

Fabrication and Characterization of SOFC Anodes formed by aqueous Nickel Impregnation on porous YSZ substrate

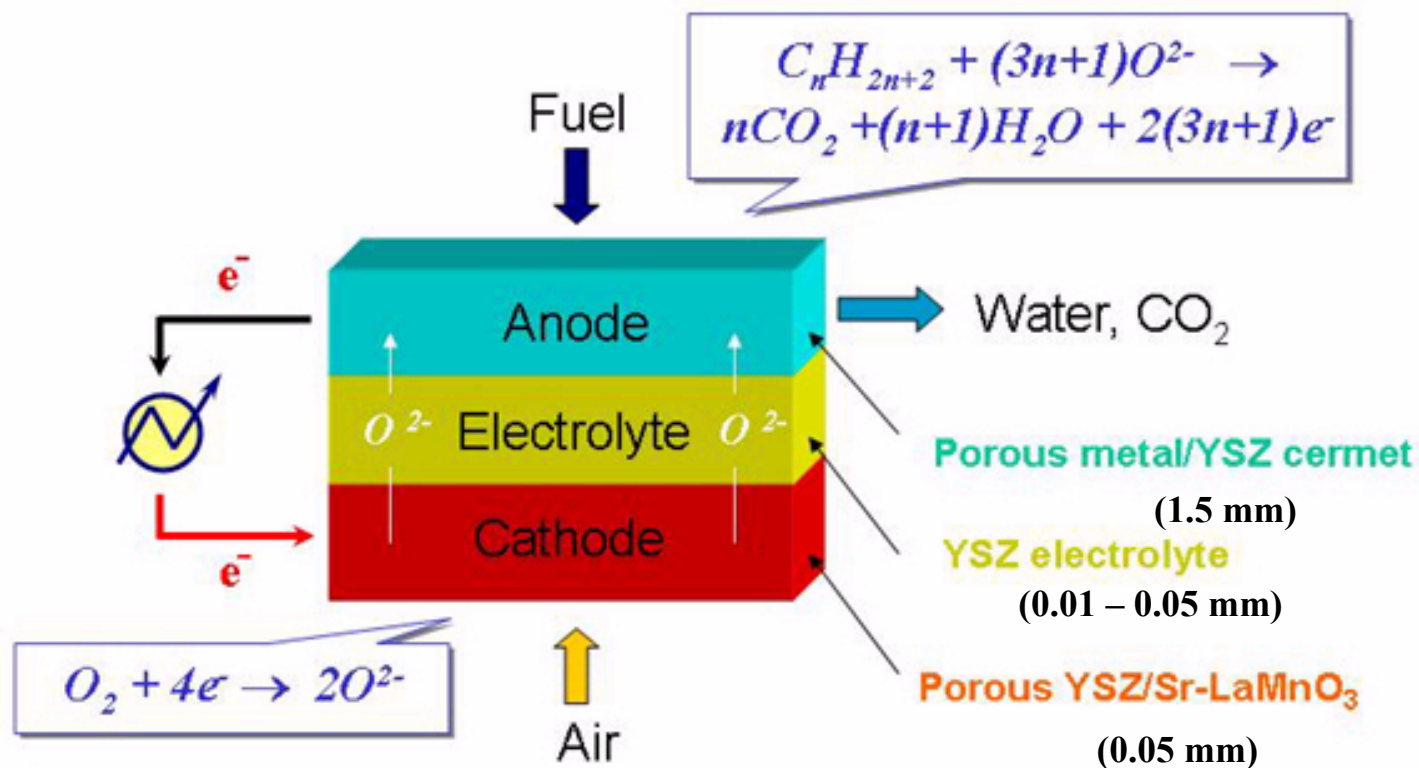


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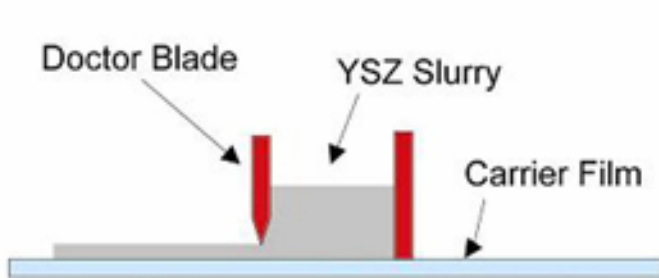


Solid Oxide Fuel Cell



YSZ – Ytria Stabilized Zirconia

SOFC Fabrication

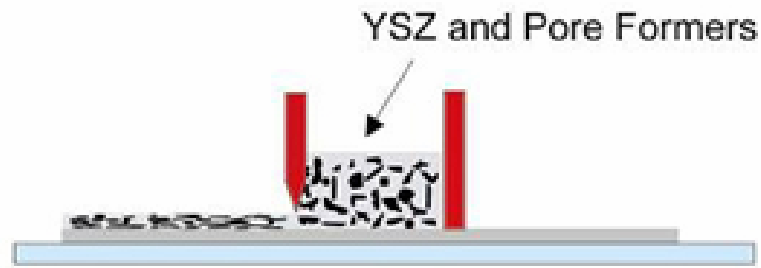


Tape casting



Electrolyte : 20 - 60 μm

Sintering 1450C – 10hrs



Multilayer Tape casting



Anode: 500 - 750 μm

Sintering 1250C- 2hrs

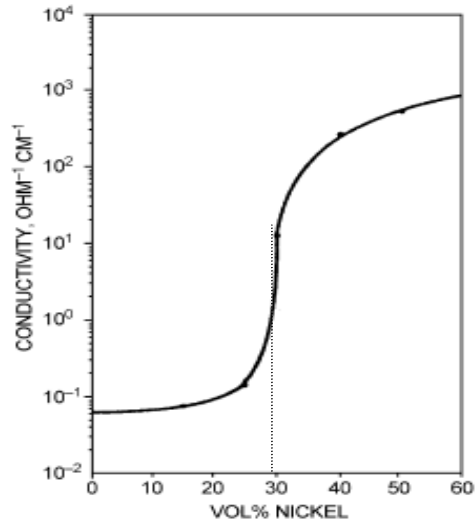


**Brush painting
LSM/YSZ**



Conventional Ni-YSZ anodes

Prepared by solid state Technique

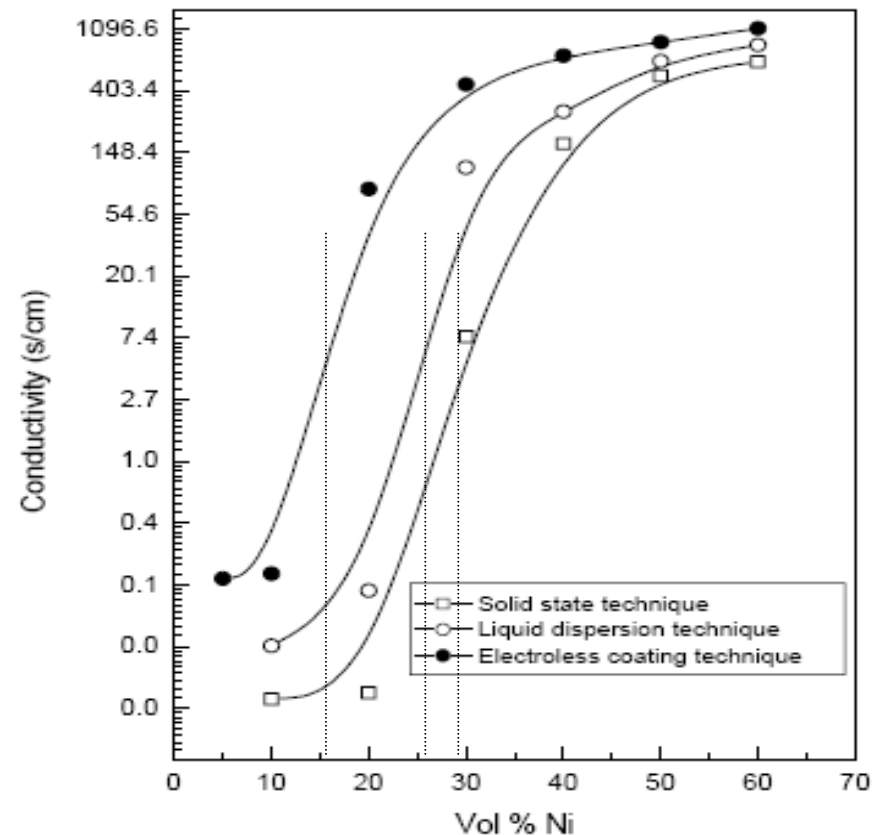


Minh, N. Q., J. Am. Ceram. Soc., 1993, 76

- To ensure **connectivity**, Ni content > 30 Vol% for percolation
- High Ni Content – Poor Redox tolerance

Alternate Ni-YSZ anodes

Improving the 'Percolation' threshold



Pratihari et al., MRS Bull. (2005), 40

Percolation threshold reduced to about 15 vol % Ni using electroless coating technique

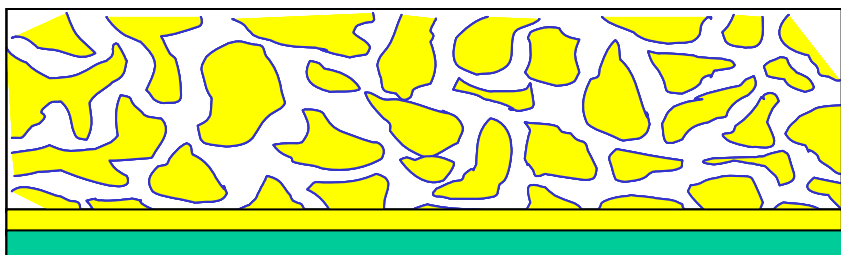


Motivation

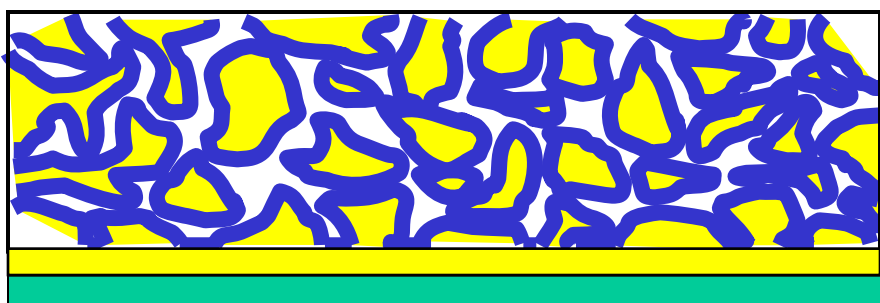
- Examine if lower Ni levels can still provide adequate conductivity and deliver performance – improvement in redox tolerance
- Impregnation and calcination of a Ni precursor solution onto a porous ceramic, such that a Ni film is formed that is well connected throughout the matrix
- Concept is successful in cases of Cu-CeO₂ anodes (Work of Gorte group, UPENN)
- Eventually obtain alternate anodes with perovskites deposited on porous anode structure – SOFC's operating directly on hydrocarbons



Anode Preparation by Nickel impregnation



Impregnation ↓ & Calcination



Important Issues?

- Conductivity and performance of Ni-impregnated anodes
- Role of pore morphology on electrical conductivity measurements and Cell performance

Characterization Techniques



- Morphology – SEM- Zeiss EVO 50
- Calcination and sintering Schedule-TGA/DTA- Seiko Instruments SII TG/DTA 32
- LSM structure-XRD-PANalytical- X'Pert PRO
- Particle size analysis- laser Particle Size Analyzer- Ankersmid C50 and Malvern
- Pore size analysis- Hg Intrusion Porosimetry- Quantachrome-Poremaster
- NiO reduction temperature-TPR- Micromeritics-Chemisorb 2720
- Ni Conc. at different points along anode-SEM-EDX- Zeiss EVO 50
- Conductivity-4 probe DC technique- Autolab PGSTAT30
- Cell Characterization- IV Curve analysis-electronic load assembled in lab
- Cell Characterization- Current interrupt method-Autolab PGSTAT30



Anode structural Parameters which affect the loading of catalyst, conductivity and performance of SOFC

Graphite based anode

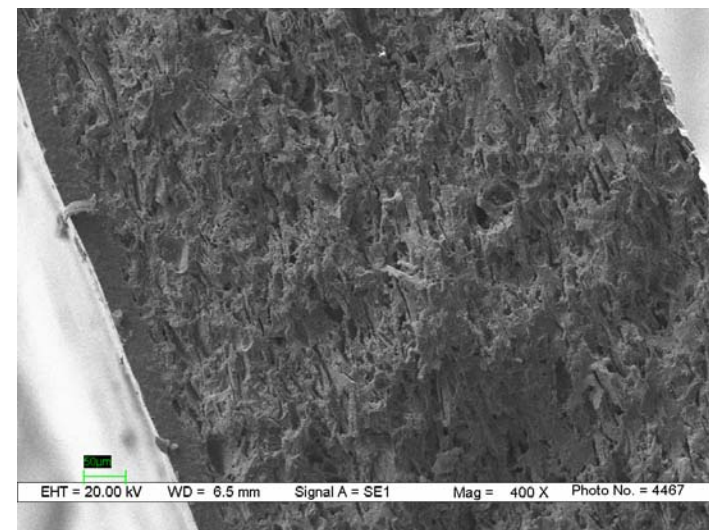
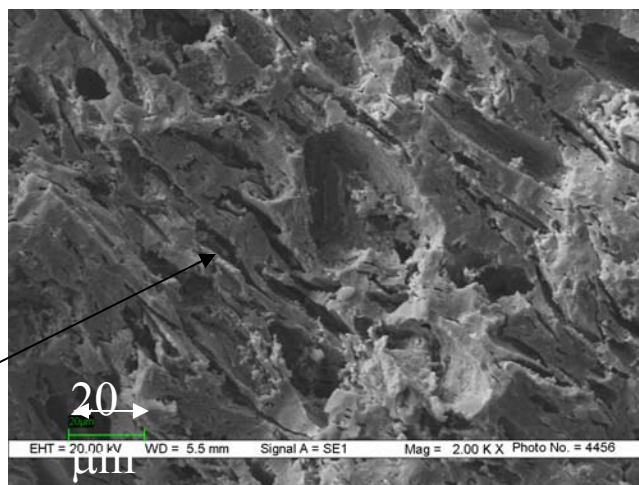
Pore shape

Flat,
spherical

Pore Size

1 -2 μm

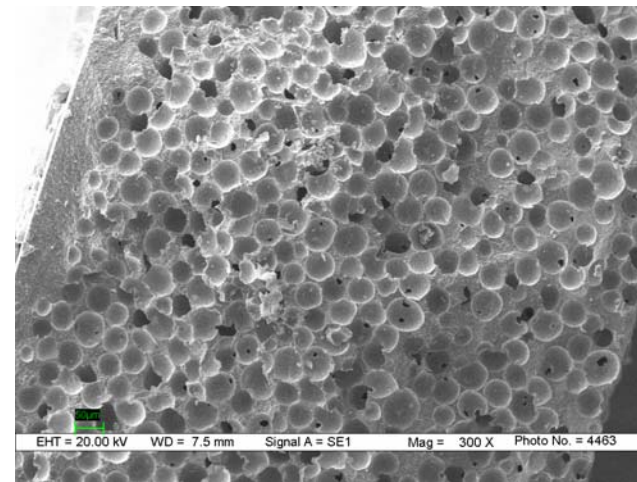
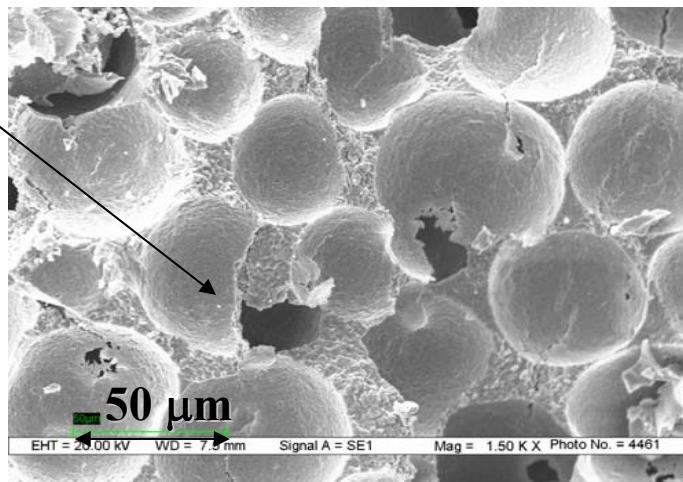
>20 μm



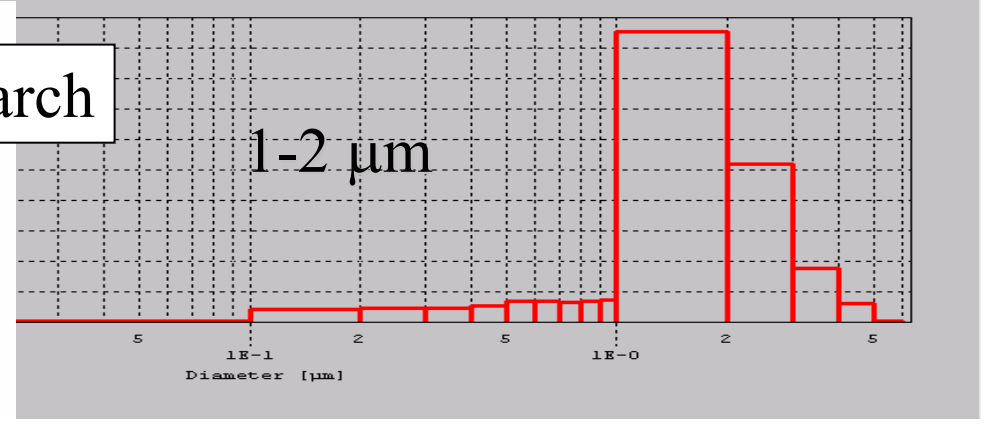
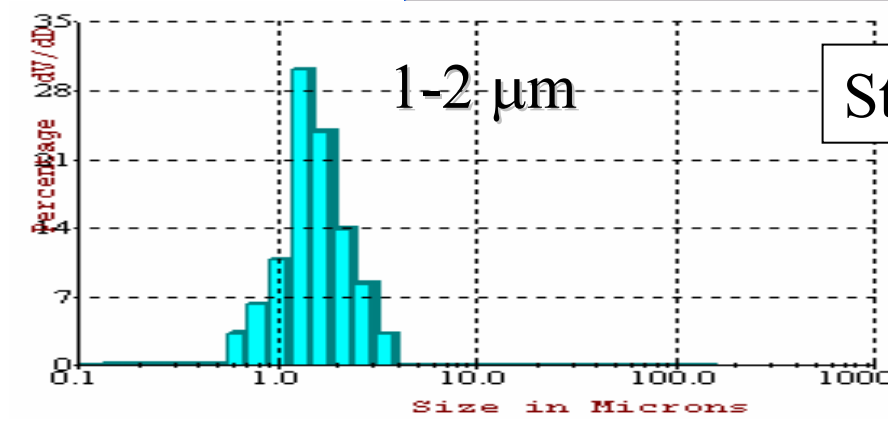
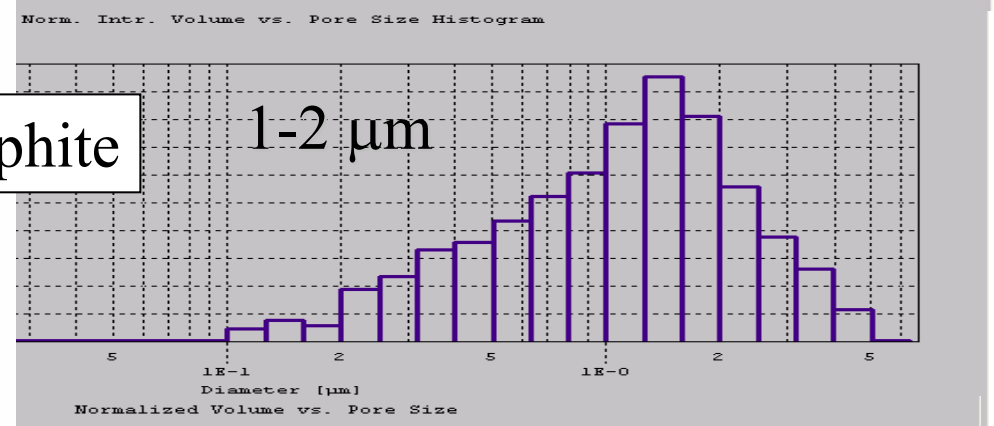
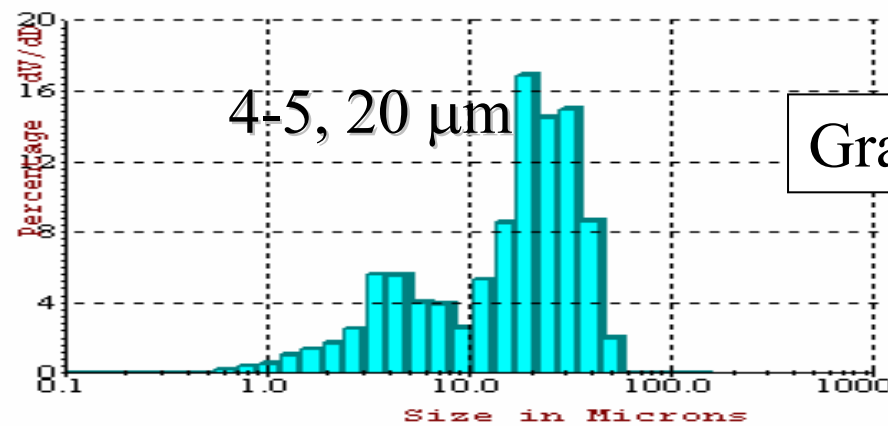
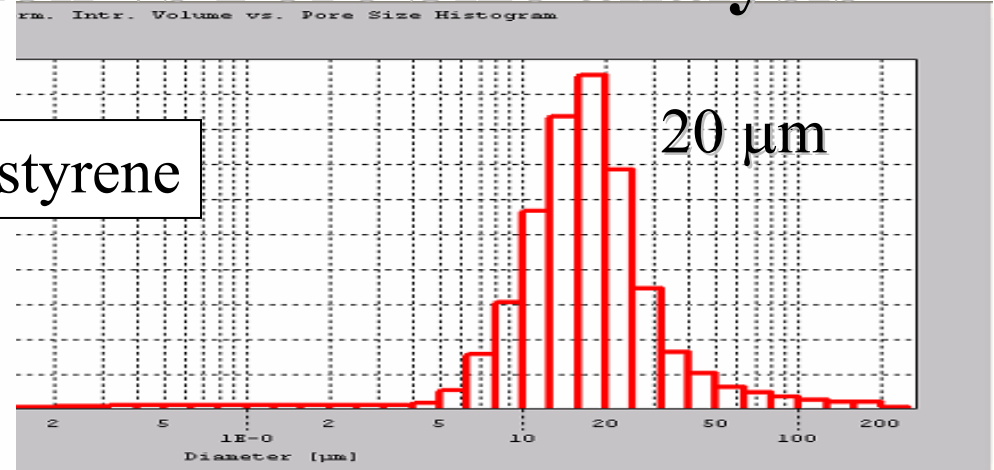
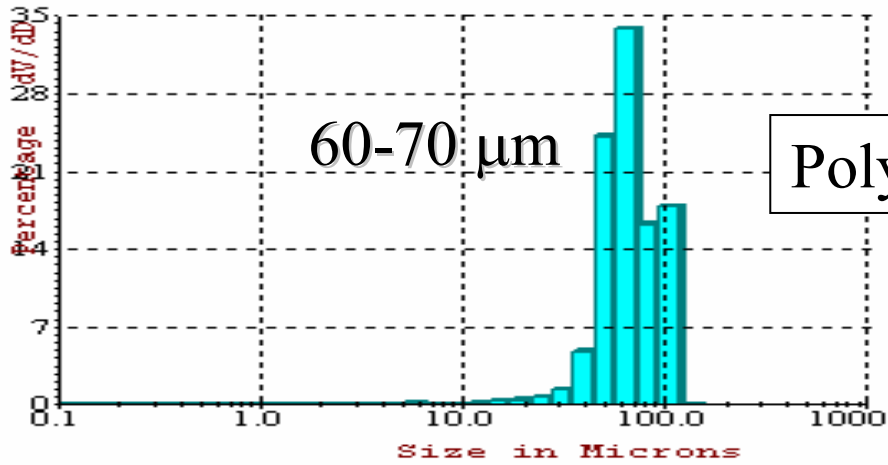
Polystyrene based anode

Porosity

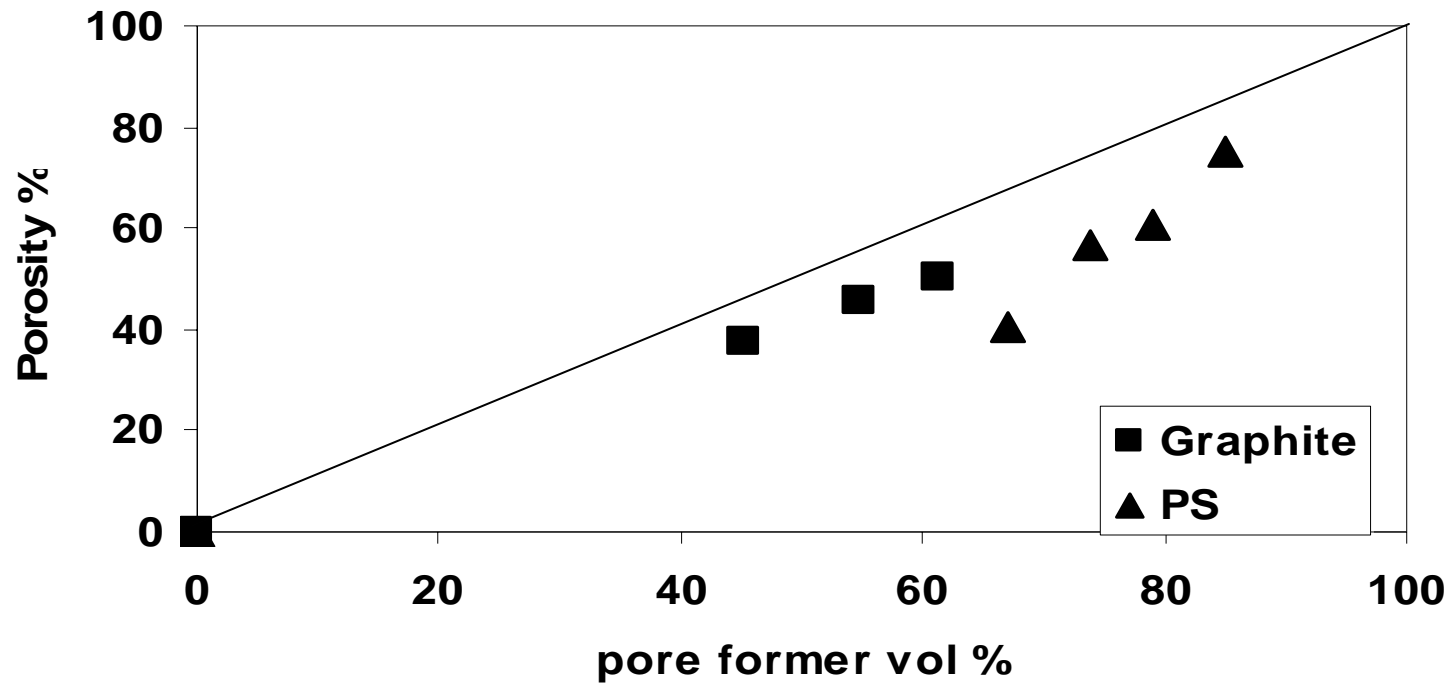
35 - 60%



Particle Size Distribution vs Pore Size analysis



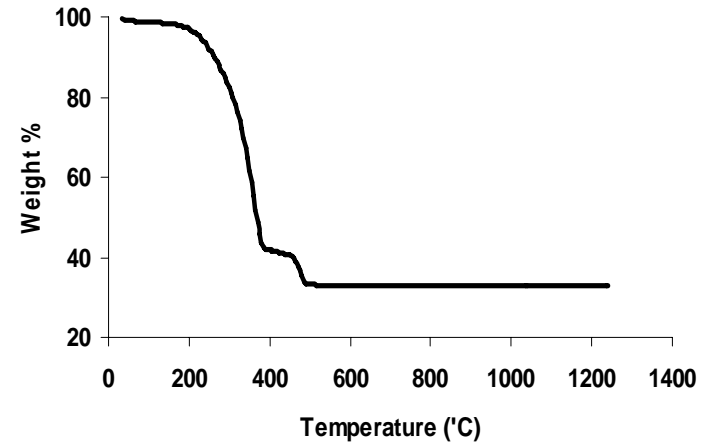
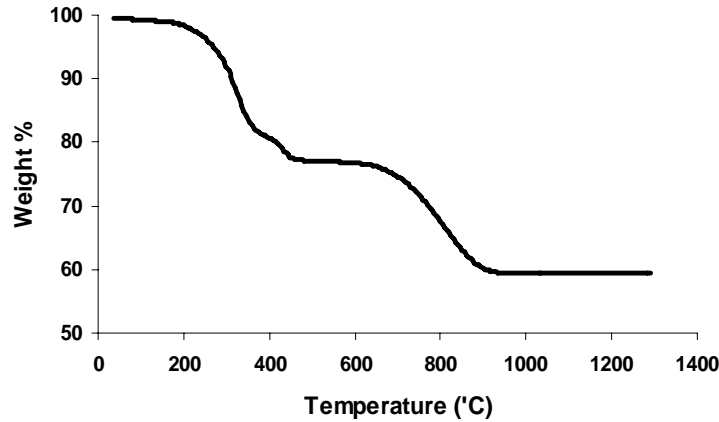
Effect of Pore former loading on porosity



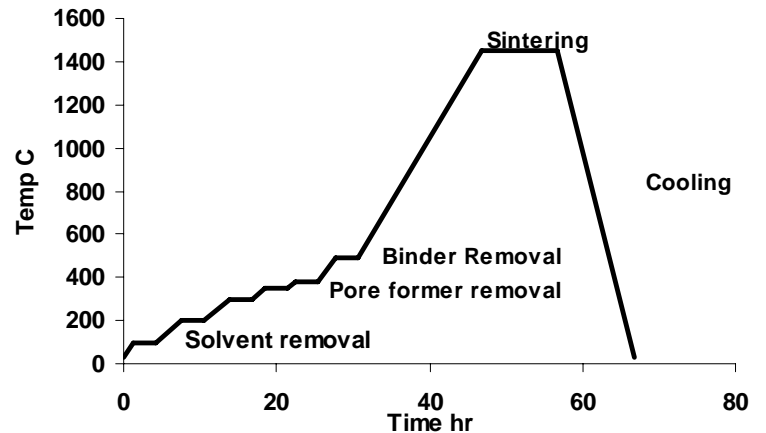
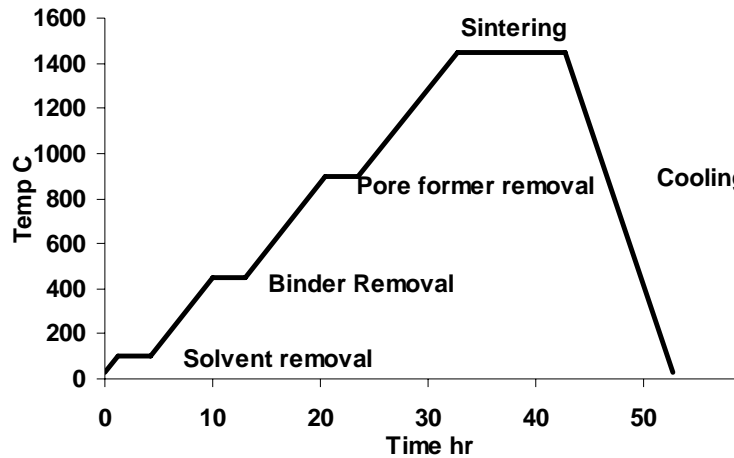
The percentage of closed end pores seems to be higher in case of Polystyrene.

Sintering Schedule

TGA



Sintering Schedule

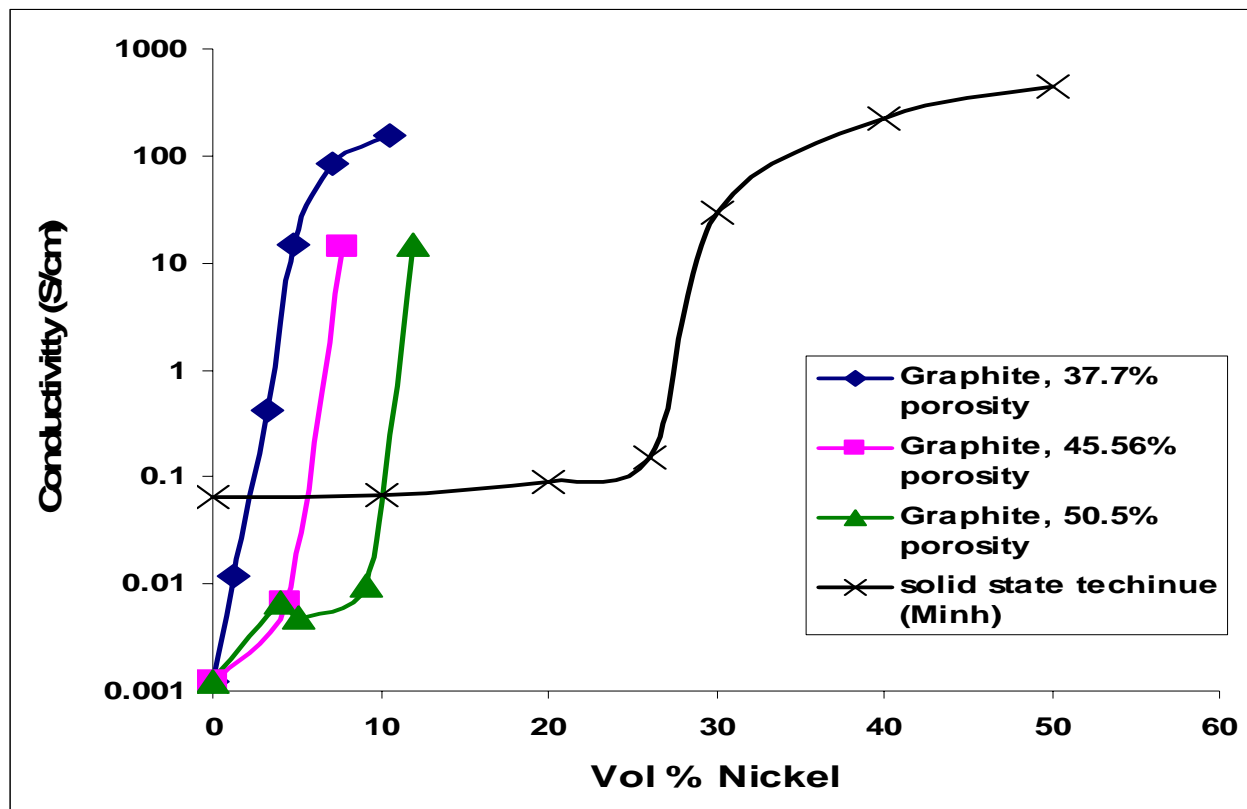
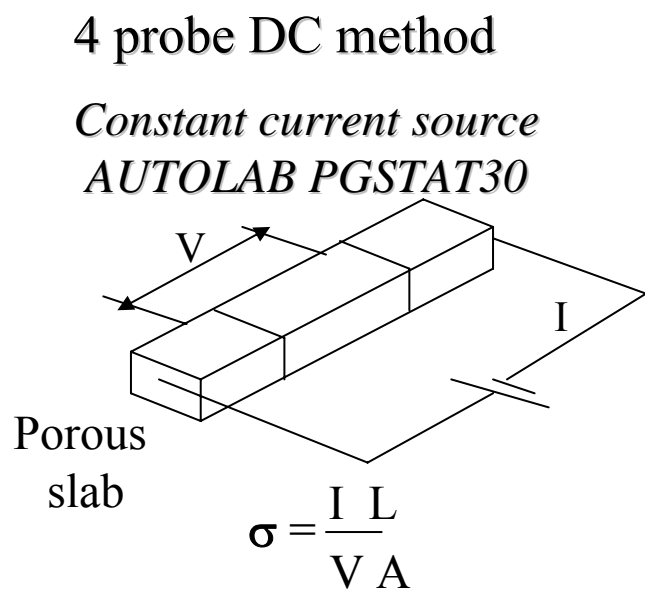


Anode with Graphite Poreformer

Anode with Polystyrene poreformer



Effect of porosity on conductivity

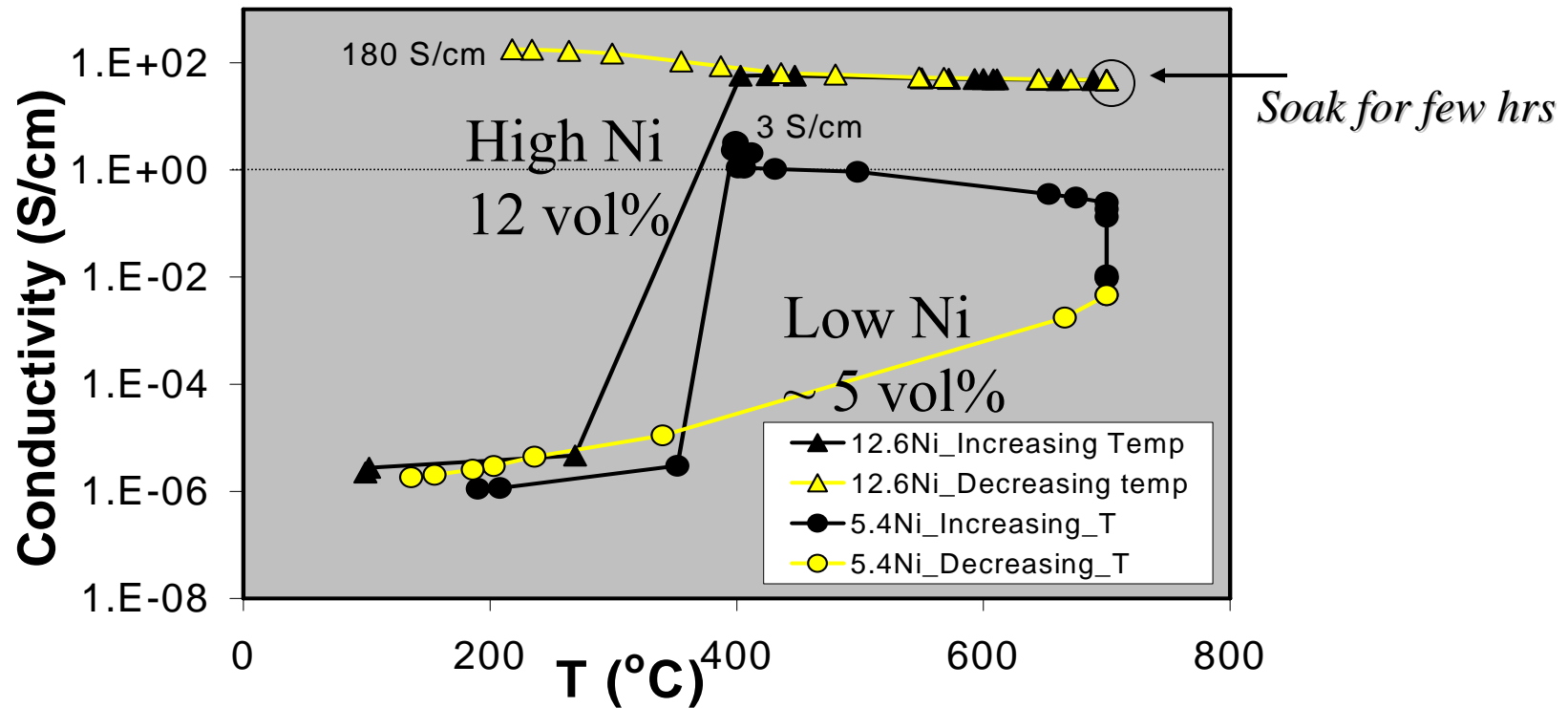


Conductivity decreases with increasing porosity for a fixed Ni content
Percolation threshold reduced to < 10 Vol% Ni

Conductivity as function of Temperature and Time



Case – Ni-YSZ prepared using Polystyrene pore-formers – porosity of 60%



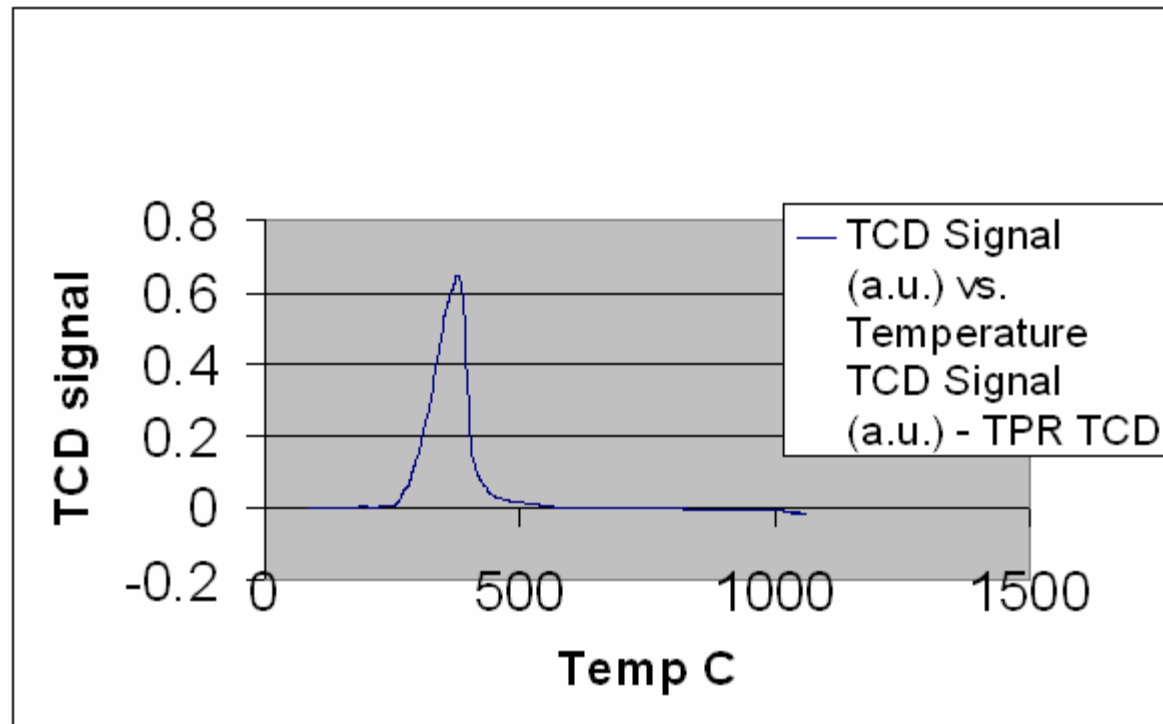
At low Ni concentrations

Drop in metallic conductivity at 700°C upon soaking, to pure YSZ levels;
YSZ behavior/ not Ni

Ni is effectively disconnected, due to sintering

Stable conductivity at 12 Vol. % Ni-YSZ loadings

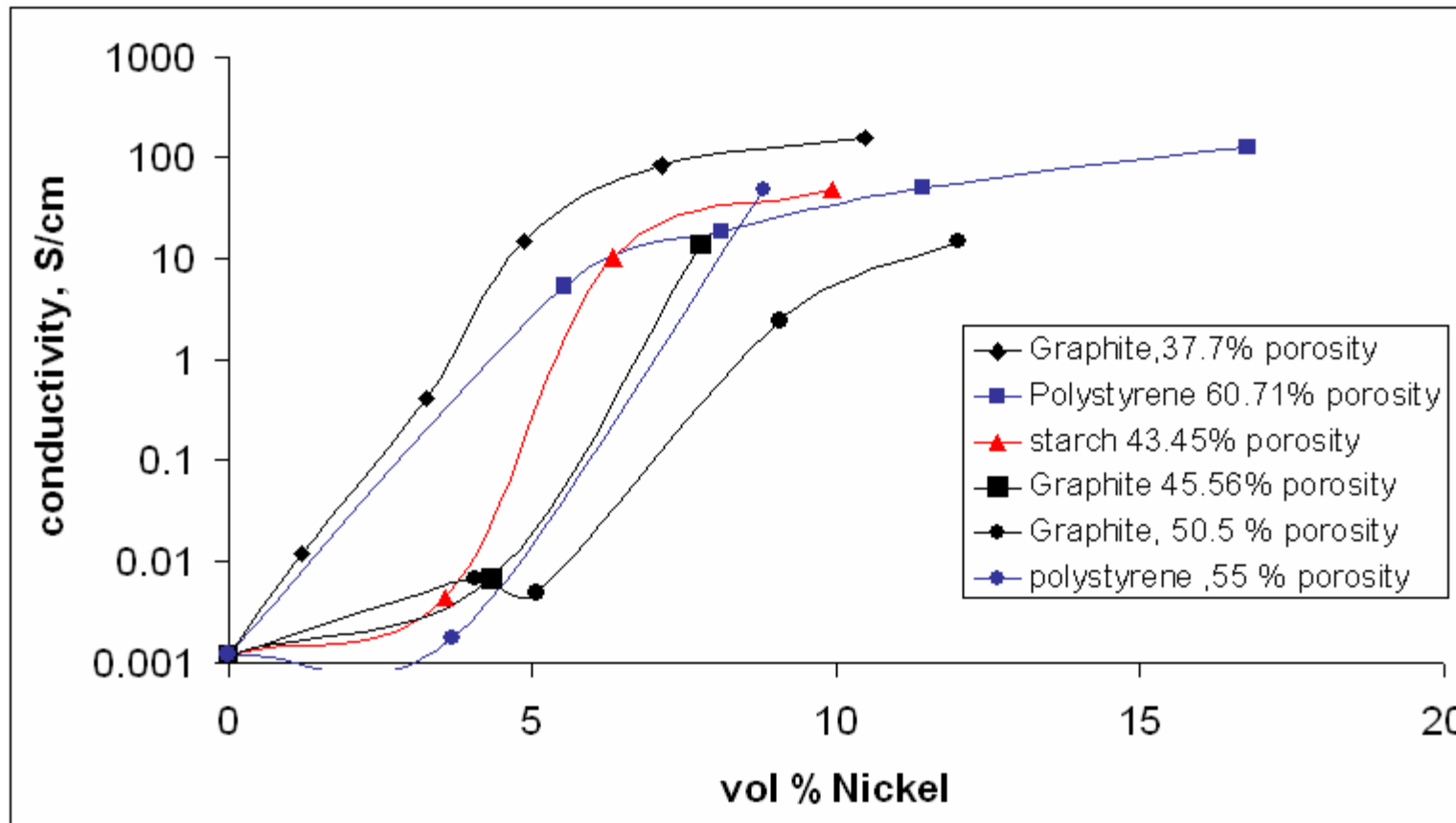
Temperature Programmed Reduction (TPR) of Ni impregnated on Graphite based Anode



The onset of NiO reduction to Ni starts at around 300C .

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Effect of porosity, pore shape and pore size on conductivity



As porosity increases conductivity decreases

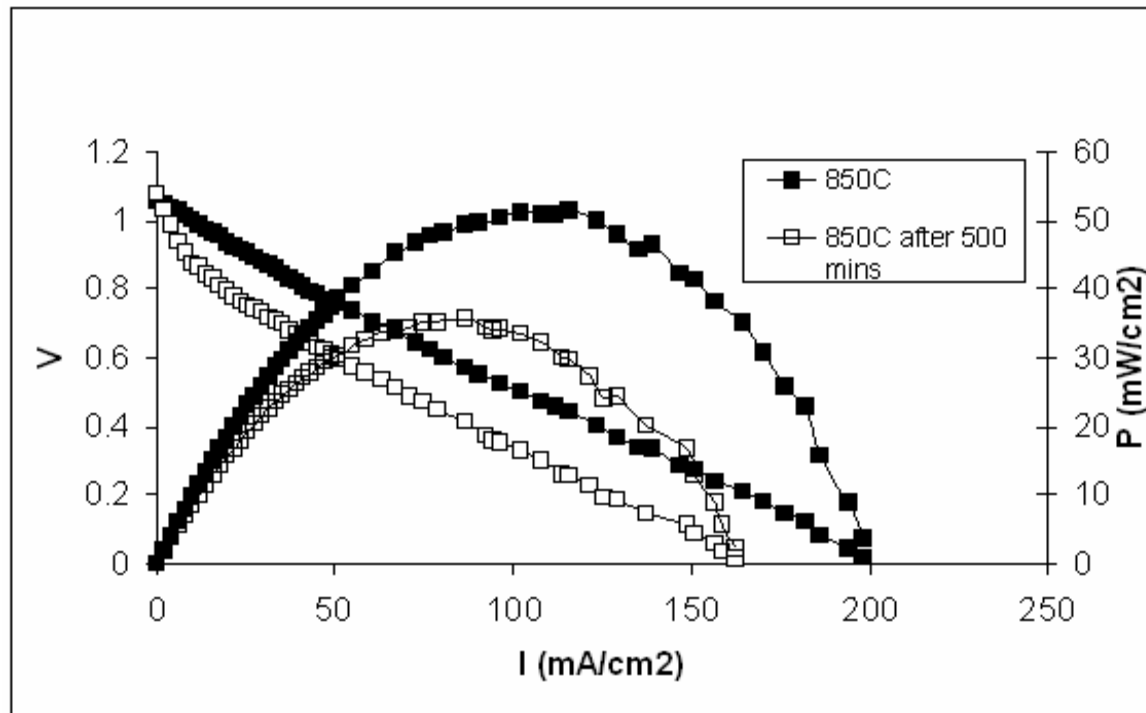
As pore size increases conductivity increases, maybe because of reduced tortuosity and hence reduced actual length.

Shape and tortuosity effects are clearly shown when graphite and starch poreformers at ca. 45% porosity are considered

SOFC Testing – Temperature Stability

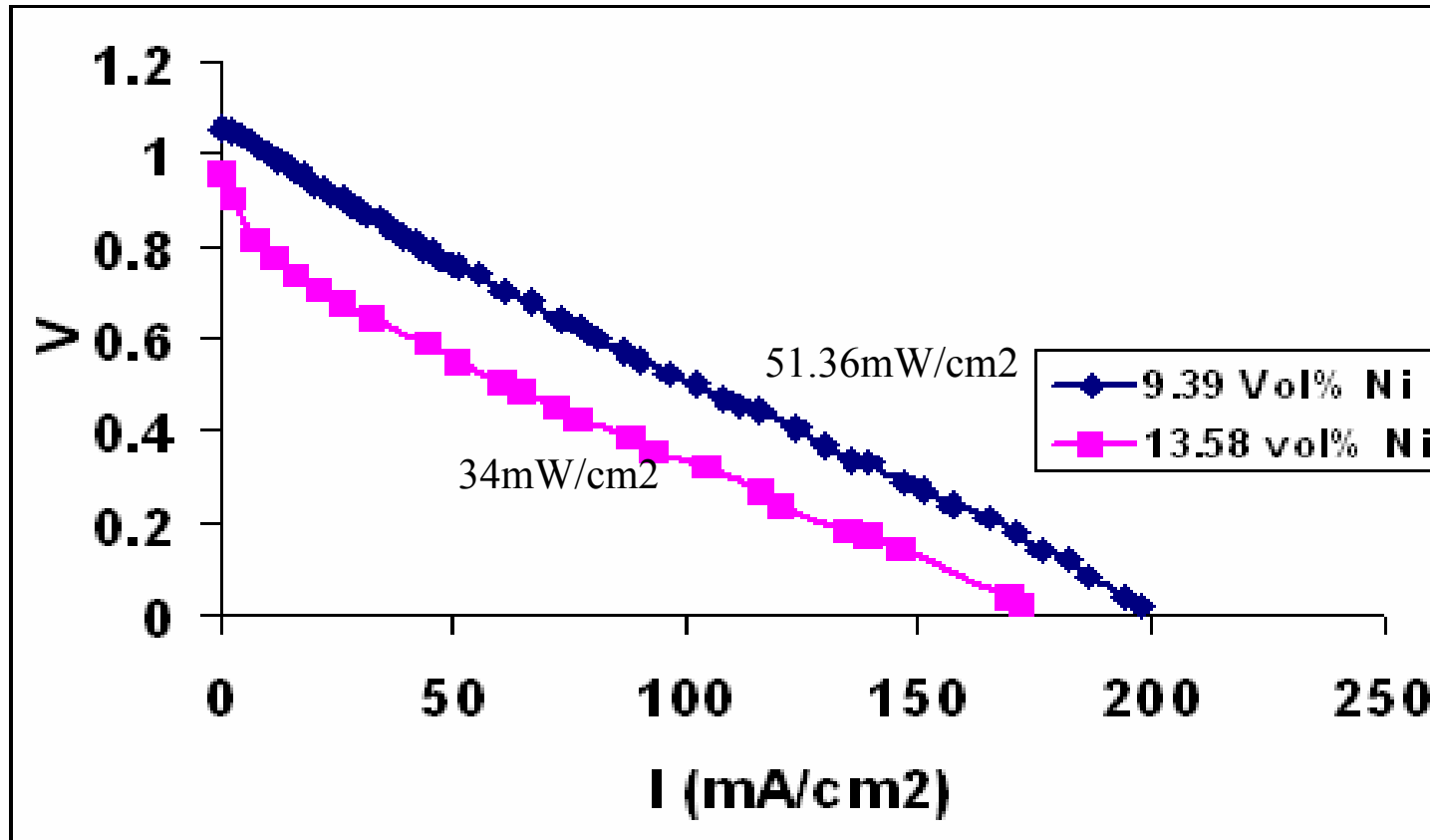


9.39 vol% Ni anode, graphite poreformer – 50.5 % porosity

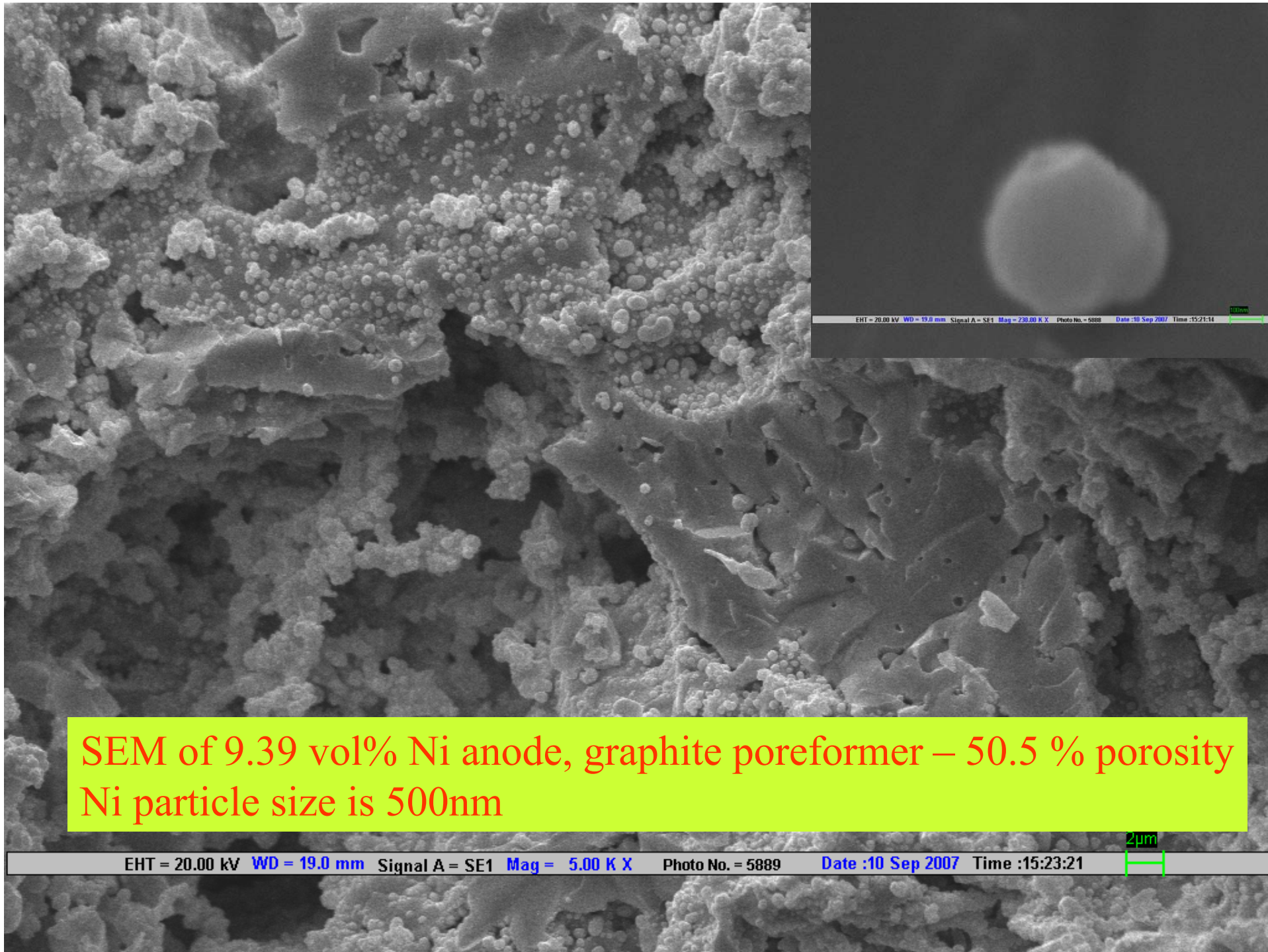


- Max Power Density is 51.36mW/cm² using H₂ as fuel
- Loss in performance is 30.62% in 500 mins
- There is an increase in activation polarization, which could mean that the effective TPB length has been reduced due to sintering.

SOFC Testing – Effect of Increasing Ni



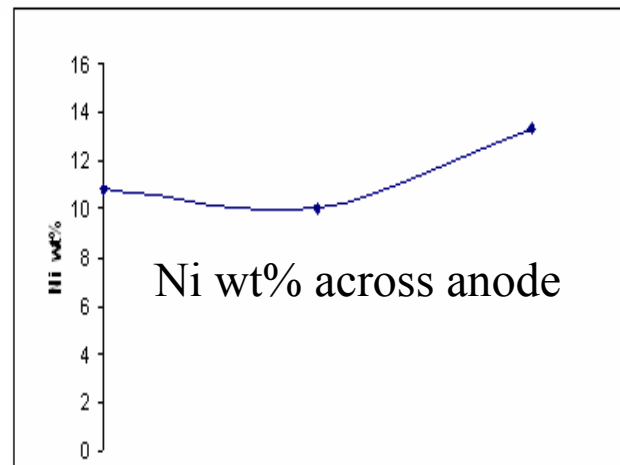
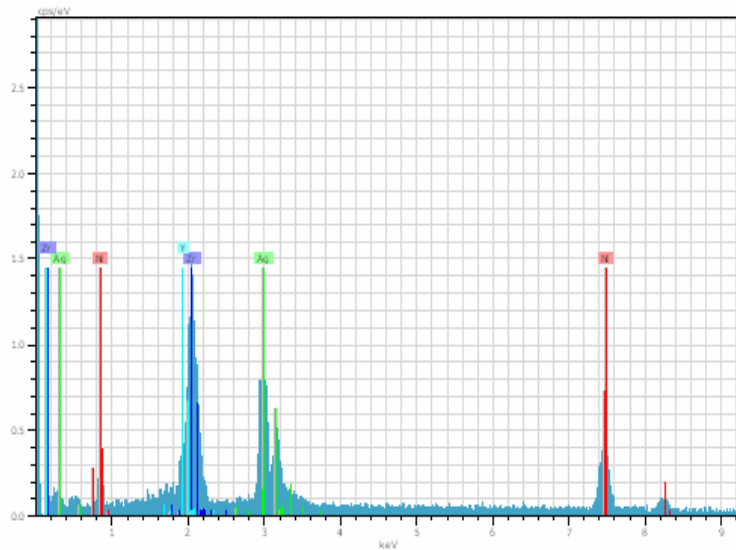
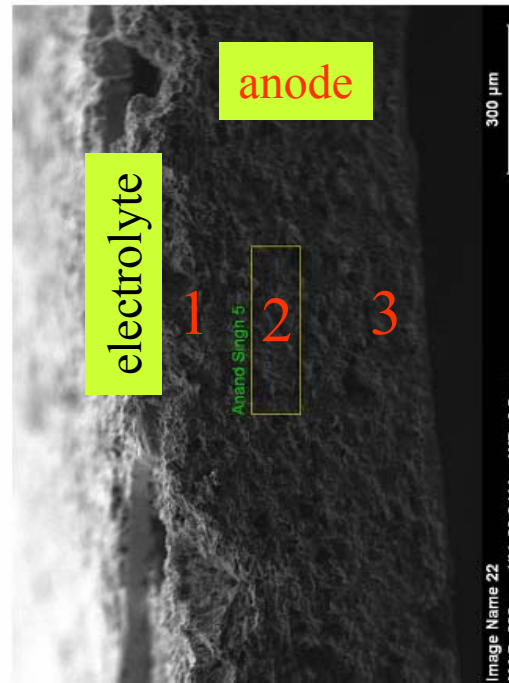
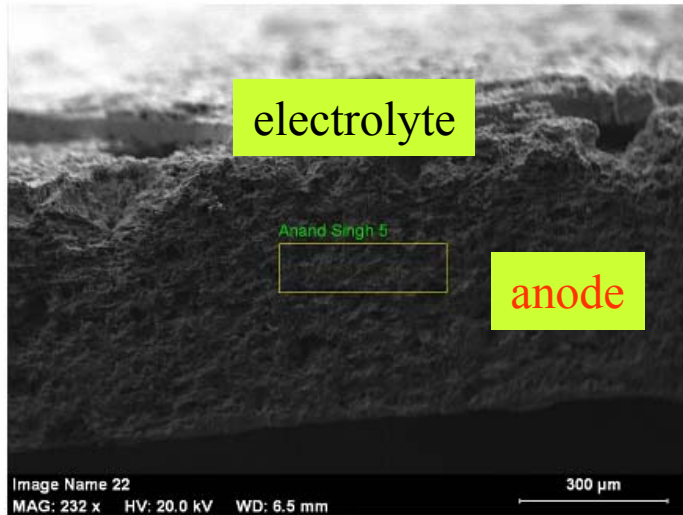
As Ni content increases performance decreases.
There is an increase in activation polarization.
But there is a small reduction in ohmic polarization.



SEM of 9.39 vol% Ni anode, graphite poreformer – 50.5 % porosity
Ni particle size is 500nm

EHT = 20.00 kV WD = 19.0 mm Signal A = SE1 Mag = 5.00 K X Photo No. = 5889 Date :10 Sep 2007 Time :15:23:21

SEM-EDX analysis



Ni levels near the TPB are significant



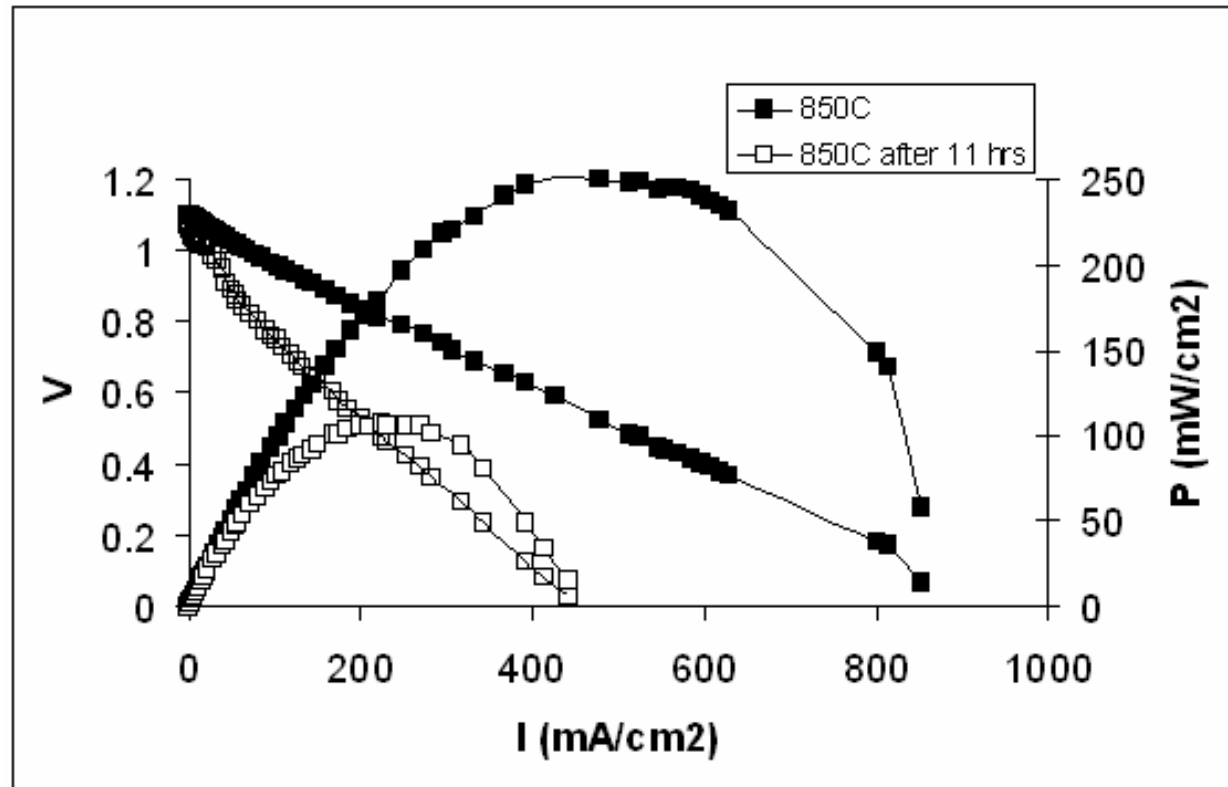
Summary and conclusions (Graphite based SOFC)

- **There is a very slight increase in performance as porosity increases.**
- **Even though the conductivity and Ni film stability will be good at low porosities, the TPB length at the interface increases as porosity increases.**
- **Since the conductivity of Ni based cermets are good, this TPB length could be the limiting factor.**
- **On increasing Ni loadings, the performance comes down**
- **This may be because of the blocking of the pore mouths and increase in diffusional resistances, without causing any real increase in TPB.
(A few impregnations are sufficient to block a 1 μ m pore.)**
- **Since the pore size is small and tortuosity high, an increase in loading may increase conductivity but may not result in an increase in TPB in the active layer and the Ni buildup may be more near the anode surface than at the interface. (as revealed by EDX)**

SOFC Testing



10.7 vol% Ni anode, polystyrene poreformer – 56.84 % porosity



- Max power density is 251.59mW/cm² H₂ as fuel.
- The IV curves after 11 hrs suggest that there is a loss in conductivity as well as the TPB length.
- The cell performance increases as Ni loading is increased.

Summary and conclusions



- **A higher Ni loading does translate into an expected increase in performance.(the pores are not blocked in this case)**
- **Loss in performance in case of Polystyrene based sofc is due to sintering and results in loss of TPB as well as conductivity.**
- **A high pore size is very critical to have a good performance.**
- **Graphite as a stand alone pore former cannot give good performance results.**
- **Graphite used along with polystyrene may give good results, as small pores will ensure that the Ni films are stable and a certain level of conductivity is maintained.**
- **For such an anode, it will be the TPB stability which has to be addressed.**
- **This can be addressed by having a novel dual layer anode.**



Work in Progress

Fabrication of The Novel Anode

- **The active layer in this case is a 10um thick NiO based ceramic mixed anode.**
- **The current collection as well as support layer is prepared using a combination of graphite and polystyrene poreformer.**
- **The active layer can have as high a Ni content as 60%, which will lead to an extremely high TPB.**
- **The support layer can have < 15% Ni.**
- **The over all Ni content will still be around 15%.**
- **This low Ni content will make the cell more redox stable.**

Hospitality at IITB – EXCELLENT!!!



THANK YOU IITB & ICAER-07