Synthesis and Processing of Nanocrystalline YSZ Thin Films for Fuel Cell Applications

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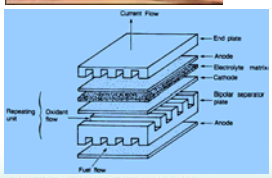
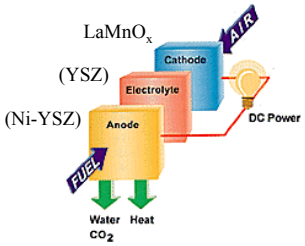
SOFC Fuel Cell Technology: Stacked Film Layers

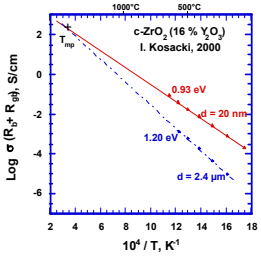




From www.poweronline.com

YSZ has Potential for High Conductivity

- Of all electrolytes, ZrO_2 is only candidate for continued development
  - Ceria microcracks due to Ce(4+) → Ce(3+) transition
  - Thin (<100μm) lanthanum gallate films fail due to phase transition at 550°C
- High purity, nanocrystalline thin films offer very exciting potential for low-temperature SOFC applications



Several issues remain

- Further enhancement of conductivity
- Understanding effects of grain boundaries, texture, materials purity, and solutes on property aging
- **Thin film development**

Electrolyte Material	Conductivity at 600°C, S/cm	Operating Temperature Range, °C	
		Bulk (100 - 200 μm)	Thin Film (~ 10 μm)
YSCZ 1-10 μm grain size	0.006	900 - 1000	800
YSCZ nanocrystalline	0.100		450 - 700
Sc-stabilized Cubic ZrO_2	0.0178	800 - 1000	550 - 700

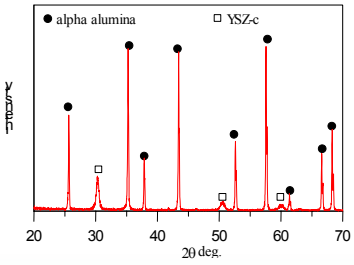
General Strategy for Thin Film Synthesis

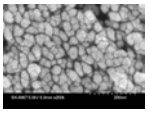
* Thin film (~ 1 μm thickness) on porous rough surface
* Conventional method such as **tape casting** won't work!

- **Solution → Sol-gel or Hydrothermal → Aqueous Sol → Coating (dip or spin)**
- **Salts + Organics → Polymeric Precursor → Coating**
- **Direct growth/deposition of film on surface**
  - **Laser abalation**
  - **CVD**
  - **sputtering**

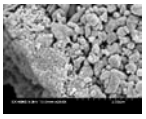
XRD Pattern of the α-Alumina Supported Yttria-Doped-Zirconia Membrane by Sol-Gel Dip-Coating Method.

(Cubic phase YSZ crystallite size ~ 21 nm — determined by XRD data)



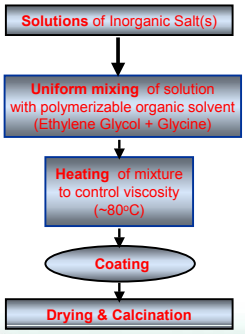


Film Surface



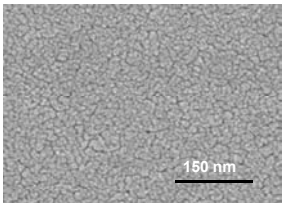
Cross-Section

Polymeric Precursors for Nanocyrstalline Films

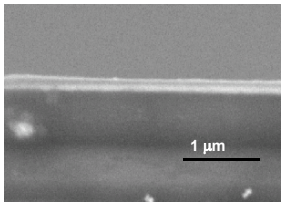


Defect-free, Nanocrystalline YSZ Film by Polymeric Precursor Spin-Coating

(~11 nm crystallite size, per XRD)



SEM Image of Film Surface

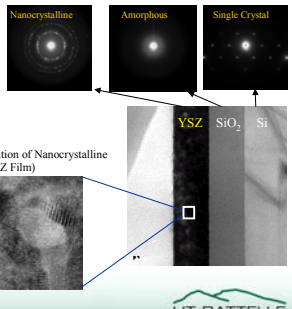


SEM Image of Film Cross-Section

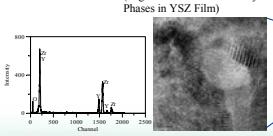
Thicker Nanocrystalline YSZ Films by Improved Polymeric Precursor Spin-Coating

- Viscosity control & heat treatment program modification
- Achieved 50~60nm thickness per coating, comparing to ~20nm thickness per coating in literature

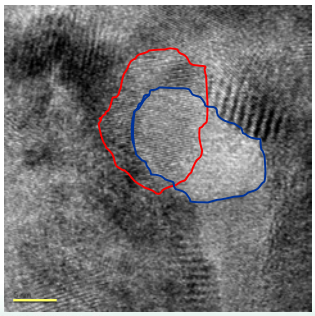
TEM images of a nanocrystalline YSZ film on silicon wafer.
(Annealed at 900oC for 20 hr; Grain size ~15 nm; Thickness ~120 nm)



(High Resolution of Nanocrystalline Phases in YSZ Film)



HRTEM: Nanocrystalline Phases in YSZ Film From Polymeric Precursor Coating

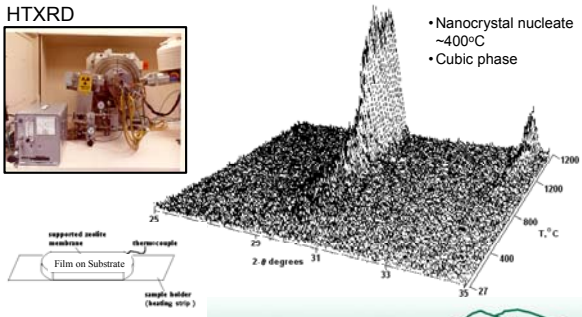


Observed grain size is in agreement with those determined by XRD (~15 nm)

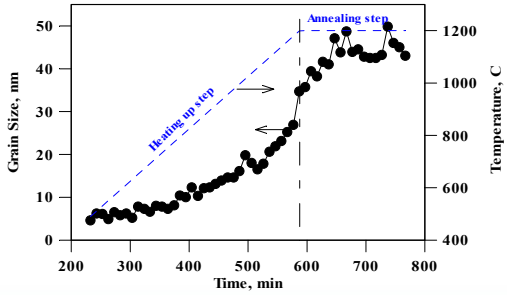
In situ High-Temperature XRD Measurements During Thermal Processing of Polymeric Precursor Film in Air

HTXRD

- Nanocrystal nucleate ~400°C
- Cubic phase

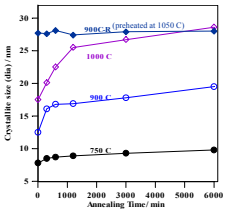


Grain Size Change in the YSZ Thin Film During Thermal Processing in Air

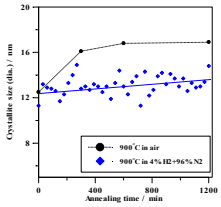


NanoGrain Growth During Constant-T Annealing Process

- At each temperature, grain size can be stabilized after certain time.
- Preheat treatment prevents further growth at lower temperature.
- Reducing atmosphere somehow inhibited the nanograin growth.



Effects of annealing time and thermal history

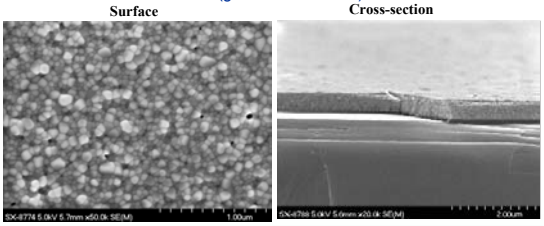


In oxidative and reducing atmospheres

YSZ Nanocrystalline Film from a Novel Seeded Precursor Method

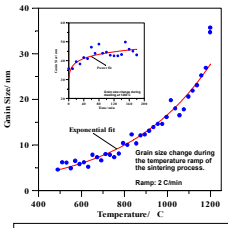
- 0.5 μm-thick (from triple coating)
- **Reduction of numbers of coatings warrants quality control, coating efficiency, and cost effectiveness**
- Annealed at 900°C for 3h (grain size ~ 27 nm)

Surface | Cross-section

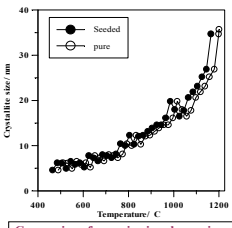


Significant Findings on Grain Growth During Firing Process

- Similar nucleation and grain growth behavior for the two precursor film during firing program
- True nanophase (<35 nm) was maintained up to 1200°C



Grain size change for pure polymeric during film firing program



Comparison for grain size change in seeded precursor film and pure polymeric film

Nanocrystal Grain Growth Modeling

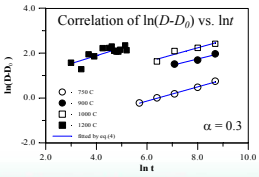
Power law kinetic expression for isothermal annealing data

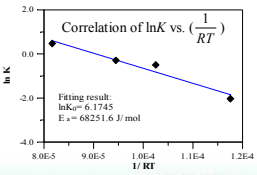
$$D = D_0 + Kt^{\alpha} \quad \text{or} \quad \ln(D - D_0) = \ln K + \alpha \ln t$$

where D - avg. grain diameter; t - heating time; K - growth rate coefficient

$$K = K_0 \exp(-E_a / RT) \quad \text{or} \quad \ln K = \ln K_0 - \frac{E_a}{RT}$$

where K_0 is the pre-exponential constant and E_a is the activation energy





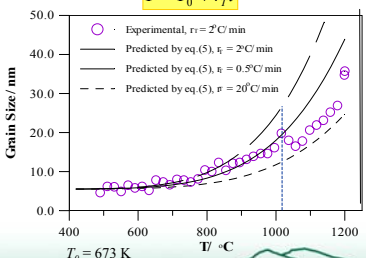
Comparison Of The Prediction By Our Model And The Experimental Data For Dynamic Nanograin Size Evolution During Thermal Processing In Air

$$D = D_0 + K_0 \sum_{n=1}^{t/\Delta t} \exp\left[\frac{-E_a}{R(T_0 + r_T t)}\right] \cdot (\Delta t)^{\alpha}$$

Temperature T is determined by the heating rate, r_T, and the time, t

$$T = T_0 + r_T t$$

- Δt is the time interval within which the temperature is considered constant
- The process is treated as being multi-stage with the number of stages defined as $t/\Delta t$
- Starting grain size (D_0) of each stage is the final grain size of the previous stage



$T_0 = 673$ K
Initial $D_0 = 5.5$nm

Summary

- **Nanocrystalline YSZ has promising properties for fuel cells**
  - **high efficiency**
  - **operating at low temperatures (<700°C)**
- **Nanocrystalline thin films have been synthesized**
  - **By polymeric precursor spin-coating (PPSC) method.**
  - **Have improved the PPSC method and also developed a seeded polymeric precursor method, allowing to coat thicker layer per coating**
- **Nanocrystal grain growth kinetics in thin film**
  - **studied experimentally**
  - **mathematical model (based on classical power-law) were developed to describe the nanograin growth under programmed thermal processing**