Elemental and Structural Analysis Techniques for Raw Materials Used to Manufacture Solid Oxide Fuel Cells

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Overview & Discussion

Introduction

Cerium Laboratories, LLC is a world class materials analysis laboratory serving alternative energy companies worldwide. We have successfully developed and used a variety of analytical techniques to characterize the chemical composition of PEM fuel cell electrolytes, electrodes, catalysts and product water and to identify leachable contaminants from associated materials of construction. Cerium recently extended its analytical offerings to include elemental and structural analysis of raw materials used to manufacture SOFC fuel cells. The purpose of these measurements is to determine the stoichiometry and purity of typical ceramic components along with their crystalline structure. This information is critical in selecting raw materials to optimize manufacturability and to correlate fuel cell construction with performance and reliability.

Elemental Analysis

Qualitative identification of the elemental composition of SOFC raw materials is accomplished using wavelength dispersive X-ray fluorescence spectroscopy. Results from this analysis are used to identify which elements require further quantitative measurements. Cerium has developed sample preparation techniques that enable complete dissolution of ceramic raw materials. Resulting solutions are analyzed by spectrochemical techniques which are calibrated with NIST traceable standards. Concentrations of major elements are used to accurately determine stoichiometry and minor contaminants may be measured at concentrations as low as 0.01 Wt%.

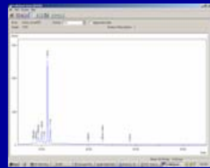
Structural Analysis

The crystalline structure of SOFC raw materials is determined using a combination of X-ray powder diffraction and Raman spectroscopy. The X-ray powder diffraction pattern provides the dimensions of the crystal lattice, while the corresponding Raman spectrum is used to identify multiple crystalline phases.

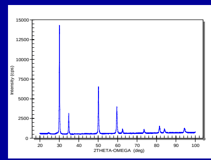
Analytical Techniques

- **WDXRF**
  - Powder over adhesive support
  - 30mm aperture
  - 40 kV, 70 mA, Rh target
  - Vacuum spectrometer
- **ICP-OES**
  - Powder fused with lithium metaborate
  - Fusion products dissolved in dilute nitric acid
  - Solutions analyzed using calibration curves prepared from NIST traceable standards
- **XRD**
  - 2Theta-Omega scans
  - 20-100°
  - Step ~ 0.02°
  - Continuous mode
  - 1.0 sec count time
  - 40 kV, 200 mA, rotating Cu anode
  - Detector slits = front 1 mm, rear 2 mm
  - Graphite monochromator
- **Raman**
  - Renishaw backscatter Raman spectrometer
  - YSZ, NiO-YSZ
    - 488 nm incident excitation
    - 10 mW power at the sample
    - ~ 1 um spot size
    - 10-30 sec scans
  - LSM
    - 514 nm incident excitation
    - 2.5 mW power at the sample
    - ~1 um spot size
    - 360 sec scan

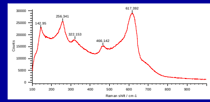
Example 1: Yttria-Stabilized Zirconia



Element	Element wt%	Oxide wt%	Oxide mol%	Spec mol%
Zr	60.71	86.02	91.85	92.00
Y	10.50	13.98	8.15	8.00
K	2.17			
Hf	1.44			
Al	0.13			
Sn	0.06			
Ba	0.04			
O*	Balance			

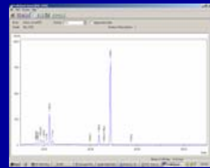


Position	Cubic YSZ		Tetragonal YSZ	
2-Theta (degrees)	2-theta (degrees)	Crystal Plane	2-theta (degrees)	Crystal Plane
30.08	30.11	<111>	30.17	<101>
34.87	34.80	<200>	34.69	<002>
50.14	50.18	<220>	50.19	<112>
59.60	59.65	<311>	59.41	<103>
62.47	62.59	<222>	62.73	<202>
73.59	73.73	<400>	73.20	<004>
81.50	81.66	<331>	81.66	<213>
84.06	84.28	<420>	84.60	<222>
94.39	94.59	<422>		

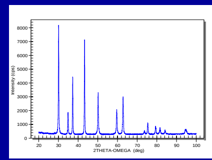


The Raman peaks at 143, 256, 322, and 466 cm^{-1} and the up shift of the cubic peak to 617 cm^{-1}, indicate that the tetragonal phase is present in the YSZ sample.

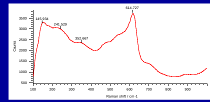
Example 2: Nickel Oxide + Yttria-Stabilized Zirconia



Element	Oxide wt%	Oxide mol%	Spec mol%
Ni	67.38		
Y	4.42	7.88	8.00
Zr	28.20	92.12	92.00

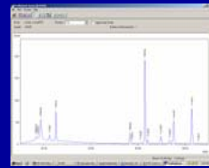


Position	Cubic YSZ		Cubic NiO	
2-Theta (degrees)	2-theta (degrees)	Crystal Plane	2-theta (degrees)	Crystal Plane
30.07	30.11	<111>		
34.86	34.80	<200>		
37.25			37.27	<111>
43.25			43.30	<200>
50.18	50.18	<220>		
59.60	59.65	<311>		
62.86	62.59	<222>	62.90	<220>
73.74	73.73	<400>		
75.36			75.44	<311>
79.37			79.43	<222>
81.56	81.67	<331>		
84.16	84.28	<420>		
94.90	94.59	<422>		

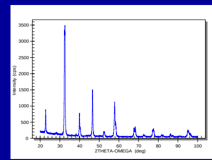


The tetragonal phase peaks of YSZ are very weak in the NiO stabilized YSZ material indicating that the material is mostly cubic.

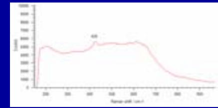
Example 3: Lanthanum Strontium Manganite



Element	Element wt%	Measured Stoichiometry	Specified Stoichiometry
La	46.72	0.79	0.76
Mn	23.43	1.00	1.00
Sr	7.30	0.19	0.19
As	1.20		
Zr	0.68		
Fe	0.14		
Co	0.03		
Ca	0.01		
O*	Balance	3.00	3.00



Position	Rhomohedral LSM		Monoclinic LSM	
2-Theta (degrees)	2-theta (degrees)	Crystal Plane	2-theta (degrees)	Crystal Plane
22.75	22.85	<012>		
32.55	32.69	<104>	32.63	<-200>
38.24	38.33	<113>	38.21	<121>
39.98	40.01	<202>	39.92	<022>
46.60	46.68	<024>	46.59	<220>
52.37	52.38	<122>	52.27	<130>
57.82	57.77	<300>	57.83	<132>
67.77	67.80	<220>	67.65	<040>
68.36	68.51	<208>	68.37	<-400>
72.70	72.93	<306>	72.77	<330>
77.66	77.83	<128>	77.66	<332>
81.80	81.73	<042>		
86.17	86.34	<404>		
87.35	87.66	<0012>		
95.00				



The Raman peak at 425 cm^{-1} corresponds to the rhombohedral phase of LSM.