



Materiales para celdas de combustible en capas delgadas

Ponente: Dr. Mario F. García Sánchez

Guillermo Santana, Betsabeé Marel Monroy, Armando Ortiz Rebollo, Aduljay Remolina Millan, Luis Andres Gómez González, Leon Hamui Balas, Carlos Álvarez Macías, Adriana Benitez Rico.

Dpto. Materia Condensada y Criogenia.
Instituto de Investigaciones en
Materiales
UNAM

Tipos de celdas de combustible

	PEFC	PAFC	MCFC	SOFC
Electrolyte	Nafion	H ₃ PO ₄	Na ₂ CO ₂ -Li ₂ CO ₃	ZrO ₂ -Y ₂ O ₃
Operating temperature (°C)	70-80	200	650-700	900-1000
Fuel	H ₂	H ₂	H ₂ , CO, CH ₄	H ₂ , CO, CH ₄
Expected efficiency (HHV) (%)	30-40	35-42	45-60	45-65
Power, current status (kW)	12.5 ^a	100 ^b	1000 ^c	100 ^d , 15 ^e
Efficiency (%)	40	40	45	43 ^d , 50 ^e

^a Allied signal.

^b Fuji electric.

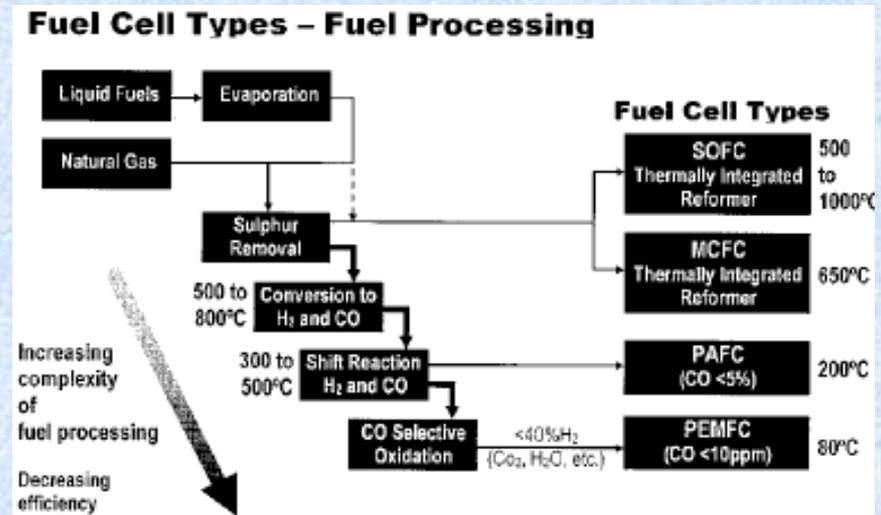
^c MCFC Research Association, Japan.

^d Siemens Westinghouse.

^e Mitsubishi Heavy Industry and Electric Power Development, Japan (at 5 atm).

O. Yamamoto / Electrochimica Acta 45 (2000) 2423-2435

B. C. H. Steele / J. Mater. Sci. 36 (2001) 1053



Selected deposition processes

Method	Example
Spin coating	0.2–2 μm YSZ films on porous or dense substrates
Vacuum evaporation	25 μm YSZ films on Ni foils
Sputtering	1–3 μm YSZ films on dense or porous substrates
Colloidal deposition	10 μm YSZ on porous NiO/YSZ substrates
Plasma spraying	10 μm cathode, 220 μm electrolyte, 10 μm anode on porous metallic support
Spray pyrolysis	5–10 μm YSZ films on anode substrates
Sol-gel	YSZ films on porous LSM cathode substrates
Electrophoretic deposition	YSZ less than 10 μm on porous NiO/Ca stabilized ZrO ₂ substrates
Laser deposition	0.5–0.7 μm YSZ films
Electrostatic assisted vapor deposition	5–20 μm YSZ on NiO/YSZ substrates
Metal organic chemical vapor deposition (MOCVD)	YSZ thin films on fused silica substrates
Electrochemical vapor deposition (EVD)	Dense 40 μm YSZ layers on porous substrates

Interfacial resistance of new electrodes by ac impedance at OCV (Ω/cm²)

	Materials	Electrolyte	600 °C		700 °C	
			1.25	0.14	0.67	0.083
Cathode	Pt-SSZ	YSZ	7.1	0.90	0.83	0.19
Cathode	(Sm _{0.6} Sr _{0.4})CoO ₃ -CYO-Ag	SSZ	8.9	1.16	0.25	0.10
Cathode	(La _{0.2} Sr _{0.2})CoO ₃ -CGO-Ag	CGO	0.25	0.10		
Anode	Ni-CSO	SSZ				
Anode	Ni-CSO	CGO				

CYO: Ce_{0.8}Y_{0.2}O₂, CGO: Ce_{0.8}Gd_{0.2}O₂, CSO: Ce_{0.8}Sm_{0.2}O₂.

M. Dokiya / Solid State Ionics 152–153 (2002) 383–392

Materials para SOFC

Developers of SOFC in anode-supported planar cell design and corresponding fabrication and design details

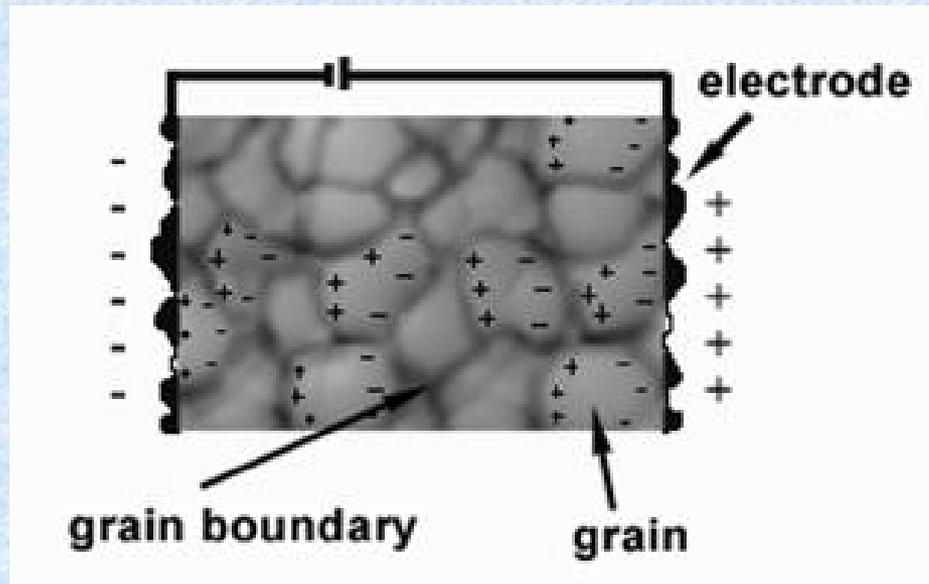
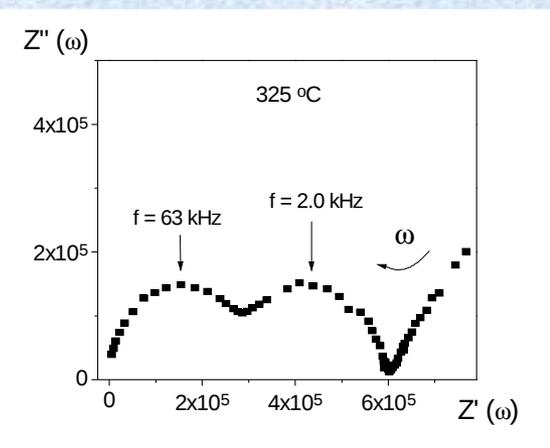
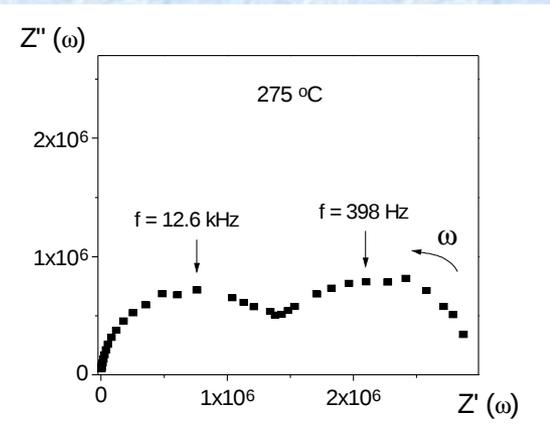
Company	Country	Component	Material	Production process	Thickness	References
Sulzer Hexis	CH	Anode substrate	Ni/YSZ	Tape casting	250–500 μm	[25]
		Electrolyte	YSZ/(Ce,Y)O ₂	Reactive magnetron sputtering	5/1 μm	[26]
ECN/InDec	NL	Cathode	La _{0.6} Sr _{0.4} Co _{0.2} Fe _{0.8} O ₃	Screen printing	ns	[26]
		Anode substrate	Ni/YSZ	Tape casting	500–800 μm	[15,16,27]
		Anode	Ni/YSZ	Screen printing	3–7 μm	[27]
		Electrolyte	YSZ	Screen printing	7–10 μm	[28]
FZJ	D	Cathode	(La,Sr)MnO ₃ +YSZ	Screen printing	ns	[27]
		Anode substrate	Ni/YSZ	Tape casting	200–500 μm	[29]
		Anode substrate	Ni/YSZ	Warm pressing	1500 μm	[6,30]
		Anode	Ni/YSZ	Vacuum slip casting	5–15 μm	[6,30]
Risø	DK	Electrolyte	YSZ	Vacuum slip casting	5–30 μm	[6]
		Electrolyte	YSZ	Reactive magnetron sputtering	2–10 μm	[31]
		Cathode	(La,Sr)MnO ₃ +YSZ	Wet powder spraying	50 μm	[6,32]
		Anode substrate	Ni/YSZ	Tape casting	200–300 μm	[33]
Global Thermolectric	CAN	Electrolyte	YSZ	Wet powder spraying	10–25 μm	[34]
		Cathode	(La,Sr)MnO ₃ +YSZ	Screen printing	50 μm	[34]
		Anode substrate	Ni/YSZ	Tape casting	1000 μm	[35]
		Electrolyte	YSZ	Vacuum slip casting	10 μm	[35]
Allied Signal	USA	Electrolyte	YSZ	Screen printing	ns	[36]
		Cathode	(La,Sr)MnO ₃	Screen printing	40 μm	[35]
		Anode	Ni/YSZ	Tape casting and calendaring	100 μm	[37,38]
		Electrolyte	YSZ	Tape calendaring	5–10 μm	[37,39]
CFCL	AUS	Cathode	Doped LaMnO ₃	Tape calendaring	ns	[39]
		Anode substrate	Ni/YSZ	Tape casting	500–700 μm	[18,19,40]
		Electrolyte	YSZ	Lamination and sintering	10–30 μm	[19,40]
		Electrolyte	YSZ	Reactive magnetron sputtering	<16 μm	[41]
Mitsui Eng. and Shipbuilding	JP	Cathode	(La,Sr)MnO ₃	Screen printing	ns	[19,40]
		Anode substrate	Ni/YSZ	ns	1000 μm	[23]
		Electrolyte	8YSZ	ns	30 μm	[23]
		Cathode	(La,Sr)(Mn,Cr)O ₃	ns	150 μm	[23]

Candidate electrolyte (Ω cm⁻²)

	550 °C	600 °C	700 °C	800 °C	900 °C
100 μm YSZ	–	2.2	0.77	0.31	0.15
100 μm SSZ	–	0.90	0.26	0.099	0.046
100 μm CGO	–	(0.59)	0.26	0.13	0.071
100 μm LSGM	0.71	0.37	0.15	0.074	–

YSZ: Zr(Y)O₂, SSZ: Zr(Sc)O₂, LSGM: La_{0.8}Sr_{0.2}Ga_{0.85}Mg_{0.15} [10], CGO: Ce_{0.8}Gd_{0.2}O₂ [9], (0.59); Ce_{0.9}Gd_{0.1}O₂ [9], CRO: Ce(rare earth)O₂.

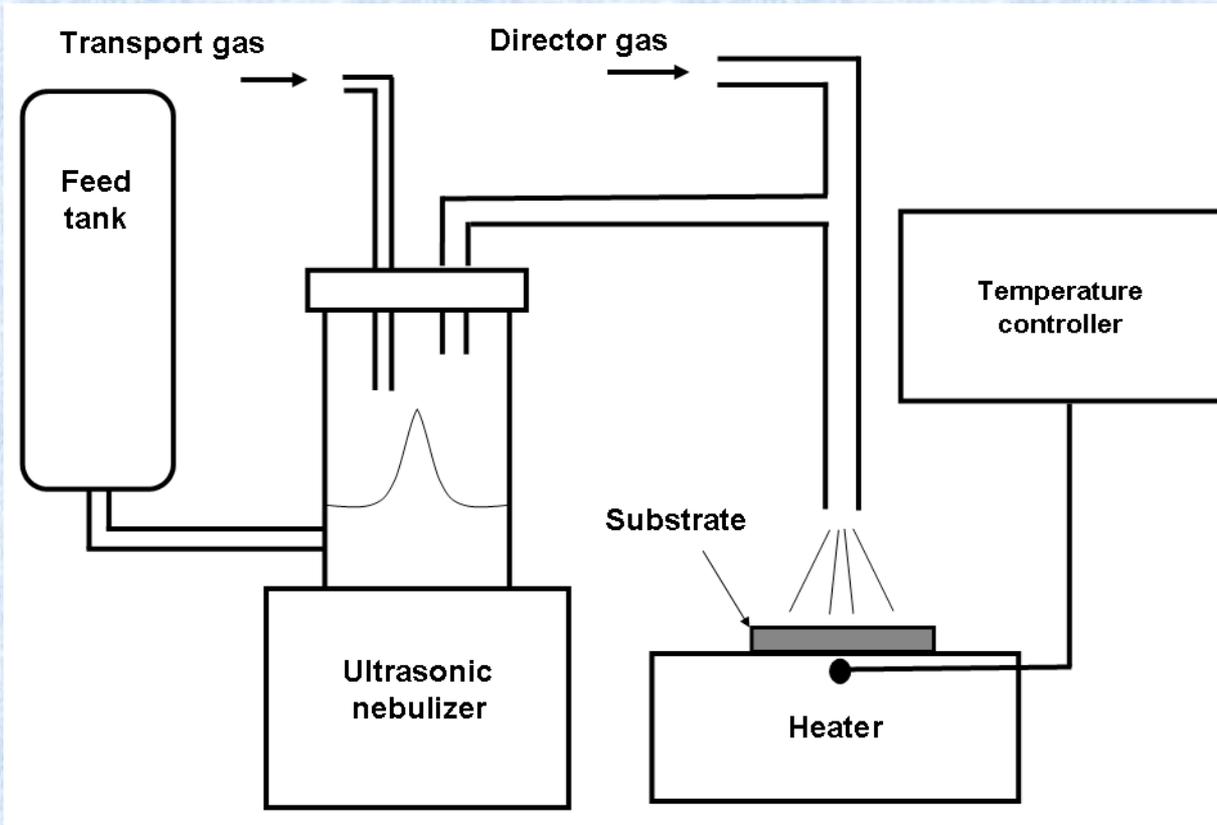
Espectroscopía dieléctrica



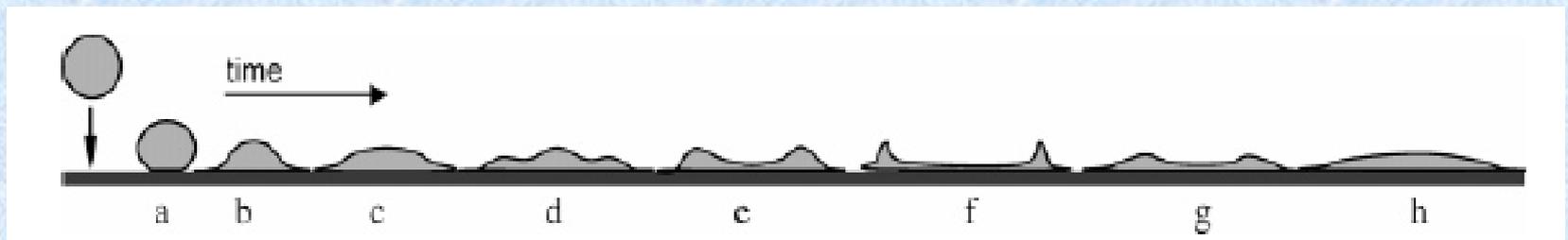
Capacitance/F	Phenomenon Responsible
10^{-12}	bulk
10^{-11}	minor, second phase
$10^{-11}-10^{-8}$	grain boundary
$10^{-10}-10^{-9}$	bulk ferroelectric
$10^{-9}-10^{-7}$	surface layer
$10^{-7}-10^{-5}$	sample-electrode interface
10^{-4}	electrochemical reactions

Arcos (numerados de izquierda a derecha por orden de aparición)	Capacidad (F) $T_{\text{sint}}=1450 \text{ °C}$	Capacidad (F) $T_{\text{sint}}=1500 \text{ °C}$	Capacidad (F) $T_{\text{sint}}=1550 \text{ °C}$
1	$(8.0 - 8.5) 10^{-12}$	$(7.8 - 8.1) 10^{-12}$	$(8.0 - 8.4) 10^{-12}$
2	$\sim 3.6 10^{-10}$	$\sim 2.5 10^{-10}$	$(4.1 - 4.4) 10^{-10}$
3	$(3.2 - 4.9) 10^{-6}$	$\sim 2.4 10^{-6}$	$(5.1 - 7.3) 10^{-6}$

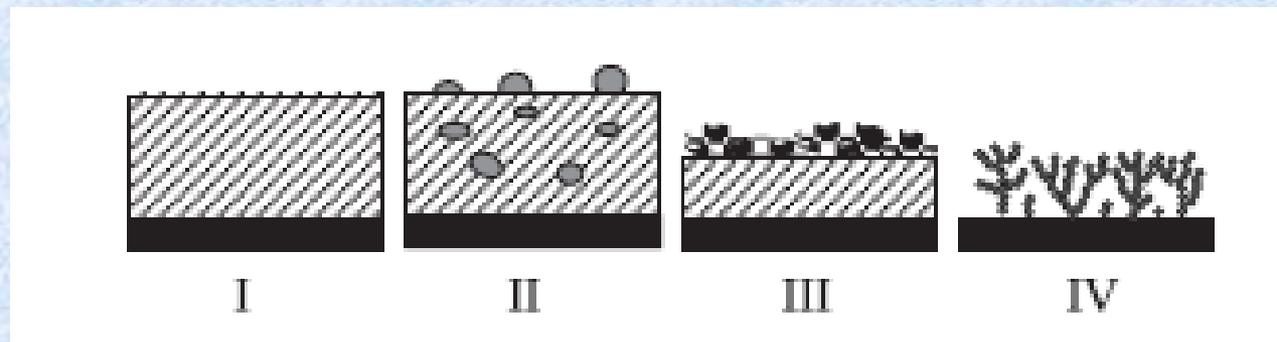
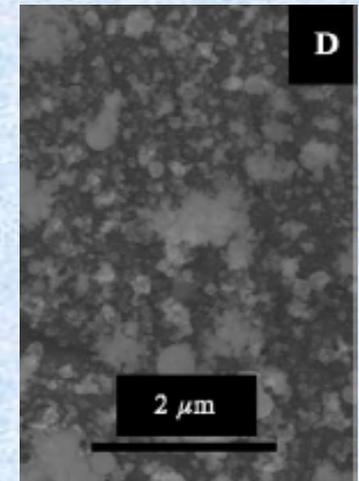
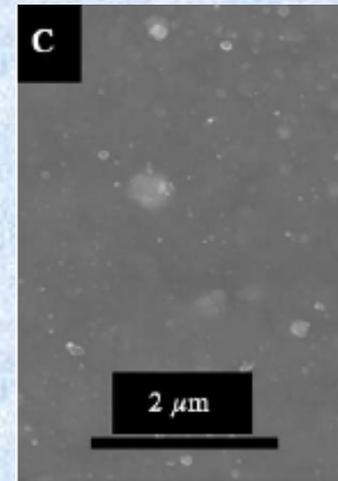
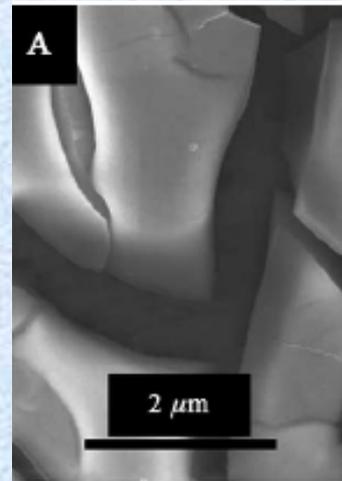
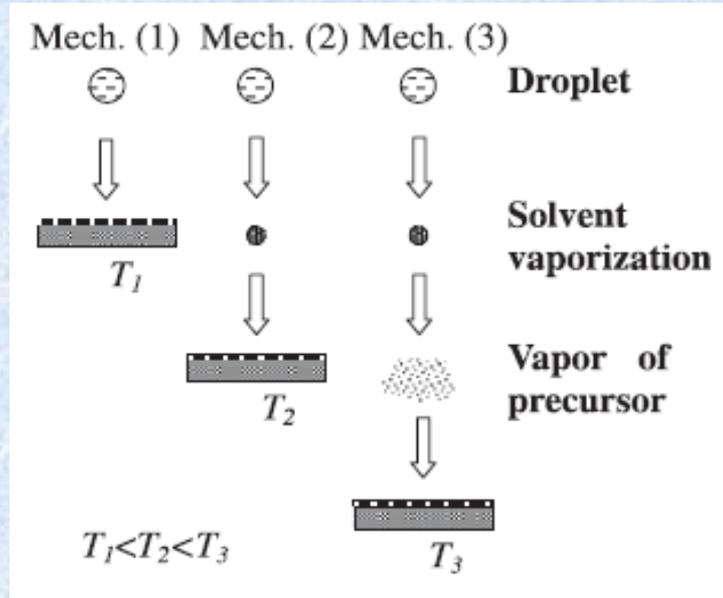
Rocío Pirolítico



- Temperatura
- Tamaño gotas
- Velocidad Flujo
- Solvente
- Tiempo
- Distancia

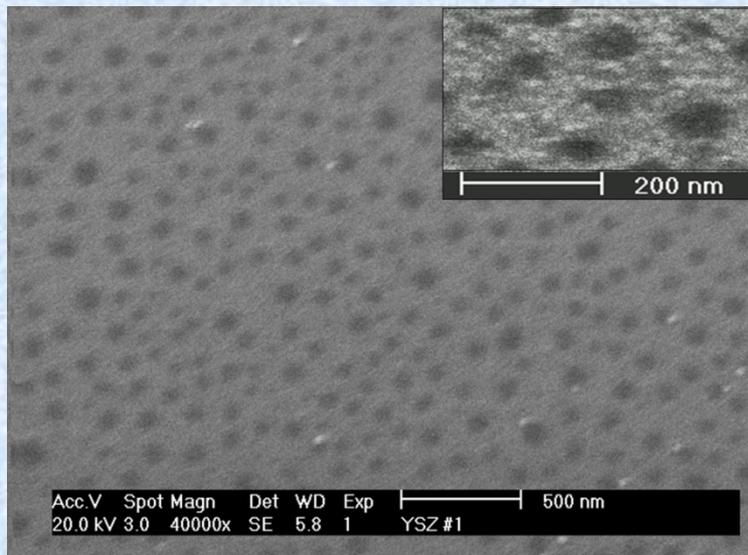


Rocío Pirolítica

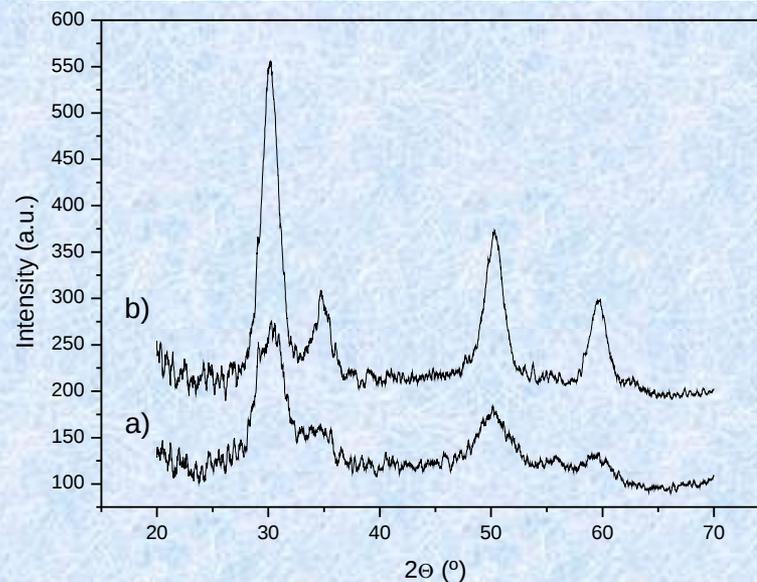
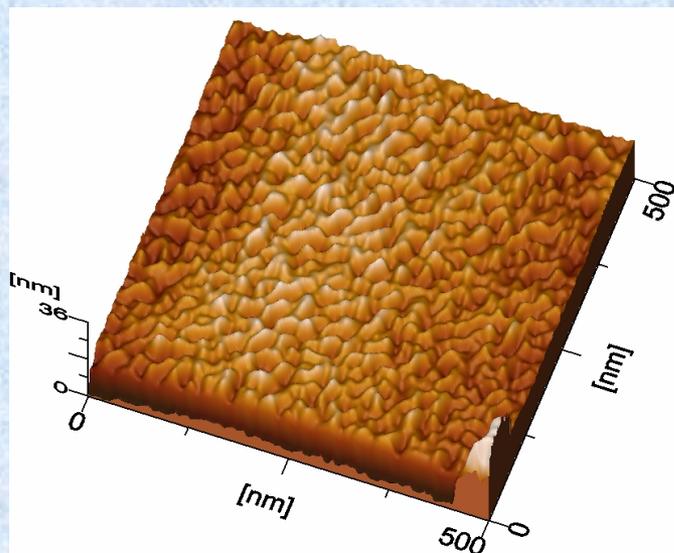
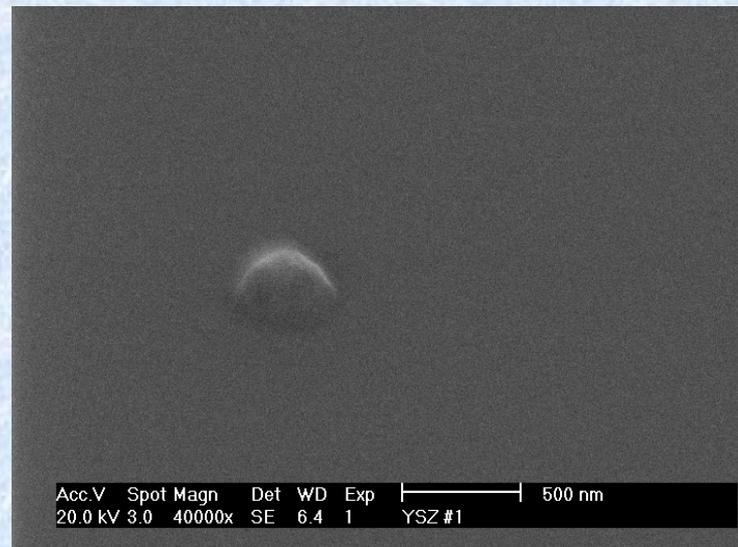


Resultados en el crecimiento de capas de YSZ

T=400 °C, t= 10min

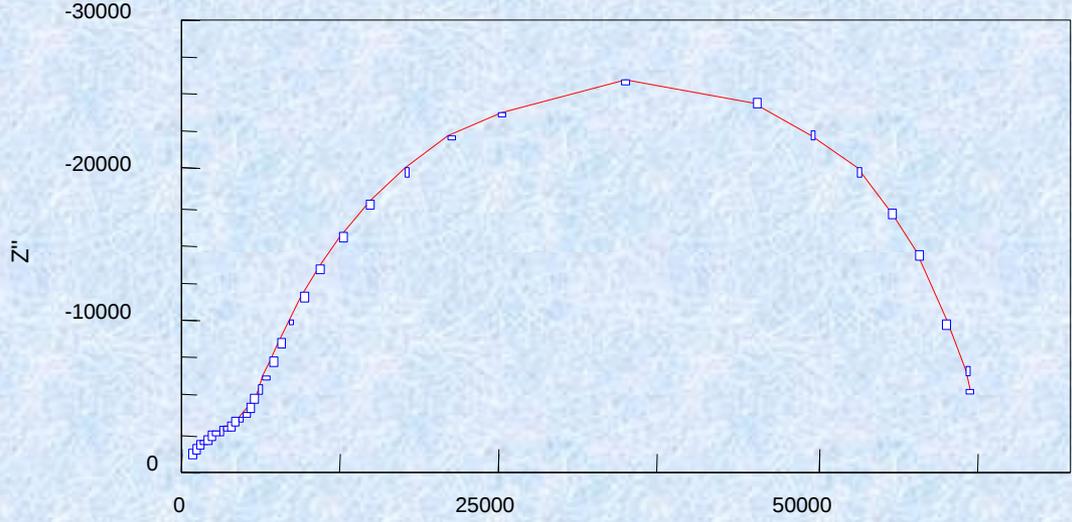


T=400 °C, t= 25 min

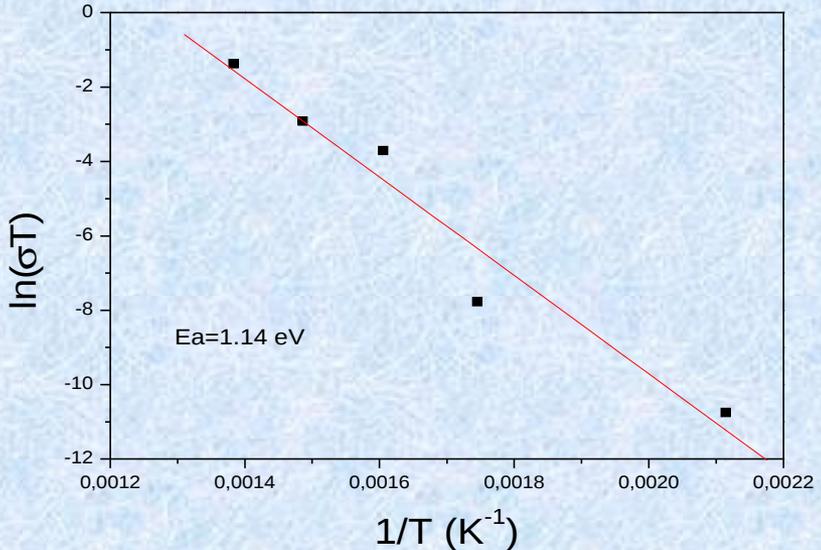


Resultados en el crecimiento de capas de YSZ

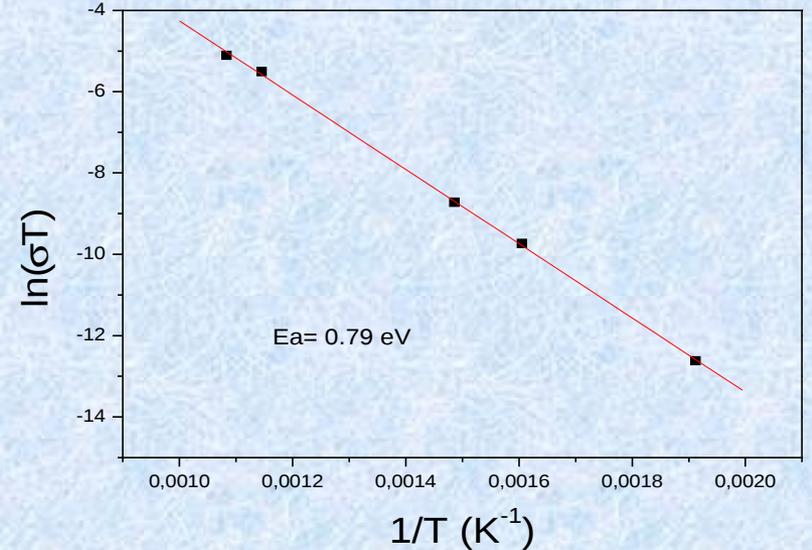
Muestra crecida a 425 °C por 10 min



Granos (Bulk)

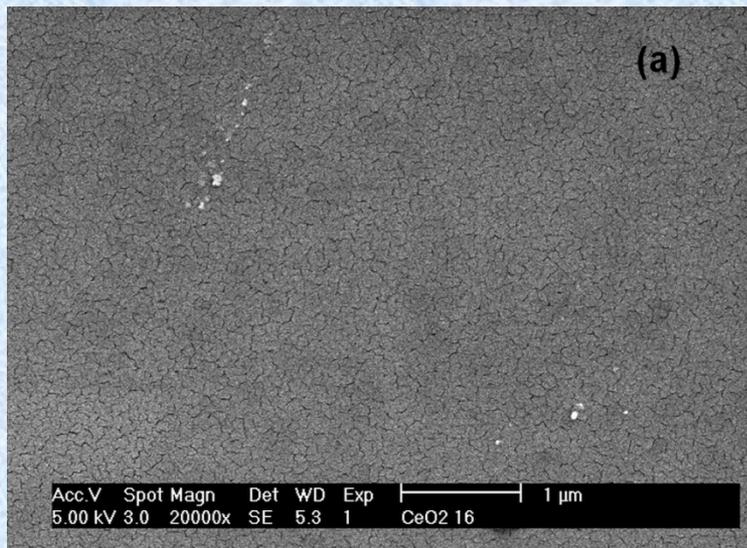


Frontera de granos

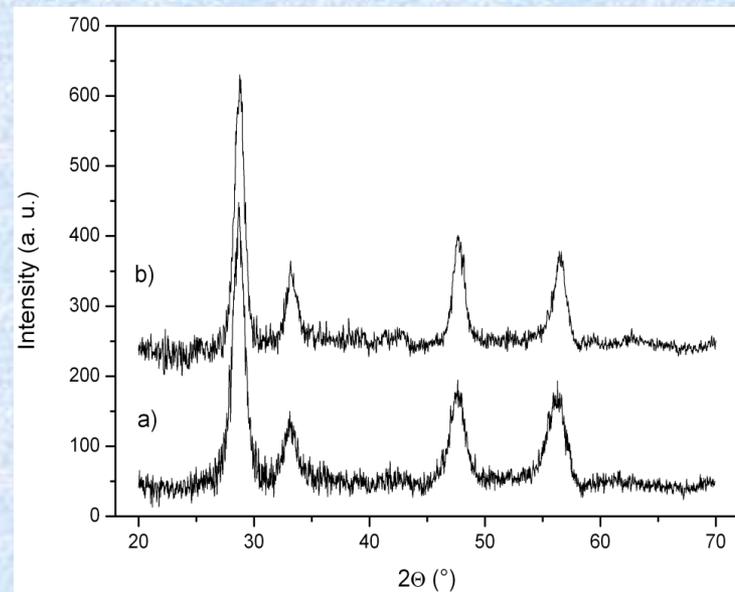
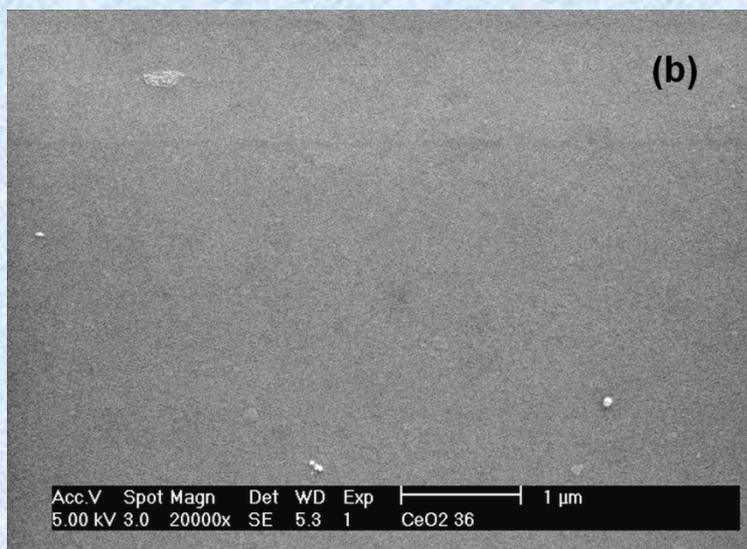
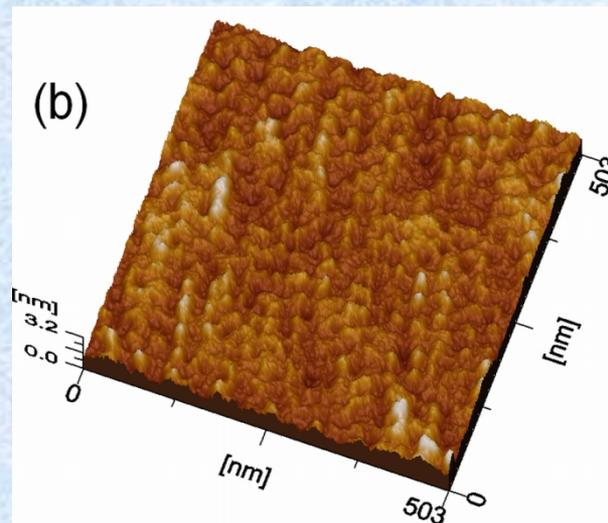


Resultados en el crecimiento de capas de CeO₂

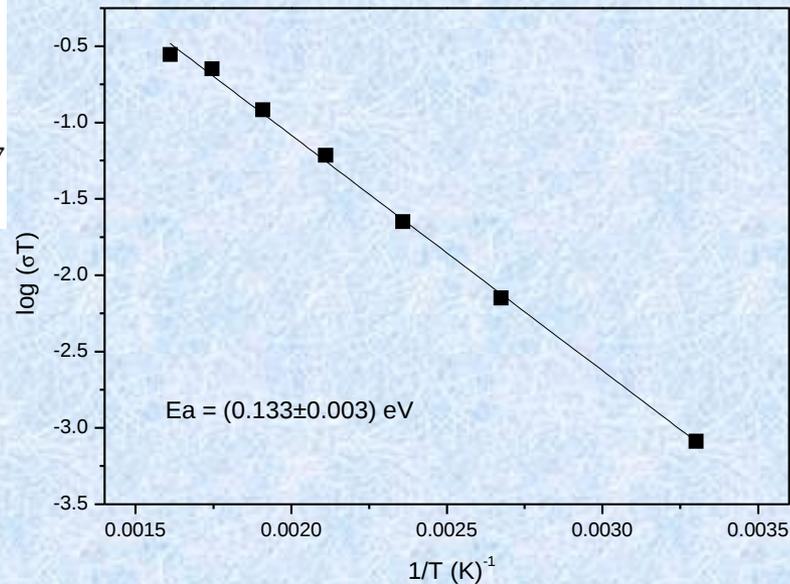
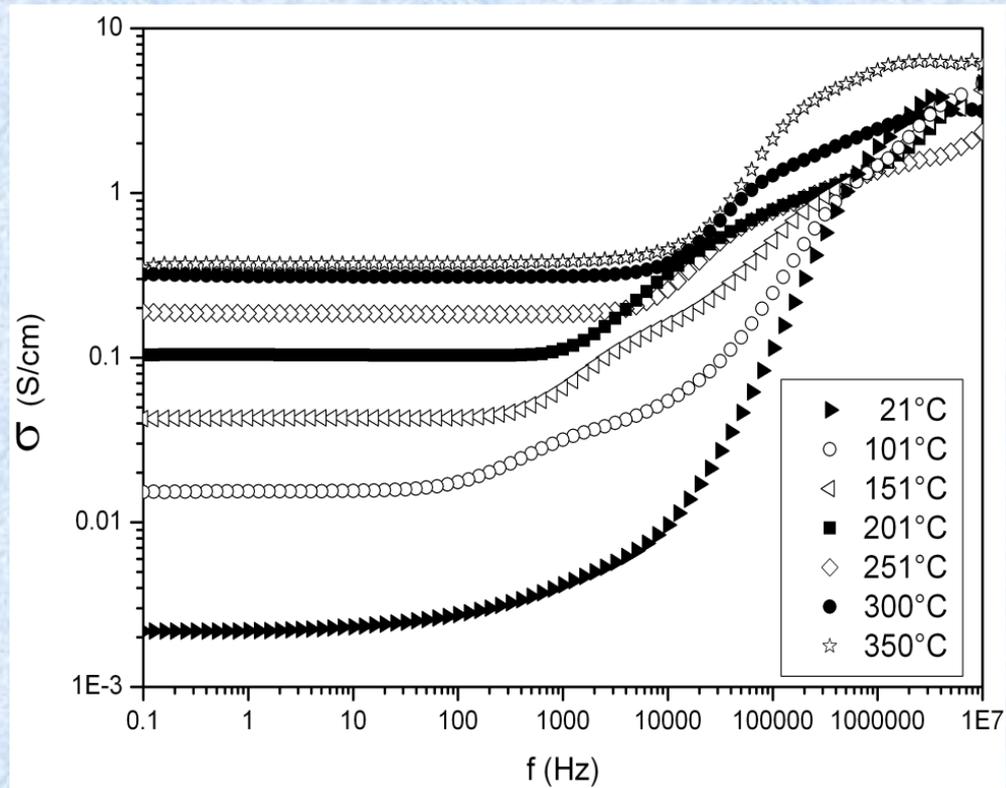
T=400 °C, t= 10min



T=425°C, t= 10min



Resultados en el crecimiento de capas de CeO₂



Conclusiones

- Optimizando las condiciones de crecimiento pueden obtenerse capas densas y homogéneas de conductores iónicos con tamaño de grano nanométricos.
- La reducción del tamaño de grano tiene una implicación importante en la conductividad total del material.

Trabajos futuros

- Comprobar la importancia del tamaño de grano en las propiedades eléctricas.
- Utilizar otros dopantes tanto en ceria como en zirconia.
- Estudiar sistemas multicapas nanoestructurados.
- Crecer por la misma técnica al menos uno de los electrodos.
- Hacer una celda de combustible en capas delgadas utilizando los materiales antes preparados y estudiar su comportamiento en condiciones de trabajo.