18th Annual Solid Oxide Fuel Cell (SOFC) Project Review Meeting; June 12-14, 2016

LSCF-CZ Cathodes for Improved SOFC Electrical Performance

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Conclusions and Acknowledgements

- Synthesized and characterized ceria-zirconia (CZ) mixtures with different molar compositions.
- Prepared LSCF-CZ cathode inks with different weight ratios.
- Quantified the electrical performance of button cells with LSCF-CZ cathodes.
- Determined the long–term voltage stability of LSCF-CZ cathodes.
- It was found that:
  - The doped ceria layer can be avoided provided low-temperature firing of the cathode inks.
  - The cell voltage appears to remain stable over relatively long-term testing.
  - The cell power density is not up to par as of yet.
  - The cathode properties need further refinements to achieve higher power densities.

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- Many thanks to Project Manager Steven Markovich and the NETL SECA program team.

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Presentation outline

- Project objectives
- Background
- Technical approach
- CZ synthesis and characterization
- Cathodes inks and pull test
- Button cell testing
- Cell post-mortem characterization
- Path forward
- Conclusion

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Project objectives

- Synthesize and characterize ceria-zirconia (CZ) mixtures with different molar compositions.
- Prepare LSCF-CZ cathode inks with different weight ratios.
- Quantify electrical performance of button cells with LSCF-CZ cathodes.
- Determine long–term voltage stability of LSCF-CZ cathodes.

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Background

- Solid Oxide Fuel Cells use cathodes that must have very specific properties.
  - Cathodes need to have high electrical conductivity and excellent catalytic activity for reducing oxygen.
  - For intermediate and low temperature SOFCs, lanthanum strontium cobalt ferrite (LSCF) cathodes are common.
  - A doped ceria barrier layer needs to be used to prevent unwanted chemical reactions at the electrolyte interface.
- There is evidence that a LSCF-CZ mixture **does not produce** the unwanted $SrZrO_3$ compounds at the electrolyte interface after sintering at 850^{o}C even without the ceria barrier layer.
  - The indication is that this mixture stabilizes the Sr^{2+} cations in LSCF and suppresses the mobility of strontium, and therefore prevents the reaction between LSCF and YSZ.
  - These studies are limited to one composition, one button cell test, and the mechanism of preventing Sr segregation in not fully explained.

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Technical approach

- Synthesize and characterize different molar compositions of CZ powders:
  - XRD, EDX, HR-TEM, and XPS.
- Prepare cathodes inks made of LSCF and CZ with different weight ratios.
- Screen print inks on commercially available anode supported bi-layers.
  - Scotch tape pull test.
- Perform button cell testing including a performance baseline.
  - V-time, VJ, and IS.
- Prepare button cell for post-mortem analysis.
  - SEM-EDX, XPS, and HR-TEM.
- Determine mechanisms of $SrZrO_3$ formation and prevention based upon results from post-mortem analysis.

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CZ synthesis and characterization

- Synthesized the following molar compositions:

Solid State Reaction (SSR)	Nitrate Synthesis (NIT)
$Ce_{0.9}Zr_{0.1}O_2$	$Ce_{0.9}Zr_{0.1}O_2$
$Ce_{0.8}Zr_{0.2}O_2$	$Ce_{0.8}Zr_{0.2}O_2$
$Ce_{0.7}Zr_{0.3}O_2$	$Ce_{0.7}Zr_{0.3}O_2$
$Ce_{0.6}Zr_{0.4}O_2$	$Ce_{0.6}Zr_{0.4}O_2$
$Ce_{0.5}Zr_{0.5}O_2$	$Ce_{0.5}Zr_{0.5}O_2$

- SSR route:
  - Zirconium and cerium oxide powders mixed with the appropriate molar ratio, milled for 1 hour in a zirconia vial, fired at 1600^{o}C for 1 hour, and then milled for 1 hour.
  - Used for comparison and training purposes.
- NIT route:
  - Nitrates of $Ce(NO_3)_3 \bullet 6H_2O$ and $ZrO(NO_3)_2 \bullet 5H_2O$ were used as precursors.
  - Hydrogen peroxide solution (30 wt%), ammonia water (25 wt%), and de-ionized water used as precipitator.
  - Precipitate formed at around 50^{o}C with stirring during the precipitation for about an hour.
  - Precipitate dried overnight, decomposed at 300^{o}C for 1 hour, and then followed by calcinations at 700^{o}C for 3 hours.
  - Resulting powders were milled for 1 hour.

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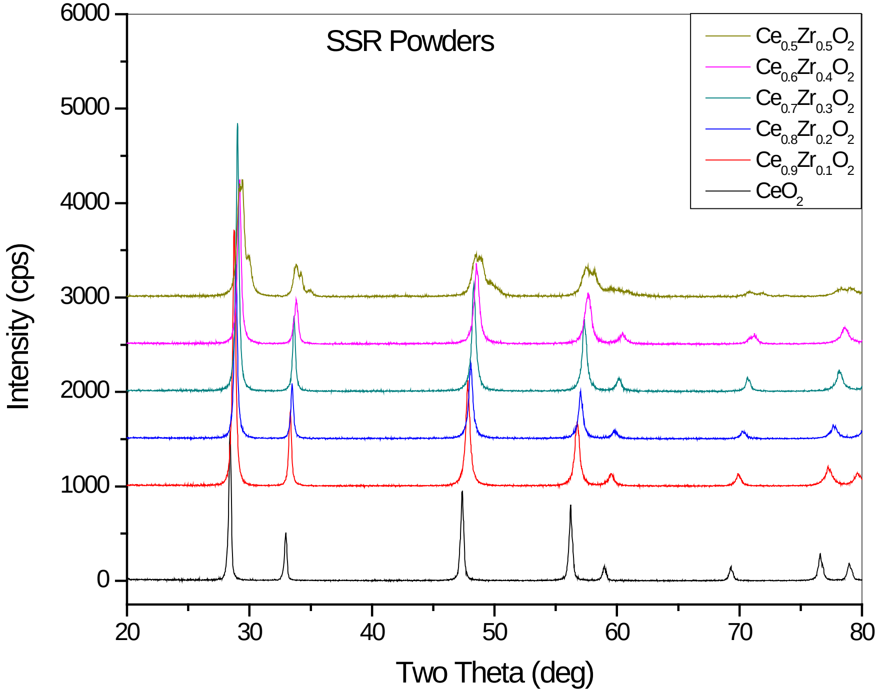
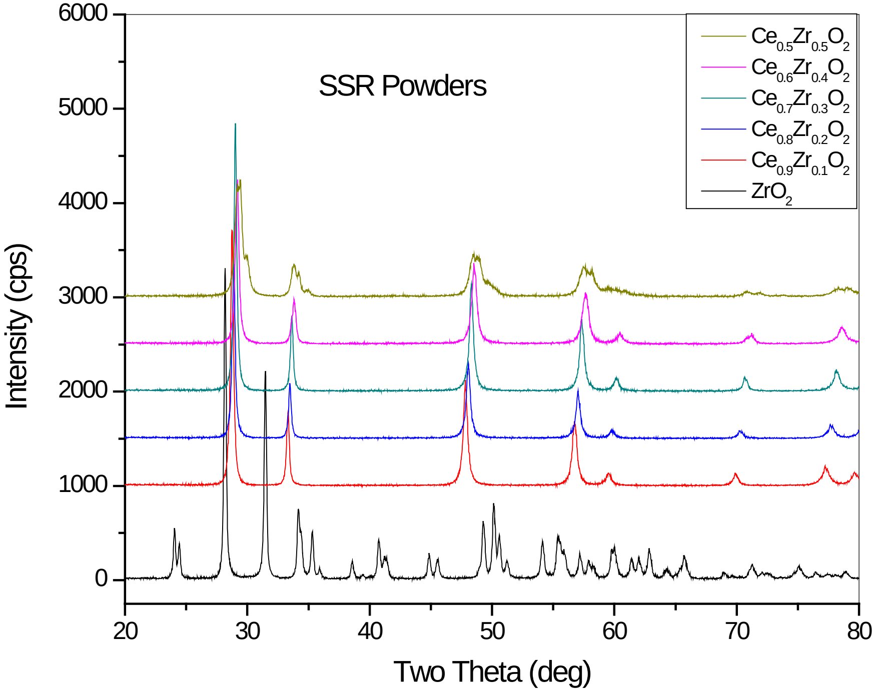
XRD characterization (SSR)

- Incorporation of Zr into the CeO_2 crystal lattice causes a slight peak shift from the pure cubic structures, indicating a change in the lattice parameters.
- This shift occurs at all Zr contents; however, it is more pronounced at higher concentration of Zr and especially on the high 2-theta range.
- The last curve (top) shows that the highest content of Zr ($Ce_{0.5}Zr_{0.5}O_2$) produces a more drastic change in the cubic structure.
- Right figure seems to indicate that a secondary phase is starting to appear at this Zr concentration which is mostly likely free ZrO_2 that has not incorporated into the ceria cubic lattice.





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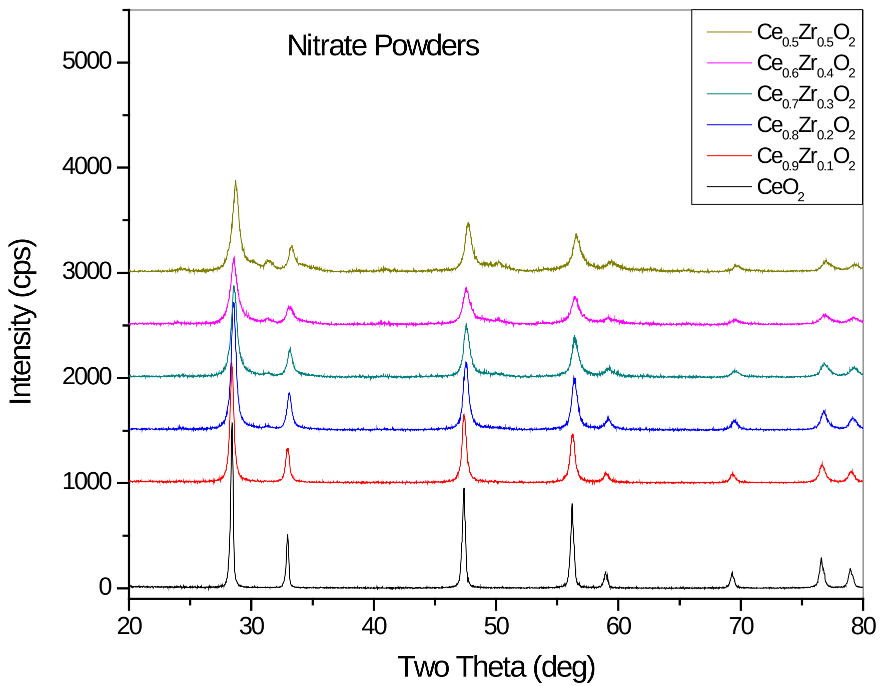
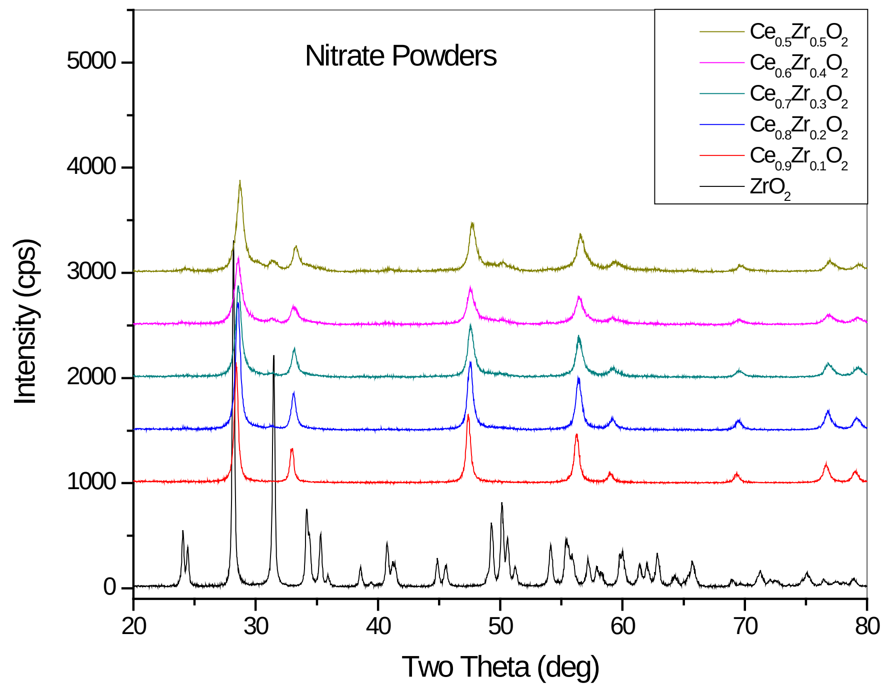
XRD characterization (NIT)

- The NIT powders do not show a peak shift like the one seen in the SSR.
- However, the data indicate that a secondary phase may be occurring at lower Zr contents.
- In the right figure, the free ZrO_2 is clearly observed with a peak at around 33 degrees, and it is visible at a Zr content of 0.3.





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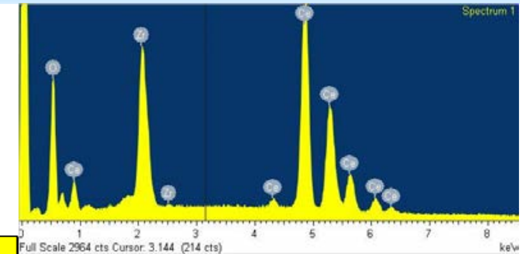
EDX characterization

- EDX results are in line with expectations.
- Zr molar composition off with lower Zr content.



SSR Powders							
$Ce_{0.9}Zr_{0.1}O_2$							
Element	Line	Weight%	Atomic%				
O	**K**	20.05	68.01		**Actual Formula**		
Zr	**L**	4.88	2.90		Ce	Zr	O
Ce	**L**	75.07	29.08		0.87	0.09	2.04
Totals		100.00	99.99				
$Ce_{0.8}Zr_{0.2}O_2$							
Element	Line	Weight%	Atomic%				
O	**K**	20.21	67.55		**Actual Formula**		
Zr	**L**	9.74	5.71		Ce	Zr	O
Ce	**L**	70.05	26.74		0.80	0.17	2.03
Totals		100.00	100.00				
$Ce_{0.7}Zr_{0.3}O_2$							
Element	Line	Weight%	Atomic%				
O	**K**	20.01	66.60		**Actual Formula**		
Zr	**L**	14.68	8.57		Ce	Zr	O
Ce	**L**	65.31	24.83		0.74	0.26	2.00
Totals		100.00	100.00				
$Ce_{0.6}Zr_{0.4}O_2$							
Element	Line	Weight%	Atomic%				
O	**K**	21.70	67.93		**Actual Formula**		
Zr	**L**	21.31	11.70		Ce	Zr	O
Ce	**L**	56.99	20.37		0.61	0.35	2.04
Totals		100.00	100.00				
$Ce_{0.5}Zr_{0.5}O_2$							
Element	Line	Weight%	Atomic%				
O	**K**	22.41	68.06		**Actual Formula**		
Zr	**L**	27.15	14.46		Ce	Zr	O
Ce	**L**	50.44	17.49		0.52	0.43	2.04
Totals		100.00	100.01				

NIT Powders							
$Ce_{0.9}Zr_{0.1}O_2$							
Element	Line	Weight%	Atomic%				
O	**K**	20.17	68.15		**Actual Formula**		
Zr	**L**	5.06	3.00		Ce	Zr	O
Ce	**L**	74.77	28.85		0.87	0.09	2.04
Totals		100.00	100.00				
$Ce_{0.8}Zr_{0.2}O_2$							
Element	Line	Weight%	Atomic%				
O	**K**	21.38	69.08		**Actual Formula**		
Zr	**L**	9.70	5.50		Ce	Zr	O
Ce	**L**	68.92	25.43		0.76	0.17	2.07
Totals		100.00	100.01				
$Ce_{0.7}Zr_{0.3}O_2$							
Element	Line	Weight%	Atomic%				
O	**K**	21.68	68.79		**Actual Formula**		
Zr	**L**	14.64	8.14		Ce	Zr	O
Ce	**L**	63.68	23.07		0.69	0.24	2.06
Totals		100.00	100.00				
$Ce_{0.6}Zr_{0.4}O_2$							
Element	Line	Weight%	Atomic%				
O	**K**	24.08	70.85		**Actual Formula**		
Zr	**L**	20.18	10.42		Ce	Zr	O
Ce	**L**	55.74	18.73		0.56	0.31	2.13
Totals		100.00	100.00				
$Ce_{0.5}Zr_{0.5}O_2$							
Element	Line	Weight%	Atomic%				
O	**K**	23.99	69.84		**Actual Formula**		
Zr	**L**	27.41	14.00		Ce	Zr	O
Ce	**L**	48.61	16.16		0.48	0.42	2.10
Totals		100.01	100.00				

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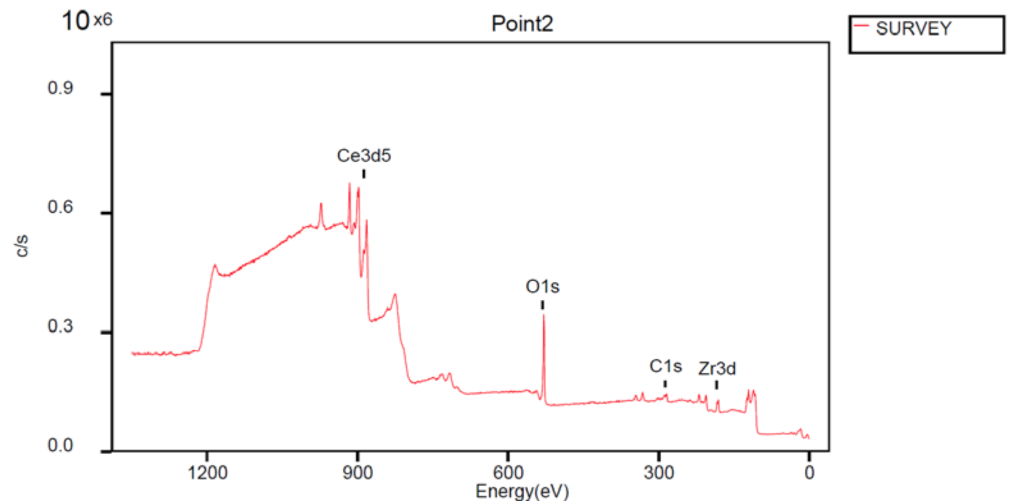
XPS characterization

- XPS results are in line with expectations for SSR samples.
- But not for the NIT samples.
- XPS is more surface sensitive while EDX is more of a bulk technique.
- Only two samples were analyzed.



SSR Powders							
$Ce_{0.8}Zr_{0.2}O_2$							
Element	Line	Weight%	Atomic%				
O	**K**	na	67.82		**Actual Formula**		
Zr	**L**	na	6.12		Ce	Zr	O
Ce	**L**	na	26.06		0.78	0.18	2.03
Totals		0.00	100.00				

NIT Powders							
$Ce_{0.8}Zr_{0.2}O_2$							
Element	Line	Weight%	Atomic%				
O	**K**	na	73.06		**Actual Formula**		
Zr	**L**	na	3.75		Ce	Zr	O
Ce	**L**	na	23.19		0.70	0.11	2.19
Totals		0.00	100.00				

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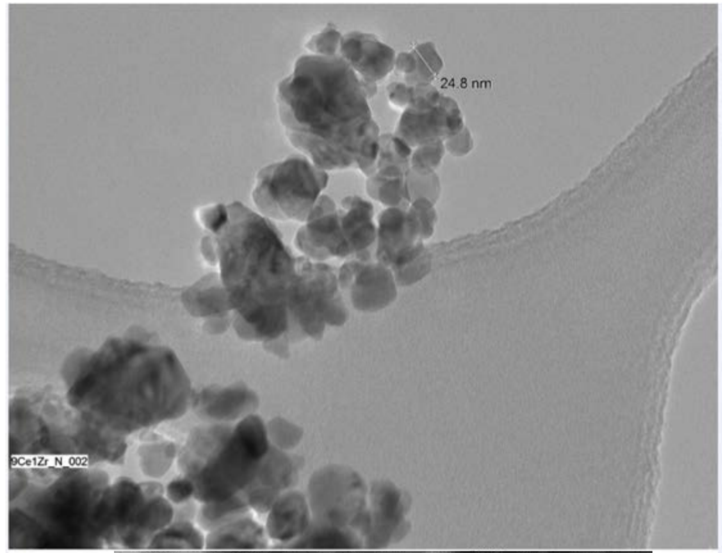
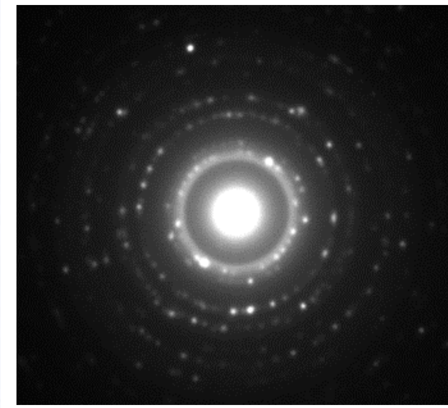
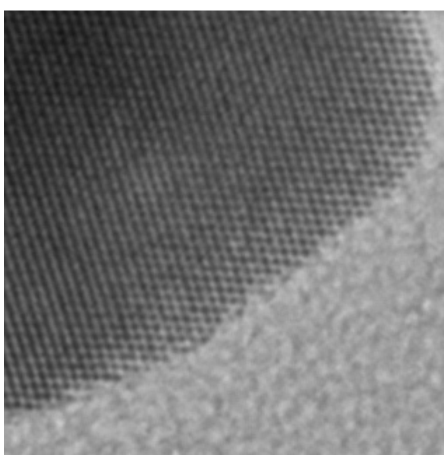
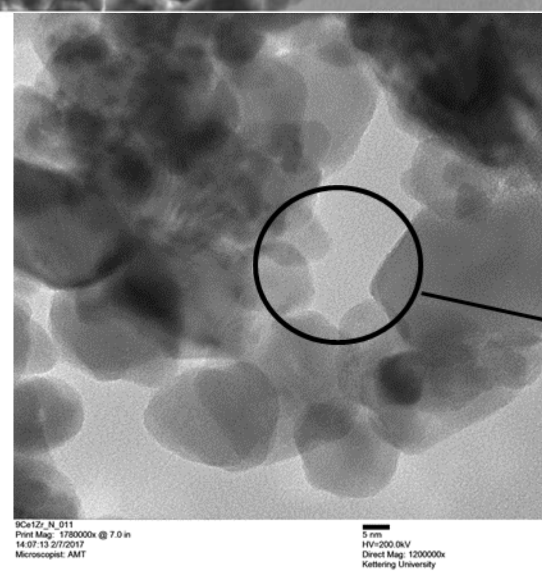
HR-TEM characterization of CZ powder

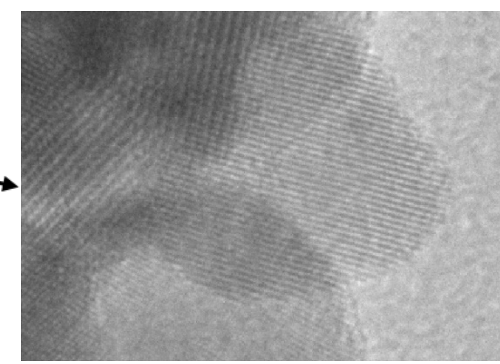
- Bright field image shows the nanosized powder of about 25 nm.
- Electron diffraction confirms cubic structure of CZ mixture.
- Lattice constant estimated to be 5.25 Å (compare to cubic cerium oxide of 5.410 Å).
- Higher magnification images illustrate the lattice.











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CZ molar composition selection

- Given the XRD results, the following two CZ compositions for the initial ink preparation were chosen:

  1. $Ce_{0.9}Zr_{0.1}O_2$
  2. $Ce_{0.8}Zr_{0.2}O_2$

- Basically, no free zirconia should be present to prevent the formation of $SrZrO_3$.

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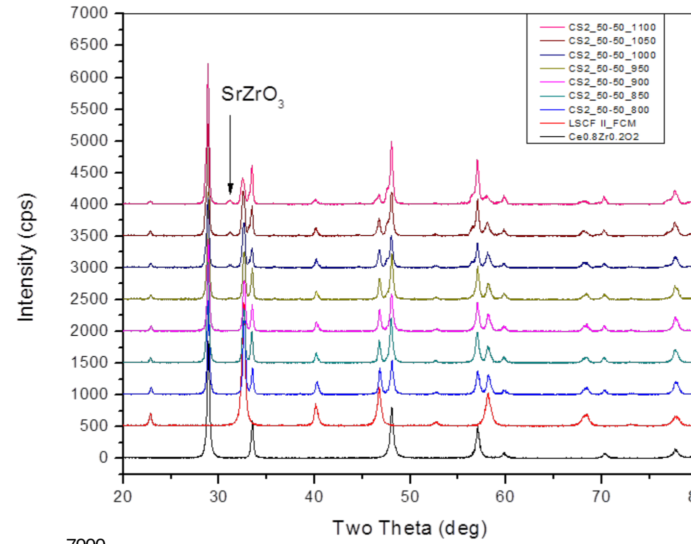
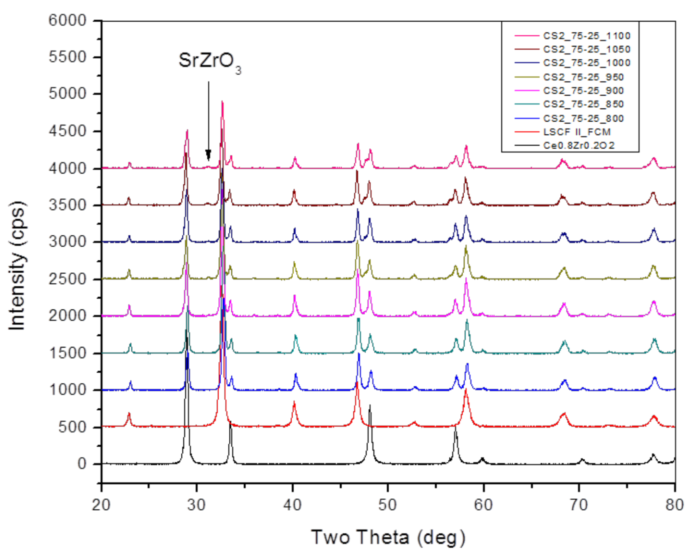
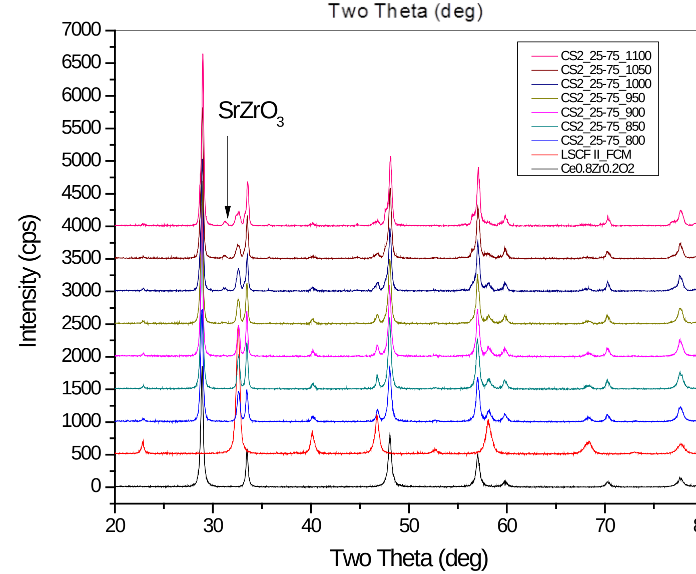
Compatibility study

- Objective of this study is to determine the temperature and weight ratios at which secondary phases may start to appear.
- Results of this study aid in determining the firing temperature of the LSCF-CZ inks for cell testing.
- Given the XRD results, cathodes should be fired below 900°C and preferably at 850°C.







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Cathodes inks

- CZ powders added to LSCF in 5, 10, and 15 wt% and mixed with an ink vehicle obtained from fuelcellmaterial.com (FCM).
- Total powder to ink loading is 60:40 as recommended by FCM for their ink vehicle.
- Six different inks were prepared for a minimum of six button cell tests.

	Mass (g)	
ID	$Ce_{0.9}Zr_{0.1}O_2$	LSCF
9C1Z+LSCF_5	0.500	9.500
9C1Z+LSCF_10	1.000	9.000
9C1Z+LSCF_15	1.500	8.500

	Mass (g)	
ID	$Ce_{0.8}Zr_{0.2}O_2$	LSCF
8C2Z+LSCF_5	0.500	9.500
8C2Z+LSCF_10	1.000	9.000
8C2Z+LSCF_15	1.500	8.500

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Pull test

- Used LSCF paste from FCM; no CZ was used.
- Anode bilayer were also purchased from FCM.
- Pull test (scotch tape) results are shown below.
- Data show that “adhesion strength” is best when fired at 950^{o}C or higher.

Sample ID	Firing Temp (^{o}C)	Firing Time (hrs)	Scotch Tape Test	Residue on Tape
PT1	850	2	Pass	Heavy
PT2	900	2	Fail	Heavy
PT3	950	2	Pass	No
PT4	1000	2	Pass	No
PT5	1050	2	Pass	No
PT6	1100	2	Pass	No
PT7	850	4	Pass	Light
PT8	850	6	Pass	Light

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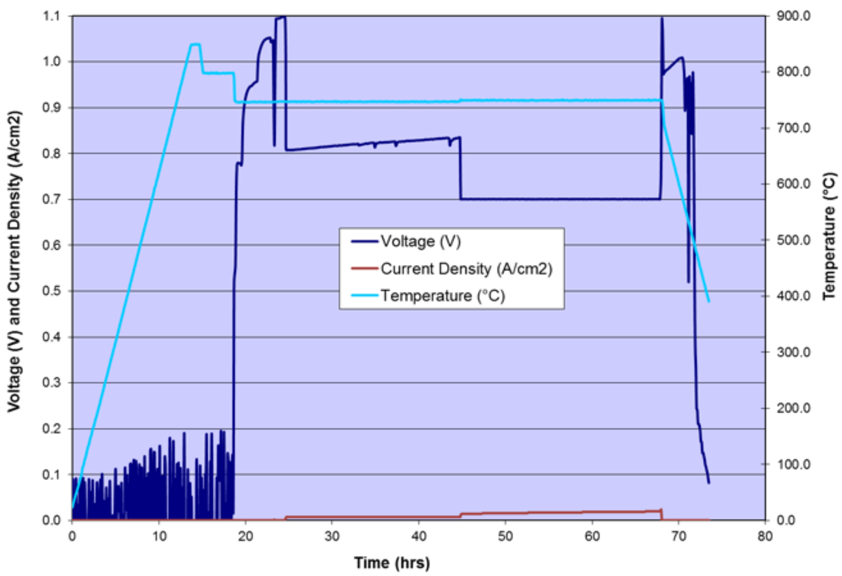
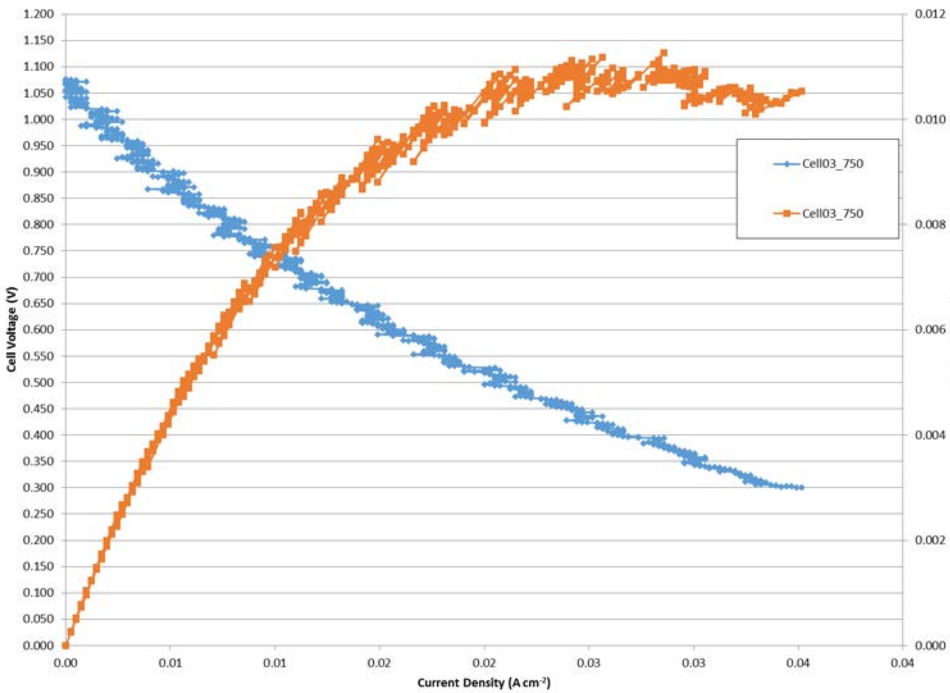
Cell 03

- Delphi bilayer and LSCF paste from FCM.
- Cathode fired at **1100ºC for 1 hour**.
- Virtually zero power is obtained due to $SrZrO_3$ formation at the electrolyte interface.
- Voltage stable; a possible indication that $SrZrO_3$ formation is complete.





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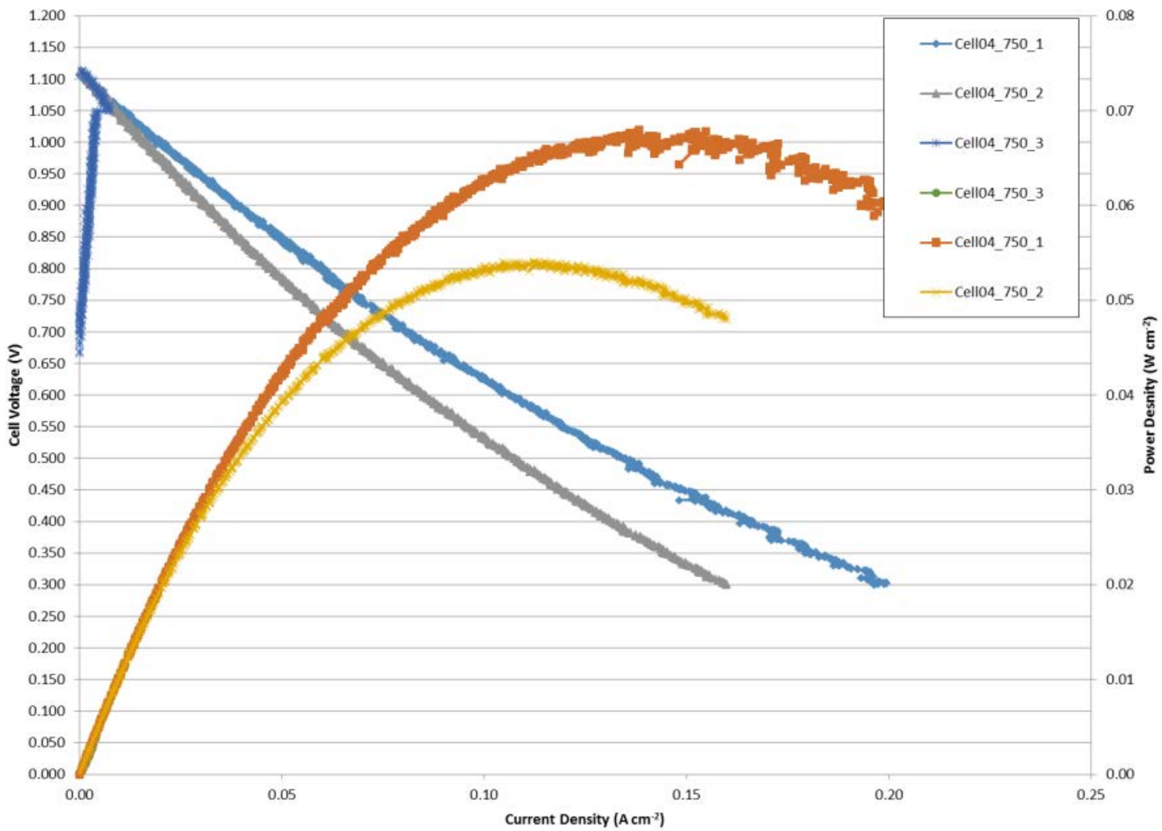
Cell 04

- Delphi bilayer and LSCF paste from FCM.
- Cathode fired at **950°C for 2 hour**.
- A little better than Cell 03 but power decays to nothing.
- Indication is that $SrZrO_3$ formation still ongoing.



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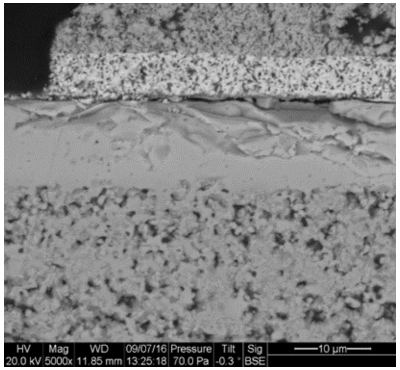
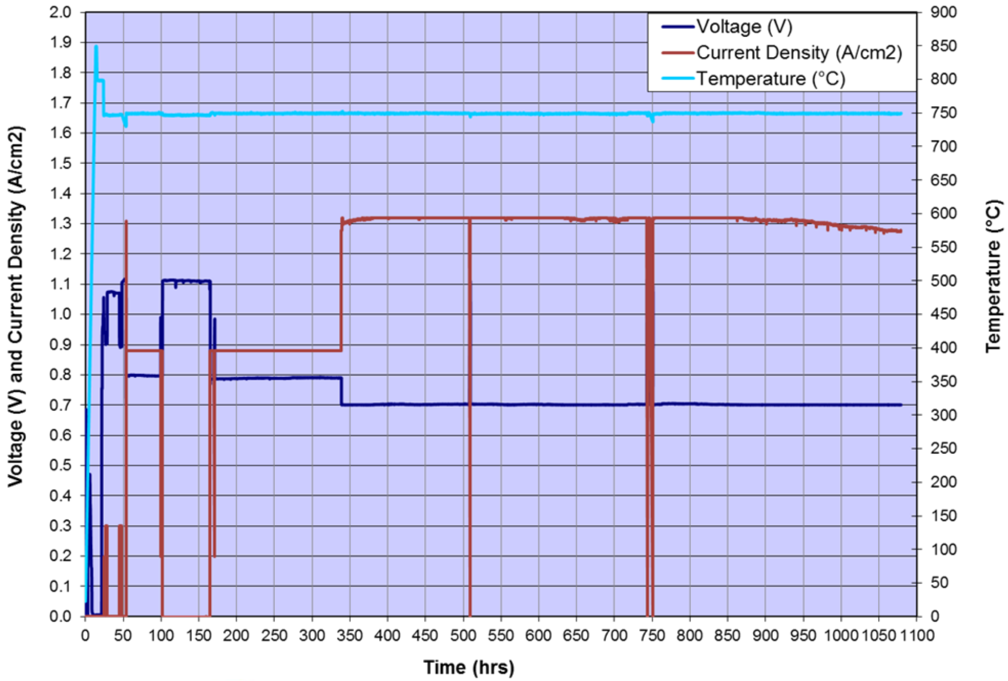
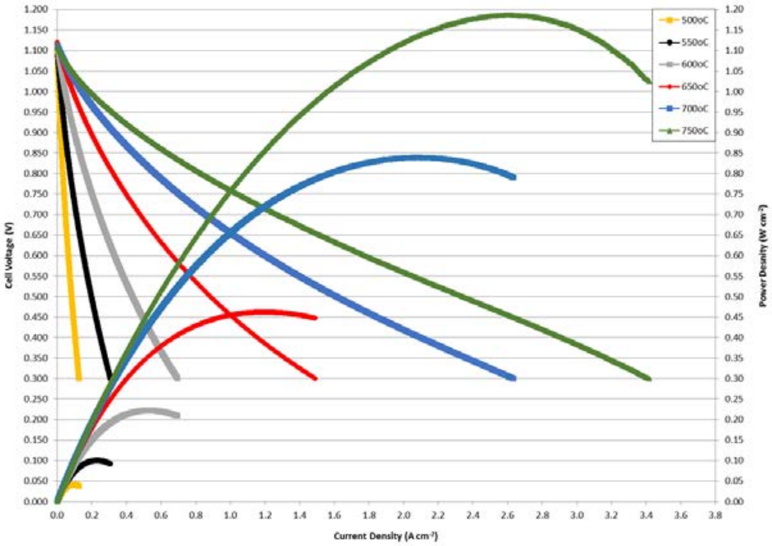
Button cell testing (baseline)

- Cell 02 Delphi baseline long-term test (Ni-YSZ/YSZ/SDC/LSCF).
- LSCF fired around 1100°C.
- Stable performance over 1000 hours.
- Current density decrease after 850 hours likely due to Arbin damage; no change in voltage when current density decreases.
- Cell performance at 750°C is quite good; irrelevant as the temperature reaches 500°C.







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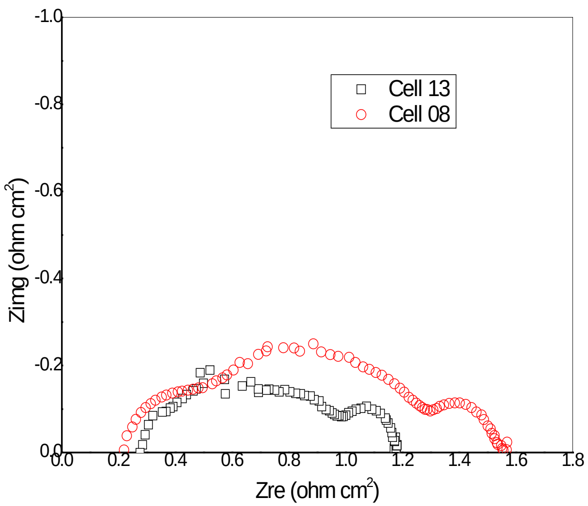
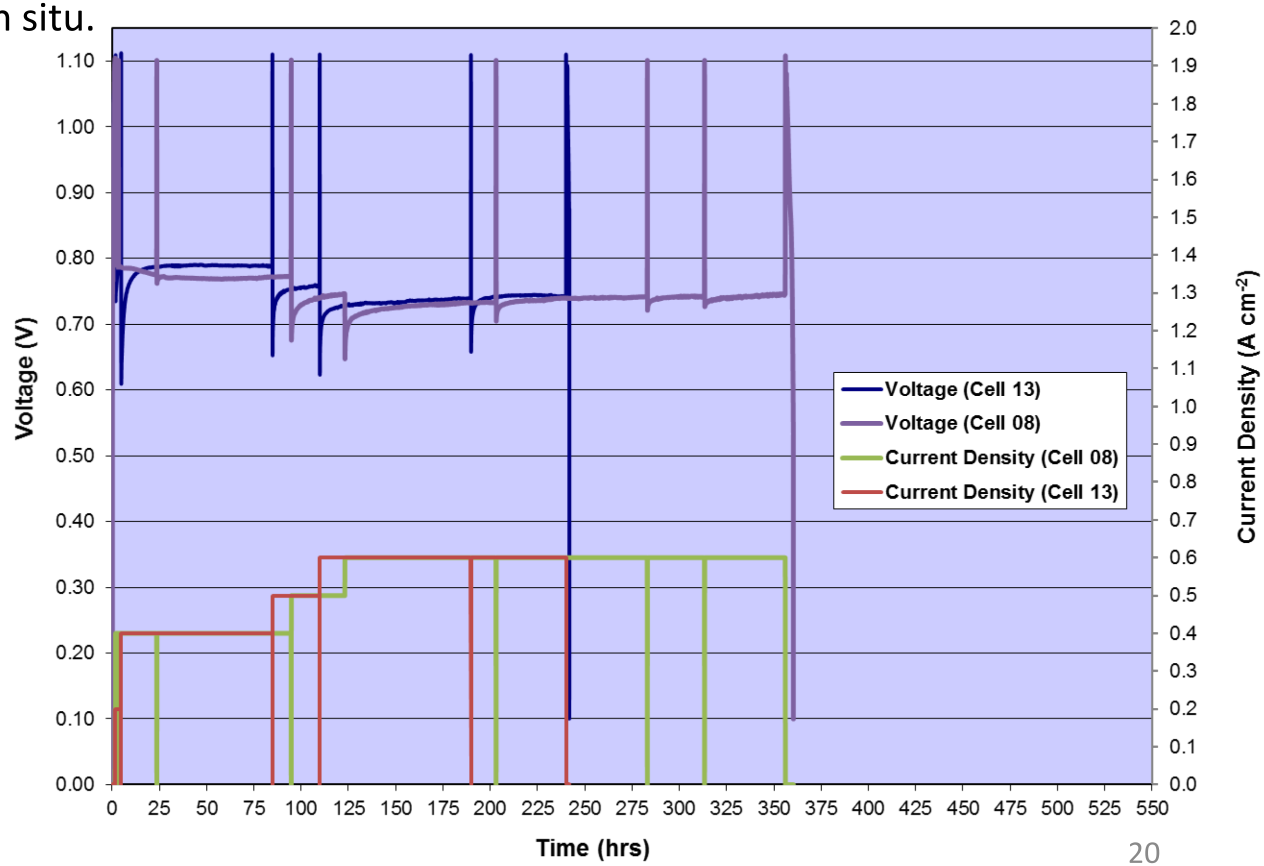
Cell testing w/o barrier layer or CZ

ID	Components	Comments
Cell 08	Ni-YSZ/YSZ/LSCF (FCM ink)	LSCF fired at 850°C/2hrs
Cell 13	Ni-YSZ/YSZ/nano-LSCF (homemade)	LSCF fired at 850°C/2hrs

- No SDC barrier layer used.
- No CZ used in LSCF.
- Fired cathode current collector in situ.
- Stable performance but cathode polarization is too large.
- Need to improve power density.





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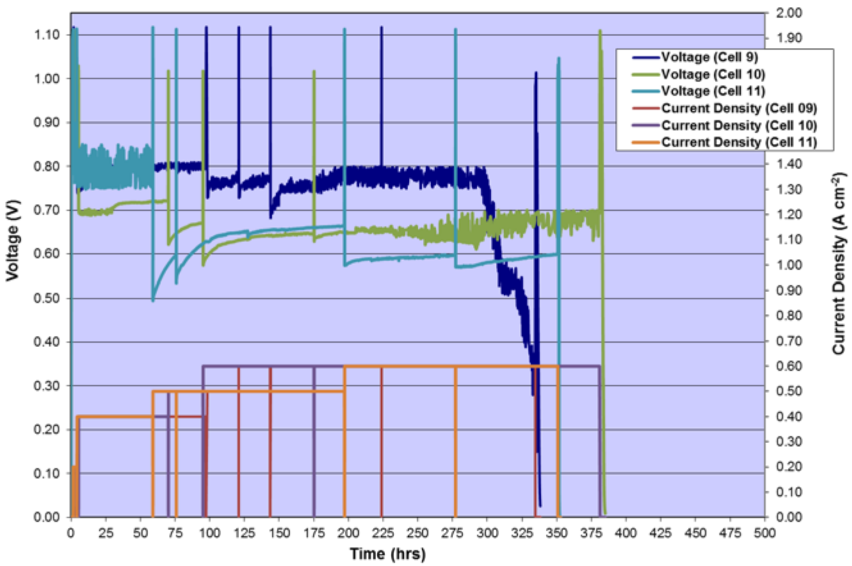
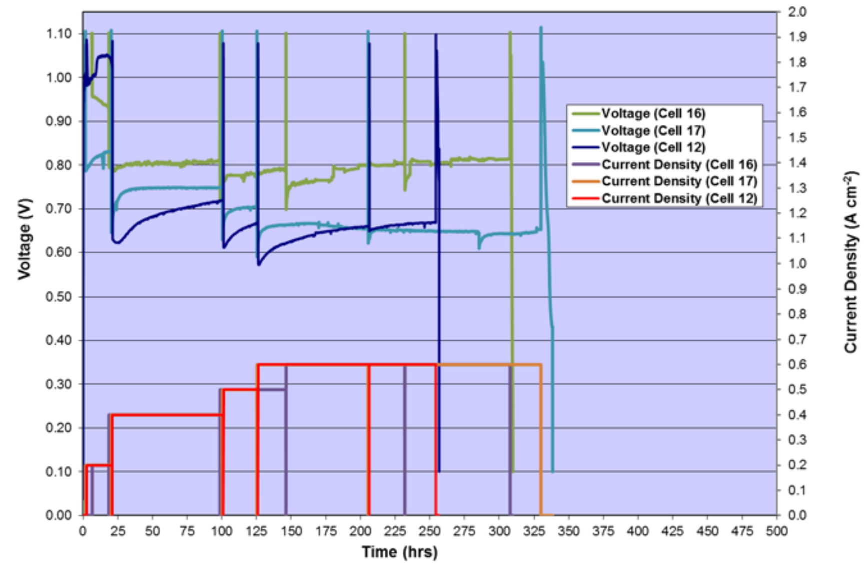
Button cell testing (LSCF-CZ)





- No SDC barrier layer used; LSCF-CZ fired at 850^{o}C/2hrs.
- Fired cathode current collector in situ.
- Stable performance in most cases.
- Higher CZ content, higher voltage.
- Relatively higher performance for $Ce_{0.9}Zr_{0.1}O_2$.
- Higher performance than pure LSCF when using 15% CZ.
- Nonetheless, need to improve power density.
- Need to optimize cathode properties such as porosity, adhesion strength, etc.

ID	Components
Cell 09	Ni-YSZ/YSZ/LSCF+15%$Ce_{0.8}Zr_{0.2}O_2$
Cell 10	Ni-YSZ/YSZ/LSCF+10%$Ce_{0.8}Zr_{0.2}O_2$
Cell 11	Ni-YSZ/YSZ/LSCF+5%$Ce_{0.8}Zr_{0.2}O_2$
Cell 12	Ni-YSZ/YSZ/LSCF+5%$Ce_{0.9}Zr_{0.1}O_2$
Cell 16	Ni-YSZ/YSZ/LSCF+10%$Ce_{0.9}Zr_{0.1}O_2$
Cell 17	Ni-YSZ/YSZ/LSCF+15%$Ce_{0.9}Zr_{0.1}O_2$

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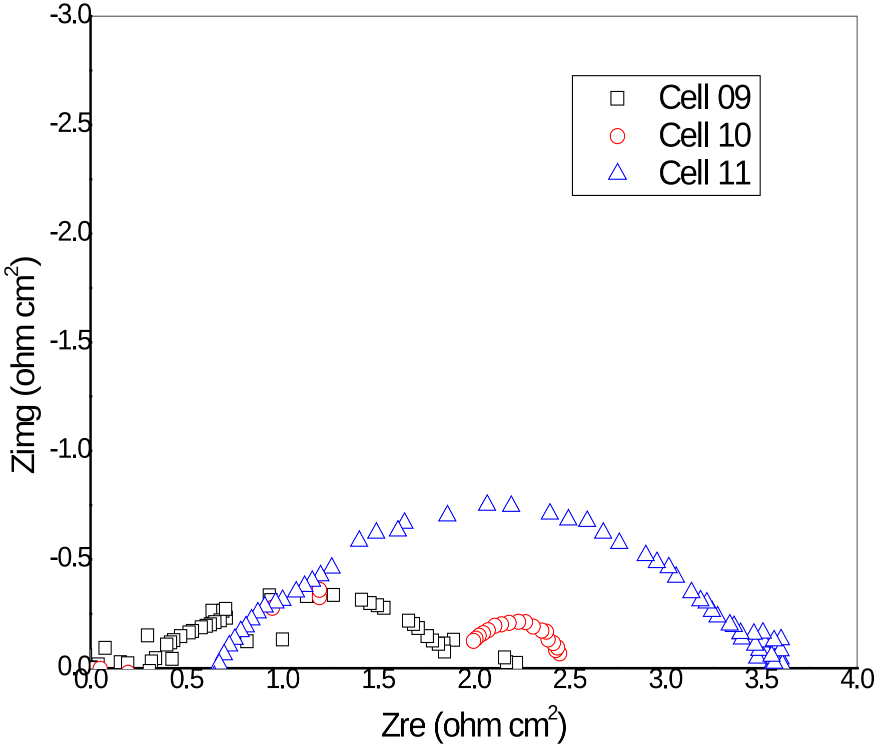
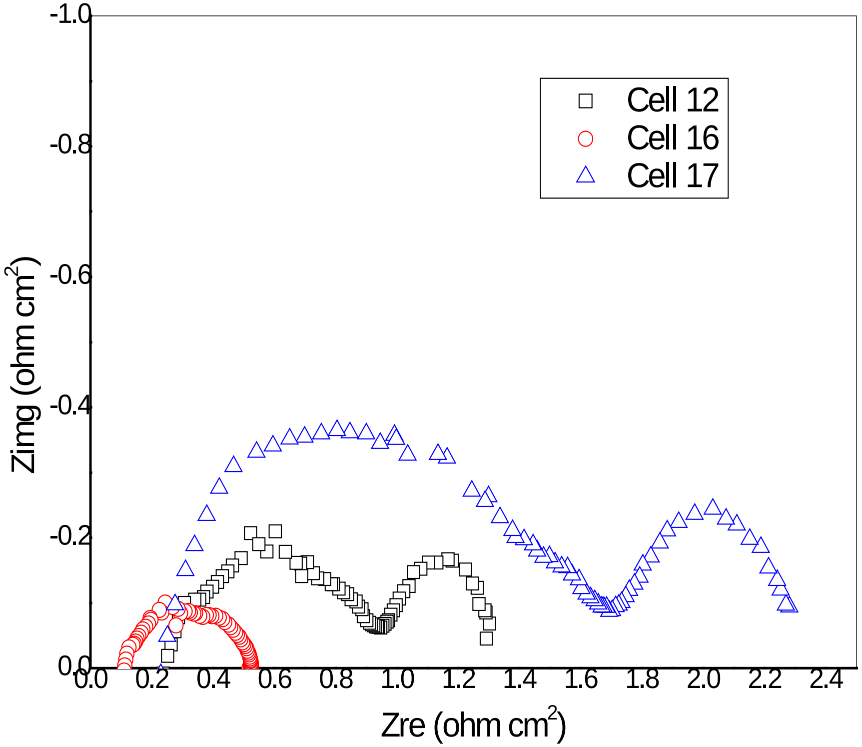
Impedance spectroscopy (LSCF-CZ)

- Cathode polarization is too high!
- Need to optimize cathode properties such as porosity, adhesion strength, etc.





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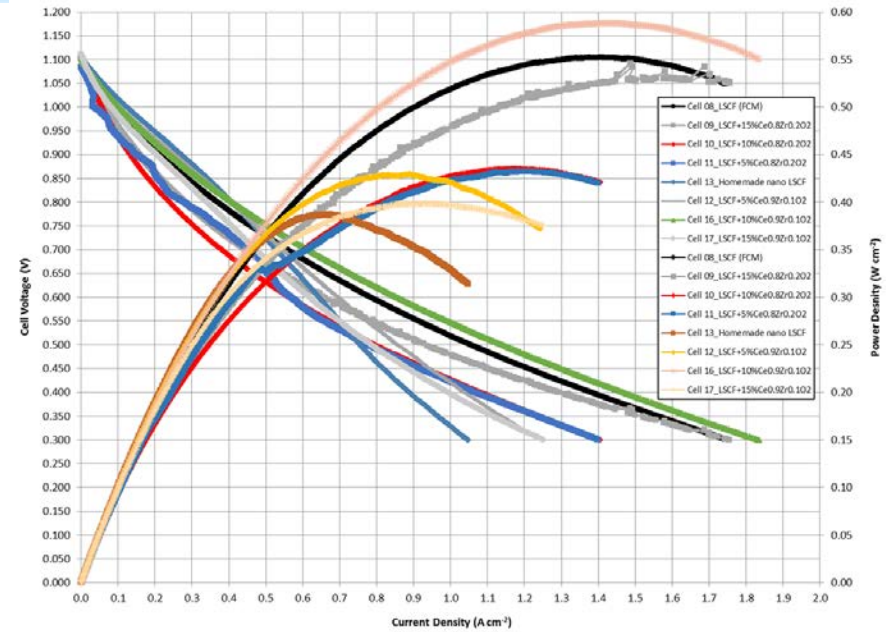
Voltage vs power density (LSCF-CZ)

- Max power density below par when compared to Delphi technology.
- Need to improve reproducibility of cell testing assembly.



ID	Components	P_{max} (W/cm^2)	Tested on	Comments
Cell 02	Ni-YSZ/YSZ/Doped Ce/LSCF	**1.19**	Q1	Delphi Cell
Cell 08	Ni-YSZ/YSZ/LSCF (FCM ink)	0.55	Q2	**Baseline 1**
Cell 09	Ni-YSZ/YSZ/LSCF+15%$Ce_{0.8}Zr_{0.2}O_2$	0.53	Q3	
Cell 10	Ni-YSZ/YSZ/LSCF+10%$Ce_{0.8}Zr_{0.2}O_2$	0.44	Q3	
Cell 11	Ni-YSZ/YSZ/LSCF+5%$Ce_{0.8}Zr_{0.2}O_2$	0.45	Q3	
Cell 12	Ni-YSZ/YSZ/LSCF+5%$Ce_{0.9}Zr_{0.1}O_2$	0.35	Q3	
Cell 13	Ni-YSZ/YSZ/nano-LSCF (homemade)	>0.45*	Q3	**Baseline 2**
Cell 16	Ni-YSZ/YSZ/LSCF+10%$Ce_{0.9}Zr_{0.1}O_2$	**0.59**	Q4	
Cell 17	Ni-YSZ/YSZ/LSCF+15%$Ce_{0.9}Zr_{0.1}O_2$	0.40	Q4	

*Power booster failure; data taken from voltage-time curve.

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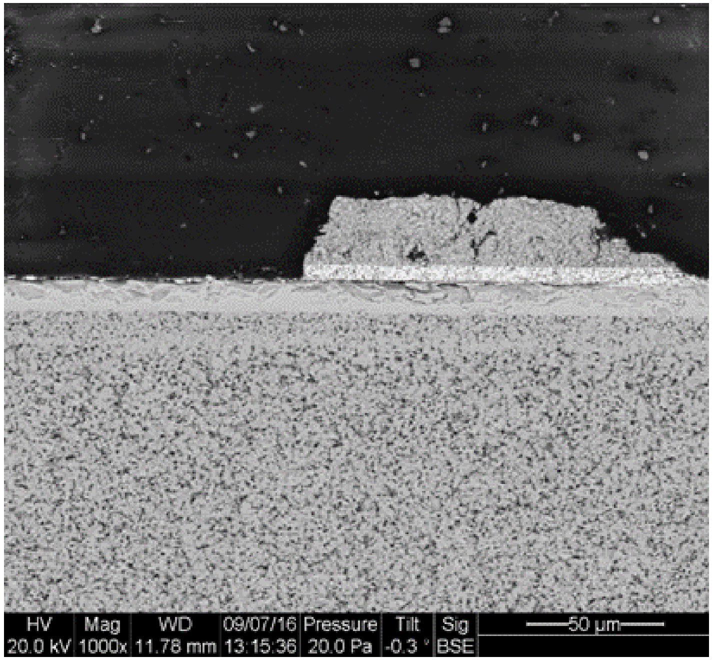
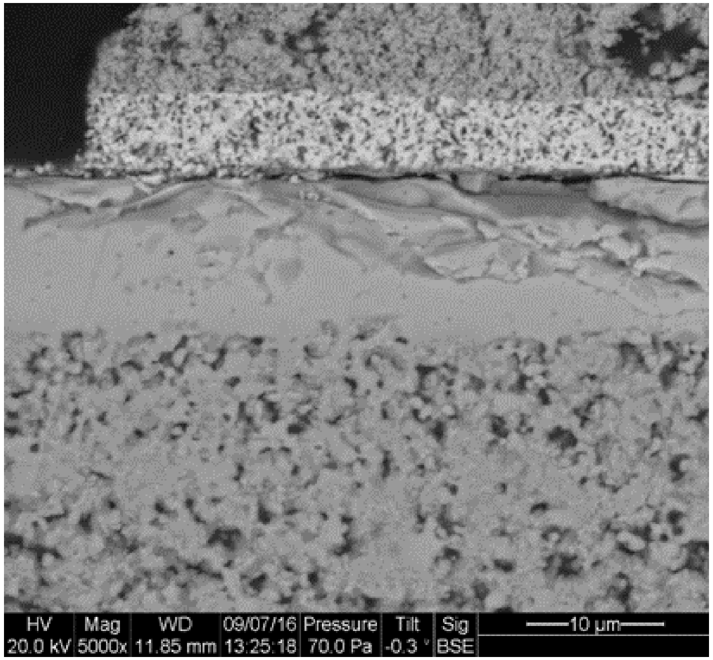
Cell post-mortem characterization (SEM)

- Cross sections of a typical Delphi tested cell:
  - Electrolyte layer about 10 µm.
  - Ceria layer about 4-5 µm.
  - Cathode **porous** layer about 30 µm.
  - Damage occurred during current collector removal and sample preparation.





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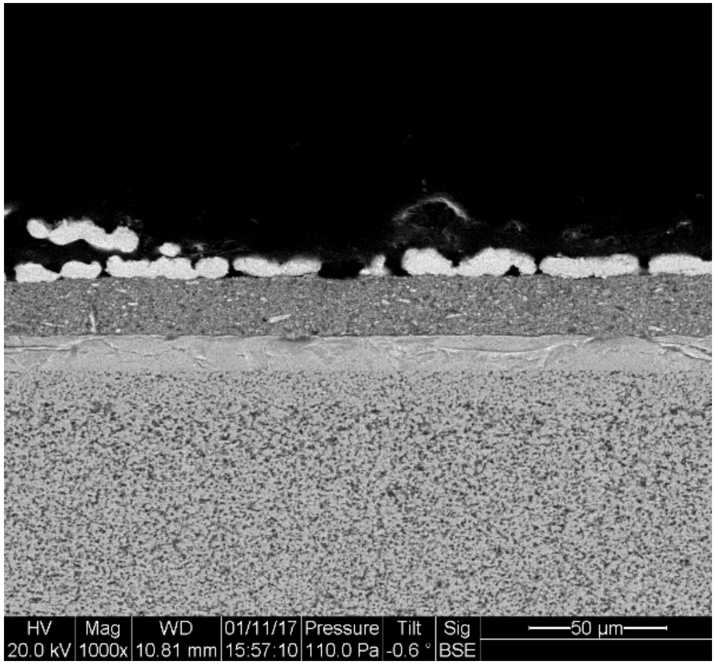
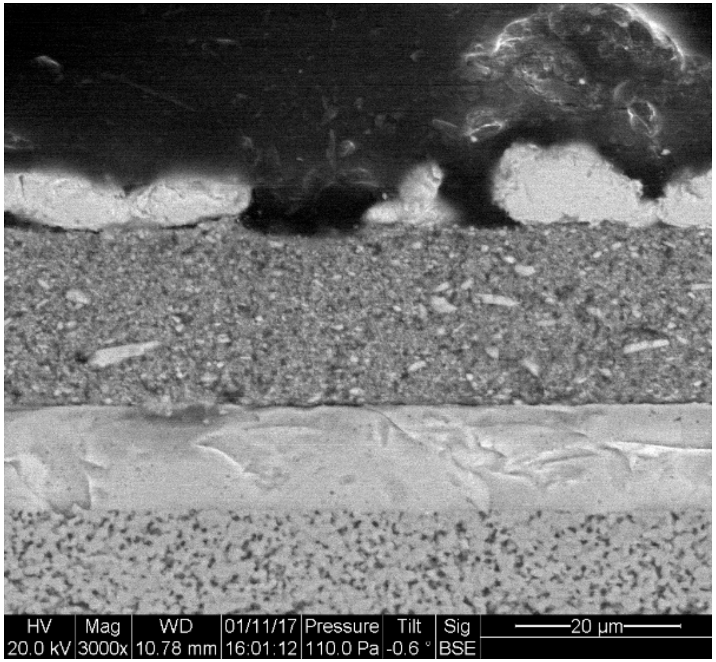
Cell post-mortem characterization (SEM)

- Cross sections of tested Cell 17:
  - Electrolyte layer about 10 μm.
  - No ceria layer!
  - Cathode **non-porous** layer about 30 μm.
  - CZ irregular shape particles clearly visible.





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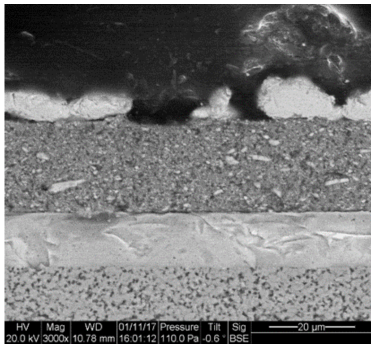
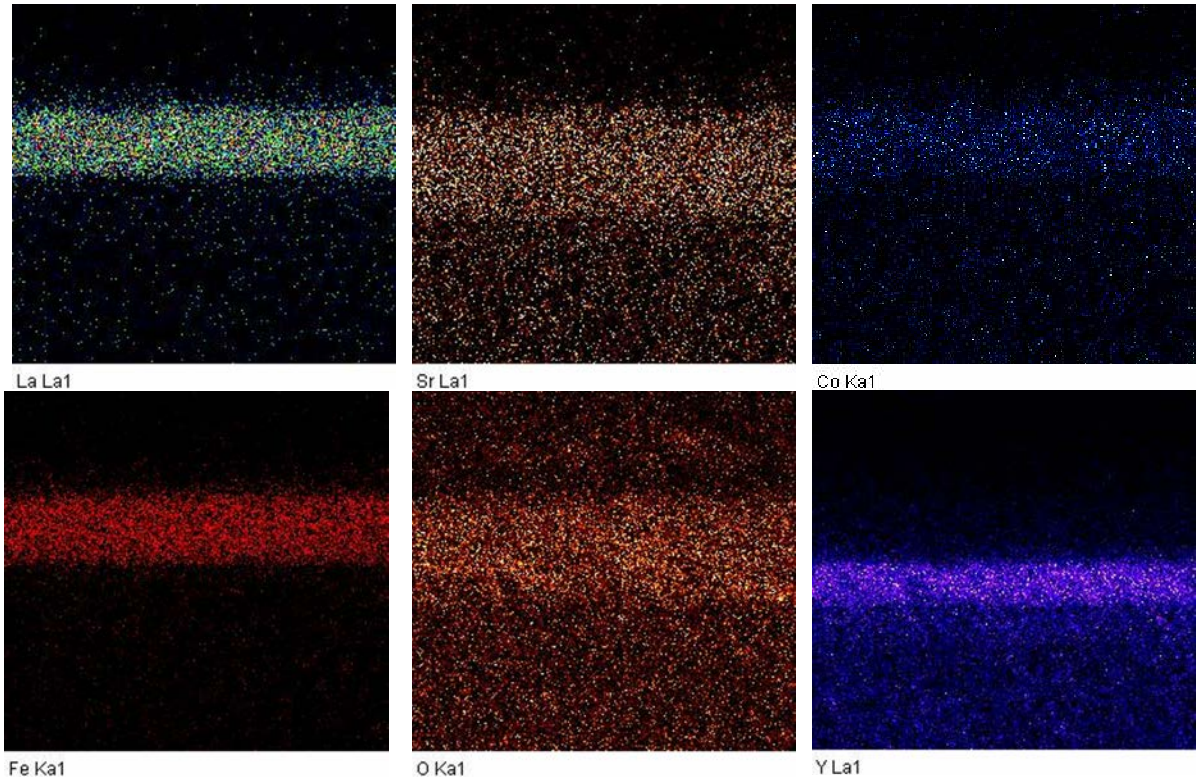
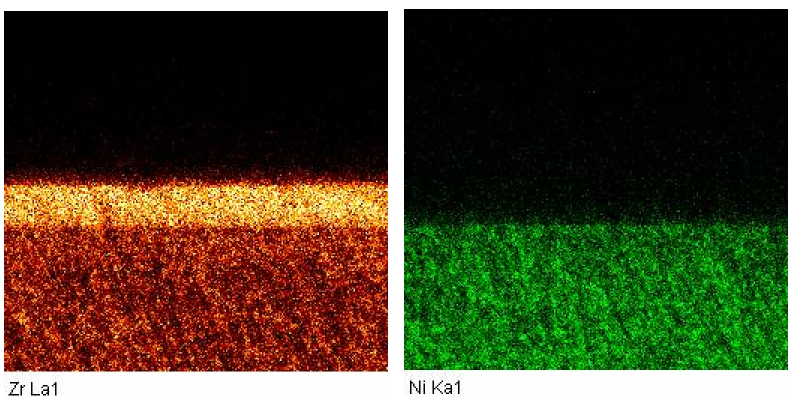
Cell post-mortem characterization (EDX)





- EDX maps of the relevant elements for Cell 17 at shown magnification.
- Sr is uniformly distributed and unable to detect any segregation.



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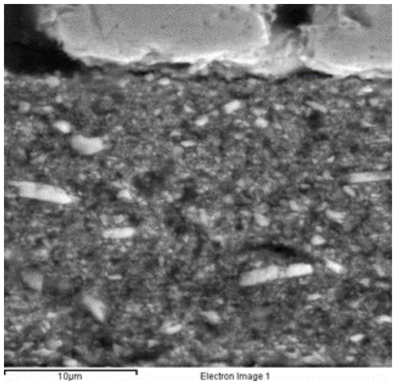
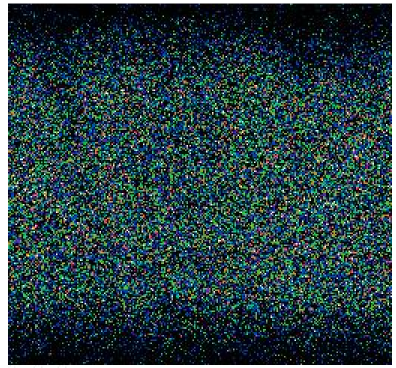
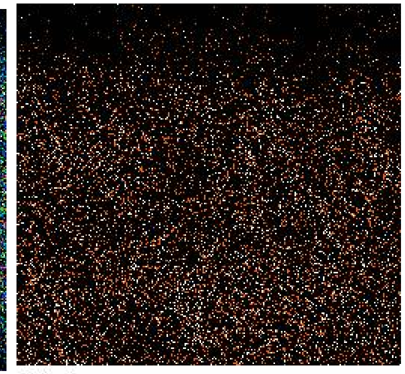
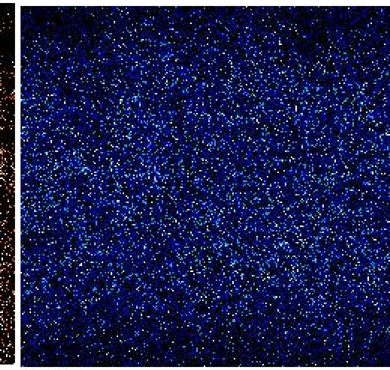
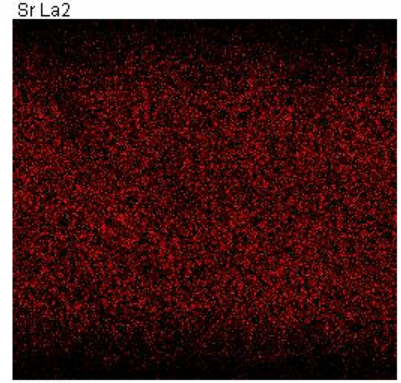
Cell post-mortem characterization (EDX)

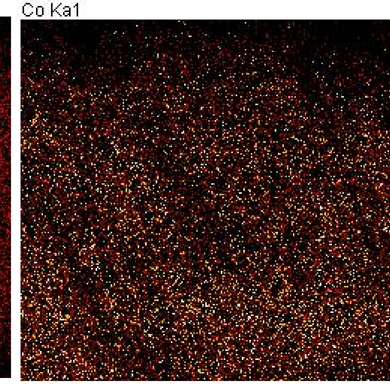


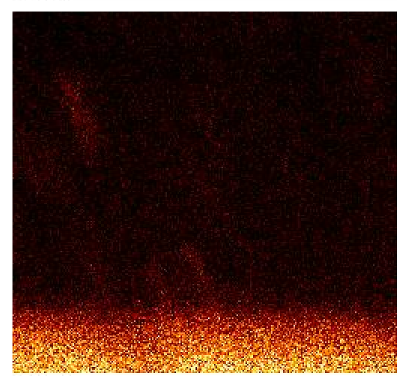

La La1

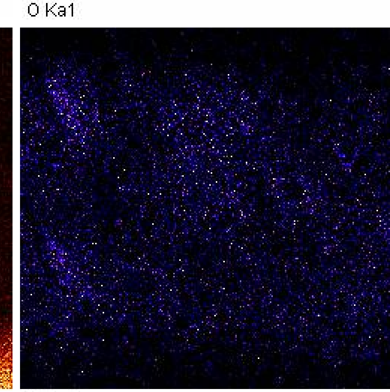

Sr La2


Co Ka1


Fe Ka1


O Ka1


Zr La1


Ce La1

- EDX maps of the relevant elements for Cell 17 at higher magnification.
- Again unable to detect any Sr segregation.

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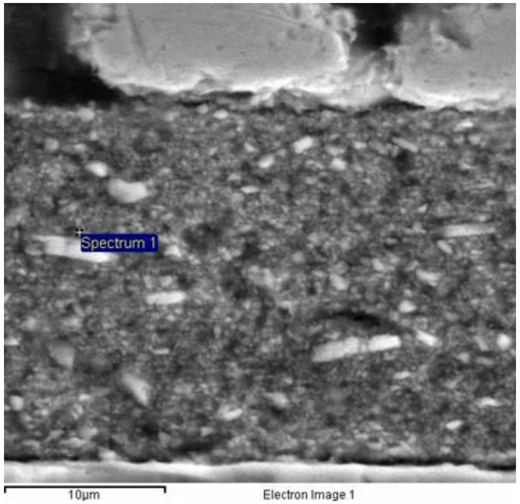
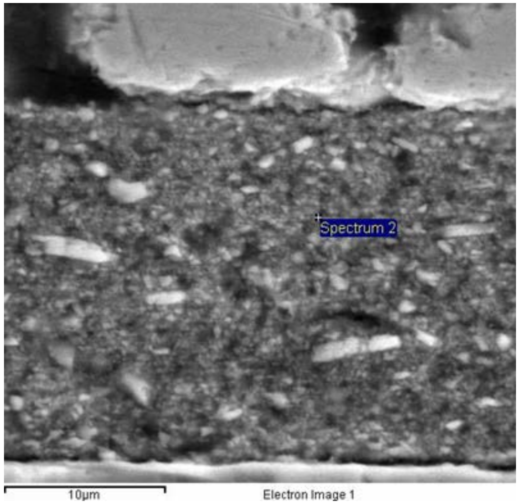
Cell post-mortem characterization (EDX)

- Spot EDX analysis for Cell 17.
- Sr numbers are within the EDX experimental error which should be around 1%.





Element	Weight%	Atomic%
O K	17.87	55.62
Fe K	15.86	14.14
Co K	4.54	3.83
Ni K	1.73	1.46
Sr L	**10.63**	**6.04**
Zr L	6.58	3.59
La L	30.22	10.83
Ce L	12.58	4.47
Totals	100.00	

Element	Weight%	Atomic%
O K	17.45	54.62
Fe K	18.02	16.16
Co K	4.61	3.92
Ni K	1.41	1.20
Sr L	**11.50**	**6.57**
Zr L	3.25	1.79
La L	33.67	12.14
Ce L	10.09	3.60
Totals	100.00	

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Path forward

- Significant results:
  - LSCF-CZ can be used to remove the ceria barrier layer .
  - Low temperature firing of the cathode prevents the formation of $SrZrO_3$.
  - The formation of $SrZrO_3$ is a strong function of temperature.
  - Stable cell voltage over long time.
- Path forward:
  - Improve cathode adhesion to the YSZ layer (nanopowders, sintering aids, etc.).
  - Improve cell power density by lowering cathode polarization.
  - Test larger scale cells.

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Conclusions and Acknowledgements

- Synthesized and characterized ceria-zirconia (CZ) mixtures with different molar compositions.
- Prepared LSCF-CZ cathode inks with different weight ratios.
- Quantified the electrical performance of button cells with LSCF-CZ cathodes.
- Determined the long–term voltage stability of LSCF-CZ cathodes.
- It was found that:
  - The doped ceria layer can be avoided provided low-temperature firing of the cathode inks.
  - The cell voltage appears to remain stable over relatively long-term testing.
  - The cell power density is not up to par as of yet.
  - The cathode properties need further refinements to achieve higher power densities.
- This project was supported by the Department of Energy under Award Number DE-FE0026168.
- Many thanks to Project Manager Steven Markovich and the NETL SECA program team.

Thank you for your time.

Questions?

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