



Roles of humidity and cathodic current in chromium poisoning of Sr-doped LaMnO₃-based cathodes in solid oxide fuel cells



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HIGHLIGHTS

- Humidity promotes chromium poisoning and degradation of cathode performance.
- Current promotes chromium poisoning and degradation of cathode performance.
- Humidity promotes greater vaporization of Cr species from Crofer interconnect.
- Cr poisoning occurs via both chemical and electrochemical pathways.
- O₂(g) and Cr vapor oxide species have similar reduction potentials.

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ABSTRACT

Performance degradation of cathodes caused by chromium deposition and poisoning is one of the major challenges to overcome for long-term operation of solid oxide fuel cells (SOFCs). To fundamentally understand the mechanisms of the degradation phenomenon, it is necessary to investigate the roles of humidity and cathodic current in chromium poisoning.

In this study, anode-supported SOFCs, with Sr-doped LaMnO₃ (LSM) based cathode are employed. These cells are electrochemically tested at 800 °C with and without chromia-forming interconnect. On identical cells, different cathode atmospheres (dry air or 10% humidified air) and current conditions (no current or 0.75 A/cm² cathodic current) are imposed. It is found that both humidity and cathodic current promote chromium poisoning. Microstructural characterizations also confirmed that larger amounts of chromium-containing deposits are present at the cathode/electrolyte interfaces of the cell tested with cathodic current and/or humidity.

Free energy minimization calculations and thermogravimetric experiments are performed to determine the chromium vapor species that form over chromia-forming alloy interconnect and result in chromium deposition. Based on the experimental and computational results, the roles of humidity and cathodic current in chromium poisoning are evaluated, and a mechanism associated to chromium vapor species deposition at the cathode/electrolyte interface is proposed.

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1. Introduction

Solid oxide fuel cells (SOFCs) have gained renewed interest due to the new discovery of fossil fuel sources [1,2]. Compared with their counterparts, SOFCs are well known for high energy conversion efficiency, low greenhouse gases emission, and fuel

flexibility [3–7]. However, one of the greatest challenges for commercialization of SOFCs is performance degradation during long-term operation [8–13]. At intermediate temperatures (700–900 °C), chromium (Cr) vapor species that form over Fe–Cr alloy interconnect [14–16], can transport and deposit in the cathode and poison its performance [17–21]. Although extensive studies have been conducted, the mechanism of Cr-poisoning still needs to be clarified due to its dependence on many factors, such as operating temperature, current, humidity, and nature of

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electrode materials [22–26].

As a well-developed cathode material, Sr-doped LaMnO_3 (LSM) has been widely used for studying Cr-poisoning [27,28]. Hilpert et al. postulated that Cr vapor species can be electrochemically reduced and deposited at the triple phase boundaries (TPB's), which inhibits further oxygen reduction reaction occurring at the same TPB's [15]. Krumpelt et al. suggested a threshold potential of about 0.9 V for chromium oxyhydroxide reduction [29]. Jiang et al. proposed a nucleation theory which is based on chemical reduction of chromium vapor species facilitated by low oxygen partial pressures at cathode/electrolyte interface at high current densities [25]. Recently, Röhrens et al. proposed a combined chemical and electrochemical explanation for cathode performance degradation caused by Cr-poisoning [26]. Up until now, no studies are available which comprehensively evaluate the roles of humidity and cathodic current in Cr-poisoning.

In the present work, anode-supported SOFCs with LSM/yttria-stabilized zirconia (YSZ) and LSM bilayer cathode were fabricated and employed. In order to characterize and compare the performances of each cell before and after Cr-poisoning, the Cr vapor species were introduced in between the electrochemical measurements. This was done with the help of the experimental setup which allowed bringing the chromia-forming alloy (Crofer22APU) to the high temperature area near the SOFC cathode during the experiment. On identical cells, cathode atmosphere and current condition were varied to study the roles of humidity and cathodic current on cell performance in the presence of Cr vapor species. The Cr vapor species and the corresponding equilibrium cell potentials for their dissociation were determined using the results of free energy minimization calculations and thermogravimetric experiments. The roles of humidity and cathodic current in Cr-poisoning of LSM-based cathode are discussed.

2. Experimental

2.1. Cell fabrication

The cells used in the present work were comprised of 5 layers: anode substrate, anode interlayer, electrolyte, cathode active layer and cathode current collector layer. As-sintered cell structures, consisting of a Ni/8YSZ (8 mol% Y_2O_3 –92 mol% ZrO_2) anode substrate, a Ni/8YSZ anode interlayer and an 8YSZ electrolyte, were commercially purchased from Materials and Systems Research Inc. (Salt Lake City, UT). The approximate thicknesses of anode substrate, anode interlayer and electrolyte are 750 μm , 10 μm and 8 μm , respectively. The approximate area of anode (and electrolyte) was 7.3 cm^2 . Two layers of cathodes were screen printed over the electrolyte: cathode active layer (LSM/8YSZ composite) and cathode current collector (LSM) [30]. For the preparation of slurry for the cathode active layer, $(\text{La}_{0.8}\text{Sr}_{0.2})_{0.95}\text{MnO}_{3-\delta}$ (Fuel Cell Materials) and 8YSZ (Tosoh Corp.) powders were mixed in a 1:1 wt ratio and ball milled for 10 h in alpha-terpineol (Alfa Aesar) with the desired amount of pore former (Carbon lampblack, Fisher Scientific) and binder (V6, Heraeus). After screen printing the cathode active layer, the structure was sintered at 1200 $^\circ\text{C}$ for 2 h. Slurry for the cathode current collector was prepared by ball milling LSM powder with the desired amount of pore former (Carbon black, Fisher Scientific) and binder (V6, Heraeus) in alpha-terpineol for 24 h. Finally, after screen printing the cathode current collector layer, the structure was again sintered at 1200 $^\circ\text{C}$ for 2 h and the cell fabrication was completed. The approximate thicknesses of cathode active layer and cathode current collector layer were 30 μm and 50 μm , respectively; their porosities were approximately 35% and 50%, respectively. The approximate cathode area was 2 cm^2 . The schematic of the cell structure is shown in Fig. 1.

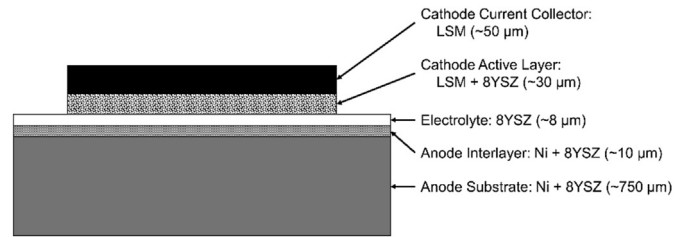


Fig. 1. Schematic of the cell structure.

2.2. Cell testing

Fig. 2 shows the schematic of the setup for cell testing. The cell test setup was comprised of two alumina tubes, with the cell sandwiched between them. A gold gasket (Scientific Instrument Services, Inc.) on the cathode side and a mica gasket (Fuel Cell Materials) on the anode side were used to seal and prevent direct contact between the cell and the ceramic tubes. Glass paste (Fuel Cell Store) was applied outside the tubes to ensure the gas tightness. Silver mesh (Fuel Cell Materials) was attached on the cathode with silver ink (Fuel Cell Materials) as cathode current collector, and nickel mesh (Alfa Aesar) was attached on the anode with nickel ink (Fuel Cell Materials) as anode current collector. Two silver wires (Alfa Aesar) on the cathode side and two nickel rods (Alfa Aesar) on the anode side were firmly pressed on the corresponding meshes, to ensure good contact on both sides. On each side, one wire/rod was used as a current lead, and the other as a voltage measuring lead. As a commonly used metallic interconnect material for studying Cr-poisoning, Crofer22APU was used as Cr source in this study. Commercially purchased Crofer22APU sheet (Fuel Cell Materials) was cut into strips with approximately 48 cm^2 total surface area. To eliminate the change of the Cr vaporization rate due to the growth of $(\text{Cr,Mn})_3\text{O}_4$ top layer [31–33], the Crofer22APU strips were preoxidized at 800 $^\circ\text{C}$ for more than 200 h. These strips were

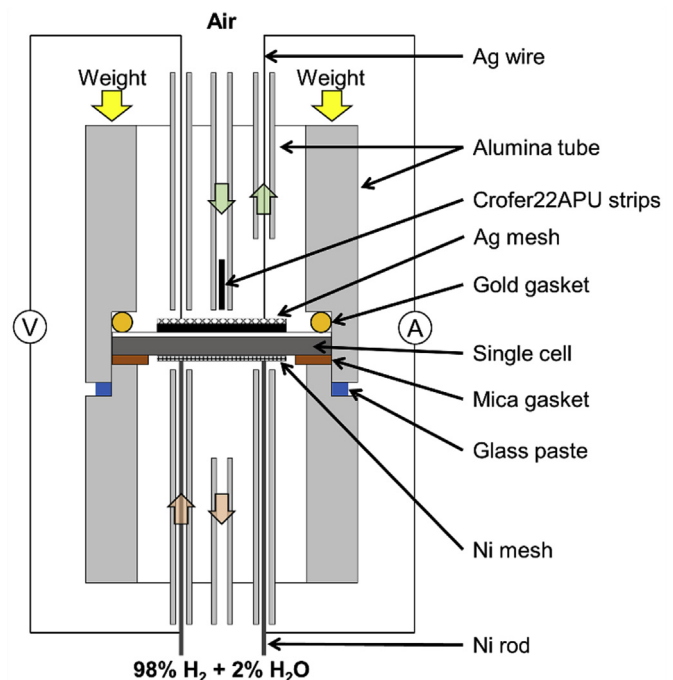


Fig. 2. A schematic of cell test setup.

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