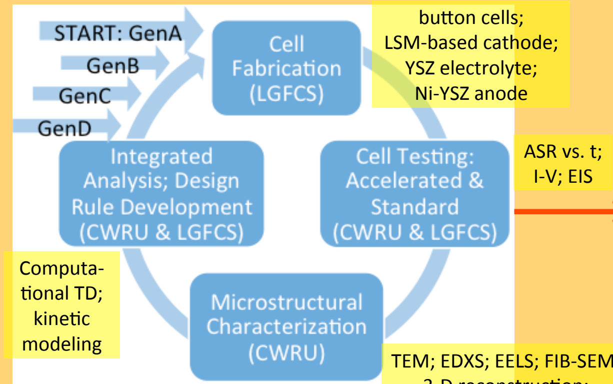
Long-Term Degradation of LSM-Based SOFC Cathodes: Use of a Proven Accelerated Test Regimen

Mark R. De Guire,[1] Arthur H. Heuer,[1] and Zhien Liu[2]

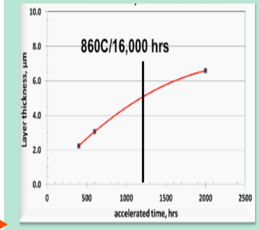
1) Dept. of Materials Science and Engineering, Case Western Reserve University, Cleveland, OH 44106;
2) LG Fuel Cell Systems Inc., North Canton, Ohio 44720

Overview

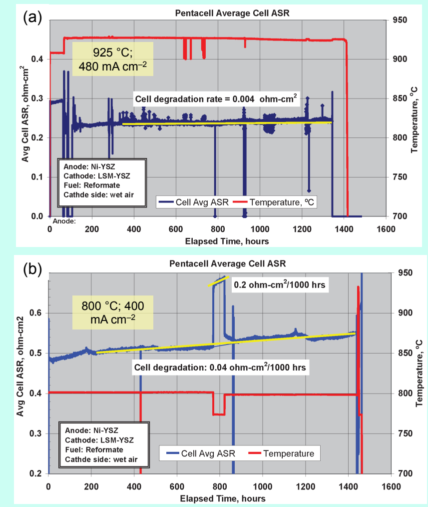
The overall goals of this SECA Core Technology Program (CTP) project are to understand the microstructural basis of performance loss in cathodes based on lanthanum strontium manganite (LSM, $(La_{1-x}Sr_x)_{1-y}MnO_{3\pm\delta}$), and to develop strategies for optimizing the long-term performance of LSM-based cathodes for commercial fuel cell systems **(Figure A)**. Here we present results from recent LGFCS–CWRU collaborations as examples of work to be carried out under this CTP project. We will implement an accelerated testing protocol, developed and validated by LGFCS, to gather performance data at CWRU in time frames of e.g. 500 h that are relevant to much longer-term normal cell operation (≥ 5 kh) **(Figure B)**, and compare these findings to results from non-accelerated tests **(Figure C)**. Tested cells will undergo detailed microstructural and microanalytical studies **(Figures D, E, F, and G)**. Analysis of performance histories, microstructural studies, and computational thermodynamic results **(Figure H)** will lead to design rules for improving the long-term stability and performance of LSM-based cathodes. We will iteratively refine the proposed design rules (GenA – GenD, **Figure A**), with a view to identifying and quantifying the mechanisms that lead to loss of performance in LSM-based cathodes.



➢ **Figure A.** Task flows and cooperative distribution of tasks between CWRU and LGFCS in the new CTP project.



➢ **Figure B.** Thickness of densified cathode layer vs. duration of accelerated testing. The vertical line indicates that 1.2 kh under the accelerated conditions produces the same thickness of densified cathode (5 μm) observed after 16 kh of testing under simulated system conditions (**Figure F**).



➢ **Figure C.** Cell ASR vs. time, with H_2O in cathode environment, as a function of operating temperature: (a) 925 °C, 480 mA cm^{-2}; (b) 800 °C, 400 mA cm^{-2}. Both cells were tested with reformate at the anode [1].

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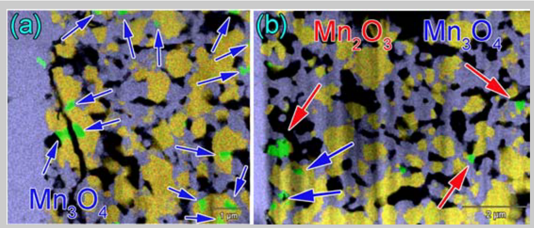
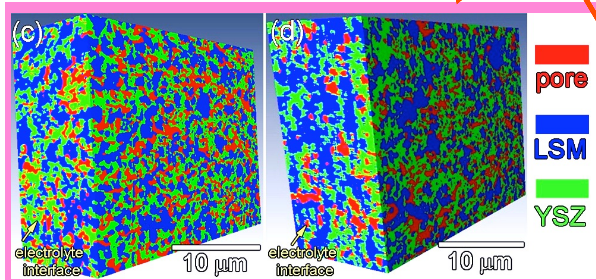
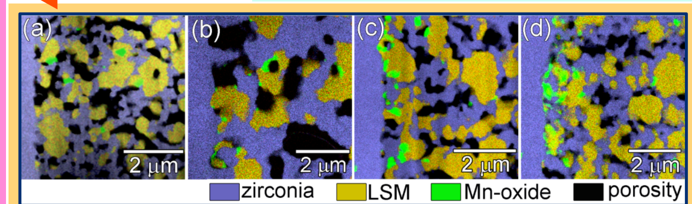


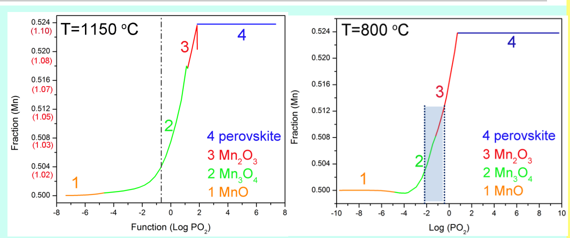
➢ **Figure G.** EDXS maps of LSM-YSZ cathodes. EELS analysis indicated that Mn-oxides in cells operated at 925 °C were Mn_3O_4 (a). Cells operated at 800 °C contained Mn_2O_3 and Mn_3O_4 (b) [1].



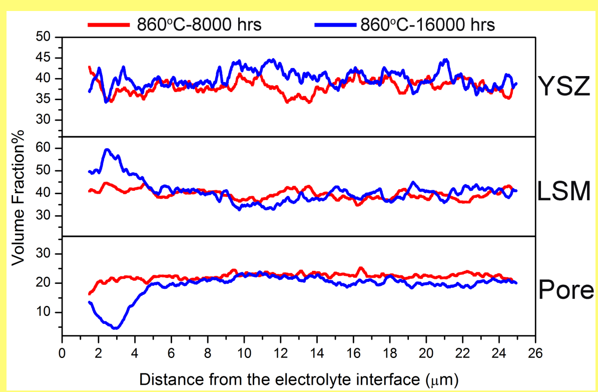
➢ **Figure E.** 3D reconstructions of the cathode (electrolyte at front left) for cells after testing at 860 °C for (c) 8 kh and (d) 16 kh [2]. (3D studies supported by Ohio Department of Development's Third Frontier Program.)



➢ **Figure D.** EDXS maps acquired near the cathode-electrolyte interface for (a) the as-fired cell; (b) the 800 °C–2 kh cell; (c) the 800 °C–8 kh cell; (d) the 800 °C–16 kh cell. (The electrolyte is at the left edge in each image.) [2]



➢ **Figure H.** Computational thermodynamic predictions of ranges of p_{O_2} over which Mn-containing oxide phases are stable at 1150 °C (left) and 800 °C (right) [3]. Fired at 1150 °C in air during cell fabrication, Mn_3O_4 formation is predicted (left). During operation at 800 °C, a typical atmosphere near the cathode-electrolyte interface should lead to coexistence of Mn_2O_3 and Mn_3O_4 (right). Both predictions are consistent with the TEM/EELS results in **Figure G.**



➢ **Figure F.** Volume fraction profiles of YSZ, LSM, and porosity in cathodes tested at 860 °C (**Figure E**) for 8 kh (red) and 16 kh (blue) [2].

Summary

The accelerated testing protocol enables the study of microstructural changes and effects on SOFC performance that are characteristic of years of testing, within time frames (~500 h) amenable to applied laboratory-scale SOFC R&D. This brings, within the scope of a three-year program, the ability to modify cathode formulations and test hypotheses for their optimization. Because one of the key challenges in advancing SOFC technology is the difficulty of studying (and understanding) the mechanisms that lead to critical long-term performance loss, the research proposed here has the potential for breakthrough impact in improving the reliability, robustness, and longevity of SOFC technology.

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References

[1] H.-J. Wang, M. R. De Guire, Z. Xing, G. Agnew, R. Goettler, Z. Liu, A. H. Heuer, Met. Trans. E (in press). [2] H.-J. Wang, N. Hilli, M. R. De Guire, R. Goettler, Z. Liu, Z. Xing, T. R. Ohrn, A. H. Heuer, 14th SECA Workshop, 23-24 July 2013 (http://www.netl.doe.gov/File%20Library/events/2013/seca/Wang.pdf) [3] H. J. Wang, Y. L. Liu, M. Chen, J. R. Bowen, and L. Theil Kuhn, *J. Power Sources* (submitted).