

Multi-scale studies on the poisoning mechanism of lanthanum strontium cobalt ferrite in solid oxide fuel cell

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Solid oxide fuel cell (SOFC) is one of the most promising devices for electricity generation with high efficiency and environmental friendliness. Among various materials developed in SOFC, lanthanum strontium cobalt ferrite (LSCF) has been recognized as an attractive cathode material for intermediate-temperature SOFC due to its high mixed ionic/electronic conductivity and catalytic activity for oxygen reduction reaction. However, its poisoning from various sources, especially sulfur and chromium, is a critical issue in hindering the cell durability [1]. The first step in the poisoning is believed to be Sr segregation from A-site in the perovskite structure. However, the form of Sr (SrO, SrO₂, Sr(OH)₂, SrCO₃, etc) is still a disputed question [1-4]. The other secondary phases were usually detected by X-ray diffraction patterns and scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS). Very limited works have been conducted down to the atomic scale and many details remain unclear [5]. Herein, extensive investigation on the poisoning mechanism is carried out by using SEM, transmission electron microscopy (TEM) and scanning TEM (STEM) equipped with EDS and electron energy loss spectroscopy (EELS). TEM specimens are lifted out by using focused ion beam (FIB)-SEM.

In this study, the poisoning is conducted on both bulk and porous LSCF at a temperature of 700 °C. For a bulk sample annealed under dry air containing 0.01 ppm SO₂, the segregation of Sr-O rich phase is visualized directly by SEM-EDS with variable working voltages and further confirmed by STEM-EDS. EDS linescan exhibits that Sr becomes deficient near the surface. The segregation of Sr and Co(Fe) becomes heavier when the air is humid. Besides the as-reported Co-Fe spinel particles, Fe-Co core-shell ones and Fe distribution in part of a big Co particle are observed, which indicate that Fe diffuses out of CoFe₂O₄ or into Co₃O₄ during annealing.

After Cr poisoning, big SrCrO₄ particles with a monoclinic structure are formed on the surface of LSCF bulk. On the surface layer, elements of Sr and Co become deficient while La and Cr are excessive. These mean that Sr positions are occupied by La in the A-sites of perovskite structure and Cr substitutes Co on the B-sites [5]. A new phase, La-(Sr)-Cr-(Co)-Fe-O, forms and it keeps the same structure as bulk LSCF by judging from high-angle annular dark-field (HAADF) images. Fe valence is found to decrease.

Details including quantitative EDS and EELS will be presented. The microscopic results on porous LSCF electrodes without and with current loading will also be discussed.

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