Advanced Ceramics: Particle Size and the Challenge of Determining Suitable Refractive Indices

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Overview

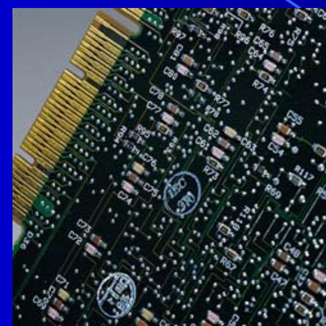
- Ceramic Formulations
- Importance of particle size
- Problems in particle sizing
- Approaches to index determination
- Examples
  - Fuel cell electrode
  - Dielectric formulation

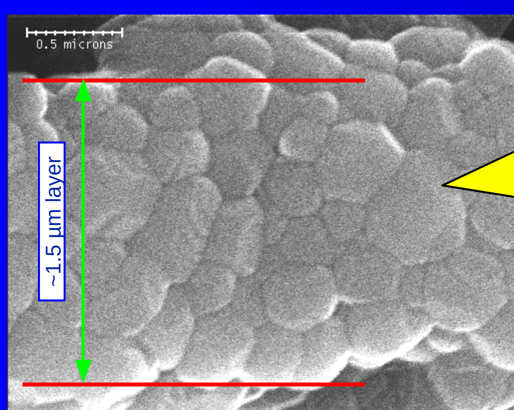
Ceramic Formulations

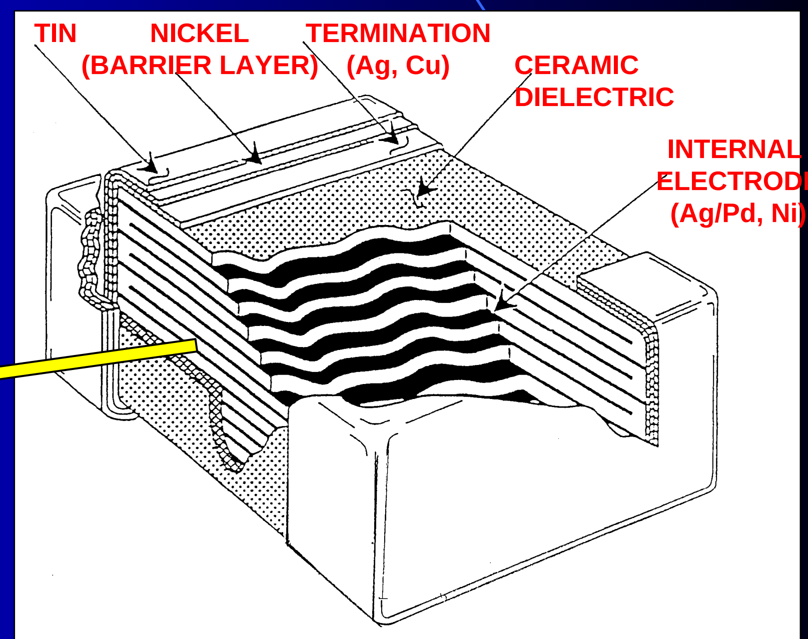
- Mixtures of two or more materials
  - Electronic Ceramics
    - Raw material mixtures
      - Oxides and carbonates of most of the Periodic Chart!
    - Doped $BaTiO_3$
      - Dopants containing >5 different materials
  - Solid Oxide Fuel Cell Materials
    - Raw material mixtures
    - $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$
    - Y_2O_3-ZrO_2
    - Gd_2O_3-CeO_2
    - Ni-Y-ZrO_2

Importance of Particle Size

- MLCC's
  - >100 in a cell phone
  - ~0.5 mm
  - 10 to >200 layers of ceramic
  - 1 – 10 µm thick
- Thinner layer = Higher capacitance

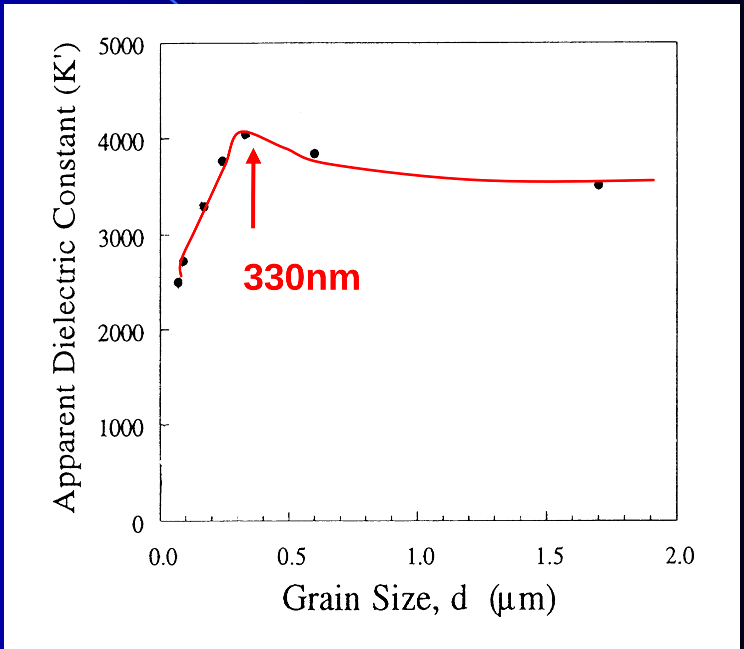






Importance of Particle Size

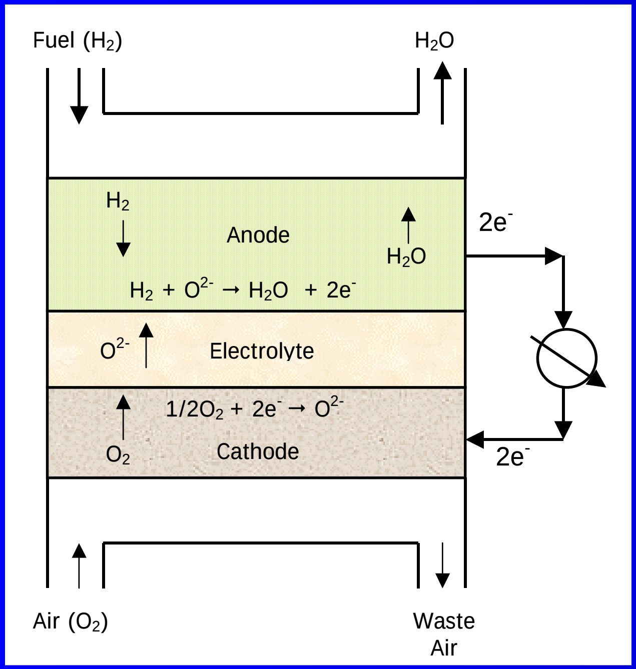
- Size Effect in $BaTiO_3$ Ceramics
  - K decreases below ~ 300 nm

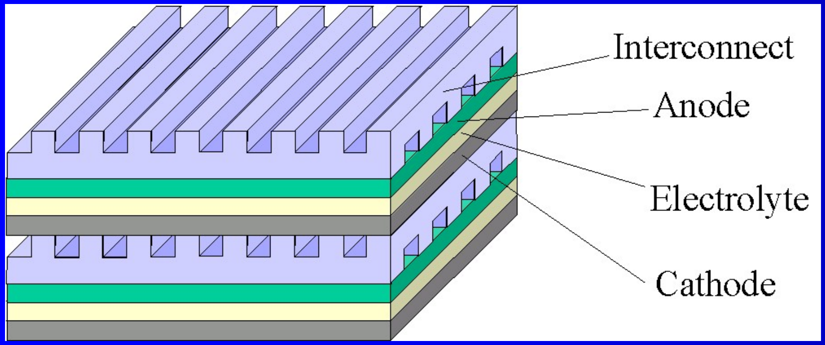


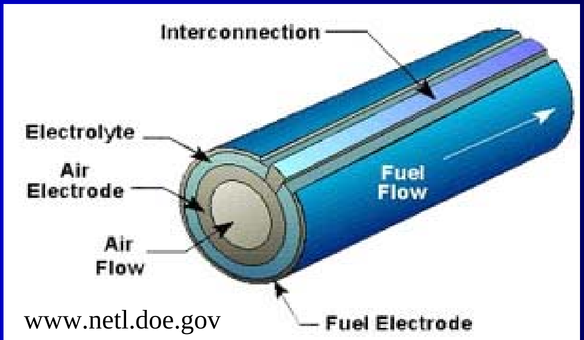
Frey *et al.*: Ferroelectrics, **206-207** 337 (1998).

Importance of Particle Size

- Solid Oxide Fuel Cell
  - Each cell ~ 1 volt
  - 3 layers/cell
  - Thin electrolyte better
    - 10 to 40 μm
  - Flat plate and tube designs

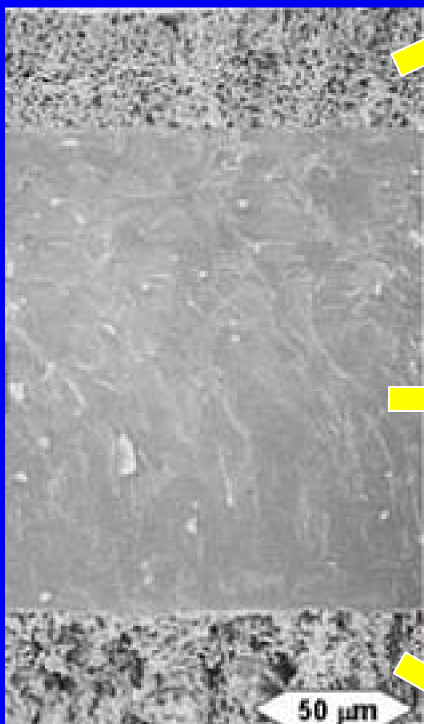


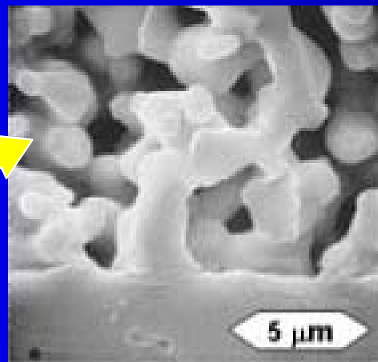




Importance of Particle Size

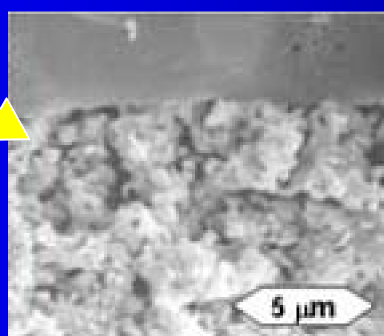
Solid Oxide Fuel Cell Structure





- Cathode
  - ~50% porosity
  - $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$

- Electrolyte
  - Fully dense
  - $Y\text{-}ZrO_2$, $Gd_2O_3\text{-}CeO_2$



- Anode
  - ~40% porosity
  - $NiO/Y\text{-}ZrO_2$

Problem

- Background
  - Laser scattering instruments are based on Mie theory for interaction of light with particles.
  - Requires knowledge of the complex refractive index of the particles.

    $n^* = n' + \kappa i$

- Problem
  - Determining a *suitable refractive index* for accurate particle size determination of mixtures by laser scattering.

Index Determination

- Approaches
  - Guess
    - OK for process control
    - When relative value is adequate
  - Mixture Rule
    - Usually suggested
    - Doesn't help with imaginary component
  - Software based
    - Statistical comparisons
    - Measured vs. calculated intensities

$n_{mixture}$ = refractive index of mixture

V_i = volume fraction of *i*thcomponent of mixture

n_i = refractive index of *i*th component of mixture

z = number of components

Software Approach

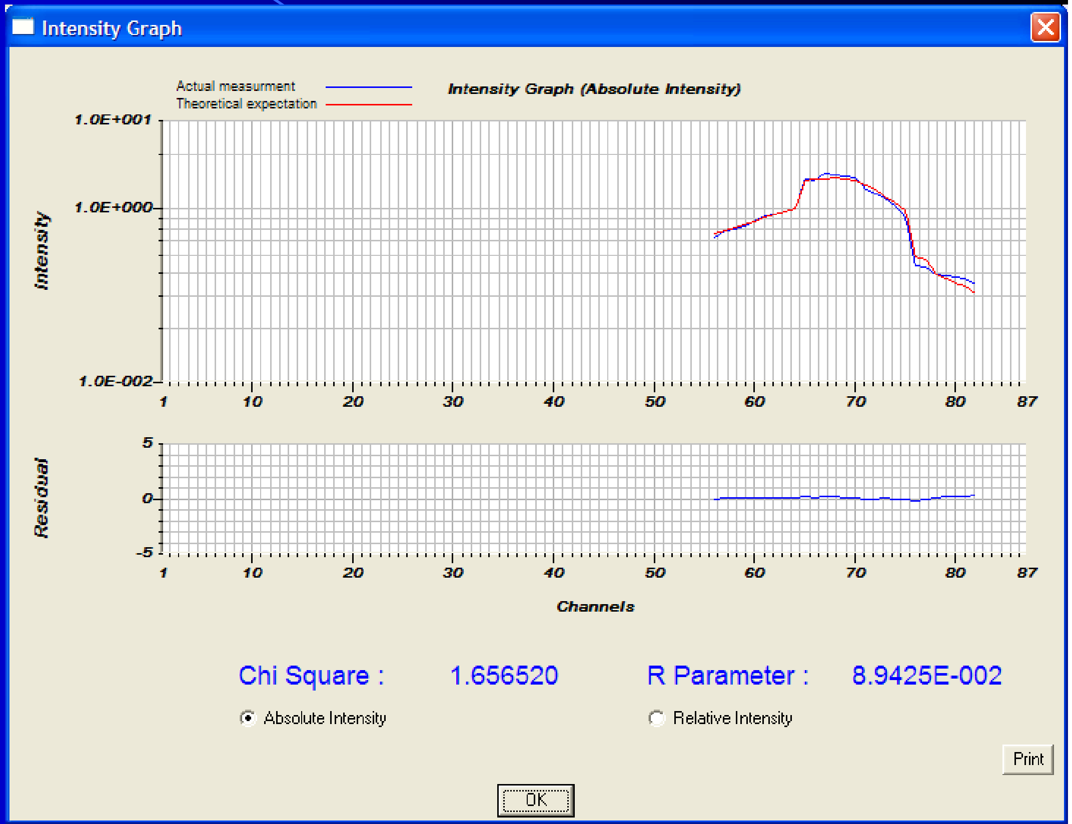
- Horiba LA-950
- Software Ver. 3.56
- Creation of new refractive index kernels
- Measured vs. Calculated Scattered Intensities
- Goodness of fit parameters:
  - Degree of similarity between distribution calculated using the input optical properties and distribution of actual scattering data.
    - Chi Square (χ^2)
    - R Parameter

Goodness of Fit Parameter χ^2

- χ^2
  - y_i = actual scattering measurement
  - $y(x_i)$ = theoretical scattering measurement
  - σ_i = standard dev. of scattering data

Intensity Data

- Software Output:
  - Intensity vs. Channel
    - Measured
    - Theoretical
    - Residual (Actual – Theo.)
  - ‼ χ^2

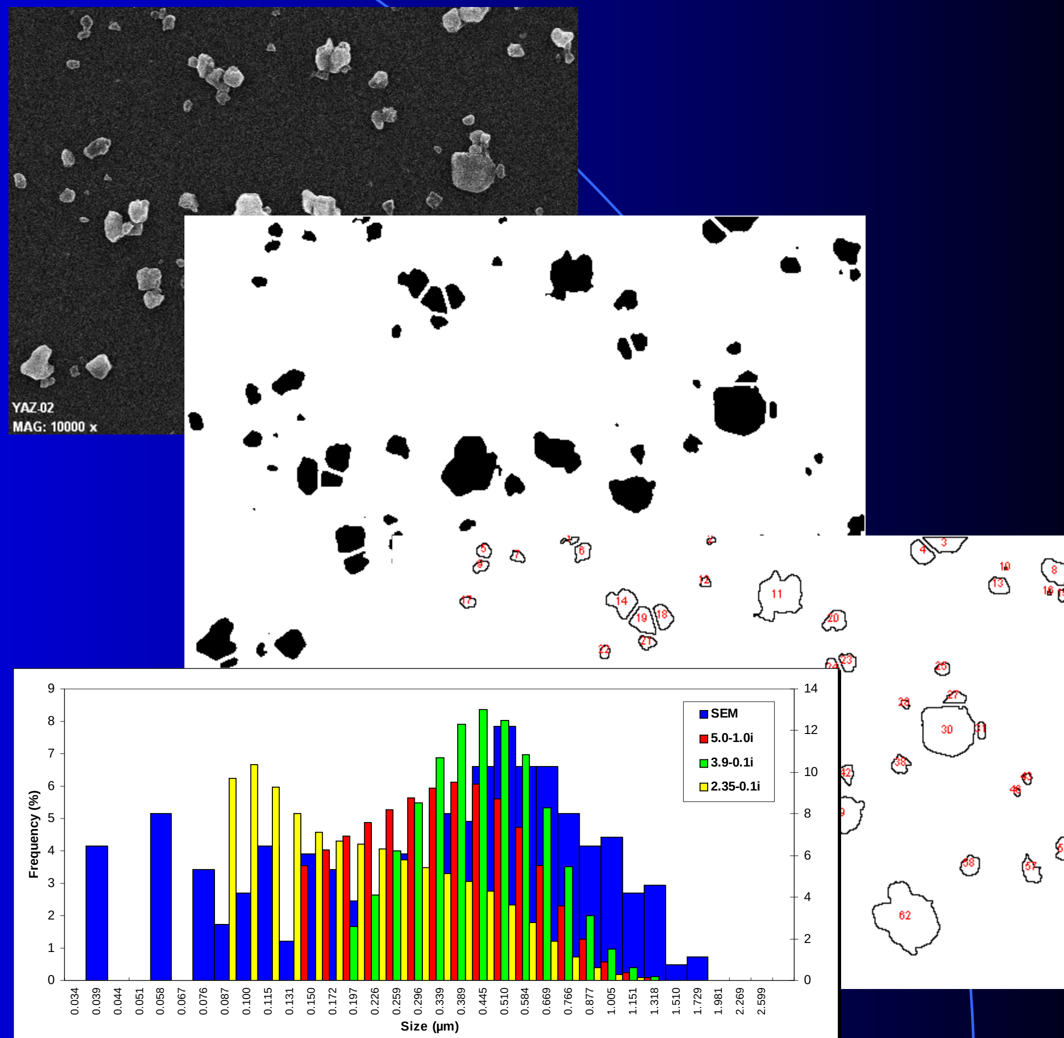


Software Based Approach

- Step 1: Make a representative measurement with best guess at R.I. (i.e. Mixture rule)
- Step 2: Vary imaginary component to minimize χ^2
- Step 3: Vary real component to minimize χ^2
- Step 4: Verify via image analysis

Image Analysis

- Deposit powder
- Collect images
- Process
  - ImageJ 1.38x Software (NIH)
- Data analysis

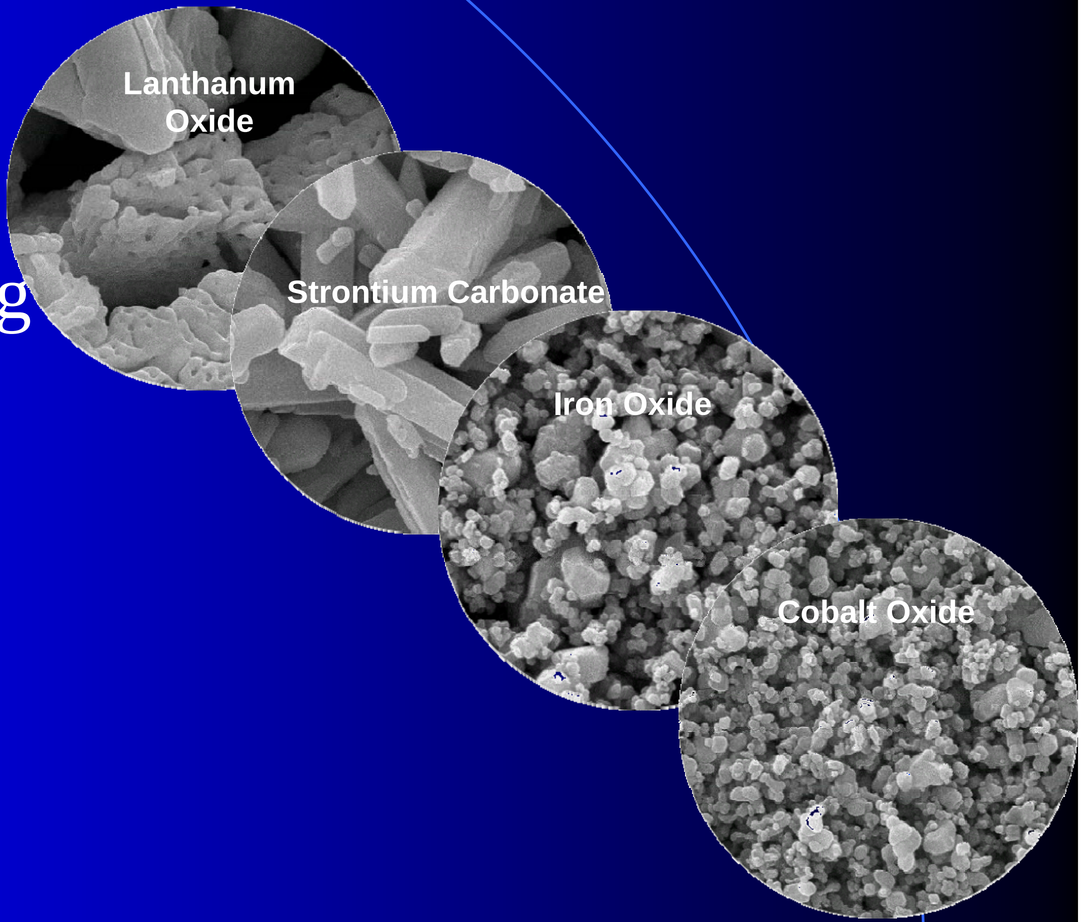


Examples

- Fuel Cell Cathode Mixture
- Dielectric Formulation

Fuel Cell Cathode

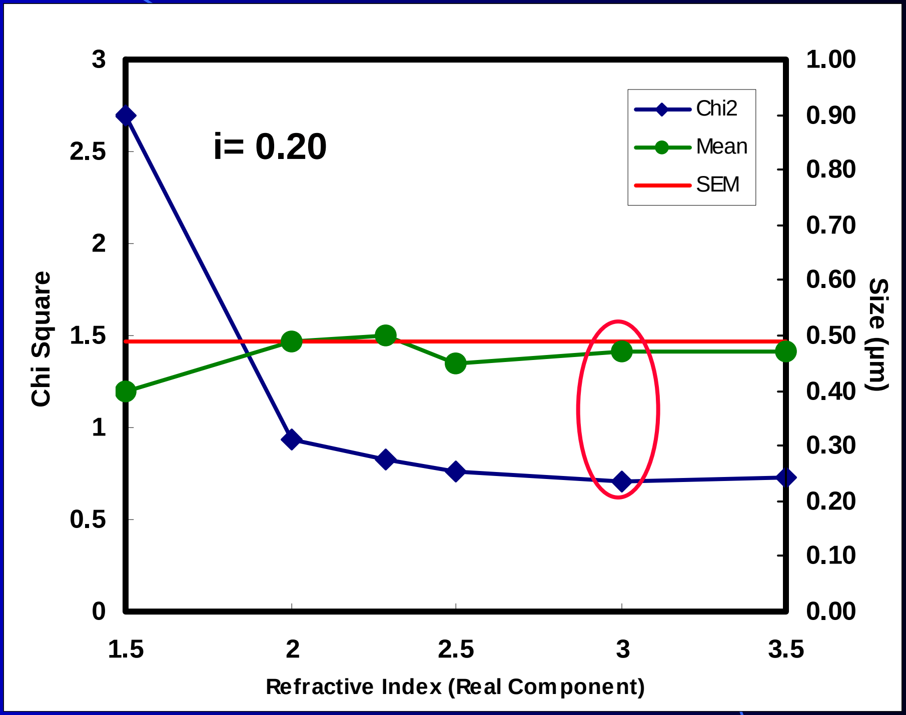
- Unreacted mixture of raw materials
  - $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$
    - La_2O_3, n = 2.51
    - $SrCO_3$, n = 1.61
    - CoO, n = 1.84
    - Fe_2O_3, n = 2.90
  - Surface Area ~ 5 m^2/g



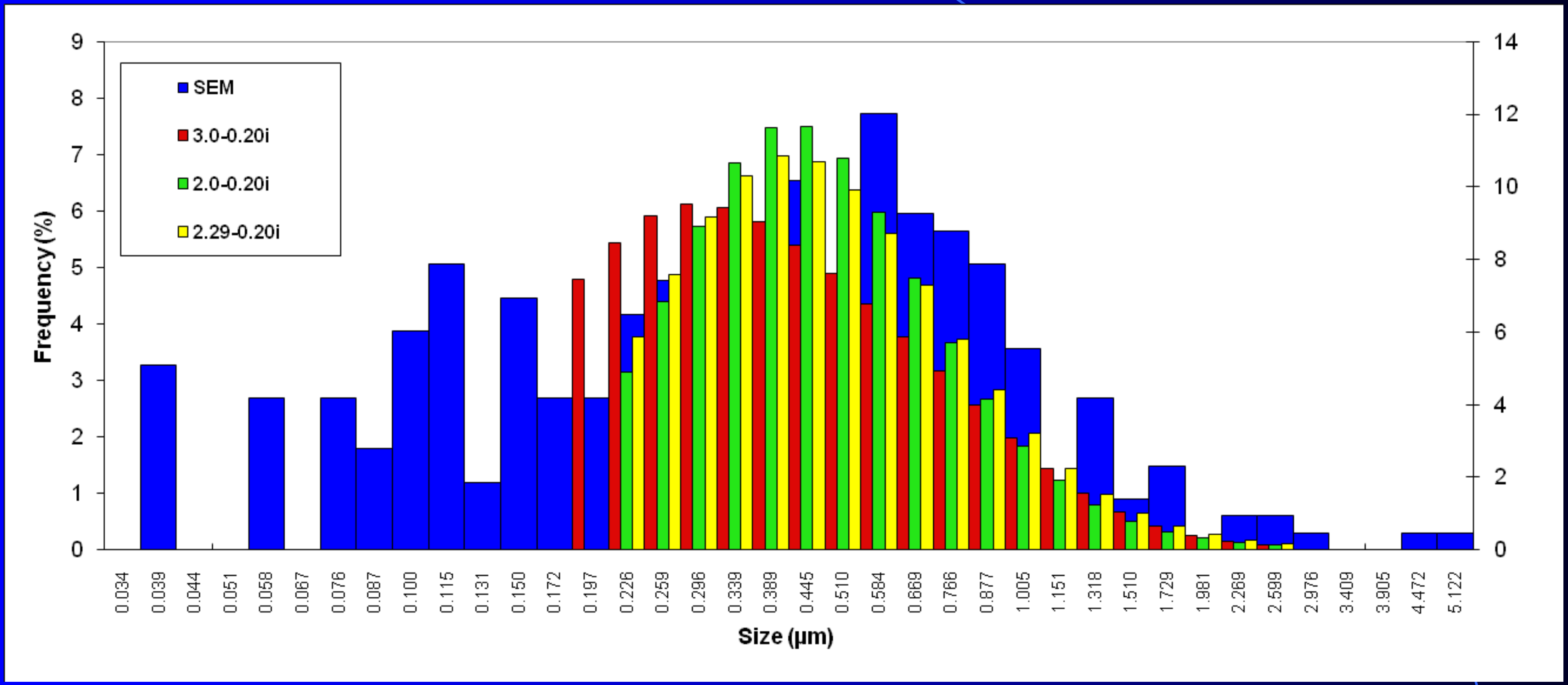
- Mixture Rule
  - $n_{mixture} = 2.29$

Fuel Cell Cathode (cont'd)

1. Make Representative Measurement
2. Vary Imaginary component
    1. 0.0i to 1.0i
    2. Take i at min χ^2
3. Vary real component
4. Verify via SEM
5. Minχ^2 at $n_{mixture}$ = 3.0-0.20i
6. Better match at $n_{mixture}$ = 2.0-0.20i



Fuel Cell Cathode (cont'd)



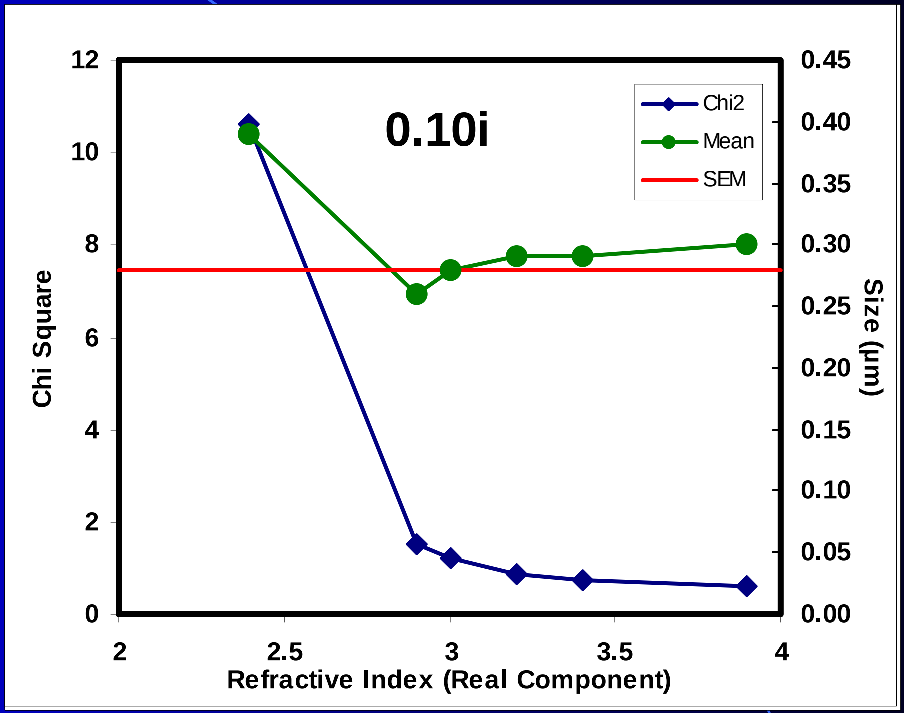
Index	*Mean*	*Median*
SEM	0.49	0.36
3.0-0.20i	0.47	0.37
2.0-0.20i	0.49	0.42
2.29-0.20i	0.50	0.42

Dielectric Formulation

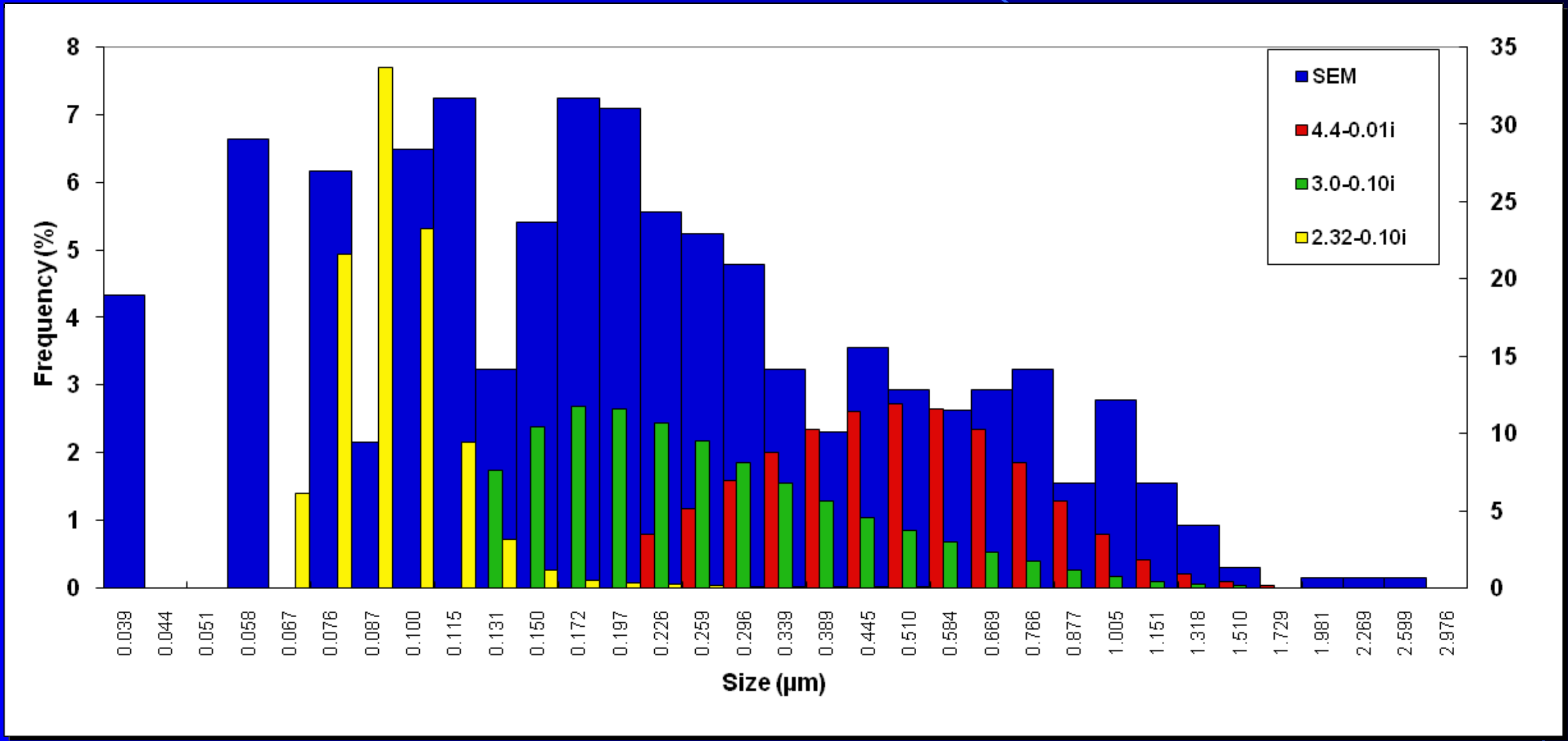
- Dielectric formulation
  - $BaTiO_3$, n = 2.39
  - Dopant mixture, n $\simeq$ 1.5
  - Surface Area ~ 5 m^2/g
- Mixture Rule
  - $n_{mixture} = 2.32$

Dielectric Formulation (cont'd)

1. Make Representative Measurement
2. Vary Imaginary component
   1. 0.0i to 0.10i
   2. Take i at min χ^2
3. Vary real component using 0.01i
4. Verify via SEM
5. No match – adjust Index
6. New imaginary – 0.10, vary Real component
7. $n_{mixture} = 3.0\text{-}0.1i$



Dielectric Formulation (cont'd)



Index	*Mean*	*Median*
SEM	0.28	0.18
4.4-0.01i	0.51	0.47
3.0-0.10i	0.28	0.22
2.32-0.10i	0.09	0.08

Summary

- Knowledge of a R.I. that provides a correct particle size is critical
- χ^2 is a good guide to find "correct" complex refractive index for a mixture
- Mixture rule calculation gives good starting point
- Must be realistic
- Still no substitute for actually looking at particles

Additional Reading

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2) Algorithm Iterations, TN149, Horiba Instruments Technical Note
3) Guide to Selecting Refractive Index, TN118, Horiba Instruments Technical Note
4) NIST/SEMATECH e-Handbook of Statistical Methods, http://www.itl.nist.gov/div898/handbook/, November, 2007.
5) http://www.webmineral.com/help/Gladstone-Dale.shtml
6) Larsen, E.S., Berman, H., The Microscopic Determination of the Non-Opaque Minerals, Second Edition, United States Department of the Interior, Geological Survey Bulletin 848, 1934, US Government Printing Office, Washington, DC.
7) Mandarino, J. A., The Gladstone-Dale Relationship: Part III: Some General Applications, Dept. Mineral. Geol., Royal Ontario Mus., Toronto, ON, Can. Canadian Mineralogist, (1979), 17[1], 71-6

THANKS!

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Expertise in ceramic formulation and processing, new product development, and characterization.