Effect of transition metal impurities on oxygen exchange kinetics in mixed ionic and electronic conducting oxides

Insaf Abdouli, Clément Nicollet

3ième réunion plénières FRH2

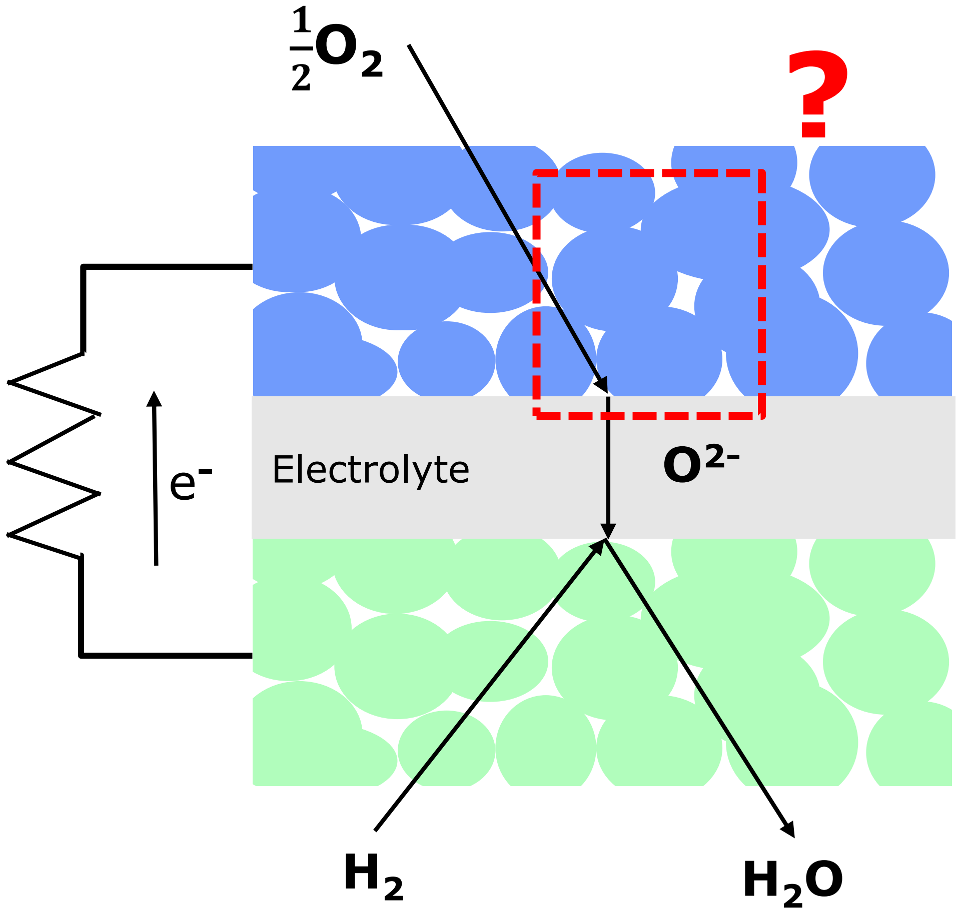
2023/05/23

IMN INSTITUT DES MATÉRIAUX DE NANTES JEAN ROUXEL

cnrs

Nantes Université

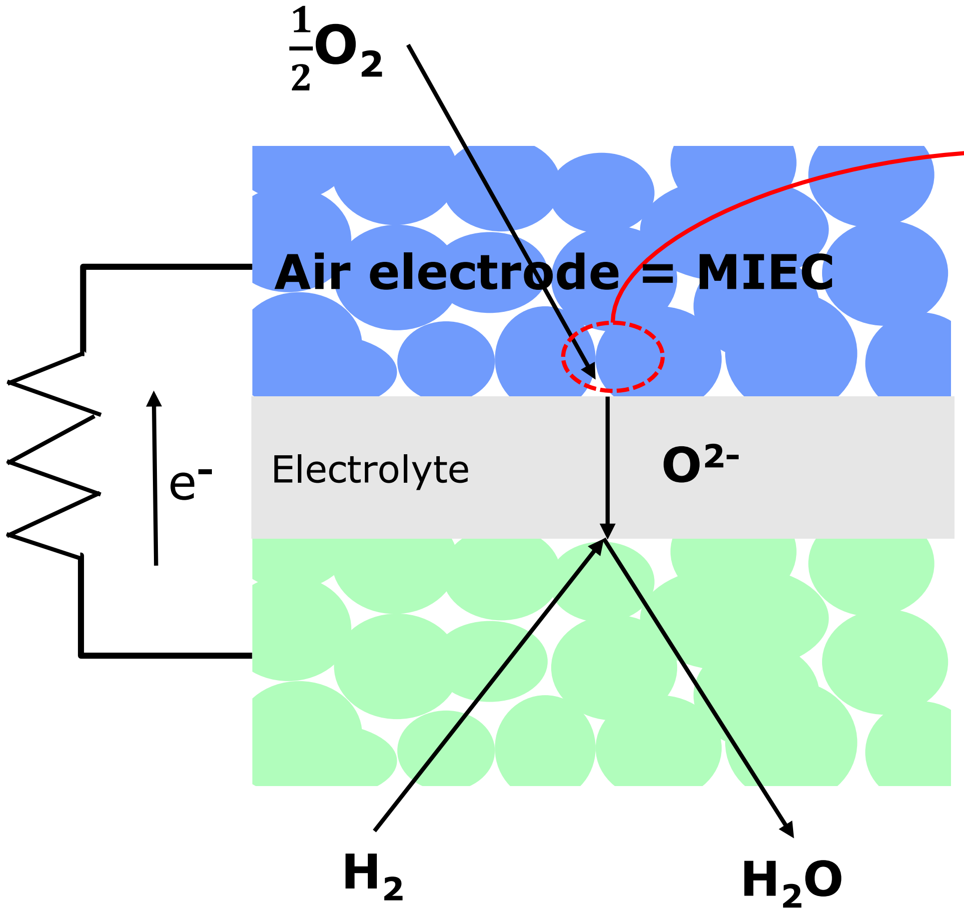
Introduction: Oxygen reduction reaction

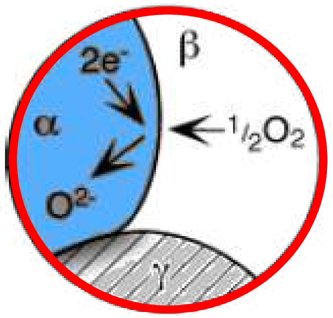


- Diffusion
- Adsorption
- Dissociation
- Partial reduction
- Charge transfer

Mechanism? Active sites?
Impurities effect?

Introduction: Oxygen reduction reaction in MIEC

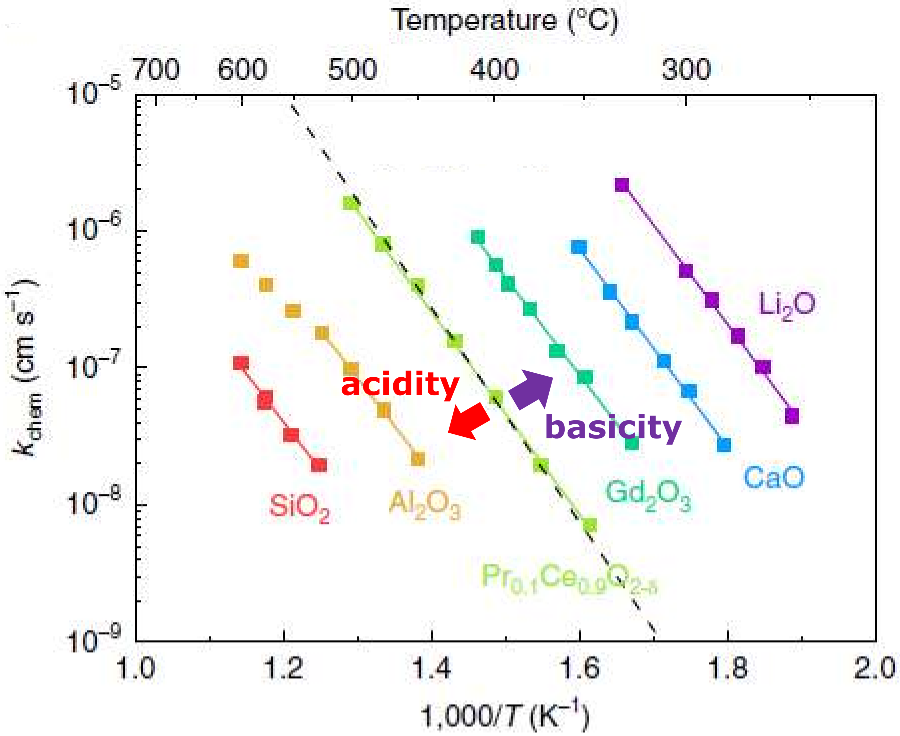




*Adler S. B., Chem Rev, **2004**, 104, 10, 4791-4843.*

$$2e^- + V_O^{\cdot\cdot} + \frac{1}{2}O_2 \rightarrow O_O^X$$

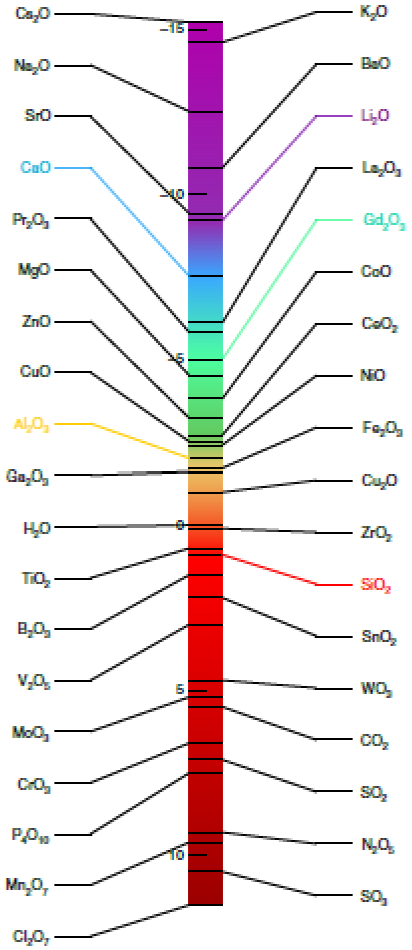
Introduction: $Pr_{0.1}Ce_{0.9}O_{2-\delta}$ (PCO10)



Same E_a

Oxygen exchange coefficient

$$k_{chem} = A \cdot e^{-\frac{E_A}{k_b T}}$$



Smith acidity scale

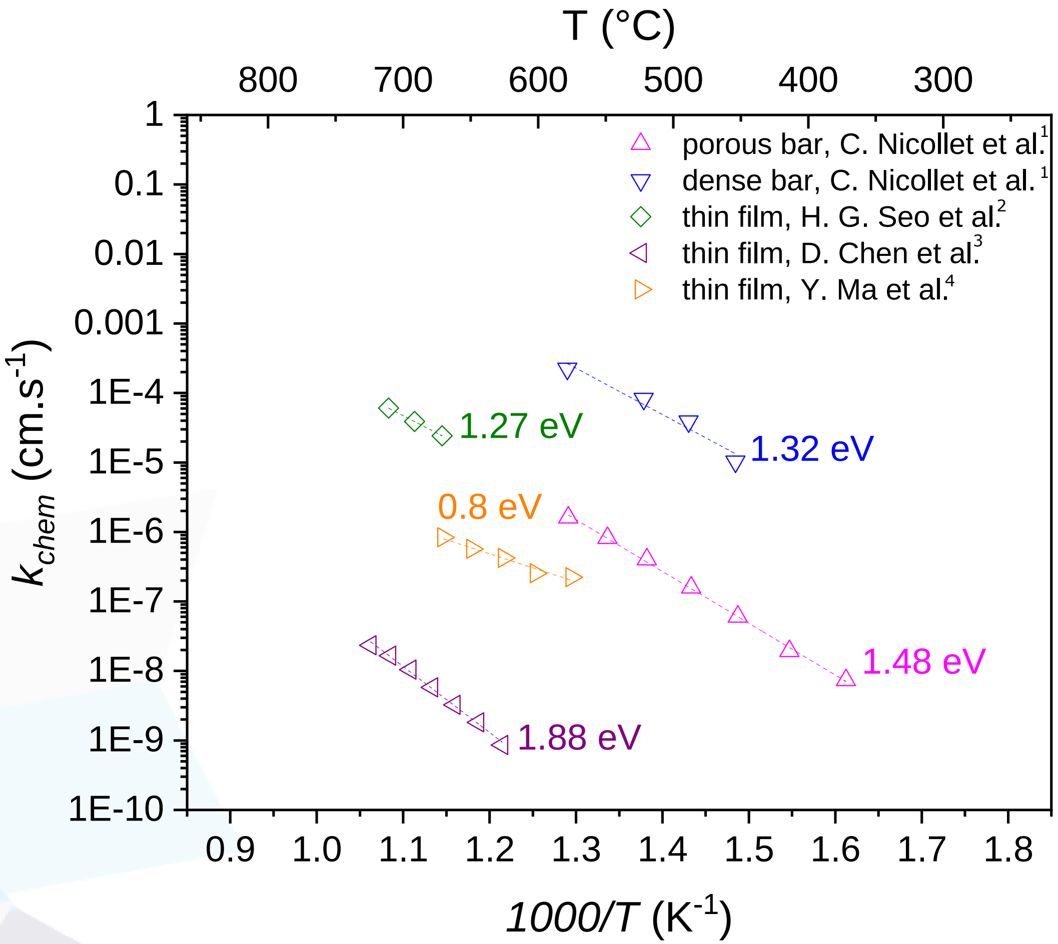
Nicollet C. et al., Nat. Catal. ***2020****, 3 (11), 913–920.*
Smith D. W., Journal of Chemical Education. ***1987****, 64, 480.*

Nantes Université

The French Research network on Hydrogen energy

IMN INSTITUT DES MATÉRIAUX DE NANTES JEAN ROUXEL

Introduction: $Pr_{0.1}Ce_{0.9}O_{2-\delta}$ (PCO10)



Oxygen exchange coefficient

$$k_{chem} = A \cdot e^{-\frac{E_a}{k_b T}}$$

different k_{chem}
different E_a

[1] *Nicollet C. et al., Nat. Catal.* ***2020****, 3 (11), 913–920.*

[2] *Seo H. G. et al., Adv. Energy Mater.* ***2022****, 12 (43), 2202101.*

[3] *Chen D. et al., J. Electroceramics* ***2012****, 28 (1), 62–69.*

[4] *Ma Y. et al., Phys. Chem. Chem. Phys.* ***2018****, 20 (43), 27350–27360.*

Nantes Université

The French Research network on Hydrogen energy

IMN INSTITUT DES MATÉRIAUX DE NANTES JEAN ROUXEL

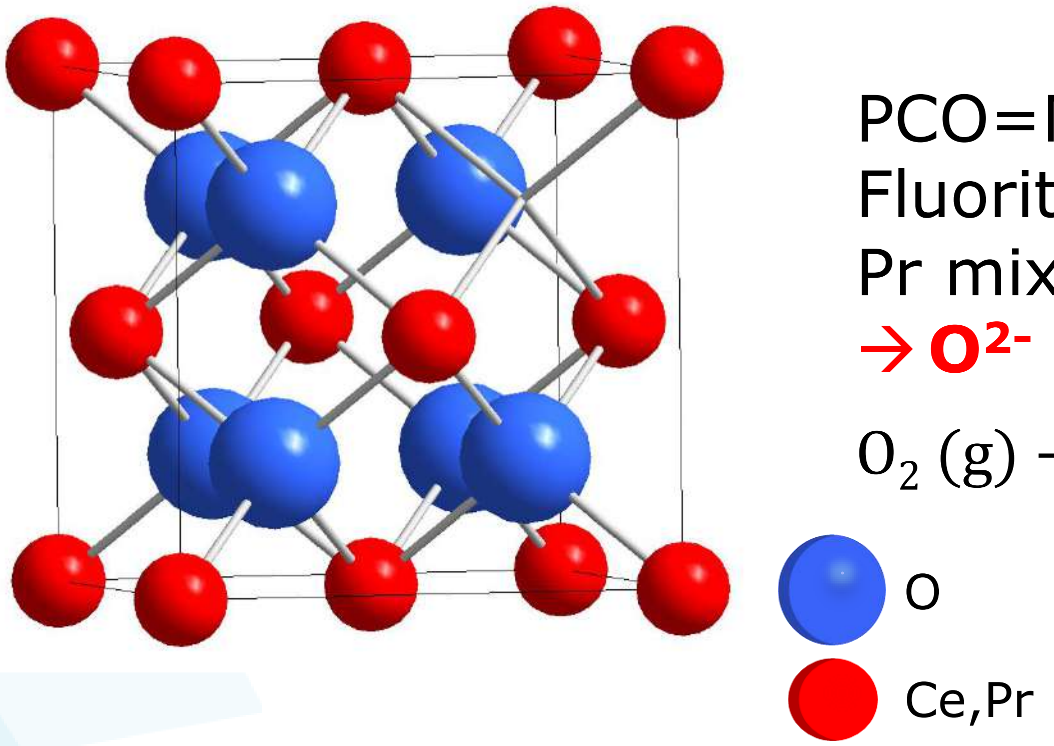
Objectives

Effect of transition metal impurities on PCO10 surface on:

- oxygen exchange coefficient
- oxygen exchange mechanism

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H 1.0079																	2 He 4.0026
2	3 Li 6.941	4 Be 9.0122											5 B 10.811	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.180
3	11 Na 22.990	12 Mg 24.305											13 Al 26.982	14 Si 28.086	15 P 30.974	16 S 32.065	17 Cl 35.453	18 Ar 39.948
4	19 K 39.098	20 Ca 40.078	21 Sc 44.956	22 Ti 47.867	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.845	27 Co 58.933	28 Ni 58.693	29 Cu 63.546	30 Zn 65.38	31 Ga 69.723	32 Ge 72.64	33 As 74.922	34 Se 78.96	35 Br 79.904	36 Kr 83.798
5	37 Rb 85.468	38 Sr 87.62	39 Y 88.906	40 Zr 91.224	41 Nb 92.906	42 Mo 95.96	43 Tc [98]	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29
6	55 Cs 132.91	56 Ba 137.33	57-71 La-Lu	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po [209]	85 At [210]	86 Rn [222]
7	87 Fr [223]	88 Ra [226]	89-103 Ac-Lr	104 Rf [267]	105 Db [268]	106 Sg [271]	107 Bh [272]	108 Hs [277]	109 Mt [276]	110 Ds [281]	111 Rg [280]	112 Cn [285]	113 Uut [...]	114 Fl [287]	115 Uup [...]	116 Lv [291]	117 Uus [...]	118 Uuo [...]

Why $Pr_{0.1}Ce_{0.9}O_{2-\delta}$ (PCO10)?



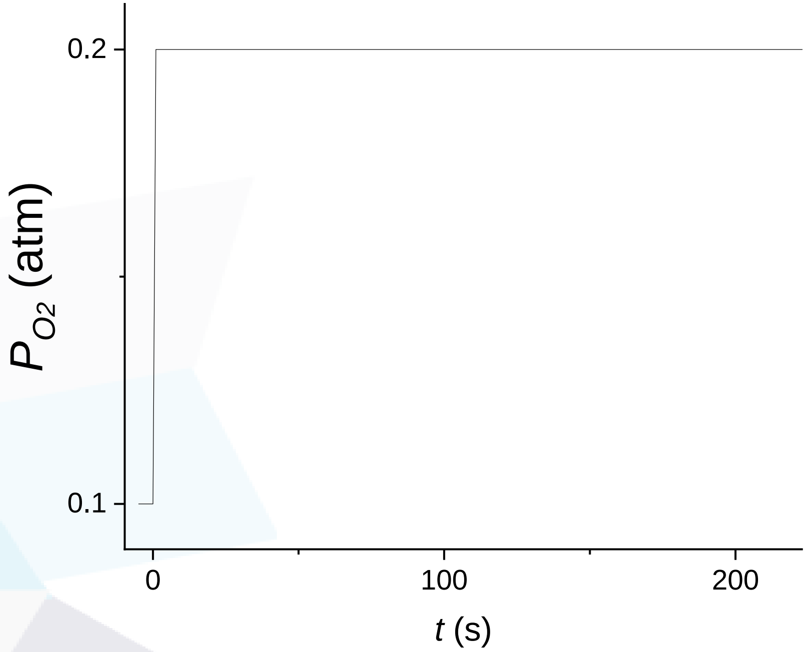
PCO=MIEC
Fluorite type structure
Pr mixed valence 3+/4+
→ O^{2-} vacancies

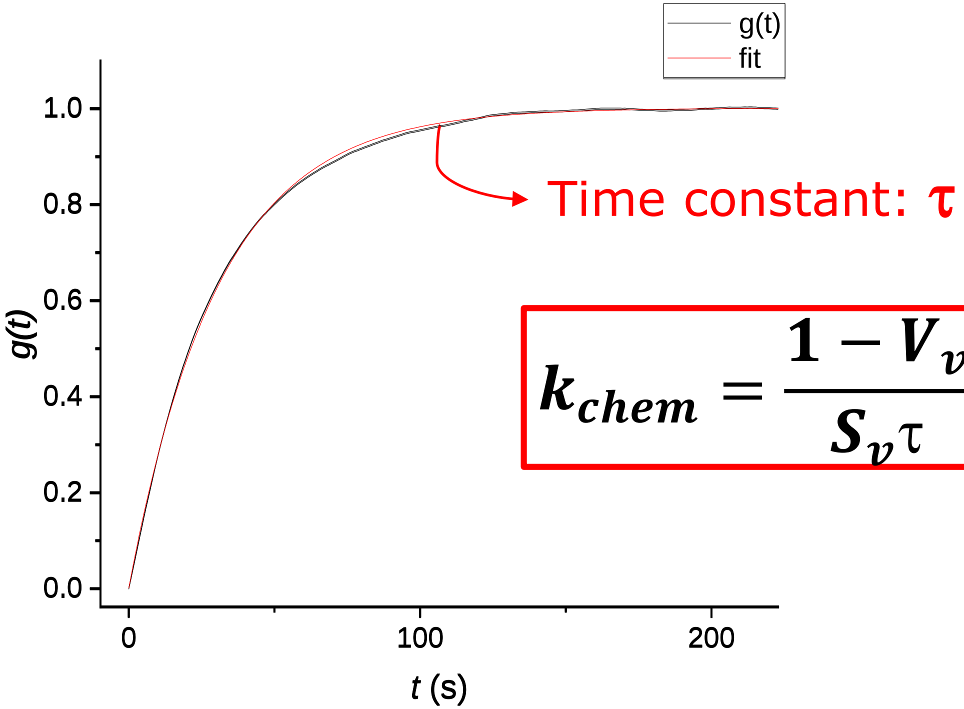
$$O_2\,(g) + 4\,Pr'_{Ce} + 2\,V_{O}^{\cdot\cdot} \leftrightarrow 4\,Pr_{Ce}^{X} + 2\,O_{O}^{X}$$

Oxygen exchange-conductivity relaxation

Porous MIEC: $\Delta P_{O_2} \rightarrow \Delta$conductivity

Normalized conductivity: $g(t)=\frac{\sigma(t)-\sigma(0)}{\sigma_\infty-\sigma(0)} = 1 - e^{-\frac{t}{\tau}}$

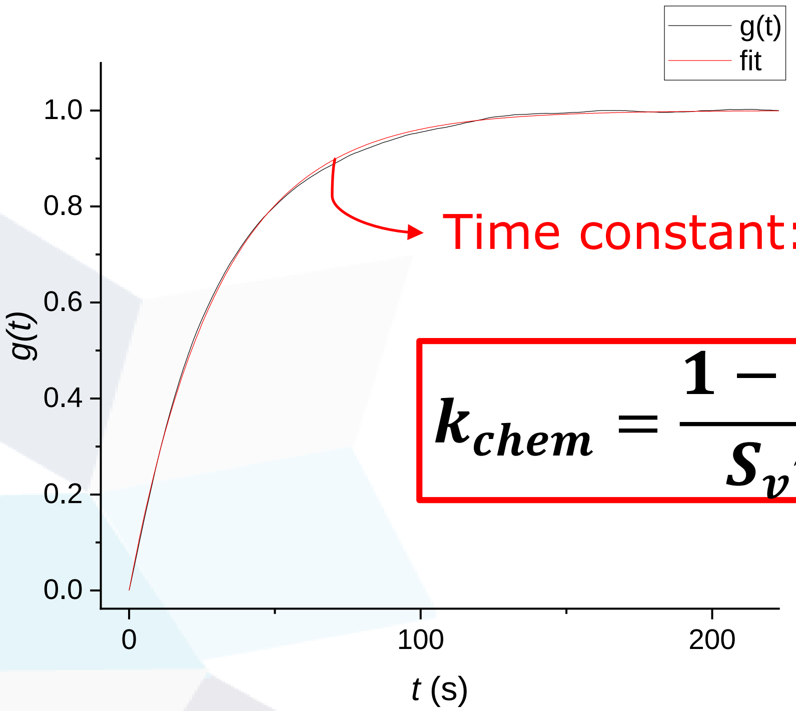




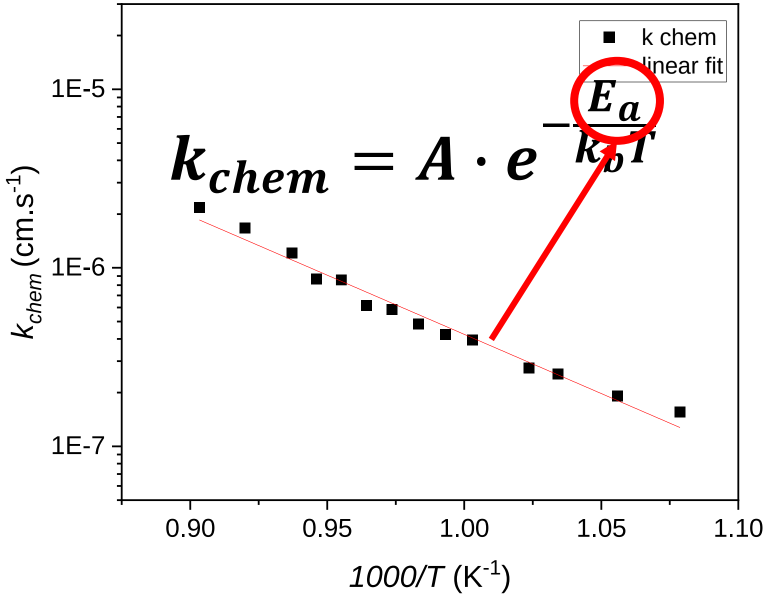
$$k_{chem} = \frac{1 - V_v}{S_v \tau}$$

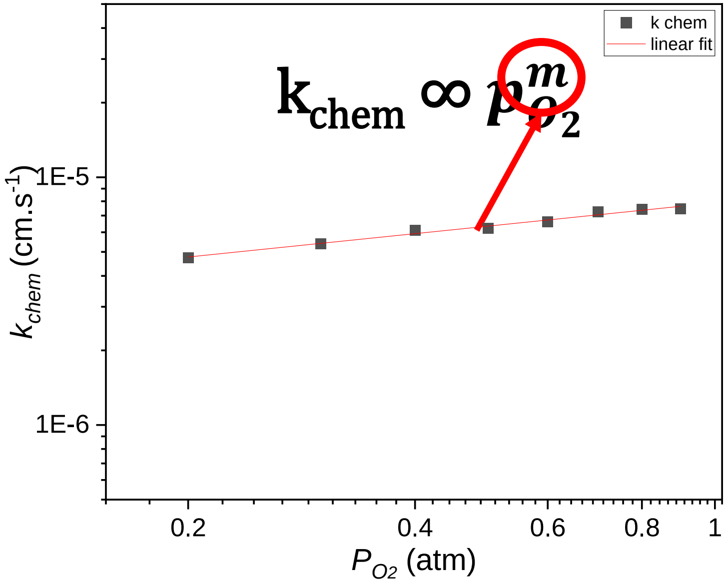
Ganeshananthan R. et al., J. Electrochem. Soc. ***2005****, (8) 152, A1620.*

Oxygen exchange-conductivity relaxation



$$k_{chem} = \frac{1 - V_v}{S_v \tau}$$



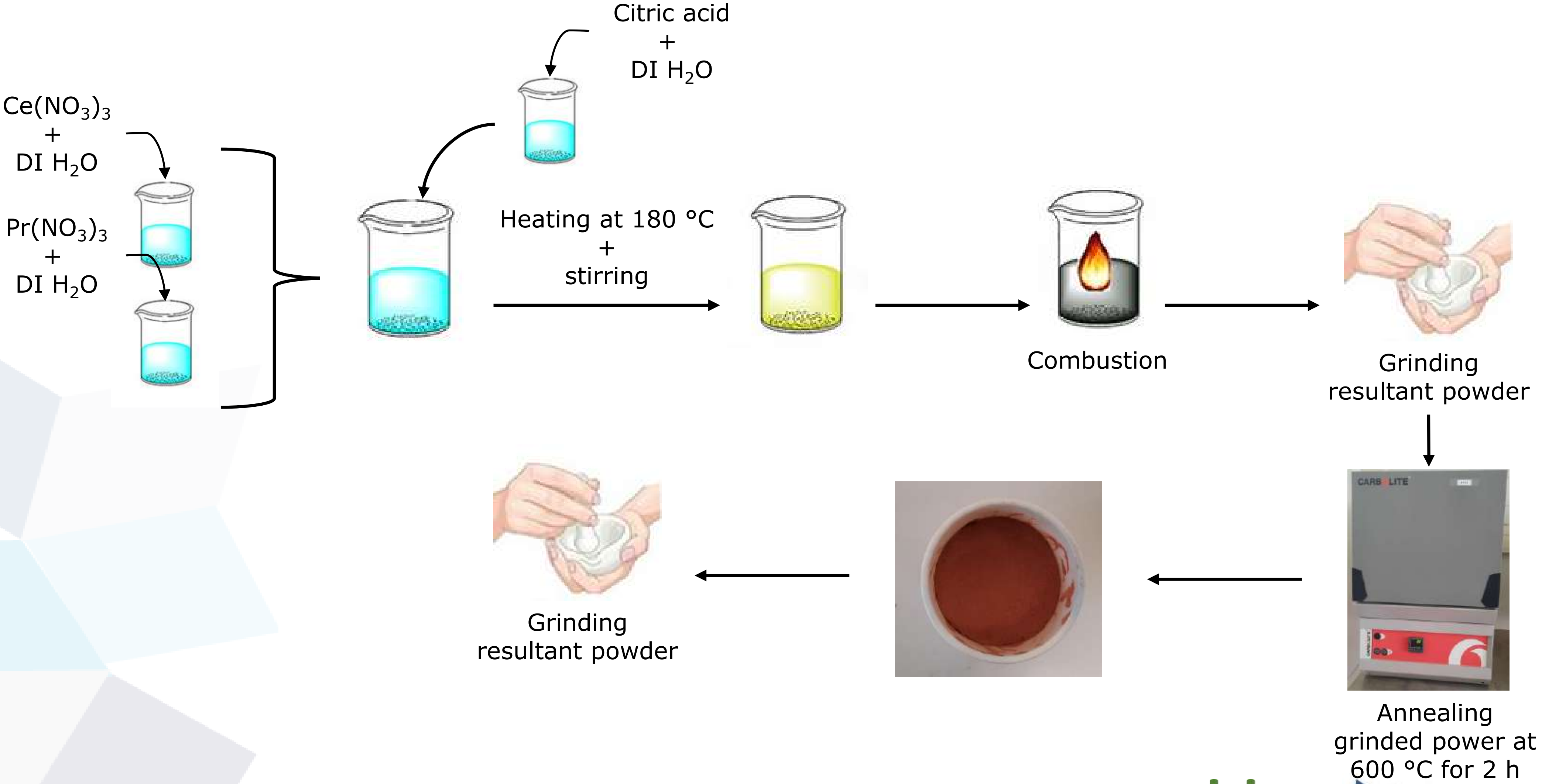


m >0.5 → the RDS involves diatomic oxygen ($O_{2(g)}$, $O_{2,ad}^{q-}$)

m <0.25 → the RDS involves atomic oxygen (O_{ad}^{q-})

Chueh, W. C. et al., Annu. Rev. Chem. Biomol. Eng. 2012, 3, 313–341.

Sample preparation: $Pr_{0.1}Ce_{0.9}O_{2-\delta}$ synthesis



Sample preparation: pellet preparation

$Pr_{0.1}Ce_{0.9}O_{2-\delta}$

Pore former: cellulose 50 µm

50:50 v:v

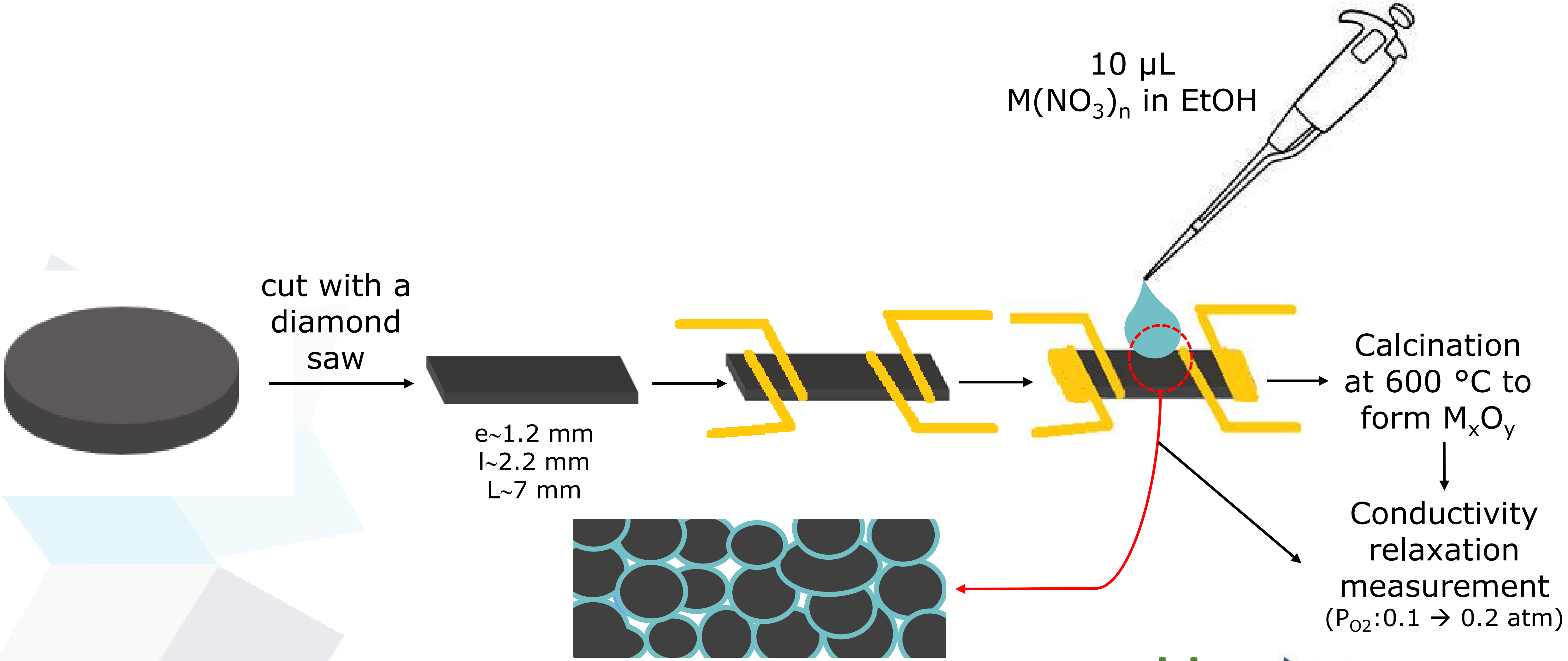
Press into a pellet

Delamination at 1000 °C for 1 h under 1 bar of O_2

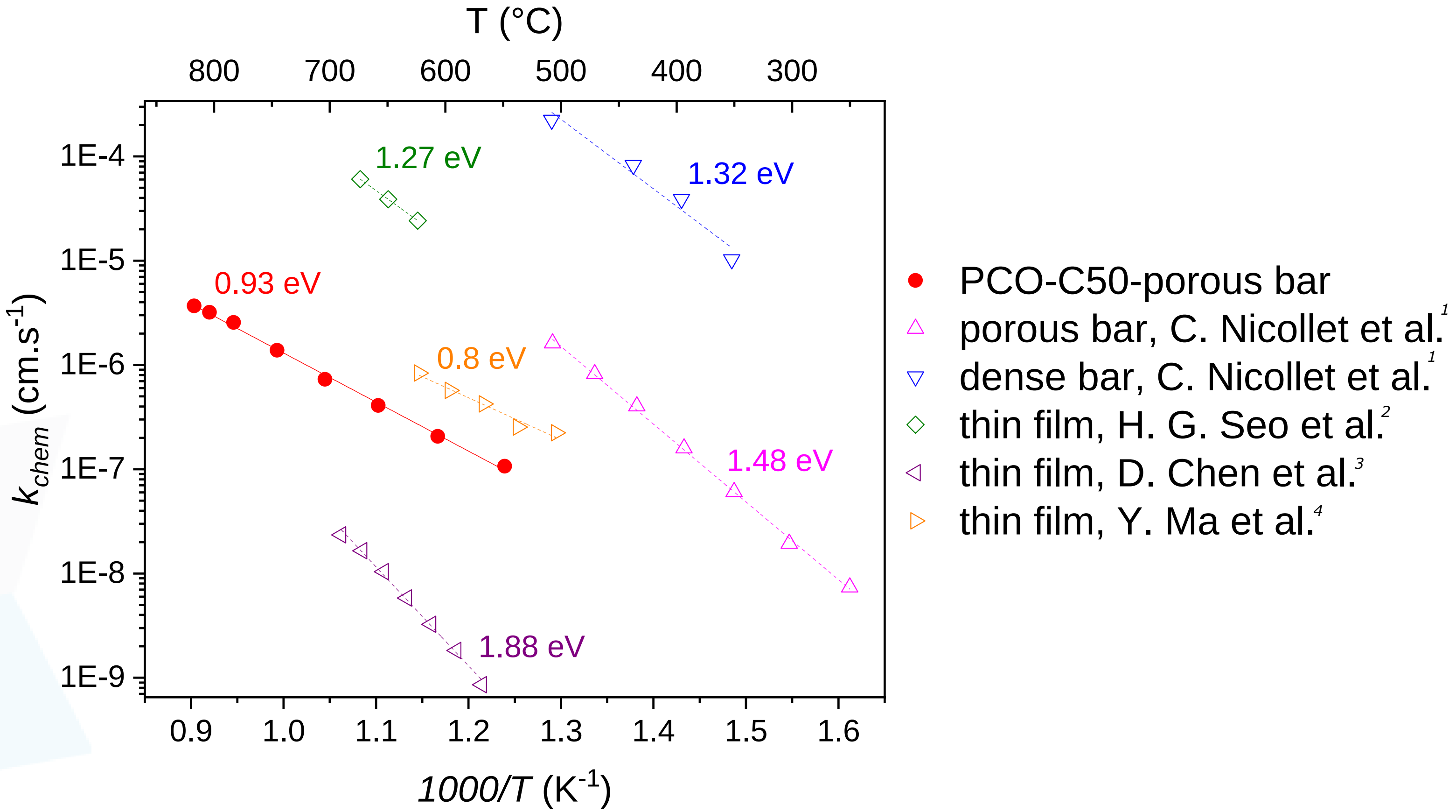
Sintering at 1450 °C for 6 h

Porosity~35 %

Sample preparation: bar preparation



PCO vs. literature



[1] *Nicollet C. et al., Nat. Catal.* ***2020****, 3 (11), 913–920.*

[2] *Seo H. G. et al., Adv. Energy Mater.* ***2022****, 12 (43), 2202101.*

[3] *Chen D. et al., J. Electroceramics* ***2012****, 28 (1), 62–69.*

[4] *Ma Y. et al., Phys. Chem. Chem. Phys.* ***2018****, 20 (43), 27350–27360.*

Thank you for your attention!