa emissão, valor total para emissão de PFCs (Vogel and Friedrich, 2018).
- (5) Estimativas realizadas em LCA (Marx et al, 2018).



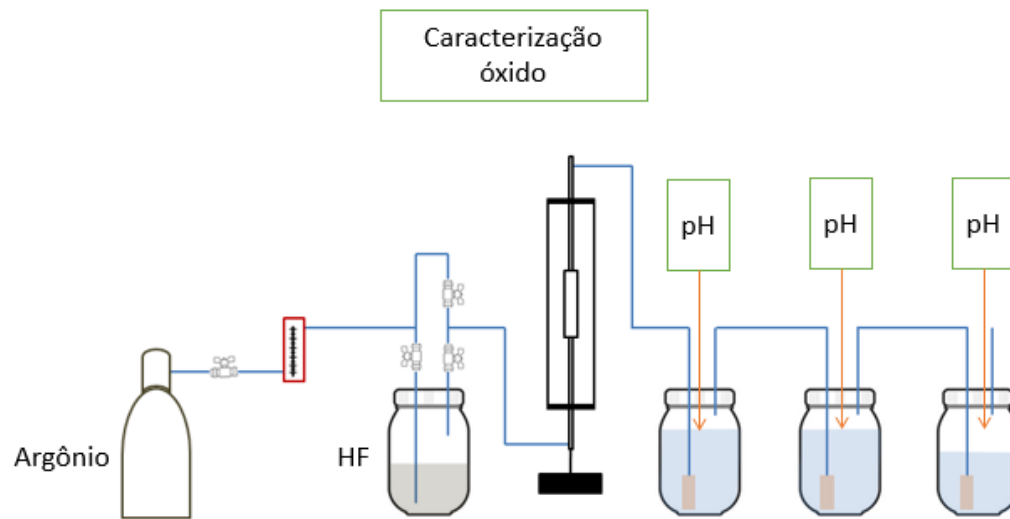
INCT - ADSORÇÃO DO HF

Mônica Yamazaki (2019)

- Realizar um comparativo entre Al_2O_3 e Nd_2O_3

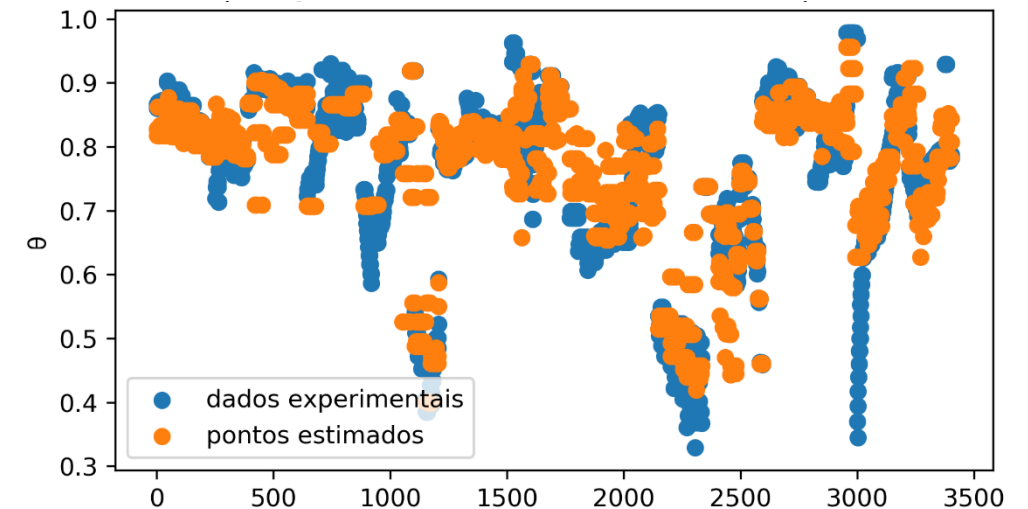
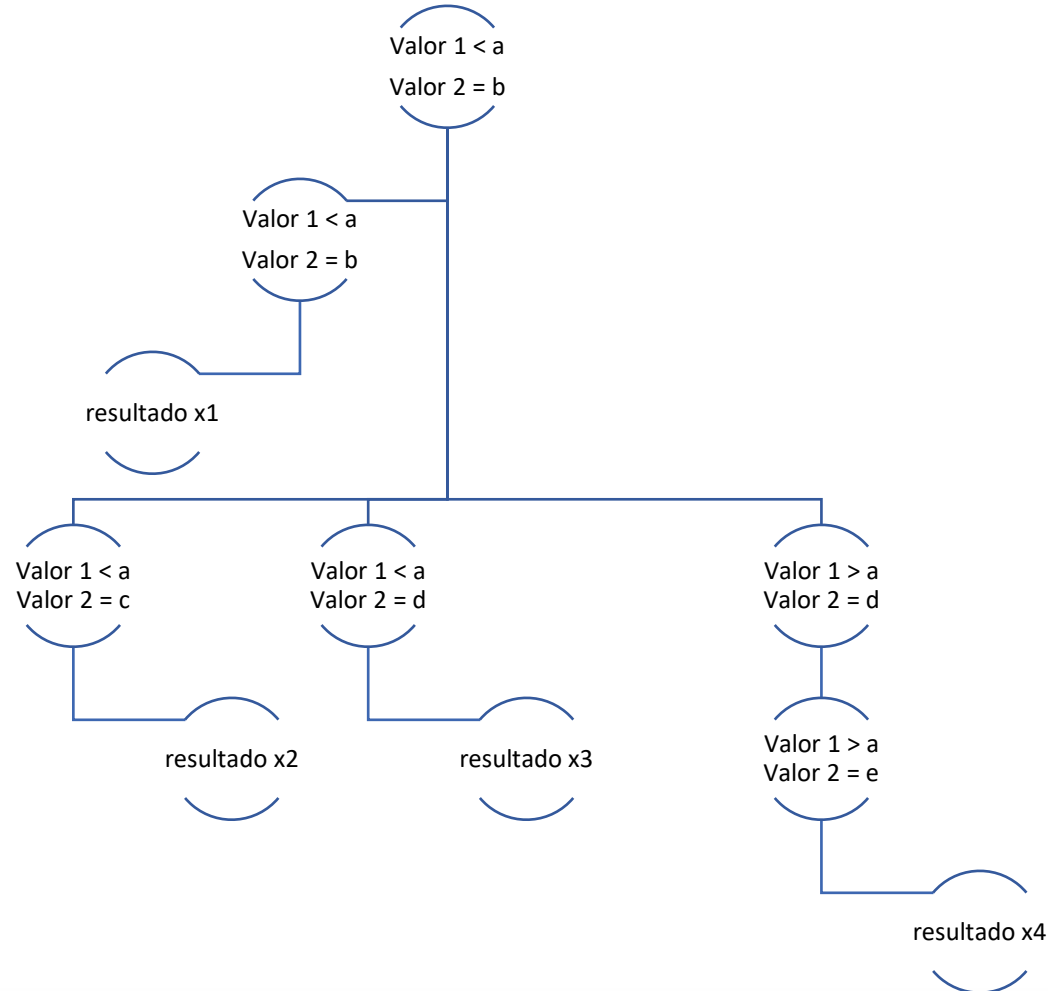


Fonte: Própria

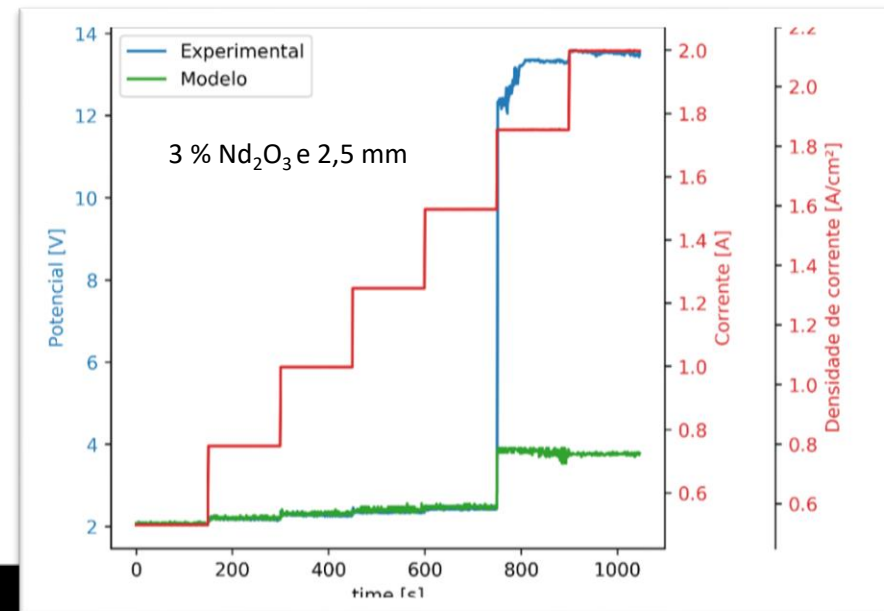
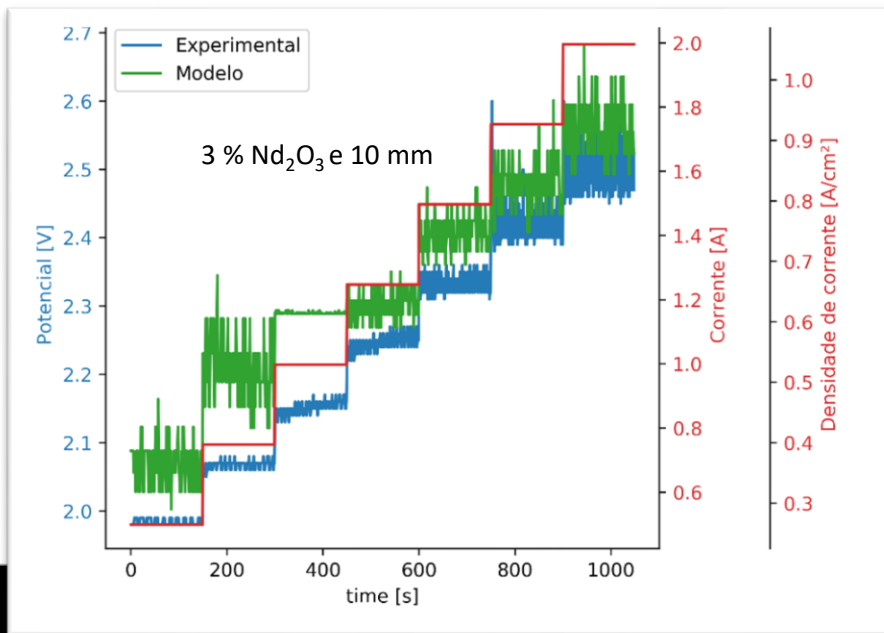
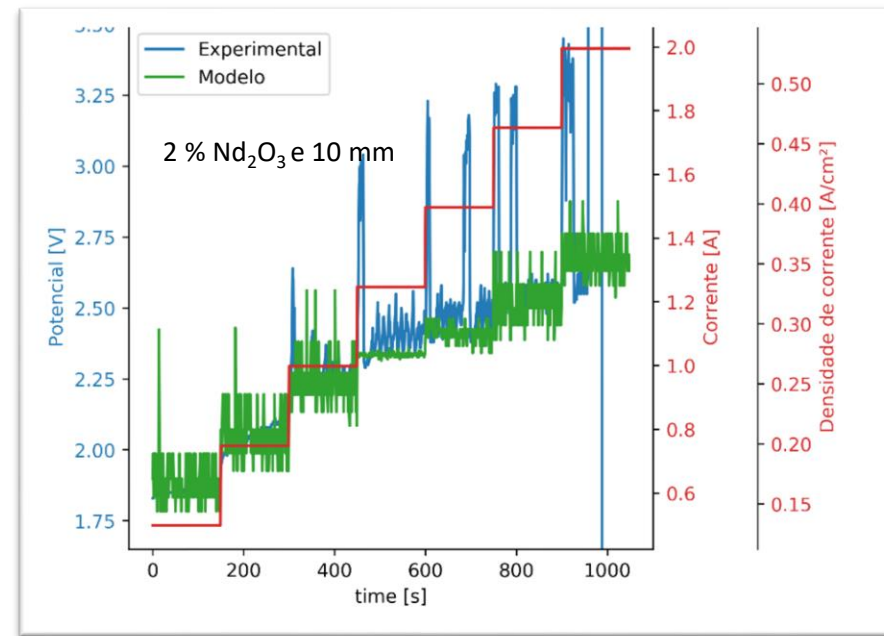
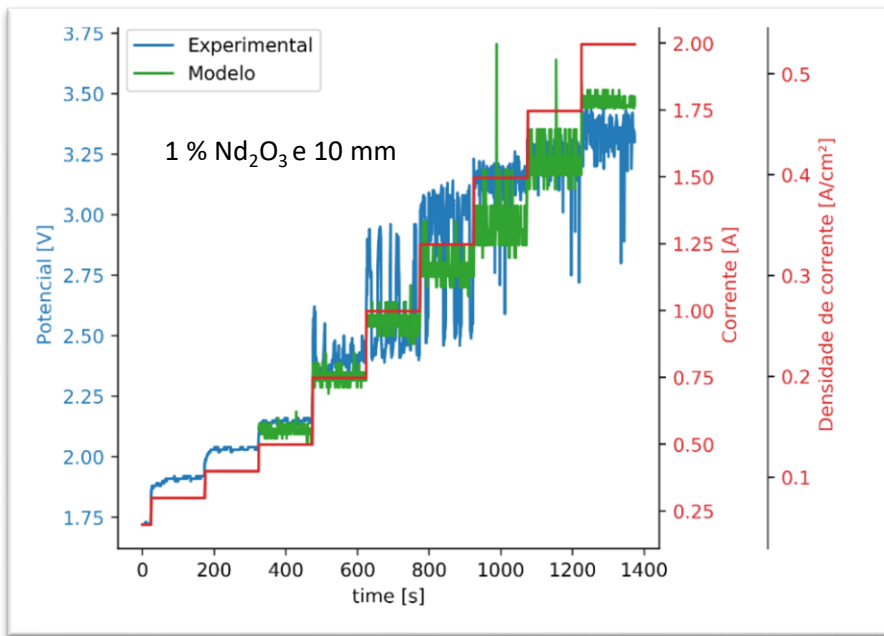


CF_4 – Não adsorve

Predição de Θ por aprendizado de máquinas (árvore de decisão)



Comparação com 75 % dos dados experimentais.





Contents lists available at [ScienceDirect](https://www.sciencedirect.com)

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci



System identification and artificial intelligent (AI) modelling of the molten salt electrolysis process for prediction of the anode effect

Ozan Kaya^{a,b}, Masoud Abedinifar^a, Dominic Feldhaus^b, Fabian Diaz^{b,*}, Şeniz Ertuğrul^c, Bernd Friedrich^b

^a Department of Mechatronics Engineering, Istanbul Technical University, Istanbul 34467, Turkey

^b IME Process Metallurgy and Metal Recycling, RWTH Aachen University, Aachen 52072, Germany

^c Department of Mechatronics Engineering, Izmir University of Economics, Izmir 35330, Turkey

REGINA 2

- Anodo inerte
 - Estudos estão em estágios mais avançados para a produção de alumínio primário

- Fonte de C renovável

Obrigado!

- Andre Nunis
- alnunis@ipt.br