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Long-term degradation of $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ IT-SOFC cathodes due to silicon poisoning

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ABSTRACT

The impact of silicon on the long-term stability of the intermediate temperature solid oxide fuel cell cathode material $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) was investigated during 2400 h at 700 °C. The area-specific resistance (ASR) of symmetric cells of LSCF on $Gd_{0.1}Ce_{0.9}O_{1.95-\delta}$ (GDC) was determined by electrochemical impedance spectroscopy (EIS) in ambient air without and with Si contamination of the electrodes. The ASR of the fresh LSCF electrode was $0.3\ \Omega\ cm^2$. During 1060 h without Si contamination, an increase in the cathode ASR by a factor of 4.5 was observed, which may be attributed to a decrease in the surface oxygen exchange coefficient of LSCF due to changes in the surface elemental composition. Subsequently, 10 nm thick silicon layers were sputtered onto the LSCF electrodes. This contamination resulted in a strong increase in the ASR by a factor of 5.9 during additional 1340 h at 700 °C. Post-test analyses by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) revealed that the degradation of the cathode is caused by the phase decomposition of LSCF within an approximately 50 nm thick surface region. A continuous La-Sr-silicate layer is formed in addition to isolated $(Co,Fe)_xO_y$ nanoparticles. In agreement with the changes in the shape of the impedance spectra, it is assumed that this impurity layer leads to limitations in the gas diffusion towards the electrode and/or oxygen adsorption on the surface of the electrode.

1. Introduction

Solid oxide fuel cells (SOFCs) are a means for the conversion of chemical energy into electrical energy with high efficiency and low emission of pollutants. In contrast to low temperature fuel cells such as polymer electrolyte membrane (PEM) fuel cells, SOFCs that are operated at 600–1000 °C can use a variety of fuels (methane and other hydrocarbons, syngas, biogas, etc.). In order to separate the fuel from the oxidant, glass or glass–ceramic seals are applied. Sealing materials are typically made of alkaline earth metal silicates, borosilicates or barium aluminosilicate glasses, which contain 20–70 mass-% SiO_2 [1]. Other Si-containing components in the SOFC system are metallic supports or interconnectors, as well as thermal insulation materials [2,3]. Under SOFC operating conditions, the cathode gas is usually ambient (humid) air. Thermodynamic data show that at 600–800 °C, $pO_2 = 0.21$ bar, and relative humidities of 20–90% significant amounts of the volatile Si-species $Si(OH)_4$ are formed in the cathode compartment from the above mentioned external Si-sources in the SOFC system [4–6]. In addition, silicon is frequently contained as an impurity in raw powders used for the fabrication of ceramic SOFC components [7–10]. However, the degradation of SOFC cathodes by silicon poisoning has so far been rarely investigated in comparison to the well-known chromium poisoning.

Yokokawa et al. [2] pointed out that typical intermediate temperature (IT-)SOFC cathode materials, such as Sr-containing perovskite-type oxides from the series $(La,Sr)(Co,Fe)O_{3-\delta}$, have a high affinity towards reaction with Si impurities due to the relatively high basicity of SrO and the relatively high acidity of SiO_2 or $Si(OH)_4$. These reactions lead to the formation of phases with higher thermodynamic stability (silicates, binary oxides) compared to the complex perovskite-type oxides. Previous studies showed that Si contaminations accumulate in the cathodes of SOFC stacks over time [3] and can cause a severe degradation of $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) [7,11–14] and similar SOFC cathode materials [15–17]. Analyses that were performed on dense Si-poisoned LSCF samples indicated that a reaction of Si with the cathode surface occurs in an approximately 20 nm thick layer [18].

In the present work, long-term tests are performed on porous LSCF cathodes by electrochemical impedance spectroscopy (EIS) at 700 °C in ambient air without and with Si contamination. The impedance spectra are analysed with respect to the impact of Si-poisoning on the cathode ASR and the kinetic parameters for oxygen exchange. The changes in the surface microstructure and phase composition of the Si-poisoned LSCF electrode are investigated with scanning electron

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microscopy (SEM) and analytical transmission electron microscopy (TEM) in order to obtain further insight into the long-term degradation.

2. Experimental details

A symmetric cell with porous $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) electrodes was prepared on a dense $Gd_{0.1}Ce_{0.9}O_{1.95-\delta}$ (GDC) tablet. The LSCF paste was provided by Fraunhofer IKTS (Dresden, Germany). The GDC solid electrolyte substrate (14.8 mm diameter, 1.787 mm thickness) was supplied by Treibacher Industrie AG (Althofen, Austria). The electrodes were deposited by screen printing and covered both circular surfaces of the substrate. Sintering was performed at 1150 °C for 2 h in ambient air. Heating and cooling rates were 5 K/min. The thickness of the sintered LSCF electrodes was approximately 30 μm. X-ray diffraction (XRD) of the sintered LSCF layer on the GDC substrate was performed with CuK_α radiation by use of an AXS D8 Advance diffractometer (Bruker) operated at 40 kV and 40 mA.

The ASR of the symmetric cell LSCF|GDC|LSCF was investigated by electrochemical impedance spectroscopy (EIS) using an Alpha A-Impedance Analyzer (Novocontrol). Measurements were performed with an ac-voltage of 20 mV in the frequency range 3 MHz–0.1 mHz. The symmetric cell was contacted by two Pt-sheets by light spring force in a sample holder, which was placed in a tube furnace. The temperature was measured close to the sample by use of an S-type thermocouple. The software ZView® (Scribner Associates) was applied for equivalent circuit modelling of the impedance data. The cathode ASR was measured as a function of temperature in the range 500–700 °C in ambient air. In order to simulate the contamination of the cathode with silicon under well-defined conditions during long-term in-situ measurements, 10 nm thick Si-layers were sputtered onto both LSCF electrodes using a MED 020 high vacuum coating system (Bal-Tec) and a 99.999% purity silicon target (Goodfellow Cambridge Limited).

The surface microstructure and the elemental composition of fresh and degraded samples were investigated by scanning electron microscopy (SEM) with energy-dispersive X-ray spectroscopy (EDXS) using an Ultra 55 electron microscope (Zeiss) with an EDAX Phoenix detector. For the analysis of Si impurities, wave length dispersive spectroscopy (WDXS) was applied using an EDAX TEX detector. For SEM analyses, an accelerating voltage of 5 kV was used. EDXS and WDXS analyses were performed with an accelerating voltage of 12 kV. For cross-sectional SEM images, the cell was cut with a diamond wire saw, embedded in cold-curing resin, ground with SiC paper and polished with diamond suspensions with particle sizes down to 1 μm. The microstructure of the cross section was investigated with a Zeiss EVO 50 SEM equipped with a LaB_6 cathode.

Samples for transmission electron microscopy (TEM) were prepared by focused ion beam milling (FIB) with a Nova 200 instrument equipped with a field emission gun (FEI). TEM lamellae were prepared from the surface-near region of the LSCF cathode and the interface LSCF/GDC, respectively. Analytical TEM was performed with a $Titan^3$ 60–300 transmission electron microscope (FEI) equipped with a C_S-corrector (spherical aberration) for the probe. Images and spectra were recorded at 300 kV. Different phases were analysed by Z-contrast images, which were obtained in the scanning transmission electron microscopy–high angle annular dark field mode (STEM-HAADF). Elemental distribution maps were acquired by EDXS and electron energy loss spectroscopy (EELS) in the STEM mode via spectrum imaging (with a step size of about 5 nm). EELS measurements were done with a high-end post-column electron energy filter with a fast electrostatic shutter (GIF Quantum ERS™ from Gatan Inc.) and EDXS measurements with a high-sensitivity SDD X-ray spectrometer (Super-X).

3. Results and discussion

XRD of the fresh symmetric cell confirmed the phase purity of the sintered electrodes. The spectrum showed only the reflections of LSCF (perovskite structure) and the underlying GDC electrolyte substrate (fluorite structure), compare Fig. 1S (Supplementary material). SEM analyses of the fresh LSCF surface showed a porous microstructure (Fig. 1a). According to EDXS elemental distribution maps (not shown), the elements La, Sr, Co, Fe and O are homogeneously distributed. Fig. 2Sa (Supplementary material) shows an overview EDX spectrum from the surface of a fresh LSCF electrode. No impurity elements were found in the fresh sample.

The ASR of the fresh symmetric cell LSCF|GDC|LSCF was measured as a function of temperature in ambient air in the range 500–700 °C (Fig. 2). At 700 °C, the ASR was 0.3 Ω cm^2. The activation energy was 1.61 ± 0.01 eV (155 ± 1 kJ/mol). Selected impedance spectra of the fresh symmetric cell are shown in Fig. 3a and Fig. 4Sa–c (Supplementary material). The impedance spectra could be described by an equivalent circuit including a Gerischer element for the response of the porous mixed conducting LSCF electrodes. The Gerischer impedance is commonly defined by the following equation [19]:

$$Z(\omega) = \frac{Z_0}{\sqrt{K_a + j\omega}} \tag{1}$$

where Z is the complex impedance, Ω is the circular frequency, K_a stands for the effective transfer rate of the chemical reaction, and $j = \sqrt{-1}$. An alternative formulation which is equivalent to Eq. (1) was provided by Adler [20,21]

$$Z(\omega) = \frac{R_{\text{chem}}}{\sqrt{1 + j\omega t_{\text{chem}}}} \tag{2}$$

where R_{chem} is the polarisation resistance and t_{chem} is a characteristic time constant.

After the temperature run, the ASR of the symmetric cell was measured as a function of time at 700 °C in ambient air (Fig. 4). In the fresh state, the ASR of the cathode was 0.3 Ω cm^2. During 1060 h at 700 °C in ambient air without Si contamination, the cathode ASR

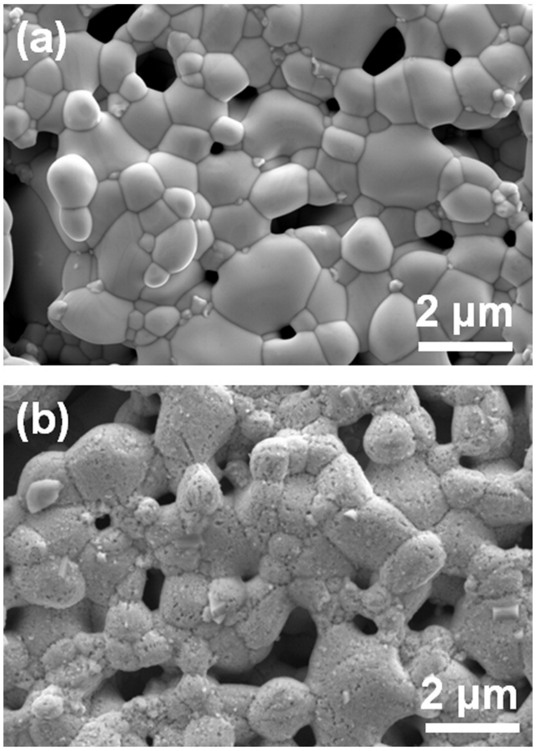

Fig. 1. SEM images of (a) the fresh and (b) the degraded LSCF electrode surface; image (b) was obtained after 1340 h of testing under Si-poisoning conditions at 700 °C.

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