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# Overview of
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## Low Temperature Cathode Supported Electrolytes

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**Presented at**
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# Low Temperature Cathode Supported Electrolytes

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## Summary

During the last few years there has been an effort promoted by the US Department of Energy to lower the operating temperatures of solid oxide fuel cells. As a result, the SOFC activities at the Electronic Materials Applied Research Center (EMARC) of the University of Missouri-Rolla (UMR) have been focussed on the fabrication of thin (0.5 to 5mm thick), dense electrolyte layers of either zirconia or ceria onto either the cathode or anode of the SOFC.

The route that has been taken is to deposit polymer precursor solutions which contain the cations of the chosen electrolyte onto a pre-sintered porous substrate of either the cathode or anode and subsequently converting the resulting polymeric films into dense layers by thermal treatment.

In this presentation, the electrolyte and porous substrate preparation and characterization techniques will be described. Optical spectroscopy and scanning electron microscopy results show that dense electrolytes on a rigid, porous substrate can be prepared at temperatures in the 600 to 800$^{o}$C range. Impedance spectroscopy and direct current measurements show that the electrical properties and single cell measurements of these electrolyte films annealed in the 600 to 800$^{o}$C range are either comparable to or exceed those obtained measured on dense sintered electrolytes prepared by other techniques.

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# Outline

- Technical Issues
- Objectives and Approaches
- Results to Date
- Goals for next Year

# R&D Objectives & Approach

- The polymer precursor technique has the potential to produce thin dense electrolyte at the temperatures 800 to 900$^{o}$C.
- It can be used for both cathode and anode supported electrolytes preparation.
- It can also be used for deposition of nanocrystalline cathode and anode reaction interlayers in combination with nanocrystalline powder.

# Technical Issues Addressed

- Currently powder based technologies are the main approach used to develop SOFC's.
- These technologies appears to have limitations because thin (1 to 5µm) electrolytes are required for 500 to 700°C operating SOFC's.
- Processing temperature need to be lowered up to the 800-900°C range to have the grain size in the range 30 to 70nm that is required for these thin dense electrolytes.
- New technological approaches need to be developed to attain these structures.

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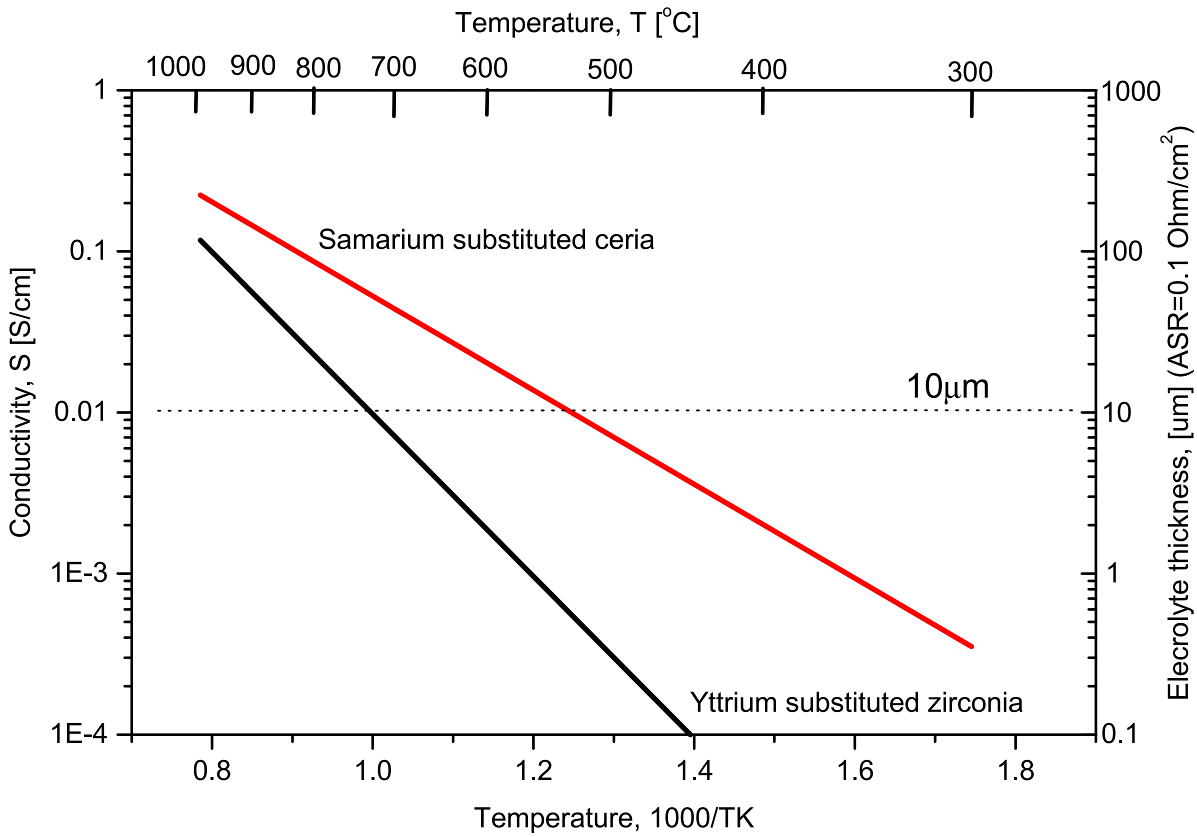
# Conductivity of YSZ and SDC and corresponding electrolyte thickness limitation

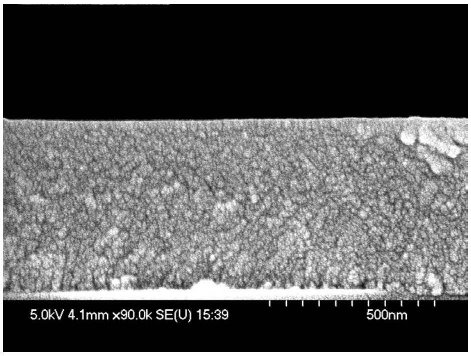


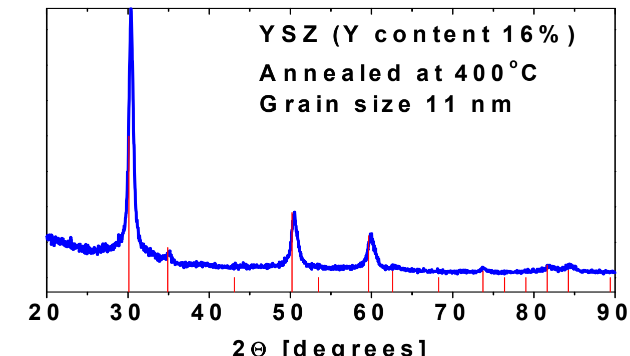

**YSZ: σ=0.12 S/cm at 1000°C, E=1eV**

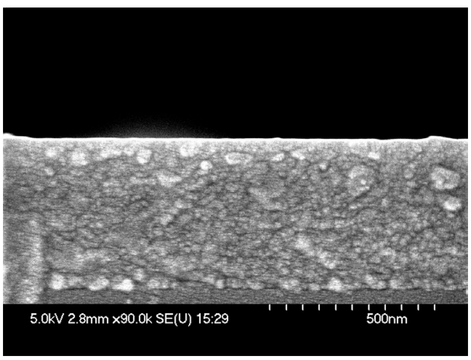
T.H.Etsell and S.N.Flengas, Chem.Rev., 70, 339 (1970)

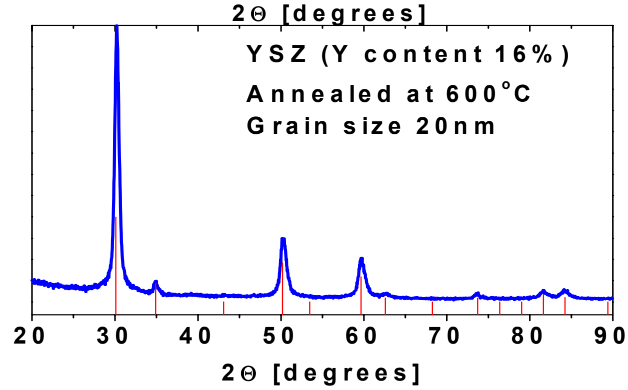
**SDC: σ=0.085 S/cm at 800°C, E=0.58eV**

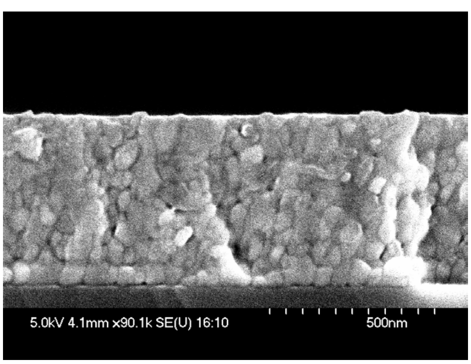
H.Yahiro, E.Eguchi and H.Arai, Sol.St.Ionics, 36, 71 (1989)

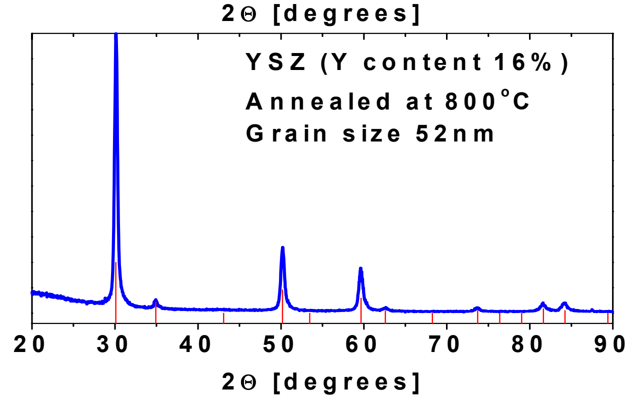

5.0kV 4.1mm x90.0k SE(U) 15:39
500nm

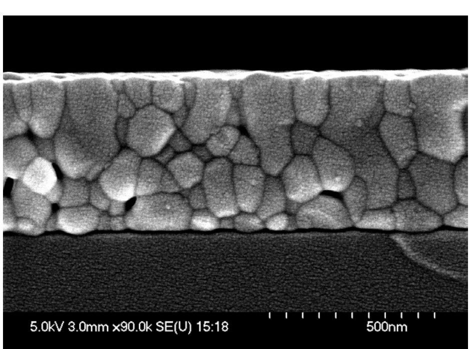

YSZ (Y content 16%)
Annealed at 400°C
Grain size 11 nm
20
30
40
50
60
70
80
90
2Θ [degrees]

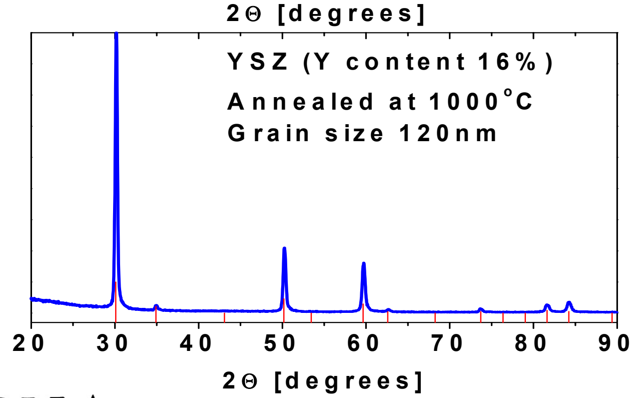

5.0kV 2.8mm x90.0k SE(U) 15:29
500nm


YSZ (Y content 16%)
Annealed at 600°C
Grain size 20nm
20
30
40
50
60
70
80
90
2Θ [degrees]


5.0kV 4.1mm x90.1k SE(U) 16:10
500nm


YSZ (Y content 16%)
Annealed at 800°C
Grain size 52nm
20
30
40
50
60
70
80
90
2Θ [degrees]

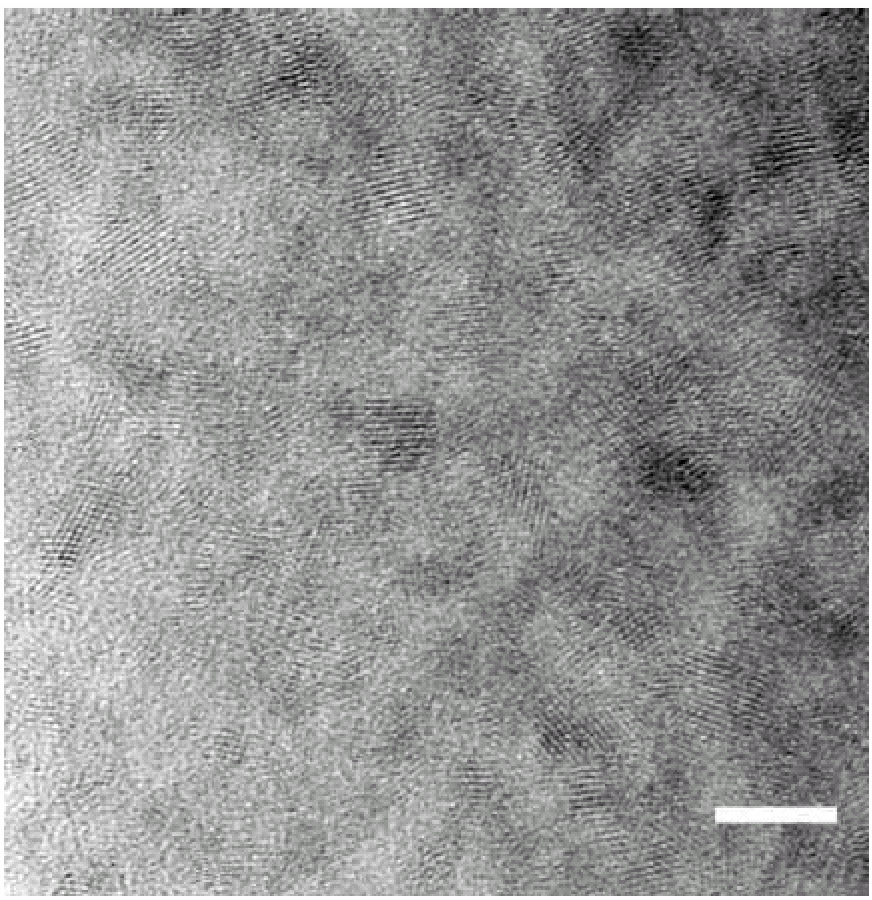

5.0kV 3.0mm x90.0k SE(U) 15:18
500nm


YSZ (Y content 16%)
Annealed at 1000°C
Grain size 120nm
20
30
40
50
60
70
80
90
2Θ [degrees]

# Results to Date

- Polymeric precursors for different zirconia and ceria based materials were developed and investigated.
- It was shown that polymer derived films formed at 400$^o$C have high initial density (~85%) and become fully dense at temperatures as low as 800 to 900$^o$C with the grain size in the submicron region (less than 100nm) .
- The electrical conductivity of these films after 800$^o$C annealing is comparable to the bulk specimens sintered at 1400$^o$C.
- The possibility was shown to control the porosity of the polymer derived films by using the mixture with the nanocrystalline powder from 50% porous up to dense state.

High resolution transmission electron micrograph of a 70 nm thick YSZ film annealed at 350°C for 1 minute. Bar = 5nm.



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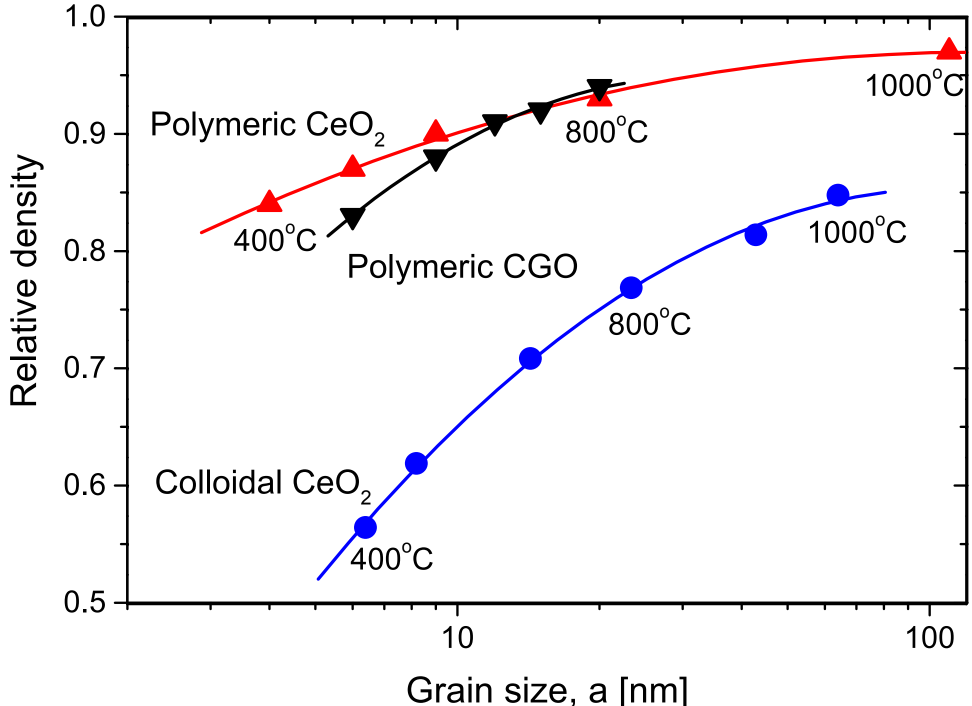
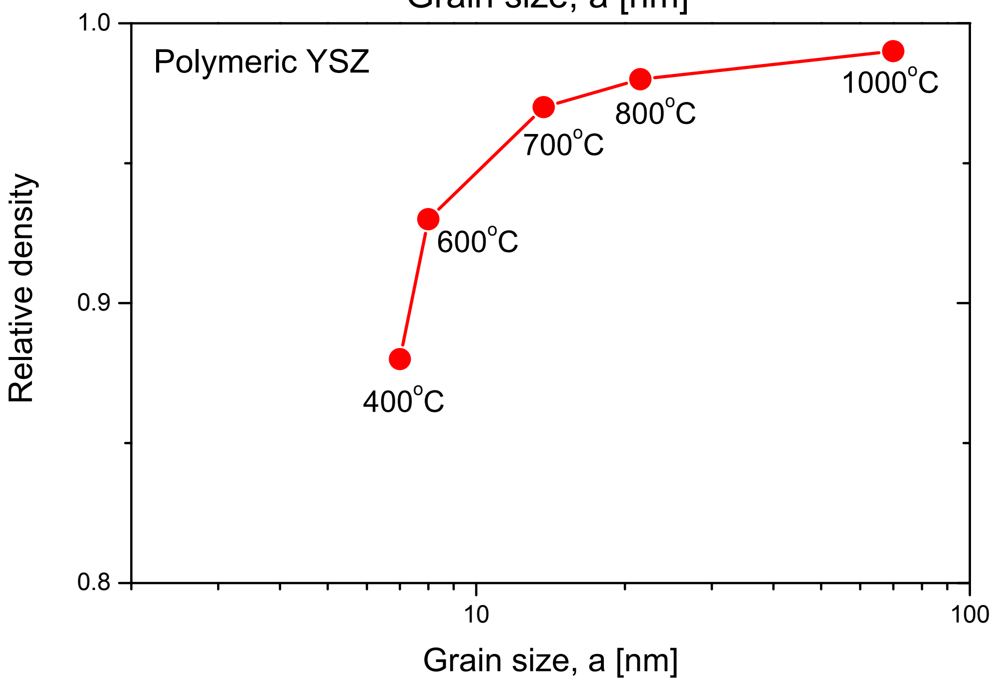
# Densification efficiency for polymeric films in comparison with colloidal suspensions



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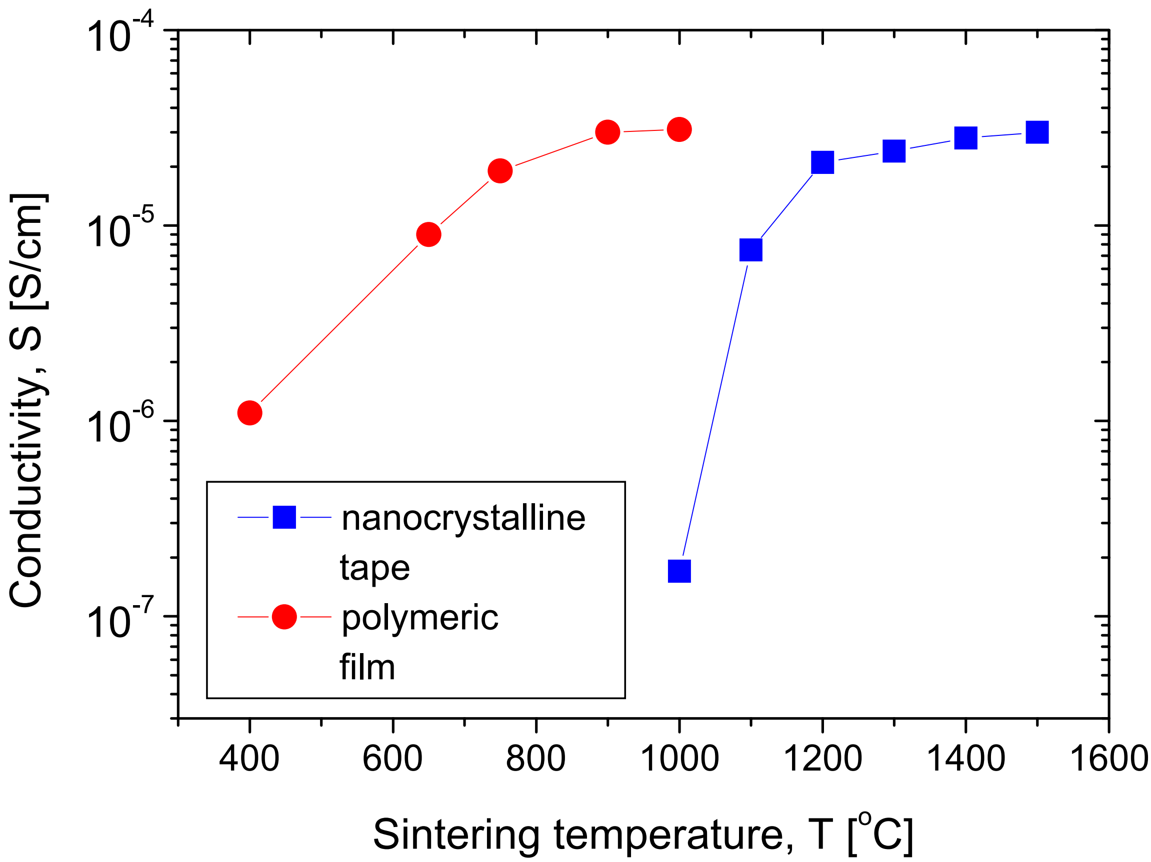
# Conductivity of YSZ tape and films as a function of annealing temperature



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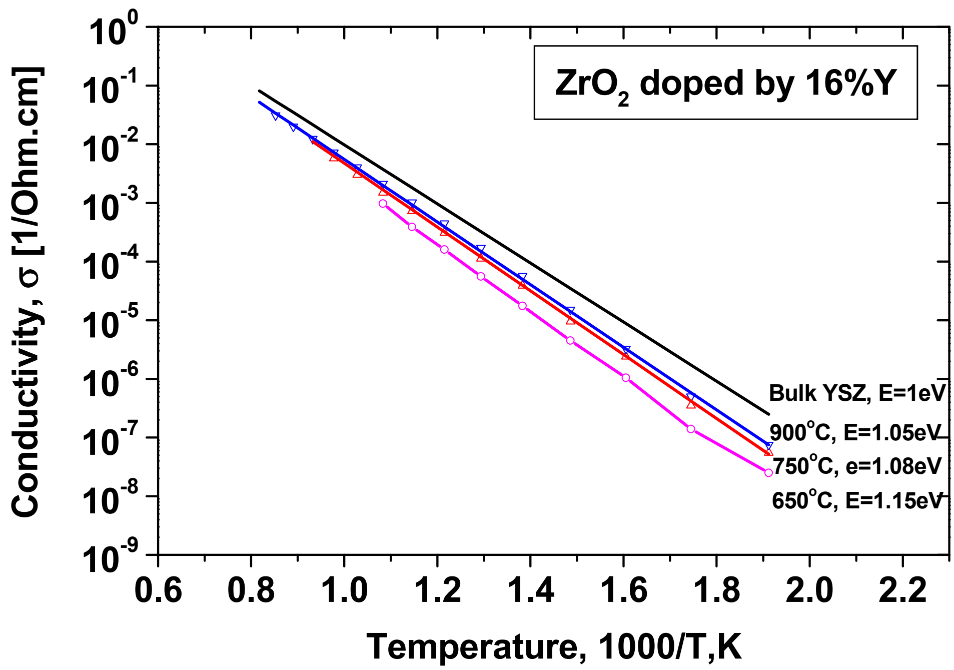
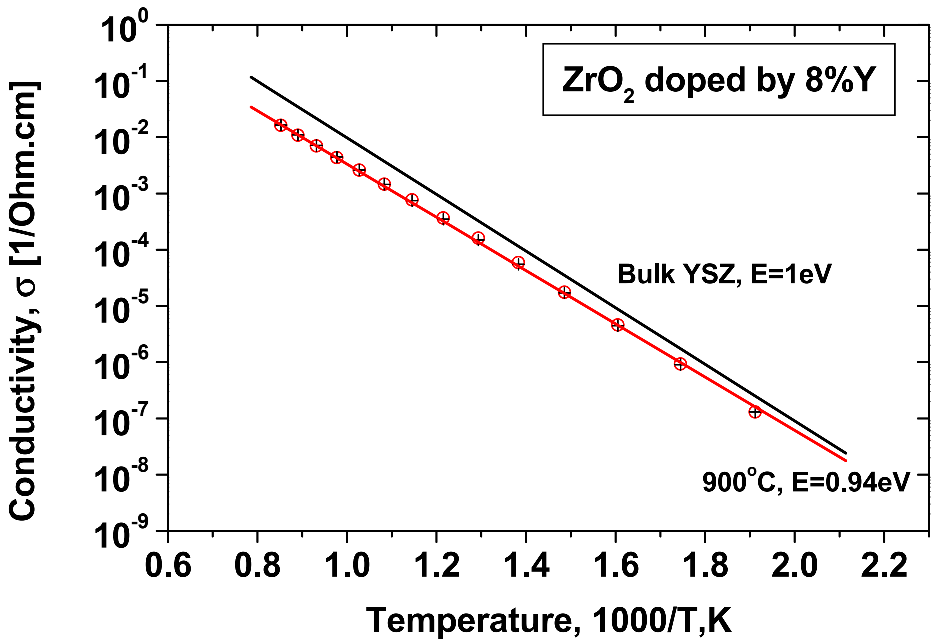
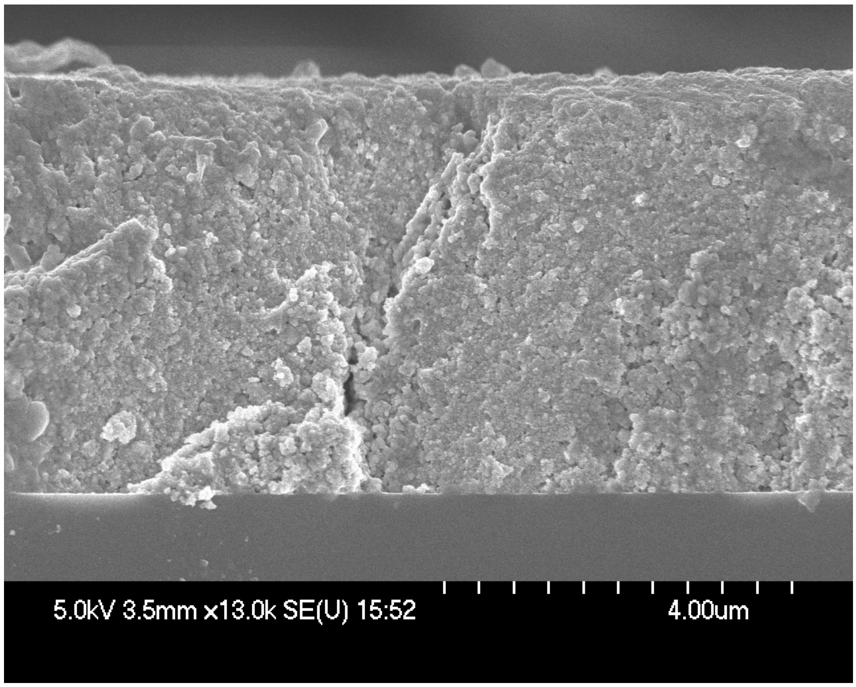
Conductivity measurements of
YSZ polymeric films (8 and 16% Y) on sapphire

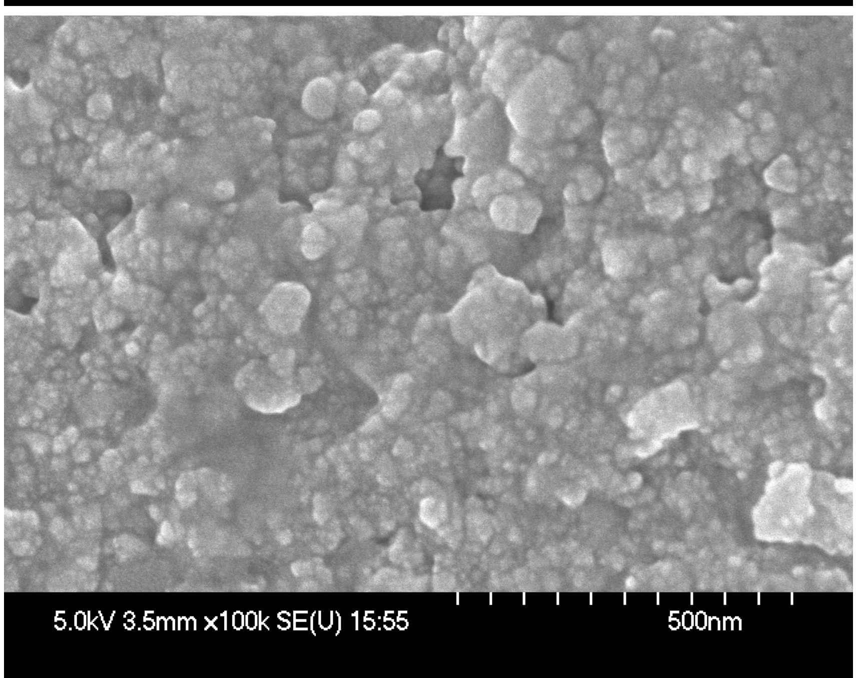


Dense YSZ-$CeO_2$ (from polymer precursor) layer on sapphire substrate.

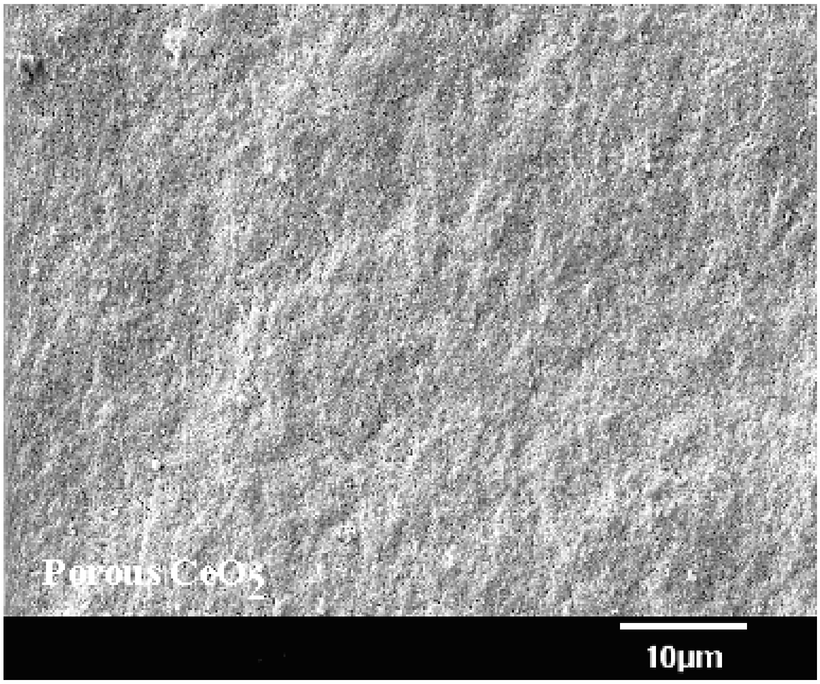



A

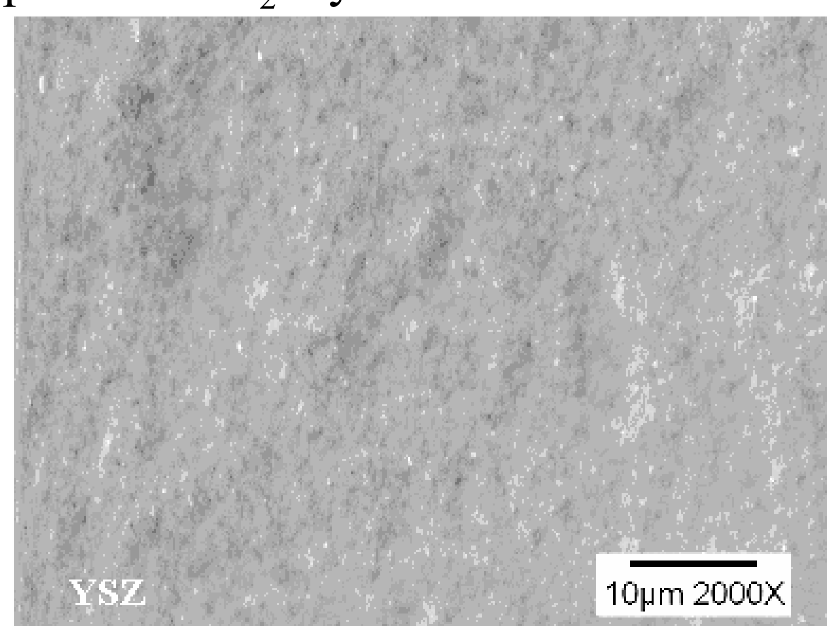



B

# SEM surface images of $YSZ/CeO_2/LSM$ composite




Nanoporous $CeO_2$ layer on LSM




Dense YSZ layer

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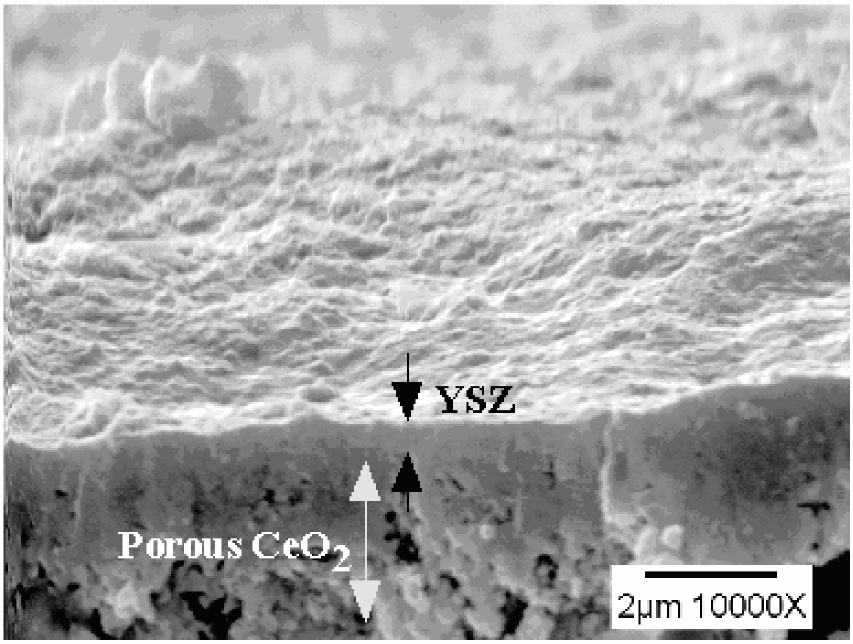
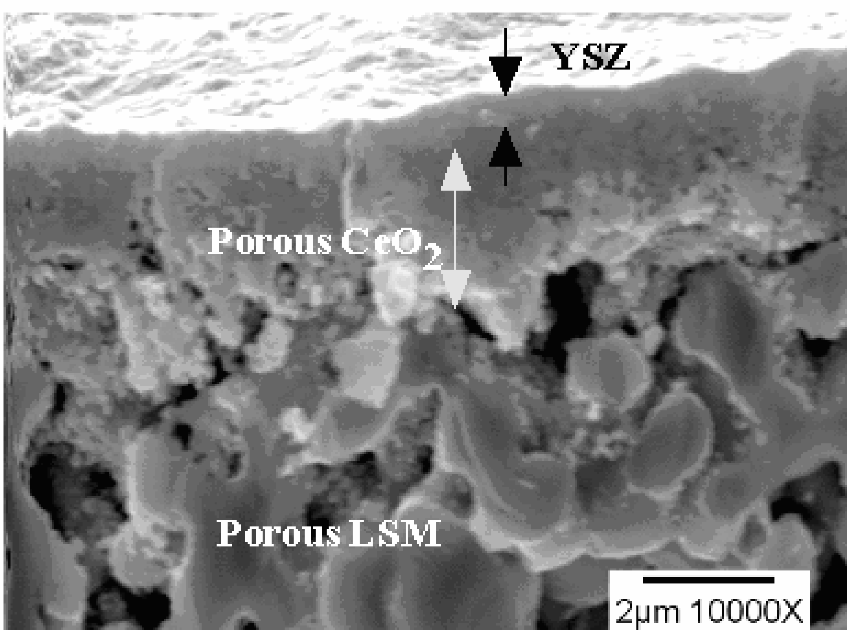
# SEM cross section images of YSZ/$CeO_2$/LSM composite



# Our goals for the next year

- Investigation and optimization of the polymer based technology is our priority for the next year.
- Precursors and deposition technique based on combination of nanocrystalline powder and metal oxide polymers will be developed for the nanocrystalline reaction interlayers.
- Finally, composite structures containing the electrolyte and reaction interlayers will be developed and tested for the both cathode and anode supported design.
- Our main goal for the next year is to show the efficiency of our approach and to build the basis for the future applications.