

Influence of architecture for nanostructured Pr_6O_{11} and GDC composite oxygen electrodes on their electrochemical properties and stability

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Programme et Equipements Prioritaires de Recherche
sur l'Hydrogène Décarbonaté (PEPR-H2)
Oxygen electrode materials



Working principle of solid oxide cells (SOC)

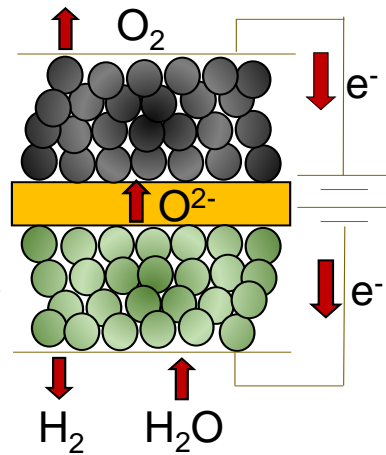
Electrolysis cell: SOEC

- $\sigma_{O_2^-}$: dense, large grains
- YSZ, GDC

+
Anode

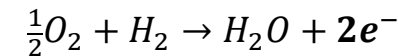
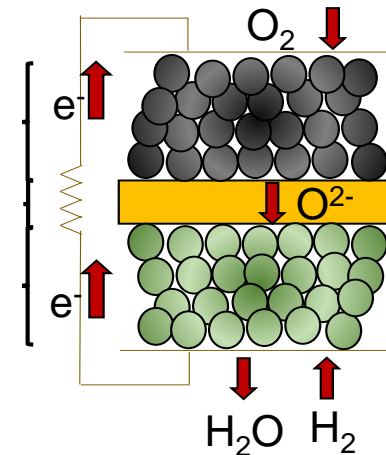
- Porosity
- Percolation $\sigma_{O_2^-} + \sigma_{e^-}$
- Chem. stability (S, C)
- YSZ/ GDC + 30 % Ni

-
Cathode



Fuel cell: SOFC

Oxygen
electrode
Electrolyte
Hydrogen
electrode

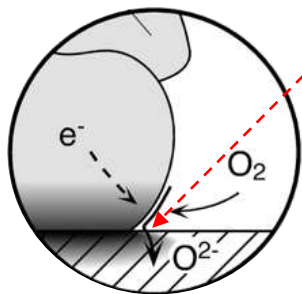


O₂ electrode characteristics

- Electrocatalytic activity
- Porosity
- σ_{e^-} (+ $\sigma_{O_2^-}$)
- Chem. stability
- Mechanical stability

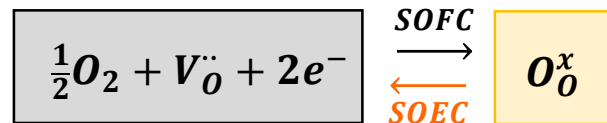
+
Cathode

-
Anode



Triple-phase
boundary (TPB)

S.B. Adler, Chem. Rev., 104 (2004) 4791

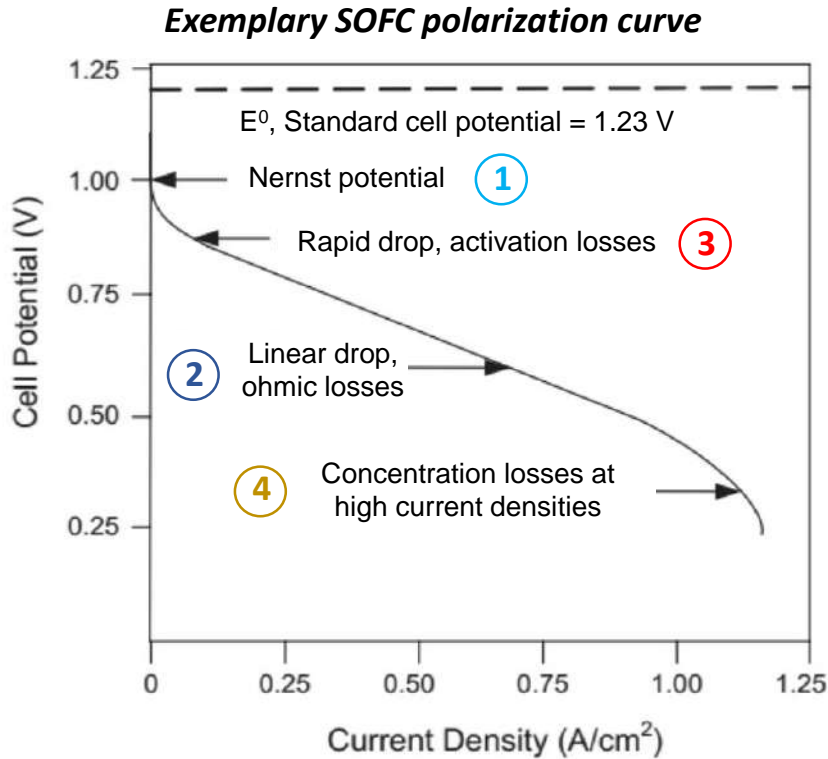


SOFC: oxygen reduction reaction (ORR)
SOEC: oxygen evolution reaction (OER)

- Oxygen electrode materials:**
1. Electronic conductors
 2. Mixed ionic + electronic conductors (MIEC)
 3. Composites

Operation condition:
 $650\text{ }^\circ\text{C} \ll T < 1000\text{ }^\circ\text{C}$

One bottleneck of SOFC – oxygen electrode



Aziz, *Int. Conf. New Trends Sustain. Energy* (2016), 228

EIS: decreasing ω

$$U_{SOFC}(j) = U_N - \eta_{ohm}(j) - \sum \eta_{activation\ polariz.} - \sum \eta_{concentration\ polariz.}$$

① $U_N = E^0 - \frac{RT}{4F} \ln \frac{p_{H_2O}}{p_{O_2}^{1/2} p_{H_2}}$

② $\eta_{ohm} = i \times (R_{electrolyte} + R_{contact}) \rightarrow \sigma_{ion} \propto \exp\left(-\frac{Q}{k_B T}\right)$

③ Processes in active layer: reaction kinetics + activation energies

④ Availability of oxygen species (depletion, accumulation)

Thermal activation

Model for area-specific polarization resistance
(porous, single-phase MIEC)

$$ASR_{pol} \propto \left(\sqrt{\frac{\tau}{(1-\epsilon)a D_o k_o c_o^2}} \right)$$

S.B. Adler, *J. Electrochem. Soc.*, 143 (1996) 3554-3564

Microstructure

τ : Tortuosity
 ϵ : Porosity
 a : Specific surface area (m⁻¹)

Oxygen transport

D_o : Oxygen self-diffusion coeff. (m²/s)
 k_o : Oxygen self-surface exchange coeff. (m/s)

Thermodynamics

c_o : concentration of oxygen lattice sites in equilibrium (mol/m³)

T-related inconveniences

- ❖ Elevated startup times
- ❖ Continuous energy demand
- ❖ Degradation promoted

Lower operation T?

- ❖ Reduced reaction kinetics
- ❖ Increased activation energy

- ✓ Electrolyte ohmic losses : doping + thin dimensions
- Oxygen electrode overpotentials :
 1. Choice of electrode materials (intrinsic properties)
 2. Modification of microstructure/architecture

Alternative oxygen electrode materials

Research towards stable, performant SOC materials

$La_{1-x}Sr_xMnO_3$ (ABO_3)

- $\sigma_{e^-} = 200 \text{ S cm}^{-1}$, 800 °C

Y Takeda, *Int. J. Electrochem. Soc.*, 134 (1987), 2656

$La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ (ABO_3)

- $\sigma_{e^-, 6428} = 300 \text{ S cm}^{-1}$, 650°C
L.W. Tai, Solid State Ion., 76 (1995), 273
- $\sigma_{ion, 6428} = 0.007 \text{ S cm}^{-1}$, 650°C
B. Fan, Solid State Sci., 13 (2011), 1835

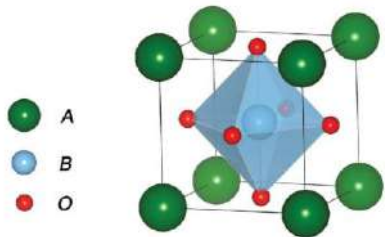
$Ln_2NiO_{4+\delta}$ ($A_{n+1}B_nO_{3n+1}$)

- La/Pr: stability/ electrocatalytic prop.
- $\sigma_{e^-} = 40\text{-}110 \text{ S cm}^{-1}$, 700 °C
E. Boehm, Solid State Ion., 176 (2005), 2717
- Decomposition under current ($Pr_4Ni_3O_{10-\delta}$, $Pr_3O_{7-\delta}$, Pr_6O_{11})
V. Vibhu, J. Energy Chem., 46 (2020), 62-70
N.I. Khamidy, J. Power Sources, 450 (2020), 227724

Pr_6O_{11} (AO_2)

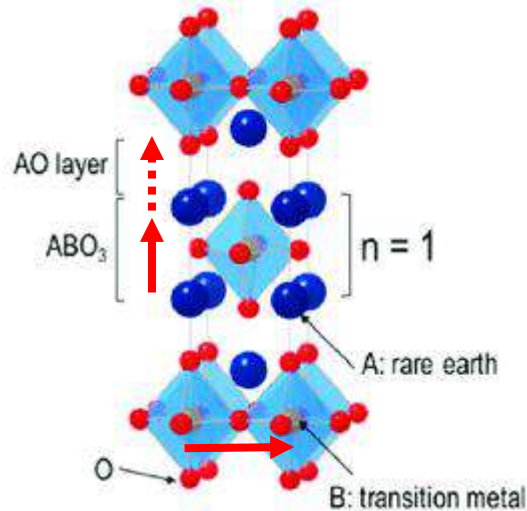
- Transition of Pr_2O_3 to PrO_2
- PrO_x with $x = 1.833$ ($PrO_{2-\delta}$)
→ mixed valency Pr^{3+}/Pr^{4+}
- $\sigma_{e^-} < 4 \text{ S/cm}$
C Nicollet, Int. J. Hydrog. Energy, 41 (2016), 15538

Cubic Perovskite



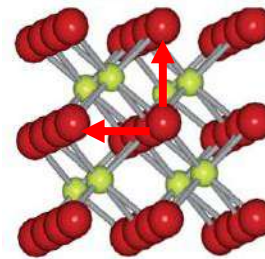
- Doping of La^{3+} with Sr^{2+} : oxygen vacancies
- Transition metals: mixed valency, σ_{e^-}

Ruddlesden-Popper (n=1)



- Vacancy mechanism in c-direction
- Interstitials in ab-plane → T-activated

Cubic Fluorite



Isotropic transport properties

Material	D^* (cm^2/s)	k^* (cm/s)
LSM ¹	5.0×10^{-8}	1.0×10^{-12}
LSCF ²	7.0×10^{-7}	5.0×10^{-8}
LNO ³	1.0×10^{-6}	1.5×10^{-8}
PNO ⁴	5.0×10^{-7}	2.5×10^{-8}
Pr_6O_{11} ⁵	3.4×10^{-8}	5.4×10^{-7}

900 °C

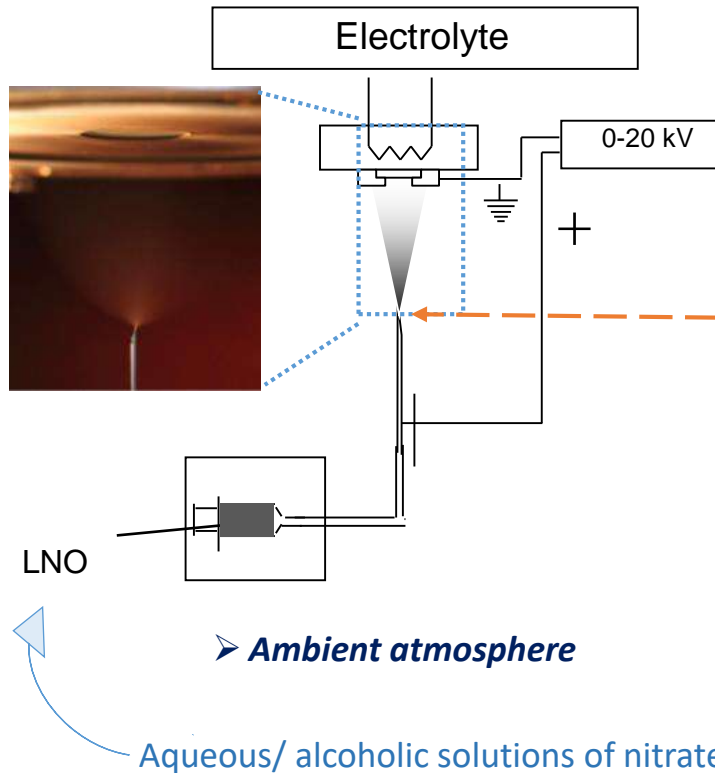
600 °C

¹ De Souza, *Solid State Ion.*, 106 (1998), 175; ² Audinot, (1999) PhD Thesis, Université de Bordeaux; ³ Skinner, *Solid State Ion.*, 135 (2000), 709; ⁴ Boehm, *Solid State Ion.*, 176 (2005), 2717; ⁵ Nicollet, *Int. J. Hydrog. Energy*, 41 (2016), 15538

Traditionally SOC via screen-printing, tape casting, ...

➤ What is the effect of reduced grain/ particle sizes?

Electrostatic Spray Deposition (ESD)



Gañan-Calvo (initial droplet size)

$$d_{size} \propto \left(\frac{\rho \epsilon_0 Q^3}{\gamma \sigma} \right)^{1/6}$$

- Surface tension, γ (N/m)
- Electrical conductivity, σ (S/m)
- Solution density, ρ (g/cm³)
- Solution flow rate, Q (ml/h)

Gañan-Calvo, J. Aerosol Sci., 28 (1997), 249

e.g. $\phi_{EtOH, 1.5 \text{ mL/h}}: 3.8 \mu\text{m}$

➤ **Microstructures with different textures, porosities, particle size**

Factors on droplet size

- 1) Initial droplet size - physicochemical properties of precursor solutions:
 - Solvent $\rightarrow T_B, \gamma$
 - Concentration $\rightarrow \sigma, \gamma$
 - Amount of solution $\rightarrow Q$
- 2) Final droplet size - deposition parameters:
 - Conditions during flight $\rightarrow T, d, t$
 - Amount of solution $\rightarrow Q$

➤ **Complex interplay of factors**

Preparation of ESD deposits on GDC

1. Deposition time
2. Deposition temperature
3. Nozzle-to-substrate distance
4. Solution flow rate

Analysis of morphology

1. SEM (surface, cross-sections)
2. TEM, XRD (grain size)

Effect of deposition time

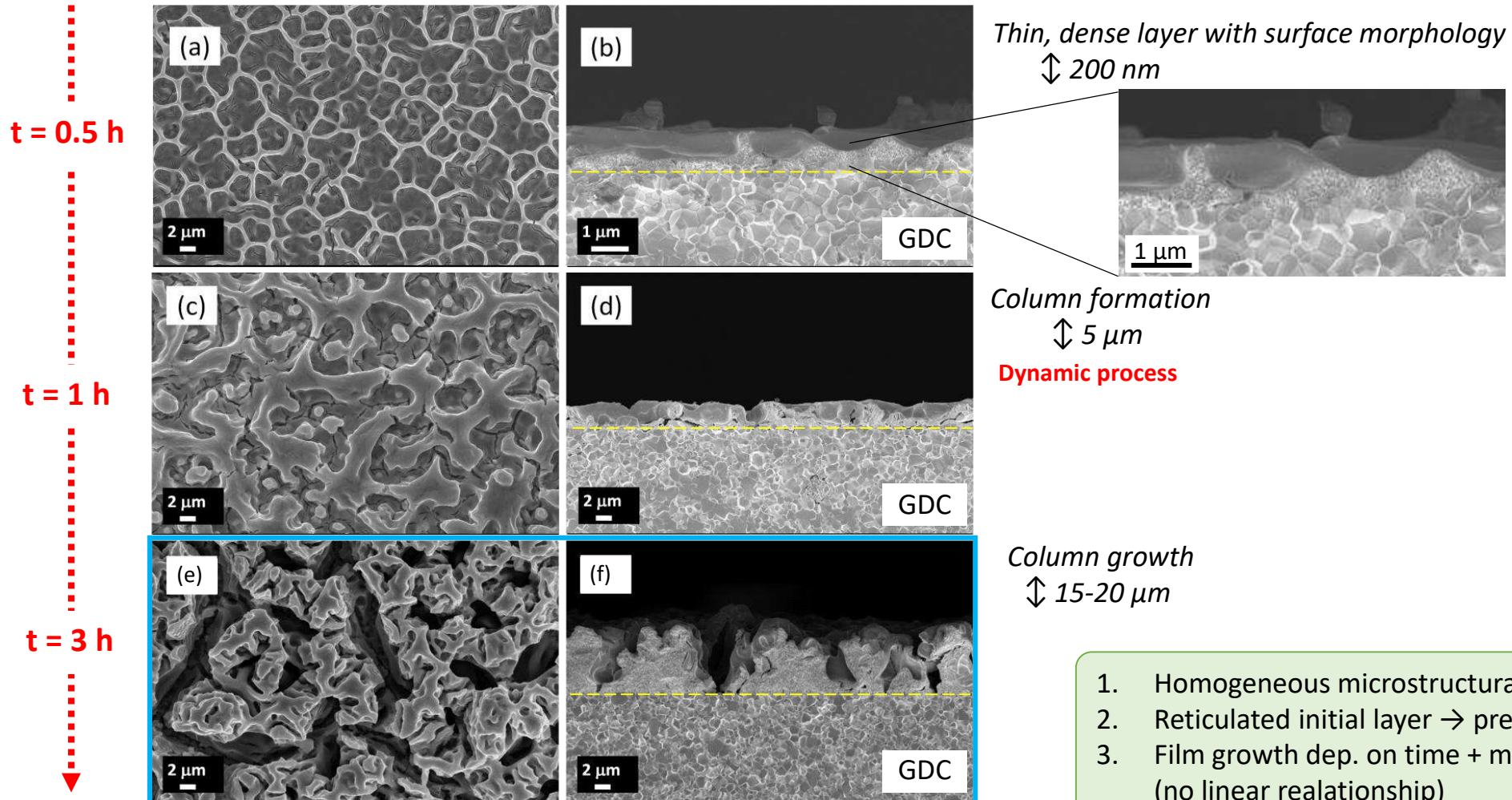
Initial droplets: $\varphi = 4.8 \mu\text{m}$

Ethanol: Butyl carbitol * (1:2, wt.), 0.02 M

Calcinated for 2 h, 700 °C

* Diethylene glycol butyl ether

$D = 20 \text{ mm}$, $Q = 1.5 \text{ mL/h}$, $T = 300^\circ\text{C}$, $E = 7.8 \text{ kV}$



- 1. Homogeneous microstructural evolution over time
- 2. Reticulated initial layer \rightarrow preferential deposition
- 3. Film growth dep. on time + microstructure (no linear relationship)

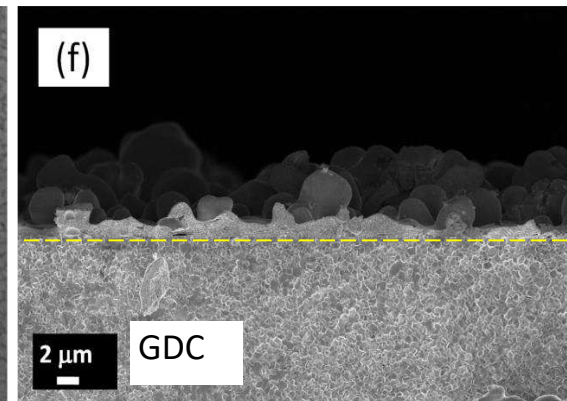
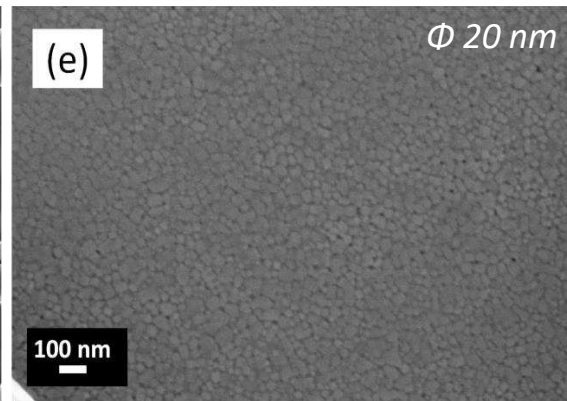
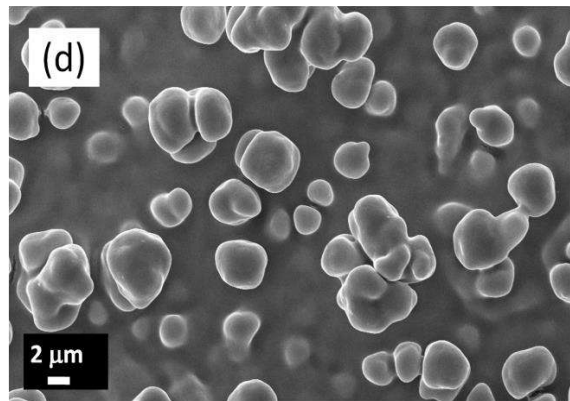
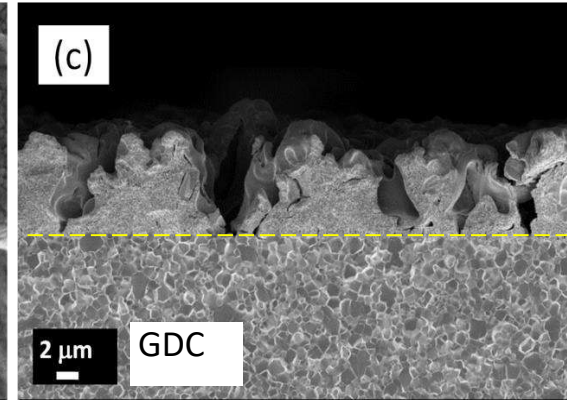
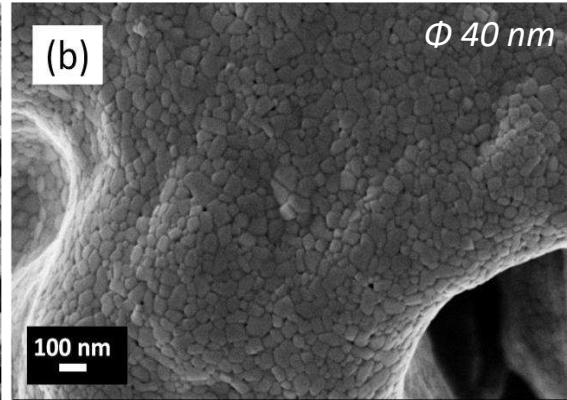
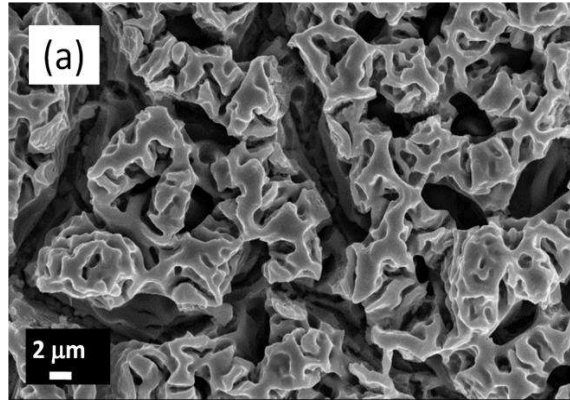
Effect of deposition temperature

Initial droplets: $\varphi = 4.8 \mu\text{m}$

Ethanol: Butyl carbitol * (1:2, wt.), 0.02 M
 Calcinated for 2 h, 700 °C
 * Diethylene glycol butyl ether

$D = 20 \text{ mm}$, $Q = 1.5 \text{ mL/h}$, $E = 7.8\text{-}10 \text{ kV}$, $t = 3 \text{ h}$

T = 300 °C
 T = 350 °C



Columns
 Simultaneous spreading
 and drying of droplets

Dynamic process

Dense layer with
 agglomerates

Ordered process

1. Particle size ↓ for T ↑
2. Grain size: 40 nm → 20 nm
3. Microstructural evolution: agglomerated particles for higher T

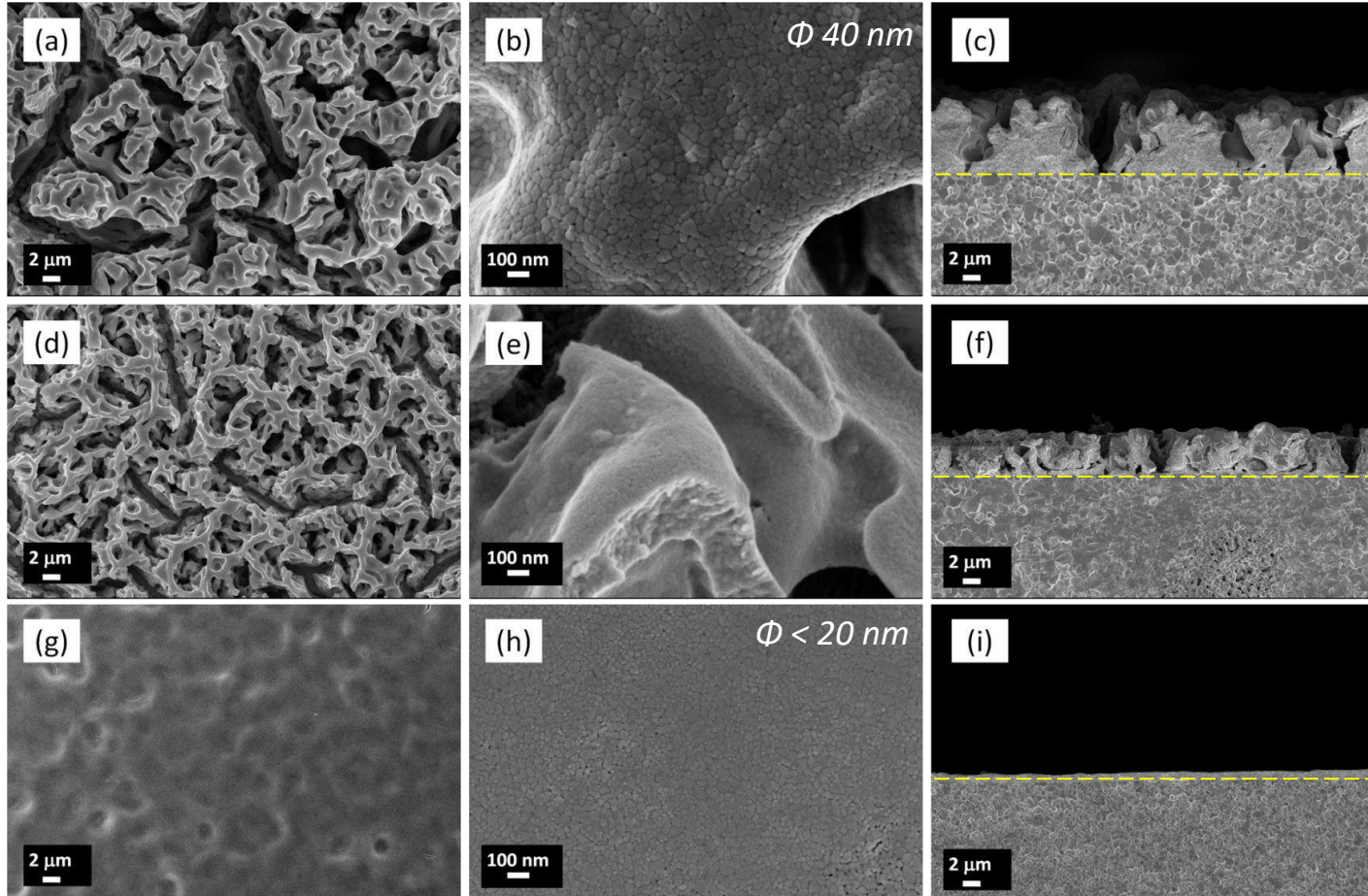
Effect of nozzle-to-substrate distance

Initial droplets: $\varphi = 4.8 \mu\text{m}$

$Q = 1.5 \text{ mL/h}$, $T = 300 \text{ }^\circ\text{C}$, $E = 7.8 \text{ kV}$, $t = 3 \text{ h}$

Ethanol: Butyl carbitol* (1:2, wt.), 0.02 M
Calcinated for 2 h, 700 °C
* Diethylene glycol butyl ether

$D = 2 \text{ cm}$
 $D = 3 \text{ cm}$
 $D = 5 \text{ cm}$



Wide columns,
large particles
Dynamic process

Thin columns,
smaller particles
→ reticulation

Dense layer,
small particles
(no agglomeration yet)
Ordered process

1. Homogeneous evolution of microstructure
2. Particle size \downarrow for $D \uparrow$
3. Grain size: $40 \text{ nm} \rightarrow < 20 \text{ nm}$

Effect of solution flow rate

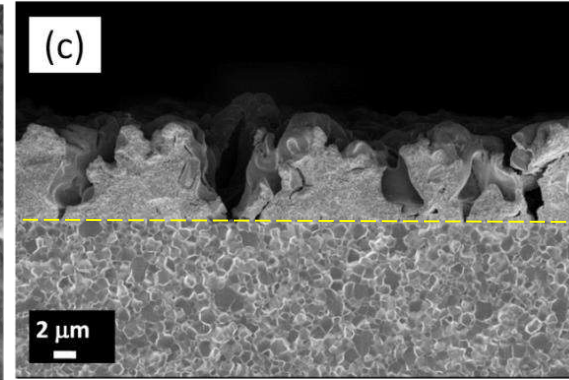
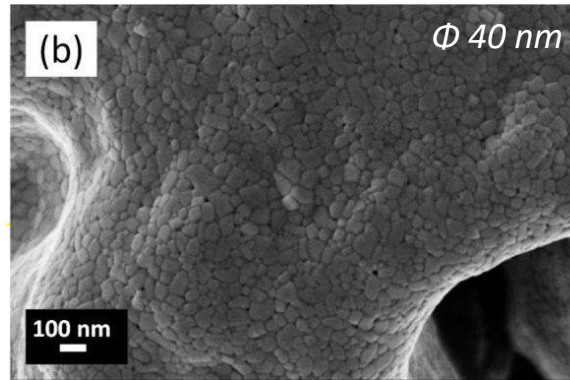
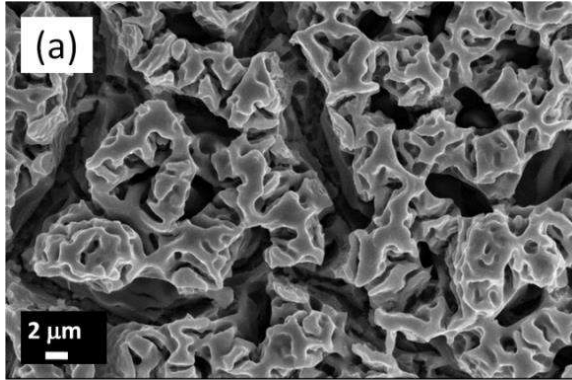
$$d_{size} \propto \left(\frac{\rho \epsilon_0 Q^3}{\gamma \sigma} \right)^{1/6}$$

Ethanol: Butyl carbitol * (1:2, wt.), 0.02 M
 Calcinated for 2 h, 700 °C
 * Diethylene glycol butyl ether

Gañan-Calvo, J. Aerosol Sci., 28 (1997), 249

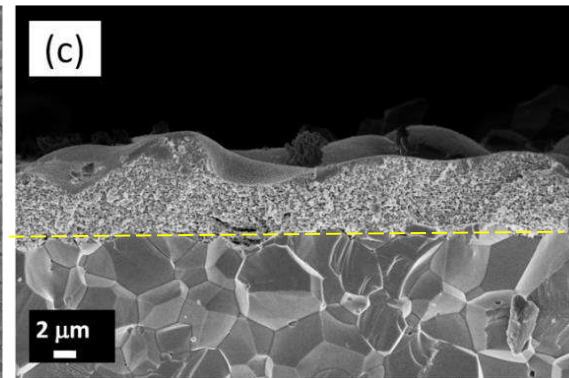
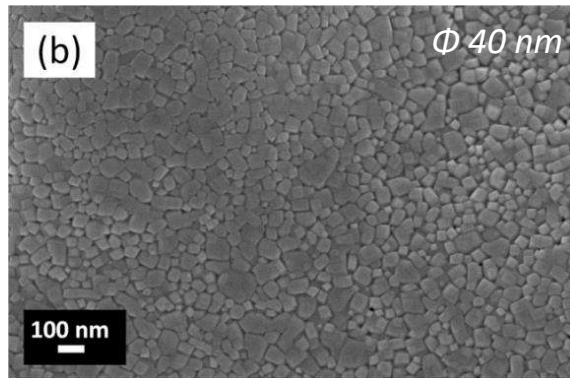
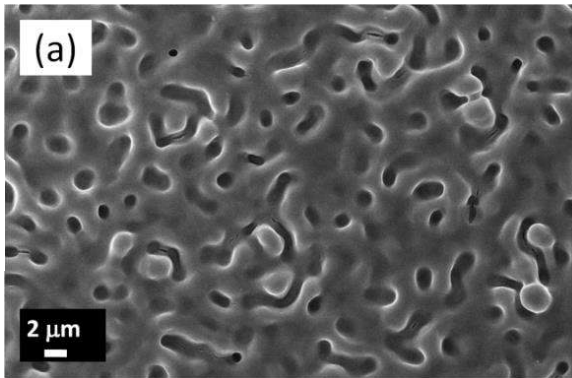
$D = 20 \text{ mm}$, $T = 300 \text{ °C}$, $E = 7.8 \text{ kV}$, $t = 3 \text{ h}$

$Q = 1.5 \text{ mL/h}$
 Initial droplets
 $\varphi = 4.8 \text{ }\mu\text{m}$



Column growth
 Dynamic process

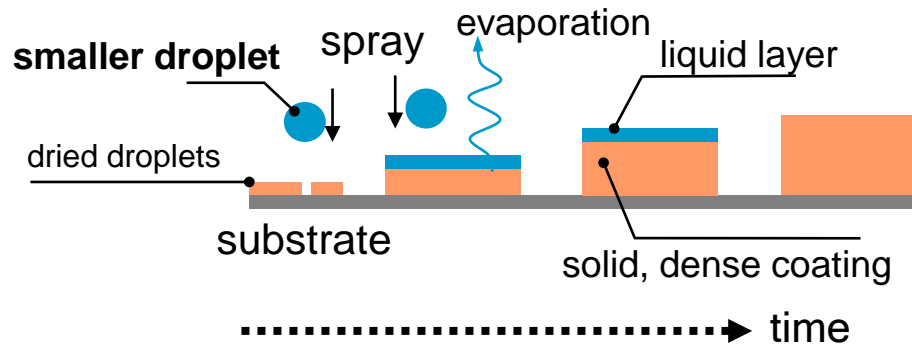
$Q = 0.5 \text{ mL/h}$
 Initial droplets
 $\varphi = 2.8 \text{ }\mu\text{m}$



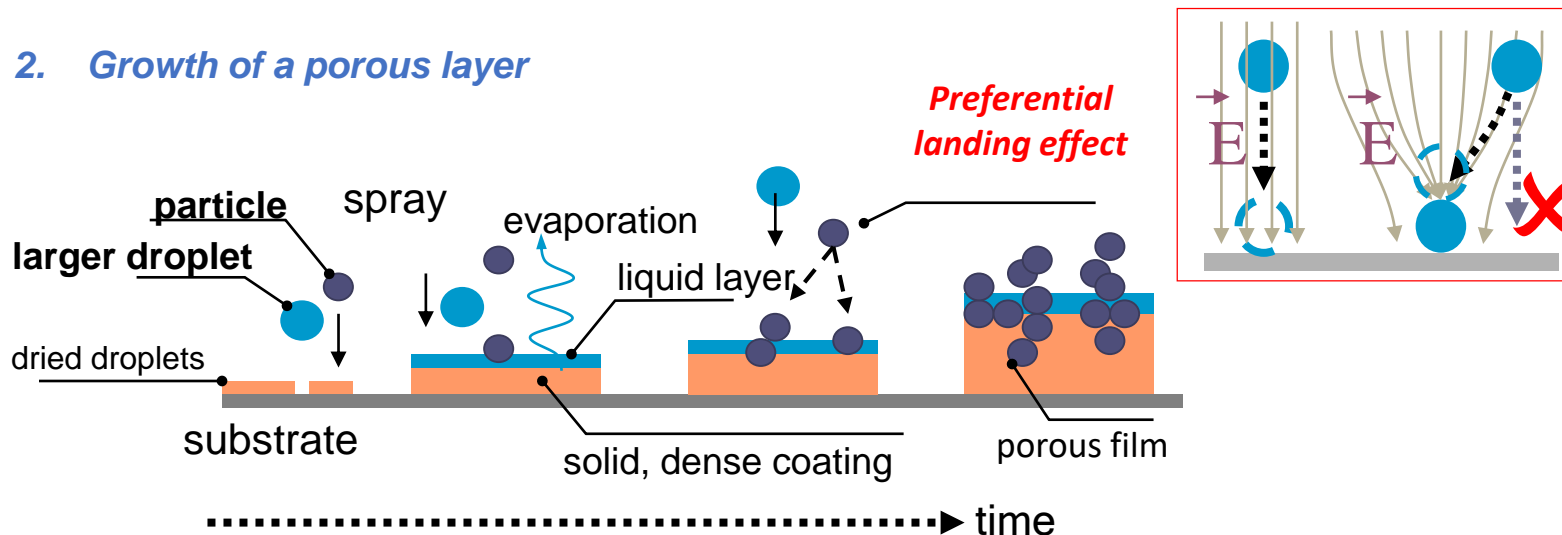
Dense layer
 Ordered process

1. Particle size ↓ for flow rate ↓
2. Grain size similar for different initial droplet sizes
3. Evolution of microstructure to dense layer

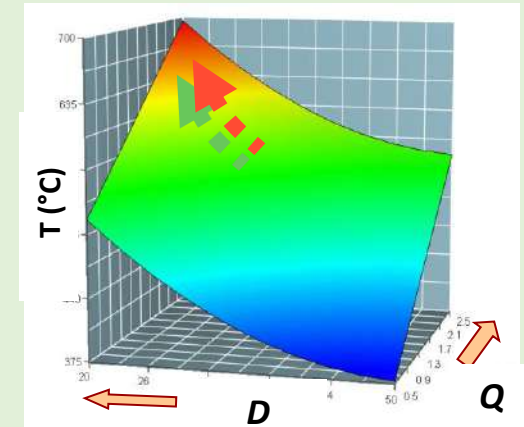
1. Growth of a dense layer



2. Growth of a porous layer



1. Equilibrium of parameters



R. Neagu, *Solid State Ionics*, 177 (2006), 1981-1984

- Plane = constant droplet size
- High T allows high Q and high D
 - Small T limits D and Q

2. Short deposition time:

Dense, thin initial layer

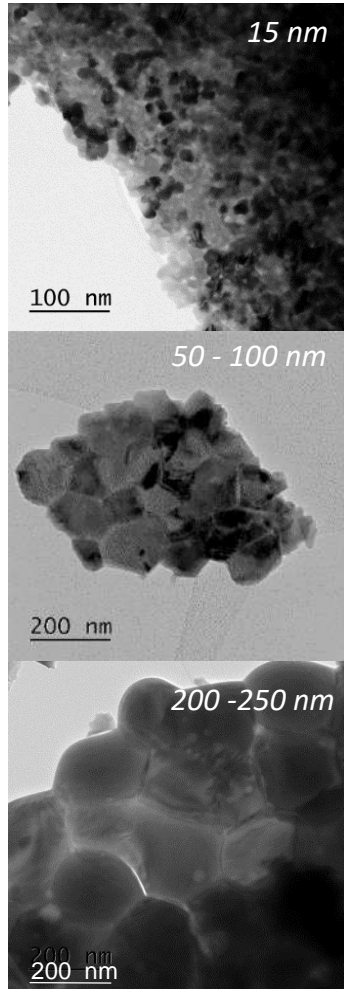
3. Longer deposition times:

Development of microstructures

- ✓ High influence on morphology and porosity via deposition parameters

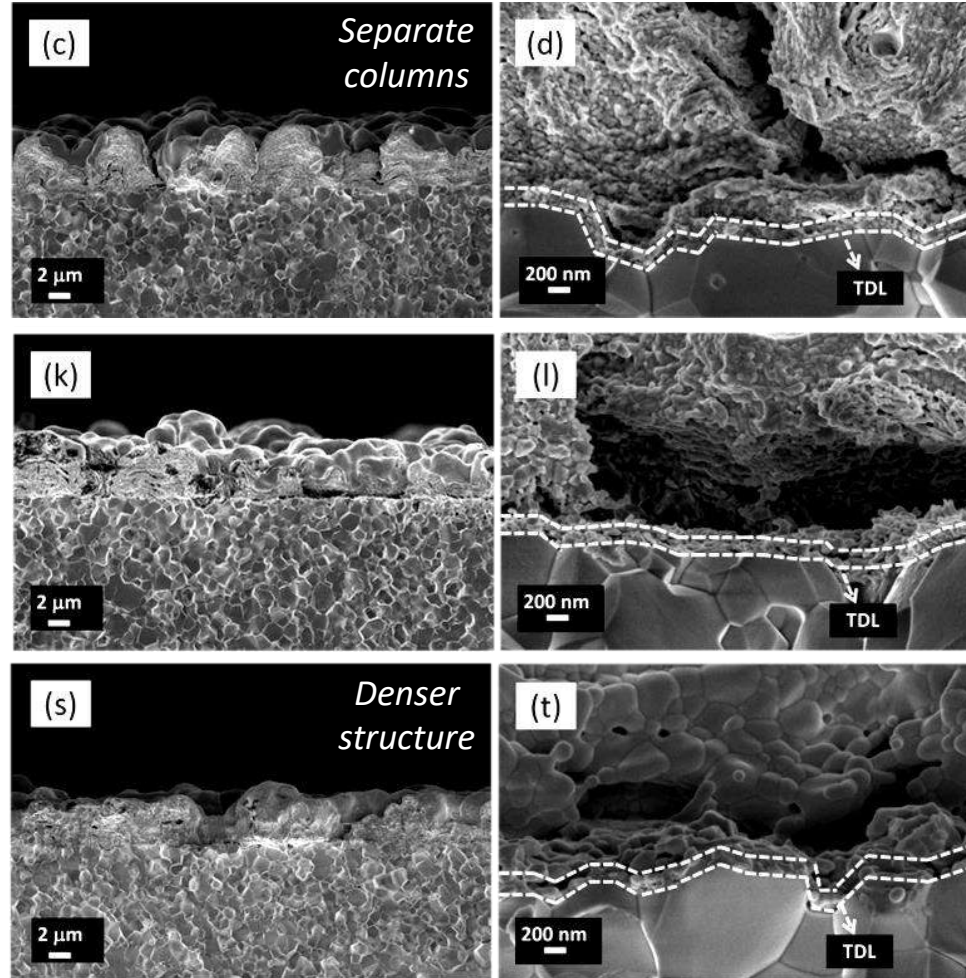
Influence of calcination temperature on crystallite size

Particles post-calcination



T = 600 °C
T = 800 °C
T = 1000 °C

Calcination of ESD deposits



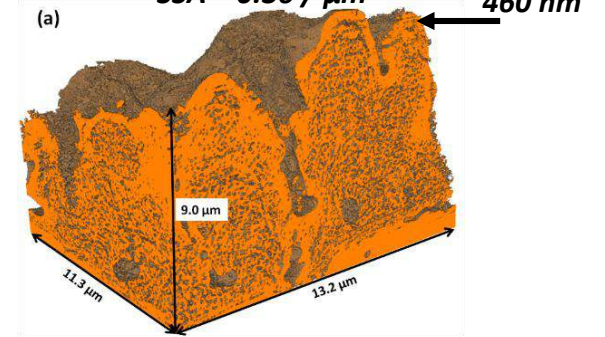
- Apparent densification (morphology maintained)
- Dense interlayer already at low T → CT_{ion}

H₂O: Butyl carbitol * (1:2, wt.), 0.02 M
 Q = 1 mL/h, T = 300 °C, d = 20 mm
 Calcinated for 2 h

FIB-SEM + 3D-reconstruction

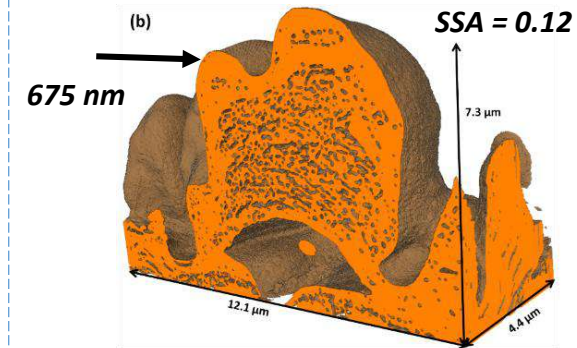
T = 700 °C (35 μm crystals)

SSA = 0.36 / μm



T = 900 °C

SSA = 0.12 / μm



- "Core-shell" structure
- Ideally low sintering temperature
- Stability?

V_{acceleration} = 200 kV, 0.19 mm resolution

Aggregate formation (XRD: 27-65 nm)

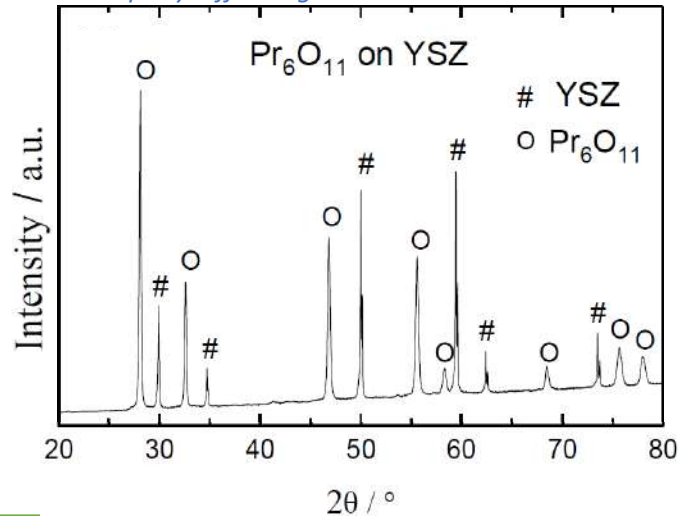
Sample preparation

1. Pr_6O_{11} (ESD, columnar, > 10 μm , 35 nm particles)
2. Composite pellets (50 % wt.): Pr_6O_{11} and GDC/YSZ



3. Thermal treatment (800 °C or 900 °C, 10 days)

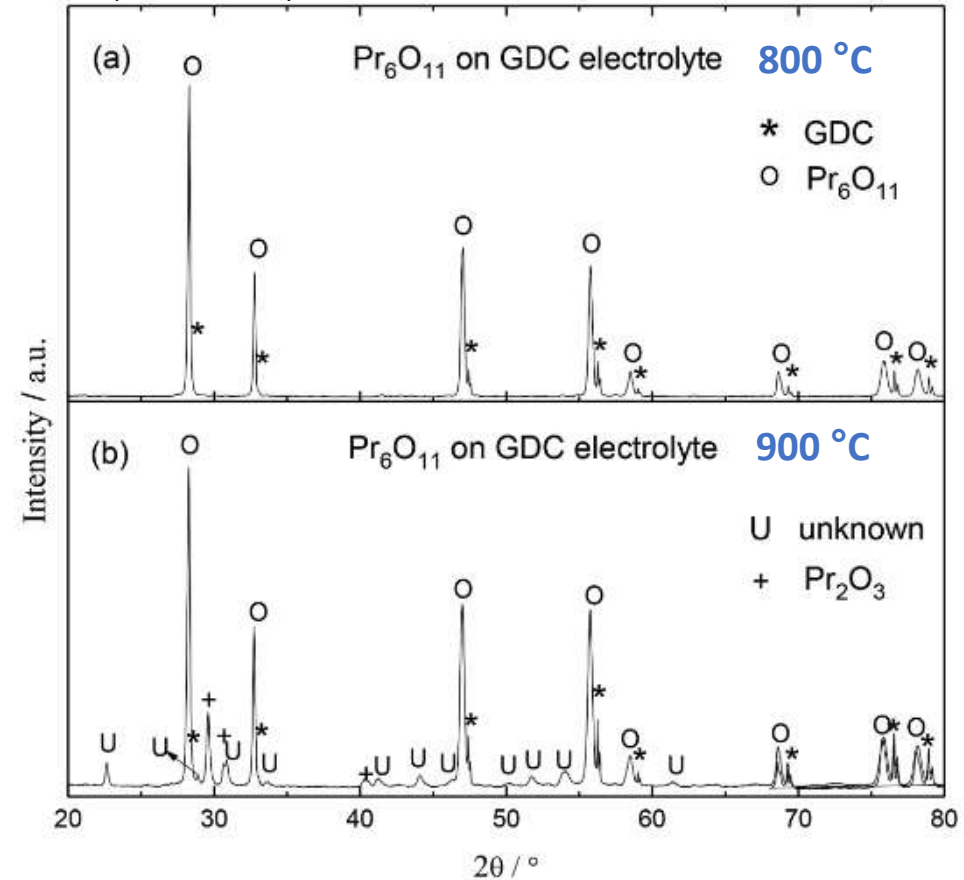
Exemplary diffractogram



✓ **Chemical stability for all samples and temperatures**

Pr_6O_{11} (ESD) – GDC

Philips X'Pert-MPD system, Cu $K\alpha$ radiation, $\lambda=1.54056 \text{ \AA}$



- ✓ **800 °C, 10 days: no decomposition**
- ❖ **900 °C, 10 days: partial decomposition, unidentified phases (ongoing)**

L. Yefsah, Solid State Ionics (submitted)

Study of symmetrical cell architectures (Focus on interface AFL/CCL)

1. Focus on AFL/CCL interface
(CCL composition, CCL thickness)
2. Optimization of AFL sintering temperature
3. Comparison of ESD morphology in practical application

Analysis of electrochemical behavior

1. EIS
($V_a = 0.02$ V, 1 MHz - 50 mHz, Au grids 1024 mesh/cm²)
2. R_{pol} extraction

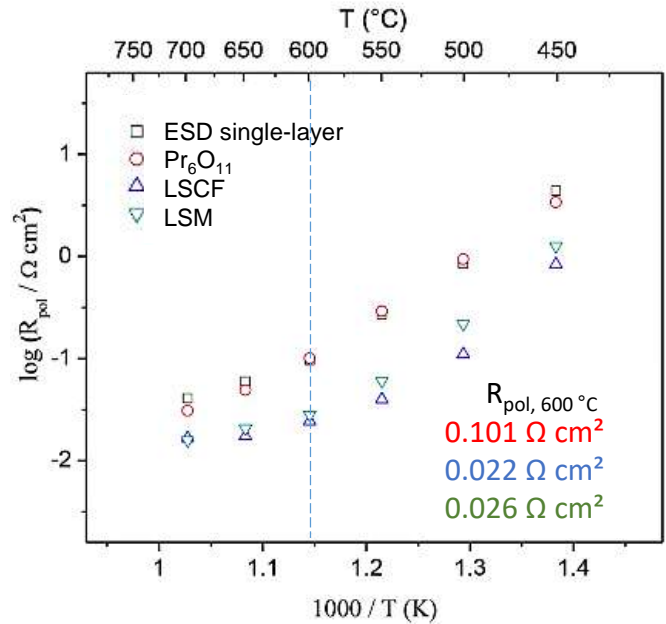
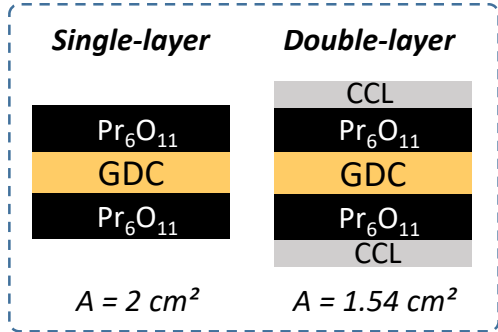
Focus on current collector layer (CCL)

CCL composition

ESD calcination: 700 °C, 2h
CCL thickness = 30 μm

Architecture (AFL + CCL)

- Pr₆O₁₁ (ESD) + Pr₆O₁₁(SP)
- Pr₆O₁₁ (ESD) + LSCF (SP)
- Pr₆O₁₁ (ESD) + LSM (SP)

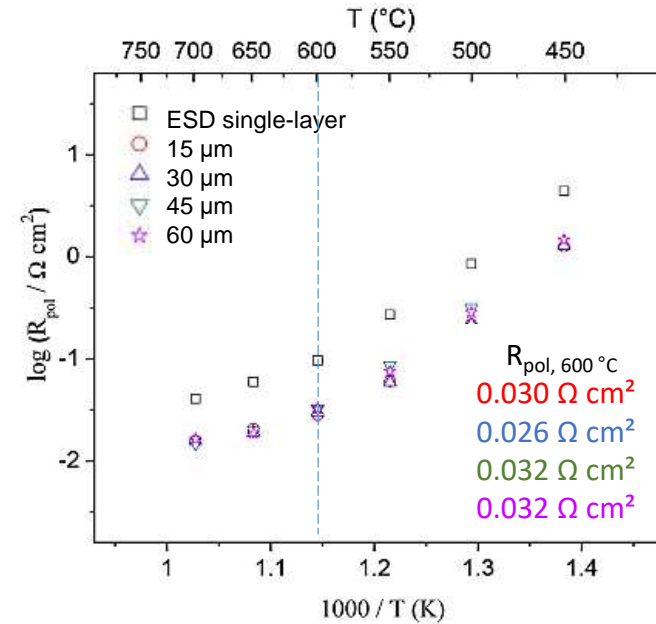


➤ T > 600 °C: LSM and LSCF as best choice

CCL thickness

ESD calcination: 700 °C, 2h

Architecture (AFL + CCL)	CCL thickness (μm)
Pr ₆ O ₁₁ (ESD) + LSM (SP)	15
Pr ₆ O ₁₁ (ESD) + LSM (SP)	30
Pr ₆ O ₁₁ (ESD) + LSM (SP)	45
Pr ₆ O ₁₁ (ESD) + LSM (SP)	60

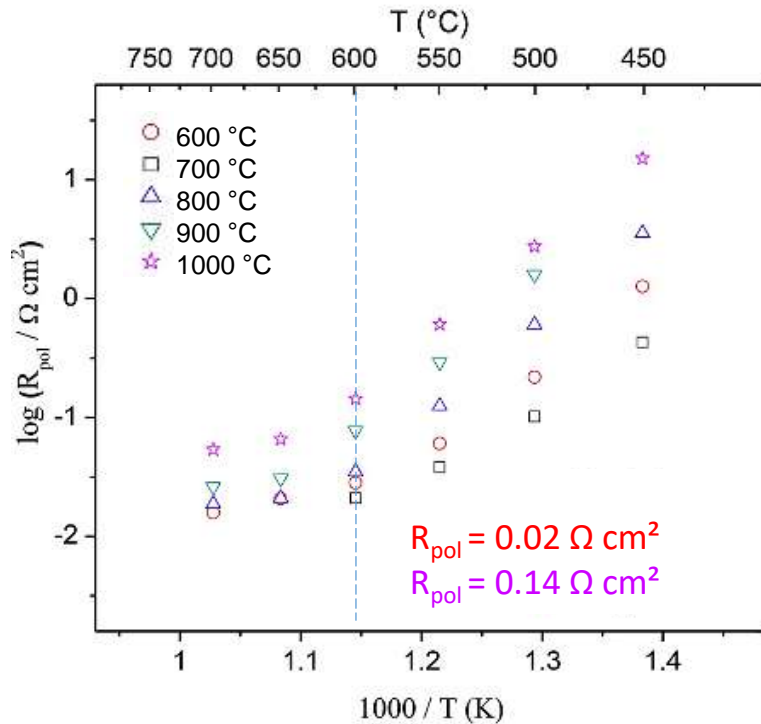


➤ Minimum CCL thickness (avoid current constriction) ca. 30 μm

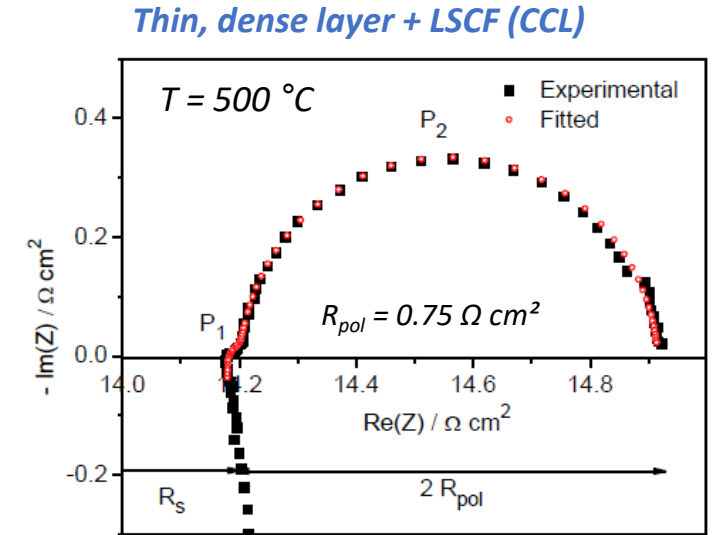
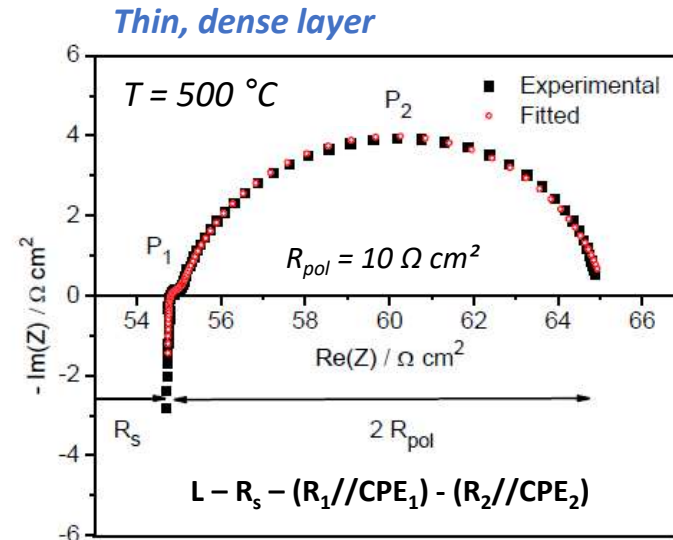
Optimization of AFL sintering temperature

LSM thickness = 30 μm

Post-ESD sintering, air	AFL particles, SEM (nm)
600 °C, 2h	< 20
700 °C, 2h	35
800 °C, 2h	50-100
900 °C, 2h	100-150
1000 °C, 2h	200-250



PGSTAT 302N, $V_a = 0.02 \text{ V}$, 1 MHz - 50 mHz, Au grids 1024 mesh/ cm^2



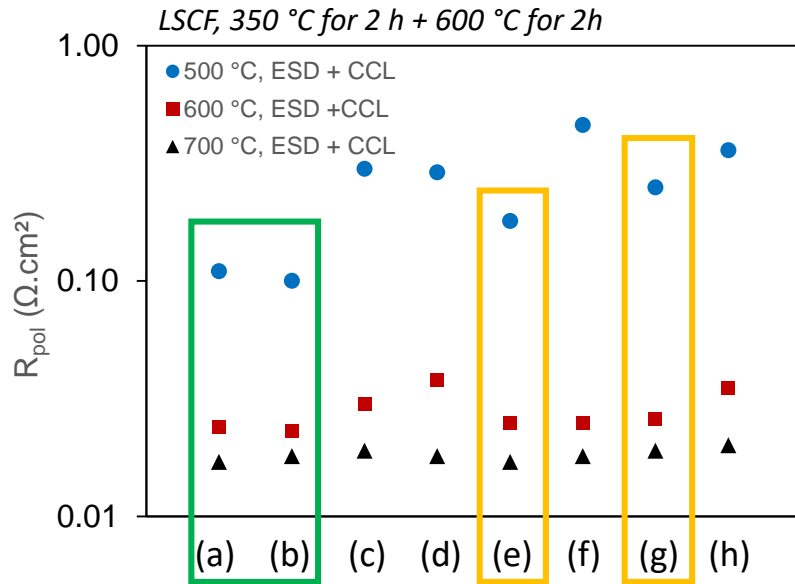
Elementary contributions:

- P_1 : Capacitance from 10^{-6} to $10^{-3} \text{ F cm}^{-2}$ (interfacial capacitance + CT)
→ Electrolyte/AFL
- P_2 : Capacitance from 10^{-3} to $10^{-1} \text{ F cm}^{-2}$ (electrode processes of oxygen species)
→ AFL/CCL

➤ Representative spectra

➤ Ideal ESD calcination temperature < 800 °C (small grains, highest surface area)

Influence of electrode microstructure on R_{pol}



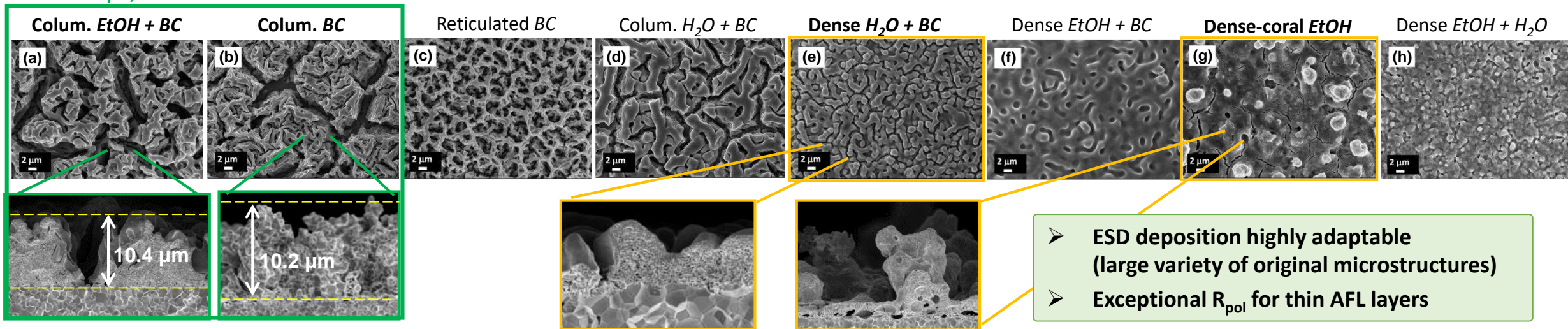
$$d_{size} \propto \left(\frac{\rho \epsilon_0 Q^3}{\gamma \sigma} \right)^{1/6}$$

Gañan-Calvo, J. Aerosol Sci., 28 (1997), 249

Solution	σ (mS/cm)	T_b^* (°C)	Droplet size (μ m)	Particle size [†] (nm)
EtOH	76.5	88.0	3.8	20
EtOH:H ₂ O (1:2)	1.61x10 ³	111.2	2.0	20
H ₂ O:BC (1:2)	3.5x10 ²	192.8	2.7	35
EtOH:BC (1:2)	17.3	193.3	4.8	35
BC	1.89	206.4	6.9	35

* TGA + DTA; [†] SEM + Image J analysis

$R_{pol, 600\text{ °C}} = 0.02 \Omega \text{ cm}^2$



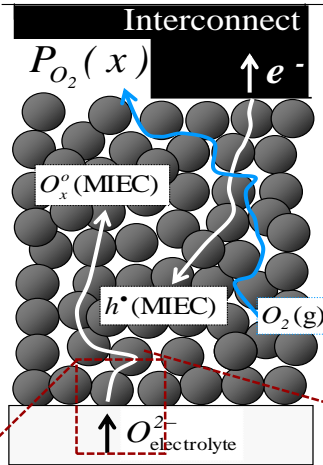
- ESD deposition highly adaptable (large variety of original microstructures)
- Exceptional R_{pol} for thin AFL layers

- Search of alternative SOC oxygen electrode materials (reduce operation temperature)
- Investigation of Pr_6O_{11} → Decomposition product of $\text{La}_{1-x}\text{Pr}_x\text{NiO}_{4+\delta}$



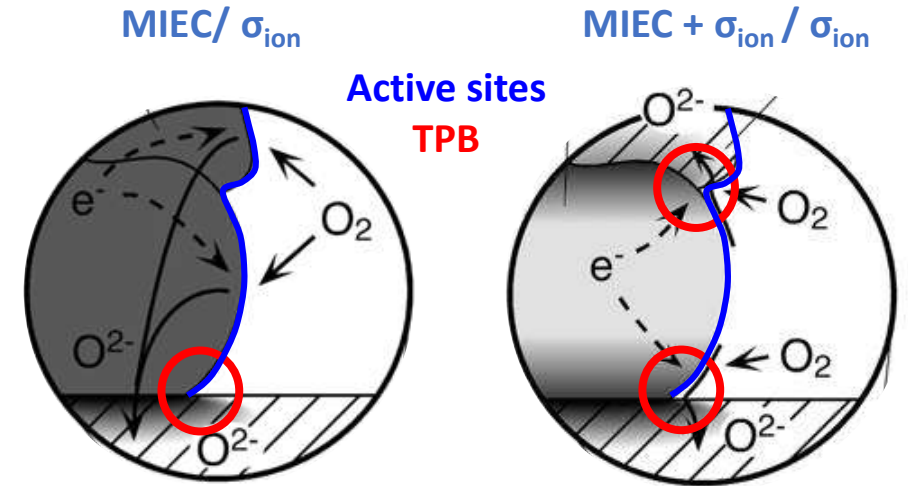
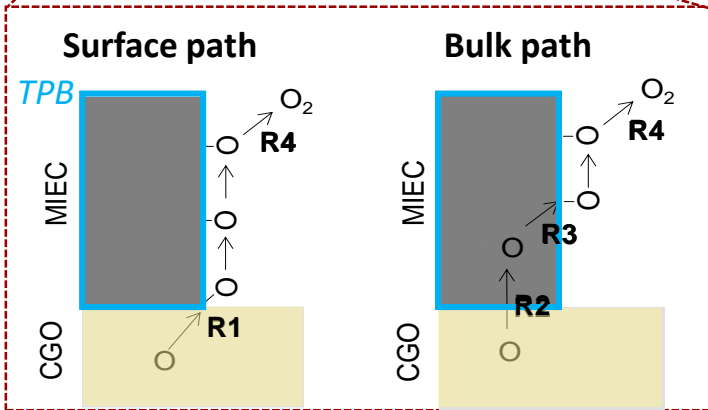
1. Synthesis of nanostructured Pr_6O_{11} electrodes for SOC by ESD → Electrostatic Spray Deposition
2. High control of process via deposition parameters (T, d, Q, t, solvent) → Microstructural studies
3. Evaluation of thermal stability window on GDC and YSZ electrolytes → 800 °C, IT-SOC
4. Preparation of symmetrical SO cells on GDC electrolytes → ESD + Screen-printing
5. Architecture of symmetrical cells optimized via EIS → ESD – calcination at 600 °C, 2h
LSM-CCL of 30 μm thickness (700 °C, 2h)
 $R_{\text{pol}, 600\text{ °C}} = 0.02\ \Omega\ \text{cm}^2$ for columnar microstructure

SOEC mode (for LNO)



- R1:** Direct oxidation at TPB
- R2:** Ionic transfer (electrolyte to electrode)
- R3:** Interstitial diffusion + excorporation + formation of adatoms
- R4:** Association + desorption

G Sdanghi, *J. Electrochem. Soc.*, 169 (2022), 034518
 L Yefsah, (2023) PhD Thesis, UGA

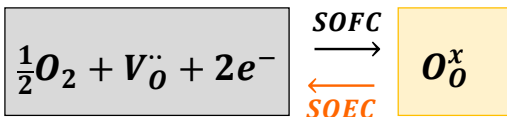


S.B. Adler, *Chem. Rev.*, 104 (2004) 4791

Dominant surface path
 → increase number of TPB

Increase interface
 MIEC/ ionic conductor

Material	D^* (cm ² /s)	k^* (cm/s)
LNO ³	1.0×10^{-6}	1.5×10^{-8}
Pr ₆ O ₁₁ ⁵	3.4×10^{-8}	5.4×10^{-7}



- ✓ SOEC: interstitial filling, parallel surface + bulk path, stable
- ❖ SOFC: depletion of interstitials (bulk path limiting)
 1. Performance
 2. Physical delamination (e.g. LNO)

➤ Pr₆O₁₁ could behave similar to LSM (detailed study of charge transfer mechanisms required)

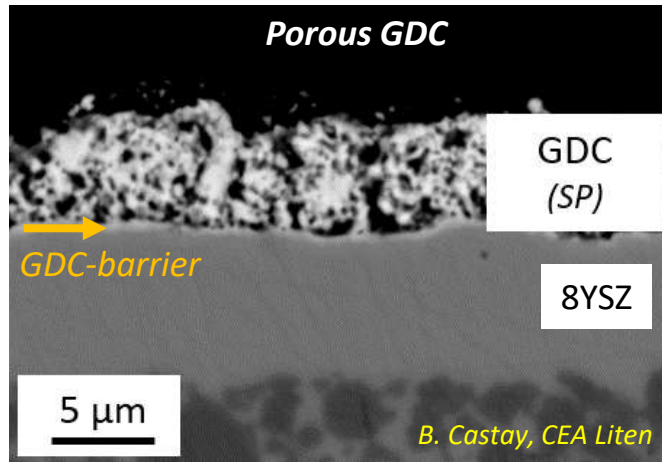
Preparation of a triple layer composite Pr₆O₁₁-GDC electrode

ESD - "infiltration" of porous GDC - conditions

$$d_{size} \propto \left(\frac{\rho \epsilon_0 Q^3}{\gamma \sigma} \right)^{1/6}$$

- **Smallest particles possible**
 Solvent = EtOH : H₂O (1:2, vol.)
 T = 350 °C
 d = 50 mm
 Q = 1.0 mL/h

Sample preparation



O₂ - electrode Active triple layer

30 μm	LSM-CCL (SP)
5-15 μm	La ₂ NiO _{4+δ} /Pr ₆ O ₁₁ (ESD)
4 μm	GDC poreux (SP)
3 μm	GDC barrière (SP)
10 μm	Electrolyte (8YSZ)
250 μm	Electrode H ₂ (Ni-YSZ)



Thank you for your attention!

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L. Yefsah (Ph.D student)

ANR ECOREVE



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C. Steil
L. Dessemond
F. Fournet-Fayard



J. Laurencin
B. Castay



Preparation of a triple layer composite Pr₆O₁₁-GDC electrode

Infiltration using precursors

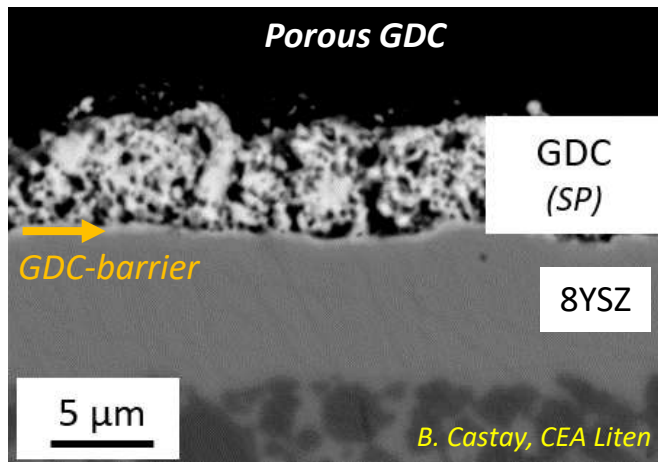
- R_{pol} (650 °C, air) = 0.16 Ω cm²
NV Lytkov, Russ. J. Electrochem, 57 (2021), 1070
- R_{pol} (600 °C, air) = 0.074 Ω cm²
M Khoshkalam, J. Electrochem. Soc., 167 (2020), 024505
- R_{pol} (600 °C, air) = 0.028 Ω cm²
C Nicollet, Int. J. Hydrog. Energy, 41 (2016), 15538
- ☐ 1.56 W cm⁻² at 700 °C (PrOx in AFL)
E Dogdibegovic, J. Power Sources., 410 (2019), 91
- ☐ - 1.5 A cm⁻² at 1.4 V (50 vol.% steam on H₂ side, 700 °C)
R Wang, Energy Technol., 7 (2019), 1801154

ESD - "infiltration" of porous GDC - conditions

$$d_{size} \propto \left(\frac{\rho \epsilon_0 Q^3}{\gamma \sigma} \right)^{1/6}$$

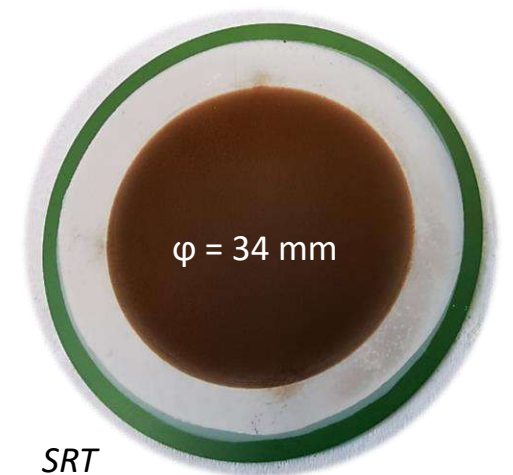
- **Smallest particles possible**
Solvent = EtOH : H₂O (1:2, vol.)
T = 350 °C
d = 50 mm
Q = 1.0 mL/h

Sample preparation

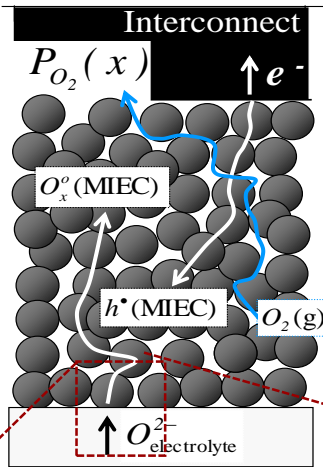


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30 μm	LSM-CCL (SP)
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250 μm	Electrode H ₂ (Ni-YSZ)

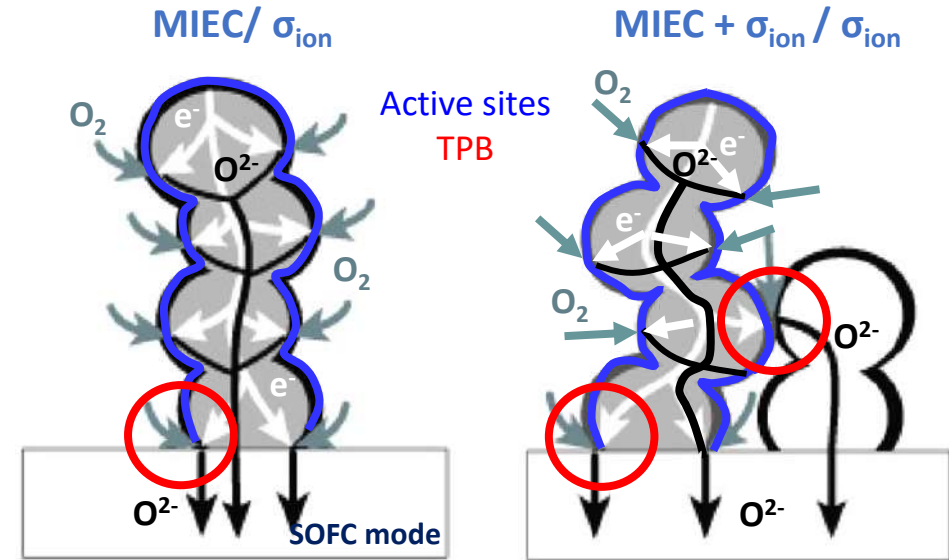
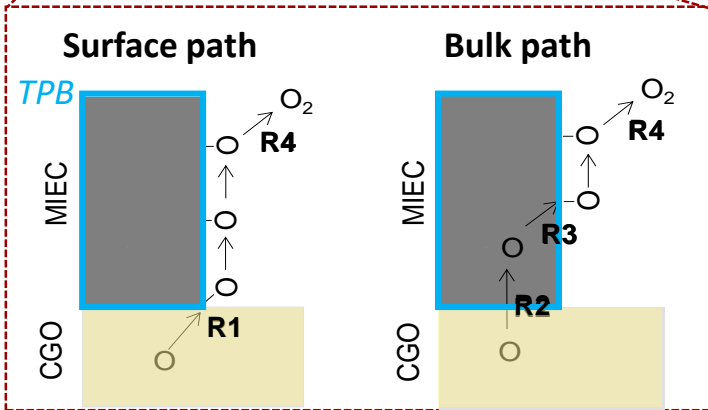


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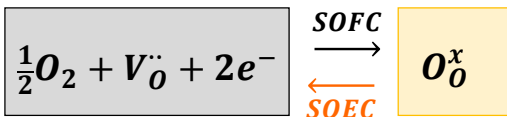
G Sdanghi, J. Electrochem. Soc., 169 (2022), 034518
L Yefsah, (2023) PhD Thesis, UGA



Adapted from: *S REY-MERMET, (2008) PhD Thesis, EPFL*

Dominant surface path
 → increase number of TPB

Increase interface with
 ionic conductor



- ✓ SOEC: filling of interstitials, parallel surface + bulk path, stable
- ❖ SOFC: depletion of interstitials (bulk path limiting)
 1. Performance
 2. Physical delamination (e.g. LNO)

Material	D* (cm ² /s)	k* (cm/s)
LNO ³	1.0 × 10 ⁻⁶	1.5 × 10 ⁻⁸
PNO ⁴	5.0 × 10 ⁻⁷	2.5 × 10 ⁻⁸
Pr ₆ O ₁₁ ⁵	3.4 × 10 ⁻⁸	5.4 × 10 ⁻⁷

⁴ De Souza, *Solid State Ion.*, 106 (1998), 175; ² Audinot, *Université de Bordeaux*; ³ Skinner, *Solid State Ion.*, 135 (2000), 70; *State Ion.*, 176 (2005), 2717; ⁵ Nicollet, *Int. J. Hydrog. Energy*, 41 (2016), 10111