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% H2O) using LSM/YSZ/Pl and LSM/GDC/Pl half-cells at 750°C. For the 100-hour tests, the electrochemical performance of the LSM/YSZ/Pl half-cell exhibited a rapid decrease with time in an I-t curve while the LSCF/GDC/Pl 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 SrCrO4 formation on the posttest LSM cathode but not on the posttest LSC 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 LSCM 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 PCrO4 and temperatures (T) while the formation of SrCrO4 was observed to be energetically favorable on LSC cathode for the experimental PCrO4-T range. Thus the calculations show excellent agreement with experimental results and the PCrO4-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 H2O (~3%), CO2 (~400 ppm), and SO2 (~0.3 ppm). Inlet air also contains chromium vapor species from balance of plant components (BoP) and metallic interconnects. Impurities namely H2O, CO2, SO2, and CrO 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)MnO3 and (La, Sr)CoO2 cathode materials in chromium species. 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:
750°C, Atmospheric air containing 3% H2O and chromium, and bias 0.5 V

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

Results and Discussion

Electrochemical performance

Figure 3. I-t and EIS plots of LSM/YSZ/Pl and LSM/GDC/Pl half cells at 750°C and 0.5 V bias in 3%H2/O-air containing Cr

Surface Morphologies & SrCrO4 Formation

Figure 4. SEM images (Left) and Raman spectra (Right) of post test LSM and LSCF cathodes exposed to Cr vapor for 100 hrs at 750°C in 3%H2O-air with 0.5 V bias

Morphologies & Compositions of Cathode/Electrolyte Interface

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 750°C in 3%H2O-air with 0.5 V bias

Comparisons of Reaction Energetics of LSM and LSC with CrO4

Figure 6. Reaction energetics of stoichiometric of (a) La0.8Sr0.2CoO4 (LSC) and (b) La0.7Sr0.3MnO3 (LSCM) with CrO4. The blue dashed rectangle shows the experimentally relevant range of PCrO4 and T.

Degradation mechanisms

CrO4 (Eq 4) forms at LSMSYS interface in humidified air in presence of Cr.
CrO4 forms at CrO4/LSM interface whereas Cr deposited mainly at LSCF surface.
Formation of SrCrO4 as favored product for LSC whereas the LSM remains unreacted for a wide range of experimental CrO4 partial pressures.

Conclusions

➢ LSM/YSZ/Pl half-cell exhibited a rapid decrease with time in an I-t curve while the LSCF/GDC/Pl half-cell only exhibited a slight decrease.
➢ Cr species deposited predominantly at LSMYSZ interface whereas Cr deposited mainly at LSCF surface.
➢ Formation of SrCrO4 as a favored product for the LSC whereas the LSM remains unreacted for a wide range of experimental CrO4 partial pressures.

References


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