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LSCF-CZ Cathodes for Improved SOFC Electrical Performance

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Conclusions and Acknowledgements

- Project started on October 2015:
  - Prepared ceria-zirconia (CZ) mixtures.
  - Prepared some of the LSCF-CZ inks.
  - Established reference button cell tests based on Delphi technology.
  - Initial button cell data available.

- This project is supported by the Department of Energy under Award Number DE-FE0026168.
- Many thanks to Project Manager Steven Markovich and the NETL SECA program team.

Presentation outline

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

Project objectives

- Study cathodes made of LSCF and CZ with different composition and determine Sr segregation prevention capabilities.
- Determine the electrical performance improvements that result from preventing Sr segregation.
- Determine the mechanism by which Sr segregation is prevented.

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Background

- Solid Oxide Fuel Cells (SOFCs) 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.
- Researchers have shown that a LSCF-CZ (ceria-zirconia) mixture **does not produce** the unwanted $SrZrO_3$ compounds at the electrolyte interface after sintering at 850°C even without the ceria barrier layer.
  - They indicate 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, 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 $Ce(NO_3)_3$•$6H_2O$ and $ZrO(NO_3)_2$•$5H_2O$ 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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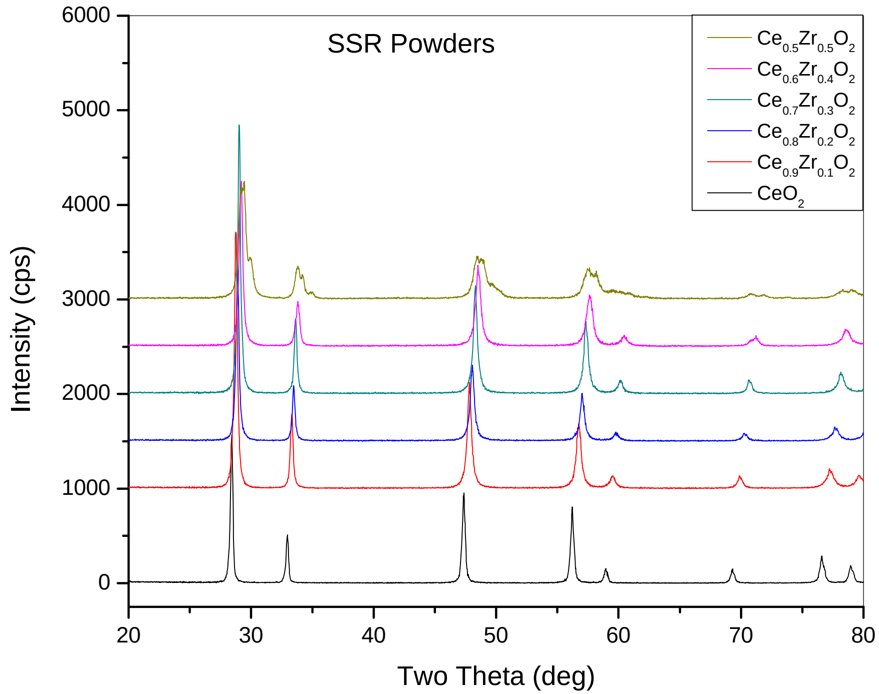
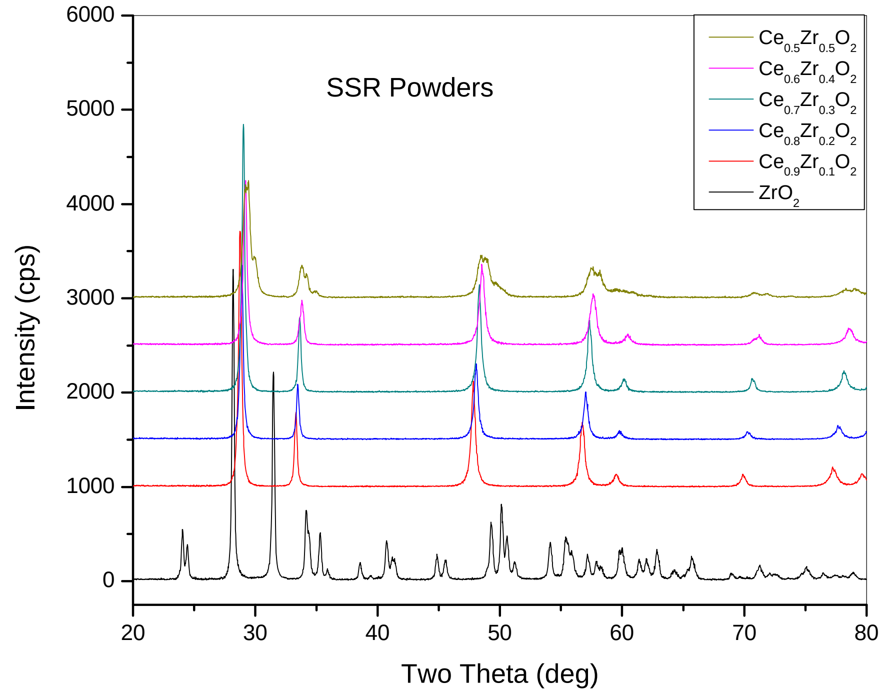
XRD characterization (SSR)

- 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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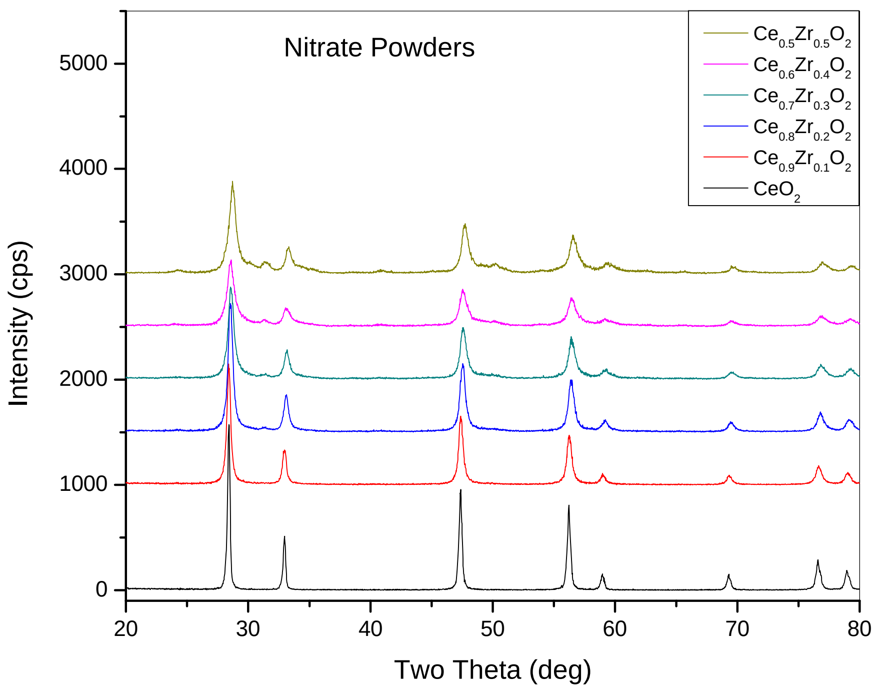
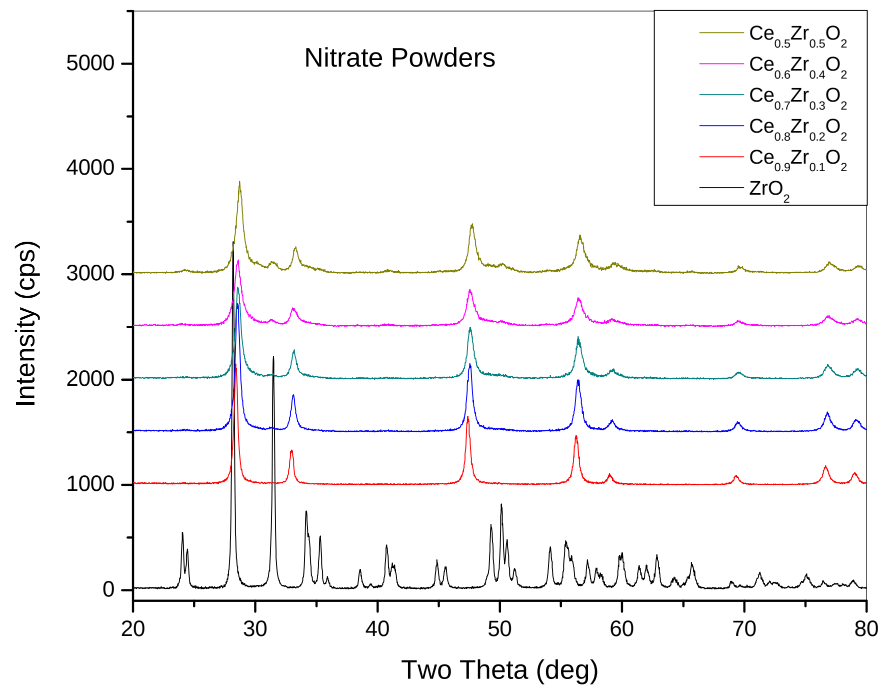
XRD characterization (NIT)

- The NIT does 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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CZ molar composition selection

- Given the XRD results, the following two CZ compositions for the initial ink preparation have been 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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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	68.31	Actual Formula		
Zr	L	4.88	2.90	Ce	Zr	O
Ce	L	75.07	29.38	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	66.90	Actual Formula		
Zr	L	14.68	8.57	Ce	Zr	O
Ce	L	65.31	24.53	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			
$Ce_{0.6}Zr_{0.4}O_2$						
Element	Line	Weight%	Atomic%			
O	K	22.41	68.36	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	2.0-
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	23.43	0.76	0.17	2.07
Totals		100.00	100.0:			
$Ce_{0.7}Zr_{0.3}O_2$						
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	2.15
Totals		100.00	100.00			
$Ce_{0.6}Zr_{0.4}O_2$						
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.
- 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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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.

	LSCF:CDZ ratio wt%		
	75:25	50:50	25:75
T (°C)	ID	ID	ID
800	CS2_75-25_800	CS2_50-50_800	CS2_25-75_800
850	CS2_75-25_850	CS2_50-50_850	CS2_25-75_850
900	CS2_75-25_900	CS2_50-50_900	CS2_25-75_900
950	CS2_75-25_950	CS2_50-50_950	CS2_25-75_950
1000	CS2_75-25_1000	CS2_50-50_1000	CS2_25-75_1000
1050	CS2_75-25_1050	CS2_50-50_1050	CS2_25-75_1050
1100	CS2_75-25_1100	CS2_50-50_1100	CS2_25-75_1100

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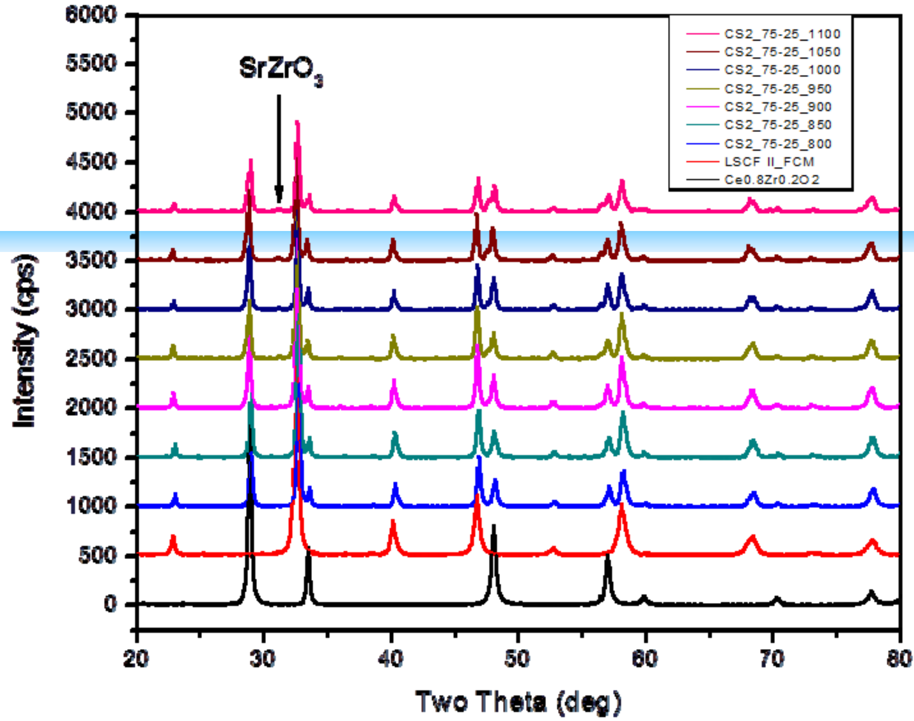

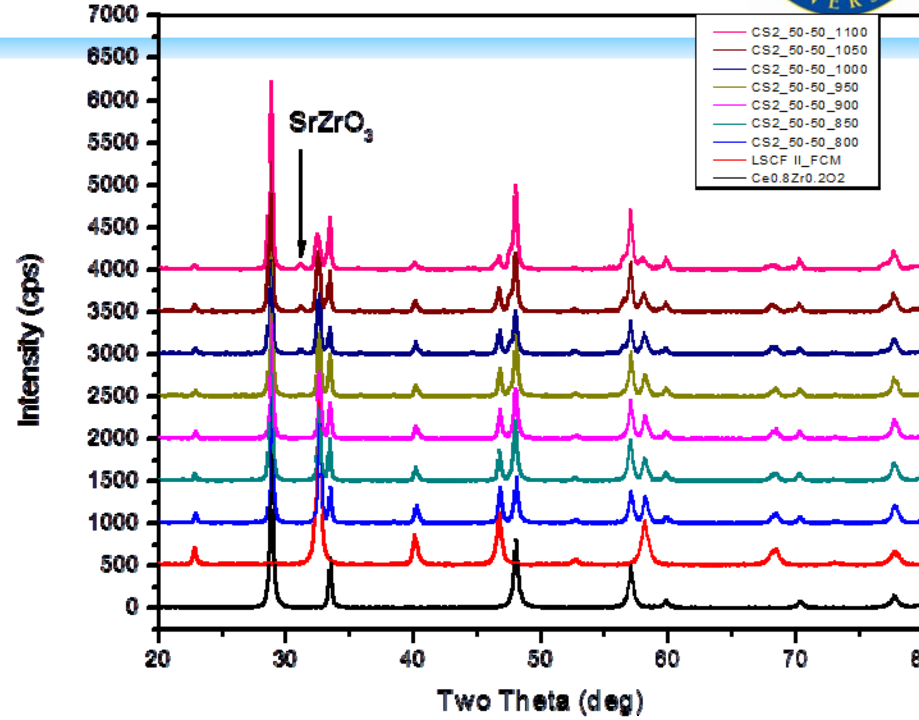

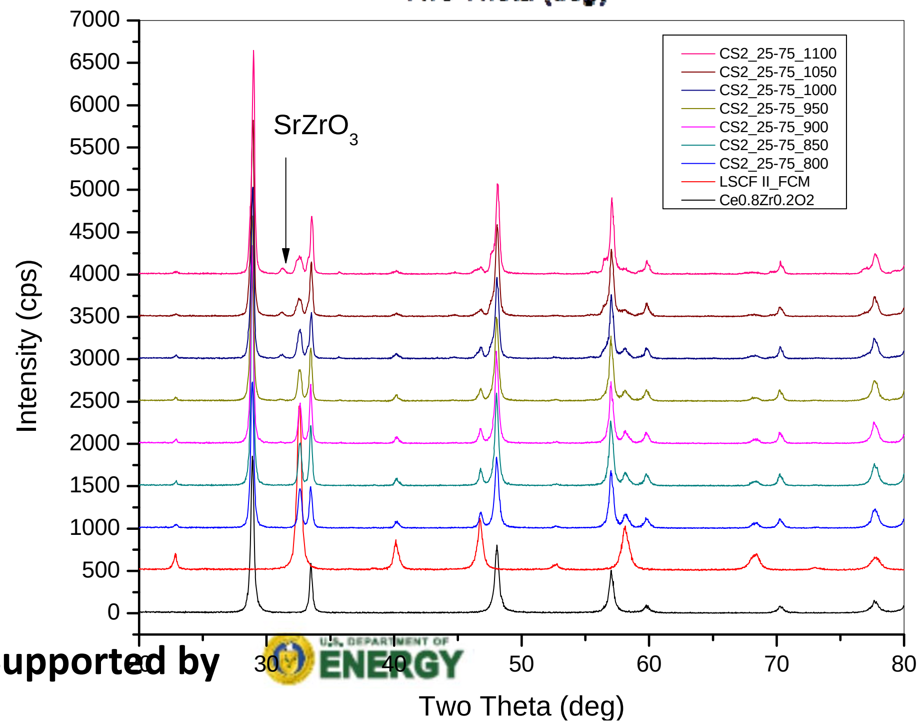

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Cathodes inks

- Initial ink makeup has been determined.
- CZ powders will be 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 will be 60:40 as recommended by FCM for their ink vehicle.
- Six different inks will be 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

Pull test

- Used LSCF paste from FCM only; no CZ used.
- Anode bilayer were purchased from FCM.
- Pull test results are the following.

Sample ID	Firing Temp (°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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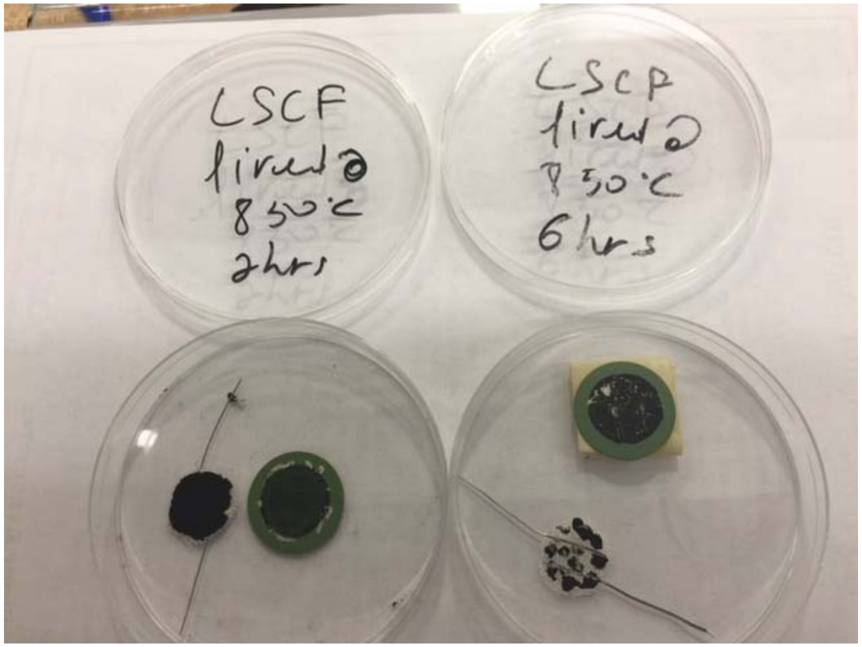
Button cell assembly

- Cathode adhesion is weak when fired at 850^{o}C/2hrs but no delamination is seen.
- Delamination occurs after firing the cathode current collector.
- Firing at 950^{o}C/2hrs eliminates delamination but no cell power.
- Modified our test rig in order to fire the cathode current collector in situ.
- For longer term adhesion needs to be improved (i.e., nano powders, sintering aid).



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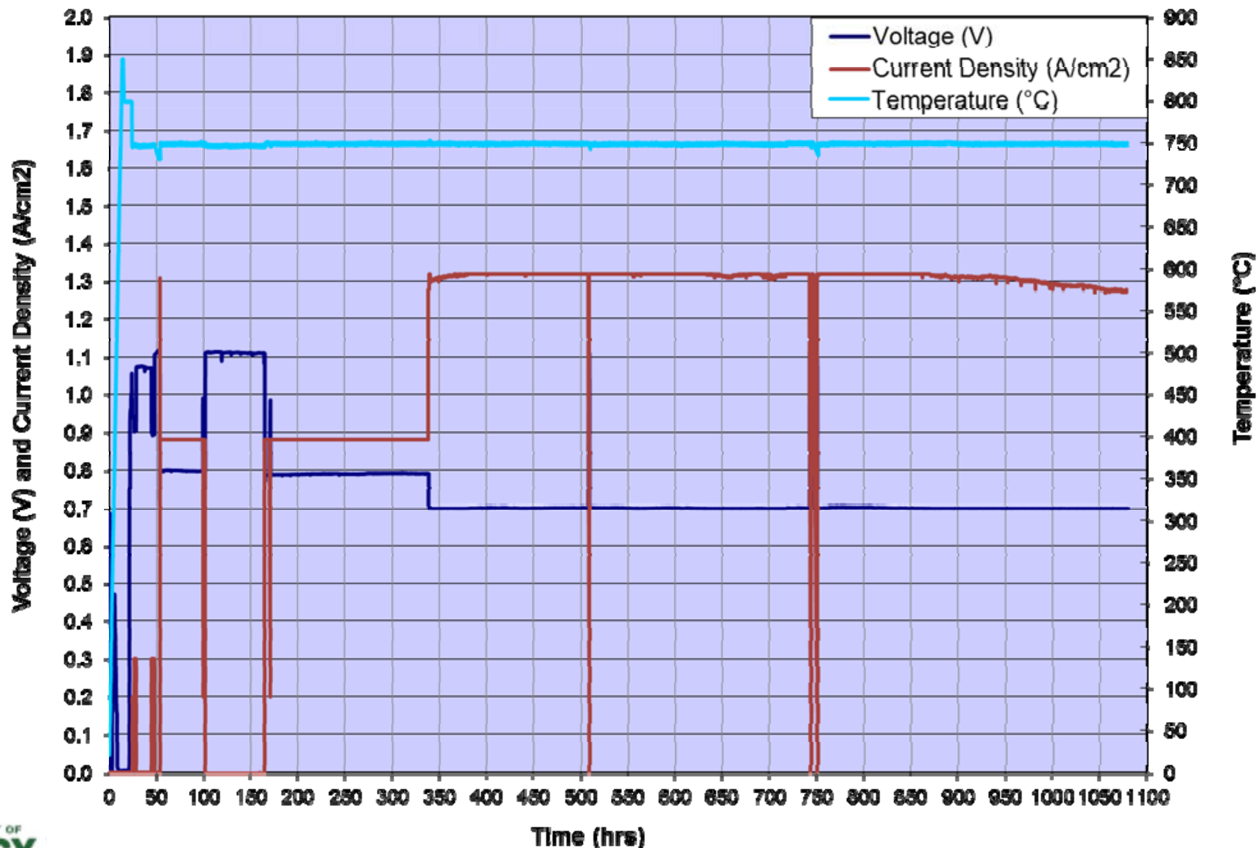
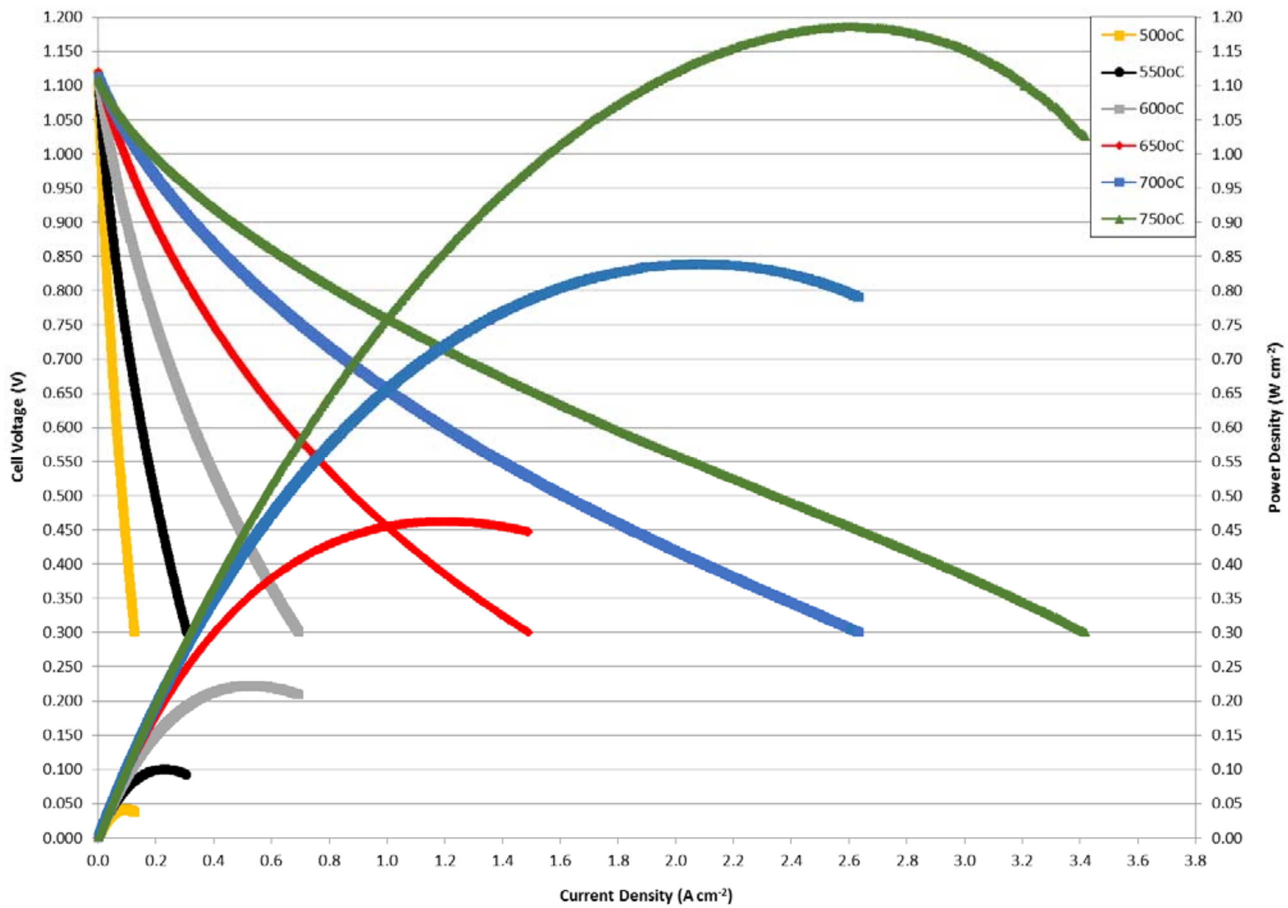
Button cell testing

- Cell 02 Delphi baseline long-term test (Ni-YSZ/YSZ/Ceria/LSCF).
- Stable performance over 1000 hours.
- Current density decrease after 850 hours likely due to Arbin damage; no change in voltage when current density decreases.



Button cell testing

- Delphi baseline performance (PARSTAT).
- Cell performance at 750^{o}C is quite good.
- Irrelevant as the temperature reaches 500^{o}C.



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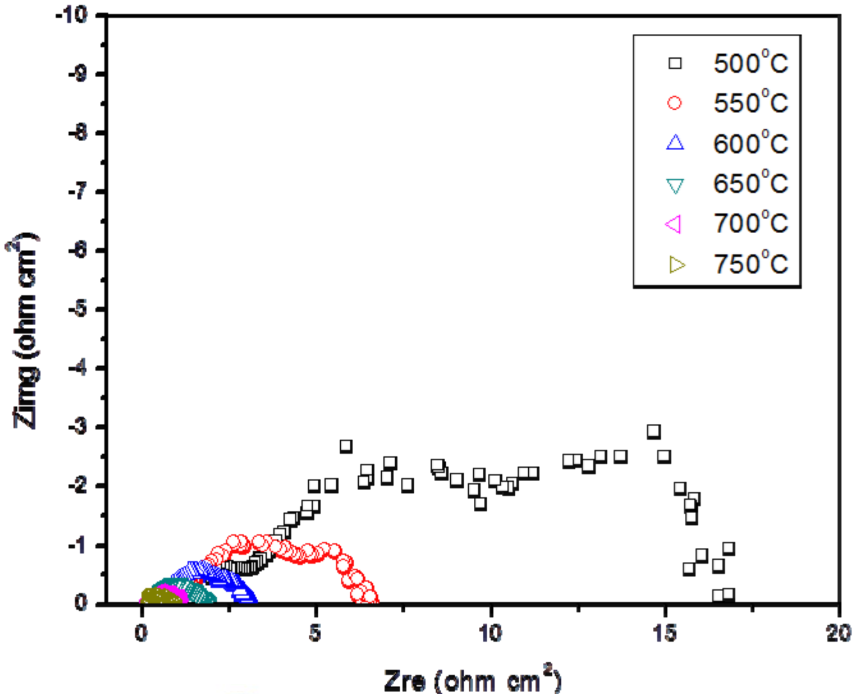
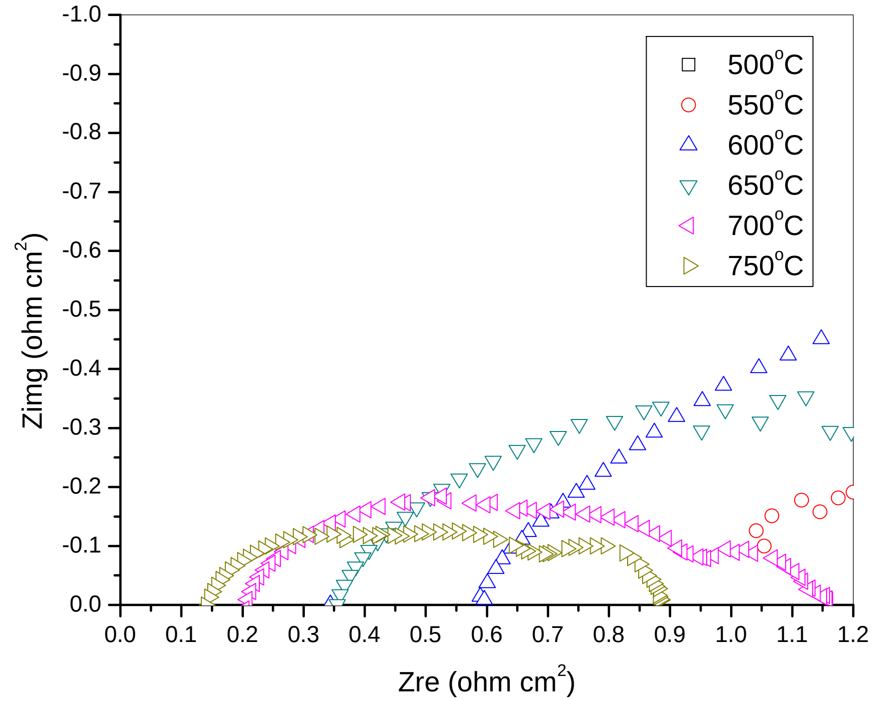
Button cell testing

- Delphi baseline performance (PARSTAT).
- Performance decline due to electrode polarization as the high frequency intercept becomes larger and larger as temperature decreases.
- Cathode electrochemical activity severely diminished with lowering temperature.
- Ohmic portion contributes to lower cell performance but much smaller than the electrode polarization; however, still a significant increase in the cell ohmic resistance is present.





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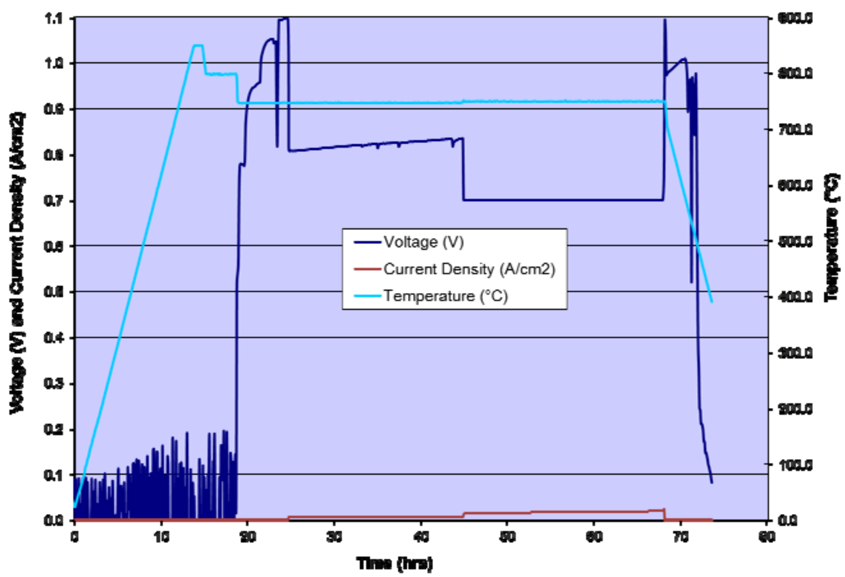
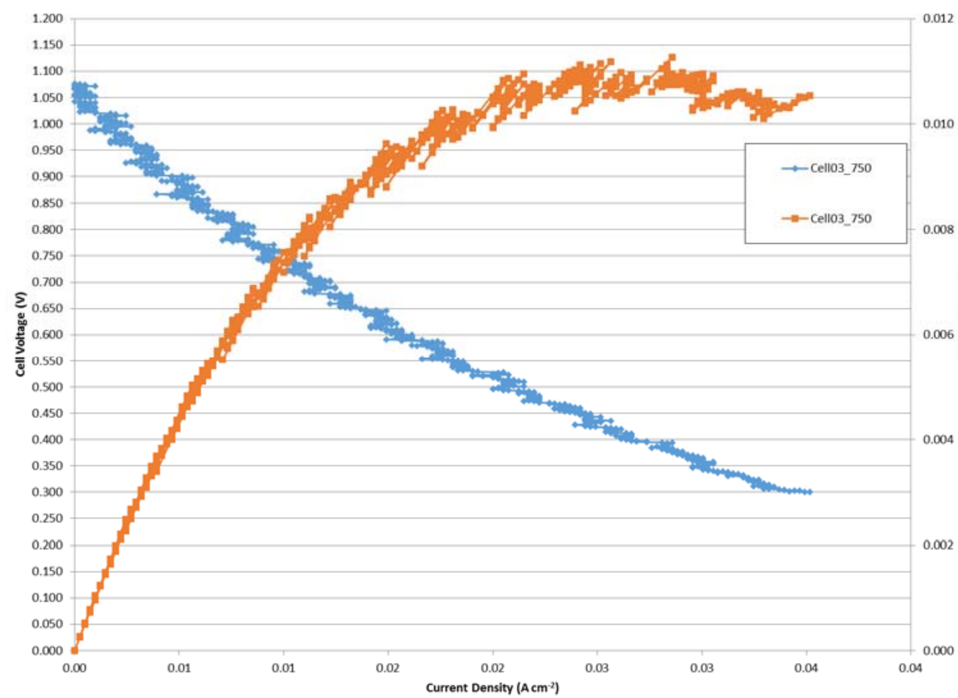
Cell 03

- Delphi bilayer and LSCF paste from FCM.
- Cathode fired at 1100°C for 1 hour.
- Virtually zero power is obtained.
- Cell will be sectioned to study the formation of $SrZrO_3$.





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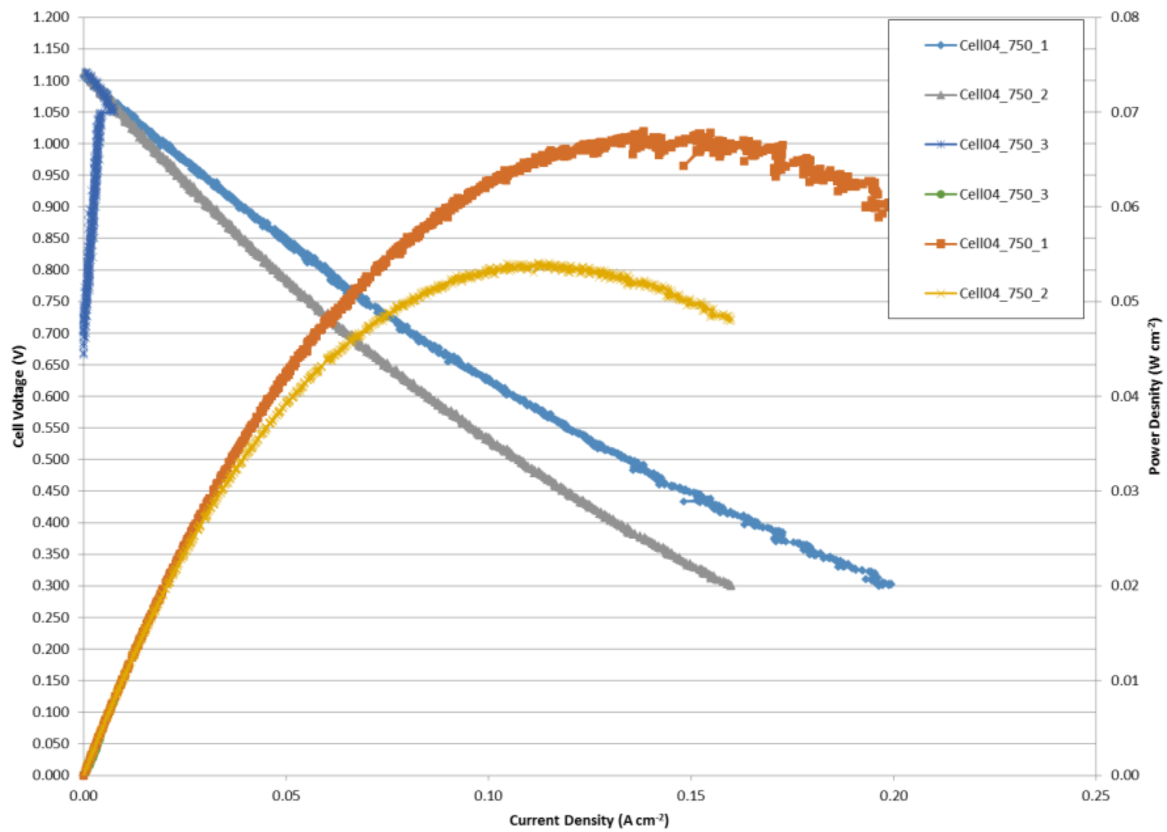
Cell 04

- Delphi bilayer and LSCF paste from FCM.
- Cathode fired at 950ºC for 2 hour.
- A little better than Cell 03 but power decays to nothing.
- Cell will be sectioned to study the formation of $SrZrO_3$.



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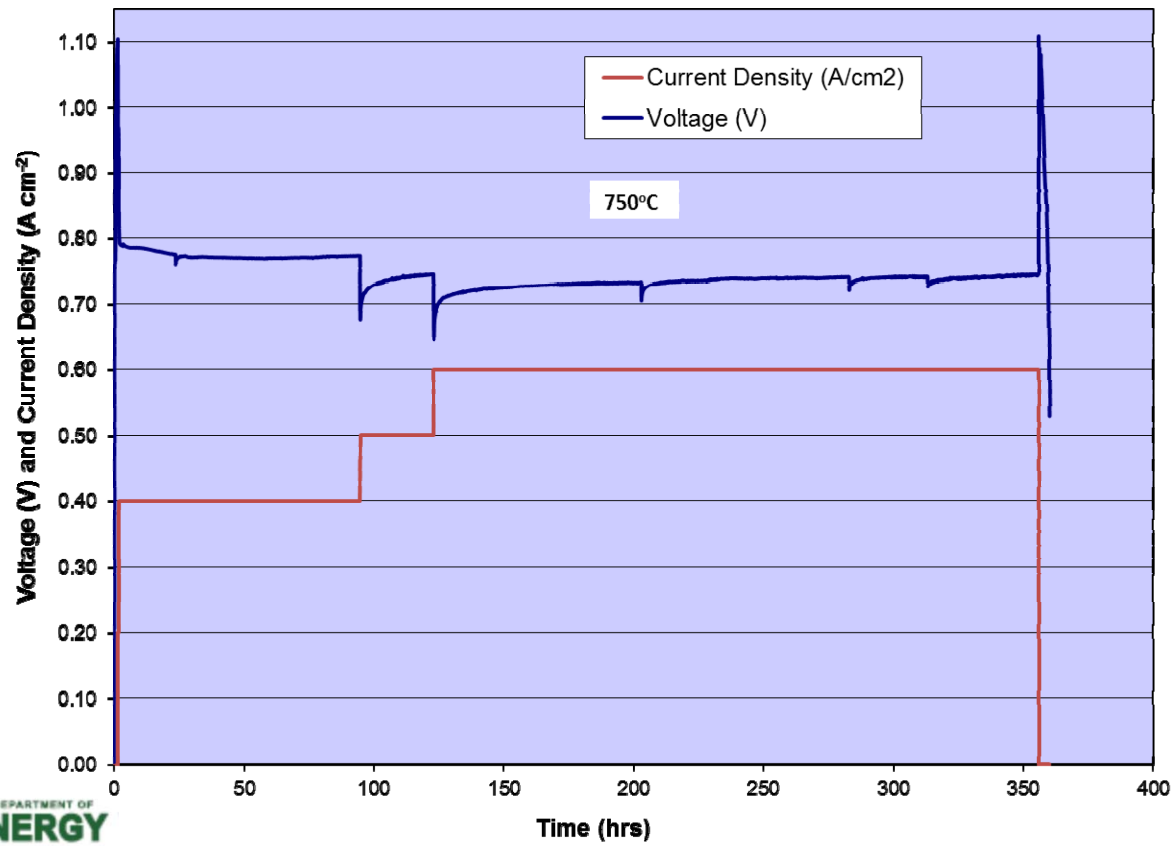
Cell 08

- LSCF fired at 850ºC/2 hours without a ceria barrier layer.
- Fired cathode current collector in situ.
- The cell voltage indicates an initial degradation, but the voltage stabilizes.
- Suggests the formation of insulating phases at electrolyte interface (complete).
- Stable performance over 350 hours.



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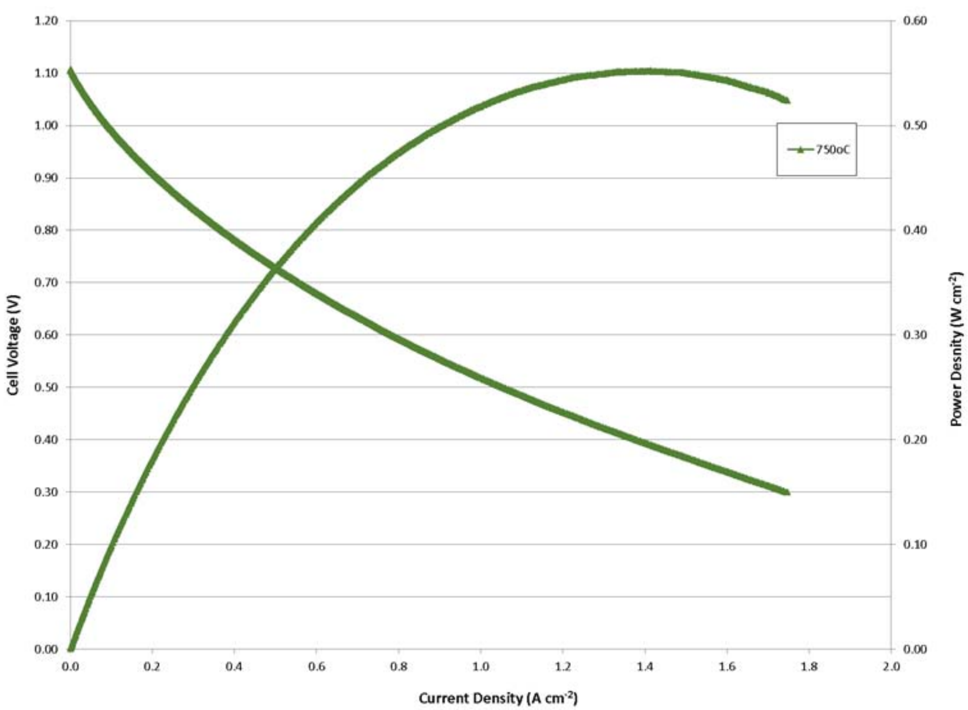
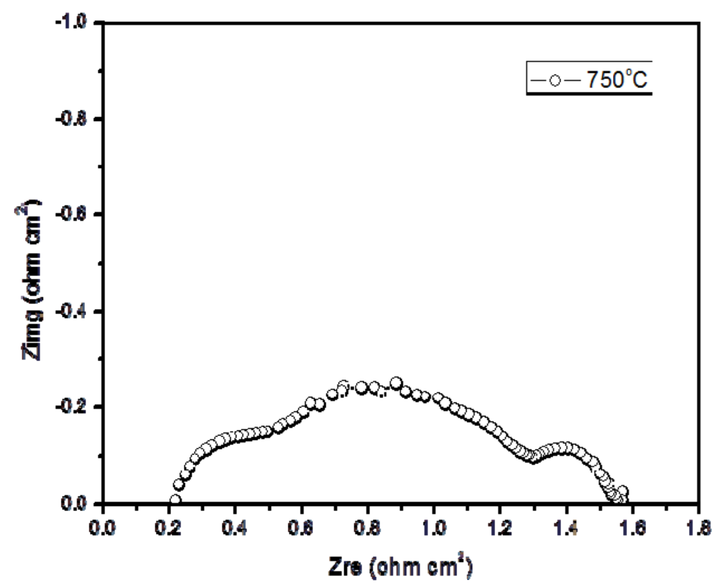
Cell 08

- LSCF fired at 850°C/2 hours without a ceria barrier layer.
- Fired cathode current collector in situ.
- The cell performance is around 50% lower than the standard Delphi cell.
- Impedance data indicates much larger electrode polarization.
- Increase in ohmic resistance also observed.





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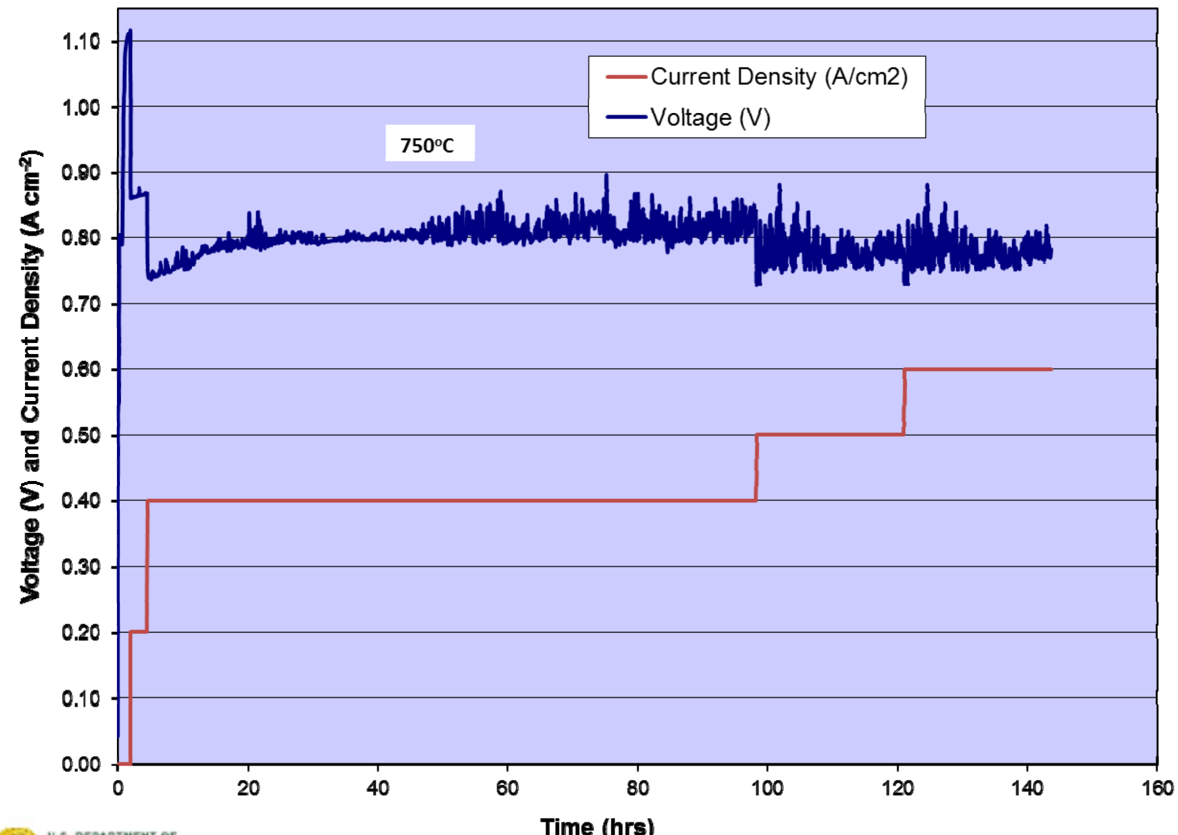
Cell 09

- LSCF+**15%** $Ce_{0.8}Zr_{0.2}O_2$ fired at 850°C/2 hours without a ceria barrier layer.
- Fired cathode current collector in situ.
- The cell voltage does not show the initial degradation and improves over time.
- The cell voltage is unstable possibly due to reactions occurring in the LSCF+CZ phase.
- Perhaps no insulating phase formed at the electrolyte interface.



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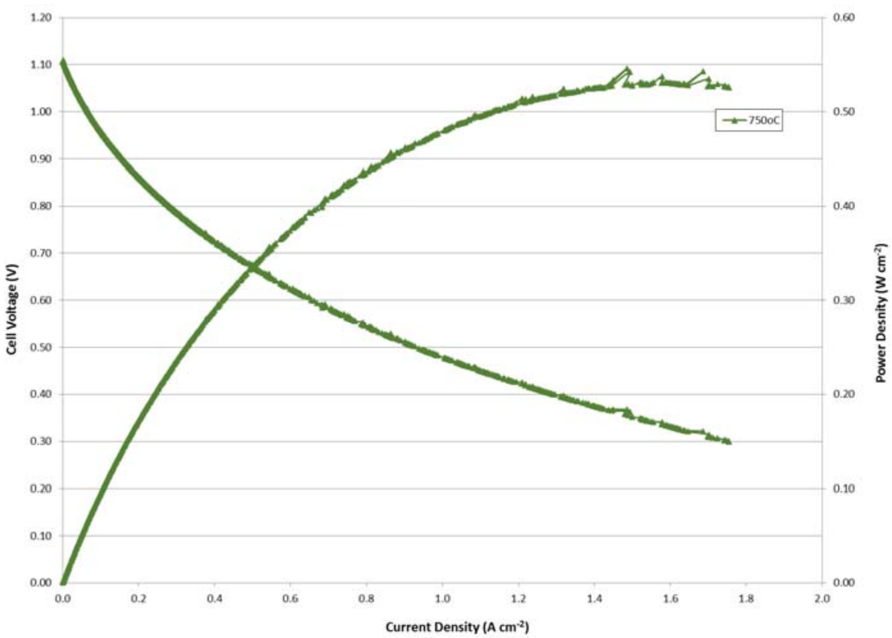
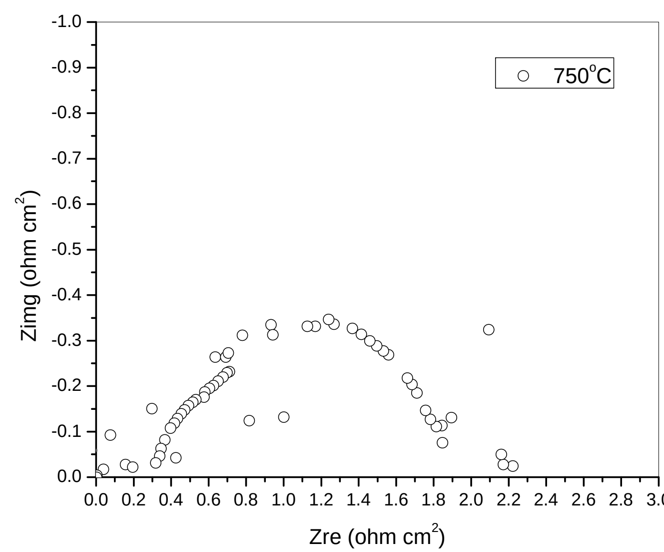
Cell 09

- LSCF+15% $Ce_{0.8}Zr_{0.2}O_2$ fired at 850°C/2 hours without a ceria barrier layer.
- Fired cathode current collector in situ.
- The cell performance is also around 50% lower than the standard Delphi cell.
- Lower cell performance when compared to Cell 08.
- Impedance data (noisy) indicates larger electrode polarization and ohmic resistance.





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Path forward

- Complete at least 5 more button cell testing.
- Improve cathode adhesion strength at 850^{o}C.
- Start post-mortem characterization of tested cells.

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Cell post-mortem preparation

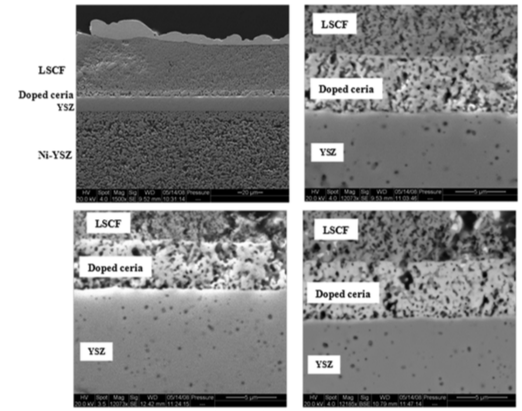
- Learning how to section and polish cells for SEM, XPS, and HR-TEM/EDS analysis.

➢ Cut

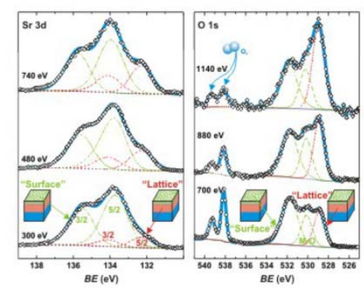
➢ Mold

➢ Polish

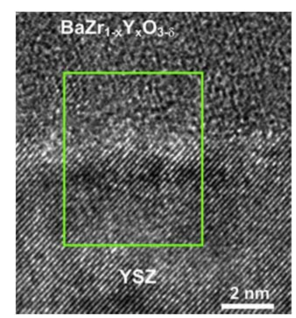
SEM

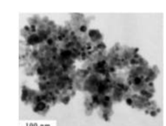


XPS



HR-TEM/EDS





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Conclusion

- Project well under way.
- Experienced some minor setbacks.
- Should not affect project schedule or cost significantly.

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Thank you for your attention.
Any questions?

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