Thermodynamic Prediction of Morphological Evolution and Chemical Stability of LSM and LSCF Cathodes in Chromium-Containing Air

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Abstract: State-of-the art cathodes namely Lanthanum Strontium Manganite (LSM) and Lanthanum Strontium Cobalt Ferrite (LSCF), have been electrochemically tested in the presence of chromium vapor and humidified air (3% H_2O) using LSM/YSZ/Pt and LSCF/GDC/Pt half-cells at 750ºC. For the 100-hour tests, the electrochemical performance of the LSM/YSZ/Pt half-cell exhibited a rapid decrease with time in an I-t curve while the LSCF/GDC/Pt half-cell only exhibited a slight decrease of electrode performance. Posttest electrode morphologies indicated that Cr species deposited predominantly at LSM/YSZ interface whereas Cr deposited mainly at LSCF surface. Raman spectra show the $SrCrO_4$ formation on the posttest LSCF cathode but not on the posttest LSM cathode. We perform first principles calculations on representative LSM and LSC, to support our experimental findings. First principles thermodynamics coupled with a linear programming approach was used to identify the reaction energetics and thermodynamically favorable decomposition pathway of LSM and LSC compounds in presence of Cr vapor. The bulk reaction energetics suggests that the stoichiometric LSM remains unreacted for the whole range of experimental $pCrO_3$ and temperatures (T) while the formation of $SrCrO_4$ was observed to be energetically favorable on LSC cathode for the experimental $pCrO_3$-T range. Thus the calculations show excellent agreement with experimental results and provide the $pCrO_3$-T range to avoid Cr poisoning.

Background

LSM and LSCF cathodes in solid oxide fuel cell (SOFC) stacks are exposed to inlet air containing intrinsic impurities such as H_2O (~3%), CO_2 (~400 ppm), and SO_2 (~0.3 ppm). Inlet air also contains chromium vapor species from balance of plant components (BoP) and metallic interconnects. Impurities namely H_2O, CO_2, SO_2, and CrO_x present in air, poison LSM and LSCF cathodes. Unlike the degradation due to water vapor, the degradation due to chromium cannot be regenerated by increase in operating temperature.

Density functional theory (DFT) offers a robust tool to study materials at the atomic level. Here we use DFT calculations to predict the stability of (La, Sr)$MnO_{3-\delta}$ and (La, Sr)CoO_3 cathode materials in chromium vapor. Combined approaches of theoretical and experimental methods reach agreement in this study. This helps understanding of chromium poisoning mechanisms for the development of robust cathodes to improve the long term stability of SOFC power systems.

Objective

➢ To identify the processes for LSM and LSCF cathode interaction with chromium species in humidified air.
➢ To determine the mechanisms for LSM and LSCF cathode degradation due to interaction with chromium originated from BoP materials and Interconnect.

Experimental & Theoretical Approaches

Cell fabricated at 1200°C in air for 2 h → Electrochemical testing

Input parameters: 750ºC, Atmospheric air containing 3% H_2O and chromium, and bias 0.5 V

Post test analysis: XRD, SEM, EDS, and Raman

Reactants → Identify elements → Product pool → Get DFT Energies (E_i) → Constrained Minimization → Get free energy of reaction → Phase Diagram
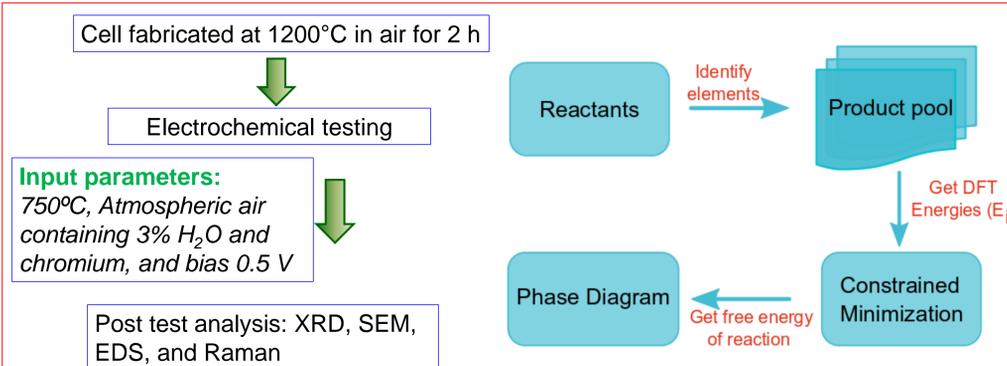
Figure 1. Configuration of a LSM/YSZ/Pt cell for electrochemical testing

Figure 2. Work flow for determination of reaction energetics through linear programming approach

Results and Discussion
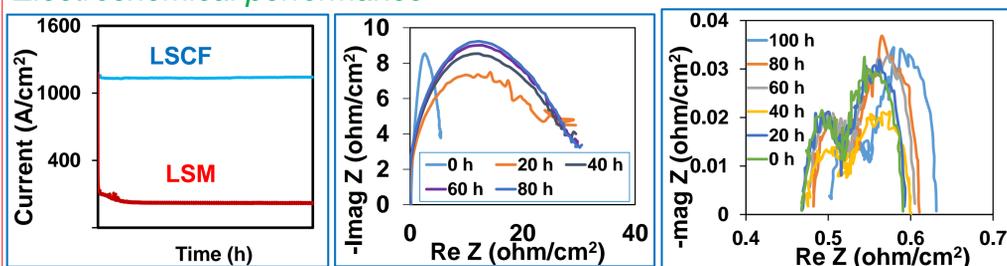### Electrochemical performance

Figure 3. I-t and EIS plots of LSM/YSZ/Pt and LSCF/GDC/Pt half cells at 750°C and 0.5 V bias in 3% H_2O/air containing Cr

Surface Morphologies & $SrCrO_4$ Formation

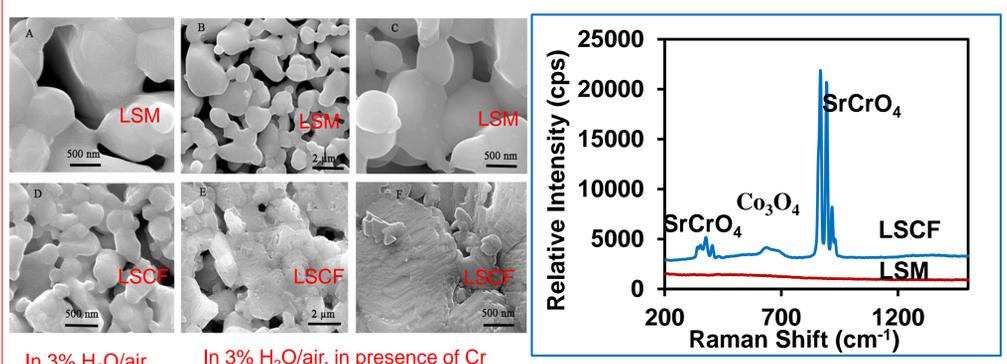In 3% H_2O/air   In 3% H_2O/air, in presence of Cr

Figure 4. SEM images (Left) and Raman spectra (Right) of post test LSM and LSCF cathodes exposed to Cr vapor for 100 hrs at 750ºC in 3%H_2O-air with 0.5 V bias

Morphologies & Compositions of Cathode/Electrolyte Interface

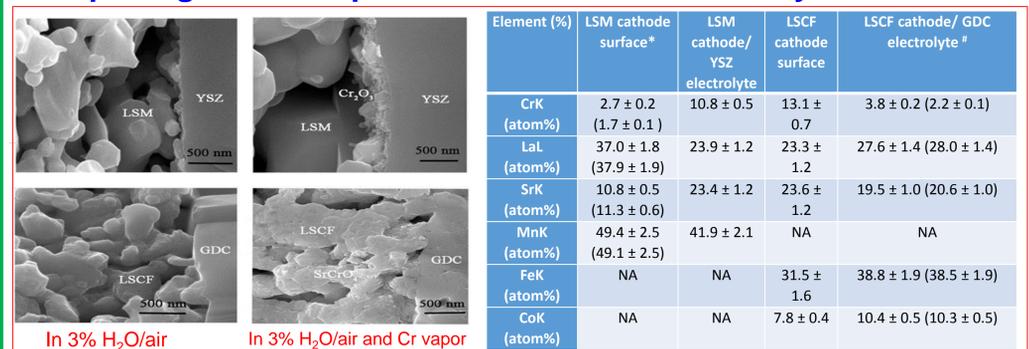| Element (%)	LSM cathode surface*	LSM cathode/ YSZ electrolyte	LSCF cathode surface	LSCF cathode/ GDC electrolyte #
CrK (atom%)	2.7 ± 0.2 (1.7 ± 0.1)	10.8 ± 0.5	13.1 ± 0.7	3.8 ± 0.2 (2.2 ± 0.1)
LaL (atom%)	37.0 ± 1.8 (37.9 ± 1.9)	23.9 ± 1.2	23.3 ± 1.2	27.6 ± 1.4 (28.0 ± 1.4)
SrK (atom%)	10.8 ± 0.5 (11.3 ± 0.6)	23.4 ± 1.2	23.6 ± 1.2	19.5 ± 1.0 (20.6 ± 1.0)
MnK (atom%)	49.4 ± 2.5 (49.1 ± 2.5)	41.9 ± 2.1	NA	NA
FeK (atom%)	NA	NA	31.5 ± 1.6	38.8 ± 1.9 (38.5 ± 1.9)
CoK (atom%)	NA	NA	7.8 ± 0.4	10.4 ± 0.5 (10.3 ± 0.5)

In 3% H_2O/air   In 3% H_2O/air and Cr vapor

Figure 5. SEM images and compositions of the cathode/electrolyte of post test LSM and LSCF cathodes exposed to Cr vapor for 100 hrs at 750ºC in 3%H_2O-air with 0.5 V bias

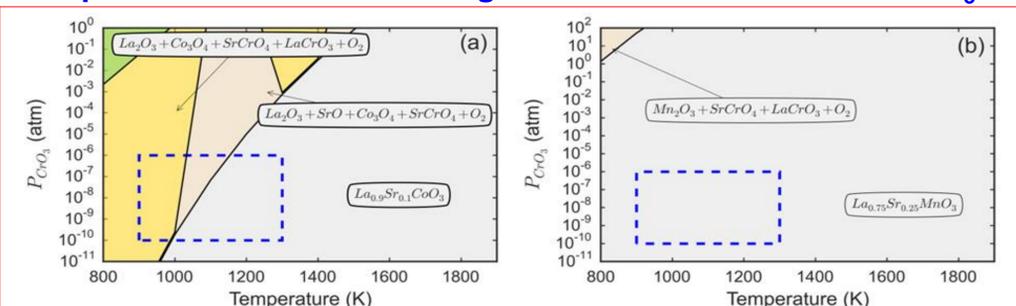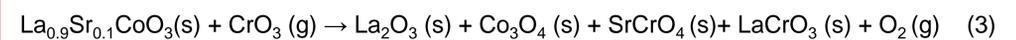## Comparisons of Reaction Energetics of LSM and LSC with CrO_3

Figure 6. Reaction energetics of stoichiometric of (a) $La_{0.9}Sr_{0.1}CoO_3$ (LSC) and (b) $L_{0.75}Sr_{0.25}MnO_3$ (LSM) with CrO_3. The blue dashed rectangle shows the experimentally relevant range of $PCrO_3$ and T.

LSM decompsotion Energy: $E_d = \min_{c_i}\{\sum_i c_i E_i\} - E_{(La,Sr)MnO_{3-\delta}} - \alpha E_{CrO_3} - \alpha\Delta\mu_{CrO_3}$ (1)

$La_{0.9}Sr_{0.1}CoO_3(s) + CrO_3 (g) \rightarrow La_2O_3 (s) + SrO (s) + Co_3O_4 (s) + SrCrO_4 (s) + O_2 (g)$ (2)

$La_{0.9}Sr_{0.1}CoO_3(s) + CrO_3 (g) \rightarrow La_2O_3 (s) + Co_3O_4 (s) + SrCrO_4 (s) + LaCrO_3 (s) + O_2 (g)$ (3)

➢ The bulk reaction energetic suggests that the stoichiometric LSM and CrO_3 (without O vacancy, $\delta = 0$) remains unreacted.
➢ Formation of $SrCrO_4$ and Co_3O_4 between LSC and CrO_3 are thermodynamically favorable at 750ºC and low Cr vapor pressure.

Degradation mechanisms

➢ Cr_2O_3 (Eq. 4) forms at LSM/YSZ interface in humidified air in presence of Cr. $CrO_3.CrO_2(OH)_2 (g) + 6 e- = Cr_2O_3 (s) + 3O^{2-}$ (ion)+ H_2O (g) (4)
➢ Formation of Cr_2O_3 at triple phase boundaries blocks oxygen reduction sites .
➢ Poor oxygen ion conductivity of LSM limits the oxygen reduction site near TPBs at interface.
➢ LSCF with excellent mixed conductivity extends oxygen reduction sites and improves cathode stability.

Figure 7. Schematic of the degradation mechanisms of LSM and LSCF cathodes in air containing H_2O and chromium vapor.

Conclusions

✓ LSM/YSZ/Pt half-cell exhibited a rapid decrease with time in an I-t curve while the LSCF/GDC/Pt half-cell only exhibited a slight decrease.
✓ Cr species deposited predominantly at LSM/YSZ interface whereas Cr deposited mainly at LSCF surface.
✓ Formation of $SrCrO_4$ as favored products for LSC whereas the LSM remains unreacted for a wide range of experimental CrO_3 partial pressures.

References

• B. Hu, M. K. Mahapatra, H. Zhang, P. Singh, J. Power Sources 268 (2014) 404-413.
• B. Hu, M. K. Mahapatra, M. Keane, P. Singh, J. Power Sources 248 (2014) 196-204.

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