



Sulphur poisoning of solid oxide electrolysis cell anodes

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ARTICLE INFO

Article history:

Received 18 September 2017

Received in revised form

12 February 2018

Accepted 26 February 2018

Available online 2 March 2018

Keywords:

Solid oxide electrolysis cell

Anode

LSM

Sulphur poisoning

Electrocatalytic performance

ABSTRACT

Sulphur poisoning for state-of-the-art $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3-\delta}$ (LSM) anodes of solid oxide electrolysis cell (SOEC) was studied under anodic current of 200 mA/cm^2 in 1 ppm SO_2 air. After polarization in 1 ppm SO_2 -containing air at 800°C for 40 h, electrode polarization resistance as well as ohmic resistance of LSM electrodes were measured $24.83 \Omega \text{ cm}^2$ and $6.09 \Omega \text{ cm}^2$, which were around 4 as well as 3 times than initial values of LSM electrodes. Sulphur deposition prefers to take place at the LSM/YSZ interface and inner layer for LSM electrodes, leading to the formation of SrSO_4 compounds, which is confirmed by XRD and then leads to the microstructural change of the LSM electrodes. The anodic polarization promotes the SrO segregation, which is supported by the observation of the deposition of SrSO_4 compounds, accelerating LSM electrodes delamination. The results indicate the obvious poisoning effect for sulphur species of electrochemical activity as well as stability of SOEC electrodes.

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1. Introduction

Recent years, people have paid much attention to develop efficient and environmental friendly methods to produce power as well as store energy [1]. Solid oxide electrolysis cell (SOEC) is one kind of excellent electrochemical devices that can generate fuels H_2 or syngas ($\text{H}_2 + \text{CO}$) from H_2O as well as CO_2 , which can meet the demand of energy crisis in the current society [1–4]. SOEC operating at temperatures of $700\text{--}1000^\circ\text{C}$ can be quite efficient due to the partial energy supplied by heat. $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3-\delta}$ (LSM) electrodes [5] are the most commonly used anodes for oxygen evolution reaction (OER) of SOEC due to their high electronic conductivities, good catalytic activities, compatibility with yttria-stabilized zirconia (YSZ) electrolytes, which are the same as solid oxide fuel cell (SOFC) cathode materials.

However, the durability of SOECs is limited by the obvious degradation of the cell, especially the decay for oxygen electrodes under high currents [6–9]. The delamination between oxygen electrodes and electrolyte interface can often be observed [10]. LSM electrodes' delamination occurred due to the formation of nanoparticles at the interface as well as LSM particles disintegration [11]. Moreover, some impurities like chromium from interconnects and boron from glass can have a severe impact on the degradation of electrode materials under both SOFC and SOEC conditions [12–17]. For instance, Cr poisoning of (La, Sr)Co-based and LSM electrodes under SOFC has been widely investigated [18–28]. One of the most acceptable mechanisms is that segregated SrO played an important role in Cr deposition for $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF) electrodes. However, there are fewer studies on the impurities poisoning of SOEC, compared to many reported works on SOFC. Wei et al. [29] studied that LSCF electrode exhibited significant degradation for OER at 800°C after Cr poisoning. It clearly showed that SrCrO_4 , $\text{CrO}_{2.5}$ as well as Cr_2O_3 were deposited on LSCF electrode surface, which were correlated to segregated SrO under anodic current condition. Moreover, Chen et al. [30] studied that LSM particles disintegrated and nanoparticles formed quickly in Cr containing alloy. Chromium deposition can take place in the LSM electrode,

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YSZ surface as well as inner surface of LSM electrode. Cr deposition was controlled by the reaction among chromium as well as segregated SrO.

There are some recent studies that have indicated ppb level of sulphur could poison SOFC electrode materials [31–40]. Kishimoto et al. [41] studied that sulphur poisoning for LSCF was influenced by the concentration of sulphur dioxide as well as temperature. We did systematic studies on sulphur poisoning for LSM and LSCF in SO₂-containing air under SOFC condition [33,42]. One of the most important results was that sulphur deposition exhibited a strong dependence on the operating temperatures, which meant that sulphur poisoning of LSCF and LSM was most severe at lower temperature (700 °C) than 800 °C. Another essential result was that sulphur deposition at both LSCF and LSM electrodes was most likely determined by the chemical reaction between sulphur gas as well as segregated strontium oxides. For LSM electrodes, sulphur deposition and poisoning was not reversible due to the formation of SrSO₄, which accelerated the Sr segregation as well as depleted the content of strontium on the A-site of LSM.

Up to now, the impact of sulphur impurity degradation on the oxygen electrode used in SOECs and its potential mechanisms have not been investigated extensively. Recently, Kushi et al. [43] did some study on the effect of sulphur poisoning on degradation phenomena of La_{0.6}Sr_{0.4}CoO_{3-δ} (LSC) electrodes in SOEC and SOFC, who reached the conclusion that SrSO₄ distributed both at the electrolyte/anode interface and within LSC bulk under SOEC, by contrary, SrSO₄ was observed in the bulk of LSC during SOFC operation. This is mainly due to the reason that higher oxygen potential at the interface strongly accelerated the formation of SrSO₄ under SOEC condition. In this paper, sulphur poisoning and deposition on LSM anodes under operating temperature of 800 °C was investigated. The effect of SO₂ on the electrochemical activity as well as stability of LSM electrode was studied under the accelerated condition. All the results showed that SO₂ could poison the electrochemical activity for LSM by forming SrSO₄ on LSM/YSZ interface region, inner and outer surface of LSM electrodes.

2. Experimental

2.1. Cell preparation

Electrolytes Y₂O₃-ZrO₂ (YSZ) was purchased from Tosoh Company. YSZ pellets (20 mm diameter, 0.5–0.9 mm thickness) were sintered at 1450 °C for 5 h. La_{0.8}Sr_{0.2}MnO₃ powders purchased from Fuel Cell Materials Company were added by organic inks to form electrode slurries and were painted on the center of YSZ pellets with the geometric area of 0.5 cm² and the thickness for LSM electrodes was around 20 μm. LSM electrodes were fired for 2 h at 1100 °C.

Pt counter electrodes (Gwent Electronic Materials Ltd, UK) were fired on the opposite surface of YSZ electrolytes. Pt ring as reference electrodes were painted on the edge of YSZ electrolytes. The cell was sealed by glass on the anode side to prevent SO₂ leakage. Dry SO₂ containing air (100 mL min⁻¹) with 1 ppm SO₂ was offered to anode for cell tests. The detailed information of cell arrangement can be found in our previous published paper [33,42].

2.2. Electrochemical tests

Polarization activity as well as electrochemical impedance were tested at 800 °C by Gamry Reference 3000 Potentiostat on a three-electrode cell. Impedance results data were collected between 0.1 Hz and 100 kHz under open-circuit conditions. Moreover, testing amplitude was 10 mV. Electrodes were initially kept stable in the ambient atmosphere before introducing SO₂. Ohmic

resistances (R_{Ω}) were collected according to the intercept of high frequency. Electrode polarization resistances (R_E) were then collected between high as well as low frequency intercept differences. The cell was also tested without 1 ppm SO₂ under the same testing condition mentioned above.

2.3. Cell characterization

The phase identification of LSM electrodes before and after poisoning tests were tested through X-ray powder diffraction (XRD) and Eva software from Bruker D8 Advances. SEM as well as EDX from NEON 40 EsB were also used to identify the microstructural change before and after poisoning. X-ray photoelectron spectroscopy (XPS) was tested by ESCALAB 250Xi instrument from Thermo Fisher.

3. Results and discussions

3.1. Electrocatalytic activity

Fig. 1 shows polarization as well as impedance curves for LSM electrode after anodic current for 200 mA cm⁻² in SO₂-free air at 800 °C for 24 h. It can be clearly seen from Fig. 1a that the overpotential was initially around 0.38 V and it changed to 0.3 V after being polarized for 24 h, which indicates that the oxygen evolution reaction activity of LSM oxygen electrode was nearly stable with the polarization time. Moreover, according to the impedance spectra result (Fig. 1b), electrode polarization resistances (R_E) of LSM oxygen electrodes changed obviously with the anodic polarization time, especially in the first 4 h. R_E was initially 7.6 Ω cm² and then increased significantly to 35 Ω cm² after 30 min, followed by the decrease to 22.5 Ω cm² after being polarized for 4 h. Moreover, R_E gradually decreased to 14.8 Ω cm² after polarized for 24 h. It indicates that the electrocatalytic activity deterioration can be partially recovered by increasing the polarization time, which was similar with the previous results reported by Chen et al. [12], who got the conclusion that R_E can be quite stable after being anodic polarized at 50 and 200 mA cm⁻² under the same experimental testing condition. R_{Ω} was also relatively stable and there was no obvious delamination after polarized at 200 mA cm⁻² for 24 h at 800 °C.

The presence of 1 ppm SO₂ can lead to the difference of the polarization as well as the impedance behaviour for LSM oxygen electrodes of oxygen evolution reaction at 800 °C. Fig. 2 shows the polarization and impedance results of LSM electrodes after being polarized under 200 mA cm⁻² in 1 ppm SO₂-containing air at 800 °C for 20 h. The overpotential was initially 0.38 V and it changed regularly with the anodic polarization time from 4 h to 20 h, and then it finally reached to around 0.4 V after being polarized for 24 h, which indicates that the oxygen evolution reaction (OER) activity of LSM oxygen electrode was affected by sulphur dioxide. As shown in Fig. 2b, in 1 ppm SO₂-containing air, the impedance spectra for LSM electrodes were identified by a depressed arc. R_E was initially 7.28 Ω cm² and then increased rapidly to 25.95 Ω cm² in the first 4 h, and finally achieved to 27.47 Ω cm² after being polarized for 20 h. The change was observed in the low frequency side. It indicates that the LSM electrode as well as YSZ electrolyte had poor interface contact, leading to the obvious electrochemical activity loss and the increase of R_E of LSM electrode. Moreover, R_{Ω} increased from 1.3 Ω cm² to 1.46 Ω cm² under the same situation. All these results can clearly illustrate that sulphur dioxide could lead to significant poisoning of LSM oxygen electrodes during the whole test.

After extending sulphur poisoning time to 40 h under the same experimental condition mentioned above, it can be seen from Fig. 3

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