



Full Length Article

Combined Cr and S poisoning behaviors of $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3 \pm \delta}$ and $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ cathodes in solid oxide fuel cells

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ABSTRACT

Although the individual effects of airborne Cr and S contaminants on SOFC cathode performance degradation have been extensively studied, the combined effects of Cr and S contaminants remain largely unexplored. Under the real SOFC operating condition where the Cr and S species coexist, their effects may compete, affecting the poisoning behavior. Our investigation reveals that the combined Cr and S poisoning behavior of LSCF remains different from those of individual Cr and S poisonings, while the combined poisoning mechanism of LSM is equivalent to the sum of those of individual Cr and S effects. For LSCF electrode, gaseous Cr species are deposited mainly at the LSCF/GDC interface by electrochemical reduction, rather than forming SrCrO_4 on LSCF surfaces (as in the case of Cr-only poisoning), indicating no reaction between Cr vapors and SrO on the LSCF surface. Thermodynamic analysis demonstrates that the SrO on LSCF surface absorbs SO_2 (g) and thereby loses the Cr-gettering effect, allowing Cr vapors to flow through LSCF and to reach the LSCF/GDC interface where the Cr deposition occurs. Unlike LSCF, LSM electrode shows cumulative effects of Cr and S, as Cr accumulation occurs at the triple-phase boundary and S absorption takes place at localized Sr-rich regions.

1. Introduction

Solid oxide fuel cells (SOFCs) have been recognized as promising candidates for next-generation power sources by offering high energy-conversion efficiency, fuel flexibility, modularity, and low pollutant emissions [1–4]. During the SOFC operation, the air-electrode is exposed to intrinsic and extrinsic airborne contaminants at high temperatures (600–900 °C), leading to their reaction with electrode materials, irreversible chemical and structural changes, and electrochemical performance degradation [5–7]. There are two most abundant and detrimental gas impurities that contaminate the air-electrodes: Cr vapors and sulfur dioxide (SO_2). It is well-known that Cr vapors, (e.g., $\text{CrO}_2(\text{OH})_2$), are generated from chromia scales (or Cr_2O_3) formed on metallic components such as balance-of-plant (BoP) subsystems for thermal management and air-handling as well as cell-to-cell interconnect (IC) and manifold in the cell stacks [8,9]. Airborne SO_2 , intrinsic to ambient air albeit low in concentration (75 ppb for the primary standard and 0.5 ppm for the secondary standard [10]), is also considered a major contaminant that affects the long term degradation of electrodes in irreversible manner [11,12].

$\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3 \pm \delta}$ (LSM) and $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ (LSCF) have been widely used as the most established air-electrode materials for

SOFC because of their high electronic and oxygen ionic conductivity, excellent oxygen reduction reaction (ORR) activity, and material compatibility with adjacent cell components during the fabrication and operation [13]. The major difference between LSM and LSCF cathodes is the ORR process as the oxygen reduction on LSM is mainly confined to triple-phase boundary (TPB; i.e., air/electrode/electrolyte) area, typically at high temperatures (800–1000 °C) [14,15], while the oxygen reduction on LSCF can occur at the two-phase interface (i.e., air/electrode) as well as TPB, allowing for lower temperature operation (600–800 °C) [16,17].

Cr and S poisoning of LSM and LSCF have been extensively studied [11,12,18–28], as summarized in Table S1. The electrode performance degradation mechanisms have been explained largely based on structural changes and secondary phase formation. LSM is susceptible to Cr poisoning since the Cr vapor deposition mainly occurs at the LSM/electrolyte interface by the reduction of Cr^{6+} to Cr^{3+} , blocking the active sites for ORR and increasing the cathodic polarization [28]. For LSCF, on the other hand, the electrode remains susceptible to SO_2 as the SrO segregated on the LSCF surface is prone to the formation of SrSO_4 , thereby reducing the active sites for ORR [12,29]. Thus, the long-term exposure of air-electrodes to ambient air flow containing traces of Cr and S species leads to contaminant accumulation at the

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