

X-ray photoelectron spectroscopy of $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$

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Abstract

Cathode electrode for solid oxide fuel cells (SOFC) consisting of strontium-doped lanthanum manganite ($\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$; LSM) was prepared with a modified sol–gel process. Its surface chemical composition was studied by X-ray photoelectron spectroscopy (XPS). As prepared LSM, the oxidation state of Mn ions is +3.5, which is consistent with oxidation state calculated from the chemical formula. The ratio of La, Sr and Mn ions is about 1/1.1/2. After the sample was heated in ultrahigh vacuum (UHV) chamber with oxygen partial pressure of 10^{-6} mbar at 600 °C for about 3 h, the oxidation state of Mn ions decreases from +3.5 to +3.3 probably due to the generation of oxygen vacancy on the surface. A little Sr-rich phase was formed on the surface due to the formation of SrO.

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1. Introduction

Currently, $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ is commonly used as the SOFC cathode material because of its high catalytic activity for oxygen reduction reaction (ORR) and thermal and chemical compatibility with yttria-stabilized zirconia (YSZ) [1]. The main function of the SOFC cathode electrode is to provide reaction sites for the electrochemical reduction of oxygen. Thus, the understanding of the active sites for ORR is important to find out the reaction processes and mechanisms. Electrocatalysts and ion transport properties of the cathodes mostly rely on the adsorption and diffusion of oxygen. The rate at which oxygen is adsorbed from the ambient environment depends strongly on the structure and composition of the outermost surface of the oxides [2]. The structure and composition of the surface may, however, differ from that of the bulk. Better understanding of the surface properties of these cathode materials is thus essential. Most of earlier

works on this material are focused on the electrochemical properties [1,3]. Few works have been done from the point view of surface science. The surface reactive sites of SOFC cathode materials for ORR are still unknown. In this communication, the surface composition and change of oxidation state of the elements in LSM are investigated in order to better understand the surface active sites for ORR.

2. Experimental

$\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ powder was prepared using a glycine–nitrate process with precursors of $\text{La}(\text{NO}_3)_3$, $\text{Sr}(\text{NO}_3)_2$, $\text{Mn}(\text{NO}_3)_2$, and glycine [3]. The powder was fired at 800 °C for 4 h in the air to form the perovskite structure as confirmed by X-ray diffraction (PW 1800). For the purpose of easier handling, the resulting powders were mixed with a PVB binder solution and pressed at 4 tons to form 1-cm diameter pellets. The pellets were then sintered for 5 h at 1000 °C in the air. XPS measurements were carried out in a multichamber UHV system combining different in-situ preparation techniques connected to a transfer chamber with the surface analysis

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system (Phi 5700). The basic pressure during the measurements is better than 10^{-9} mbar. Al $K\alpha$ radiation ($h\nu=1486.6$ eV) from a monochromatized X-ray source was used for XPS measurements. All the binding energies are referenced to the Fermi energy (E_F).

The intensity ratio among La, Sr, and Mn was calculated as

$$R_{1,2} = \frac{I_1/A_1}{I_2/A_2} \quad (1)$$

where I is the intensity taken from the XP spectrum after background correction, and A is atomic sensitivity factors.

3. Results and discussions

Fig. 1 shows the survey XP spectrum of LSM. Only La, Sr, Mn, and O elements are observed on the sample surface. No additional lines related to the contaminations were detected. The O1s core level XP spectra of LSM are shown in Fig. 2. One main emission line is detected accompanied by a small but broad shoulder peak on the spectrum Fig. 2a. The binding energies are determined as 529.5 and 531.0 eV, respectively. According to their binding energy, the main line is assigned to O^{2-} ion of the metal oxide [4], while the broad shoulder peak is probably due to the water and hydroxide absorbed on the surface [5,6]. It is worth noting that after the sample was heated at 600 °C in UHV chamber for about 3 h, the intensity of the shoulder peak decreases dramatically due to the evaporation of the water and the hydroxide species (see Fig. 2b). But a smaller shoulder peak appeared at even higher binding energy. The binding energy shift of the shoulder peak suggests that the nature of the shoulder peak has changed. The surface should be cleared from the water and other hydroxide species after annealing in UHV chamber at 600 °C for quite a long time. Liang and Weng [7], who studied the $La_{0.3}Sr_{0.7}MnO_3$ and related compounds, have attributed the peak at 531.6 eV to surface oxygen associated Sr. Similar spectra have been found for other substituted ABO_3 compounds [8,9]. Therefore, we could effectively assume that the contribution of shoulder

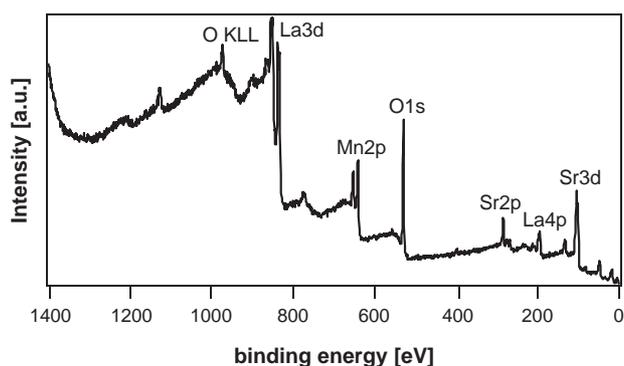


Fig. 1. The survey XP spectrum of LSM.

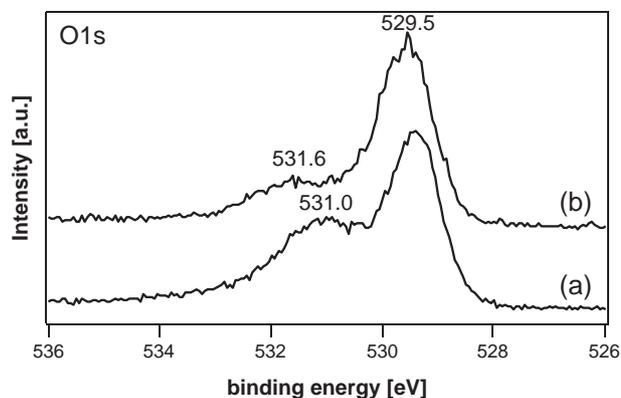


Fig. 2. The O1s core level XP spectra of LSM, (a) as prepared, (b) after heated in UHV chamber with oxygen partial pressure of 10^{-6} mbar at 600 °C for about 3 h.

peak at 531.6 eV is mainly from the Sr oxide, which will be further confirmed by the Sr3d emission.

The Sr3d XP spectra, as shown in Fig. 3, contain a doublet, whose binding energies are 132.8 and 134.6 eV, which can be assigned as $Sr3d_{5/2}$ and $Sr3d_{3/2}$ lines, respectively. Their binding energies are very close the similar compounds [10], which can be contributed to the Sr^{2+} ions in LSM. After annealing at 600 °C, a shoulder peak grows up at about 135.2 eV in spectrum Fig. 3b. It is known that the binding energy of Sr ions in SrO is about 135.0 eV [11]. It is believable that the shoulder peak at 135.2 eV has originated from SrO due to the heating treatment at high temperature. The binding energies of Sr3d main lines for Sr ions in LSM do not change before and after heating treatment. In Fig. 4, the La3d states of LSM are shown. It is well-known that the La3d states in the XP spectra are split not only due to a spin-orbit interaction into two lines $3d_{5/2}$ and $3d_{3/2}$, but additionally, each line is split due to a transfer of an electron from oxygen ligands to the

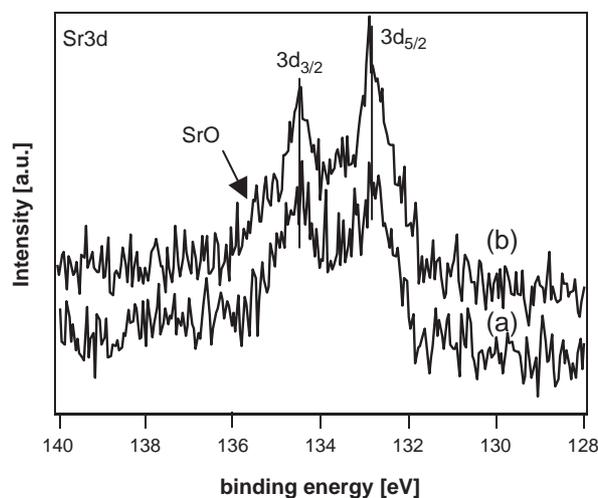


Fig. 3. The Sr3d core level XP spectra of LSM, (a) as prepared, (b) after heating treatment.

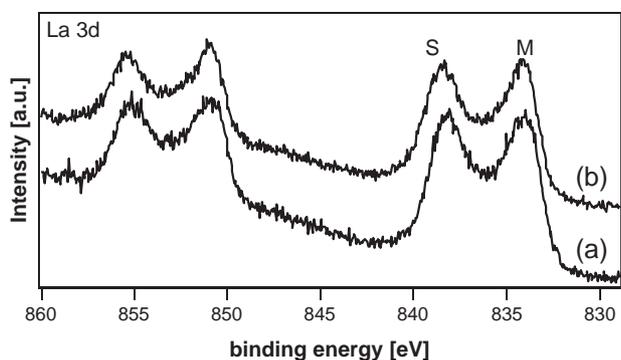


Fig. 4. The La3d core level XP spectra of LSM, (a) as prepared, (b) after heating treatment.

La4f (initially empty) [12]. The La3d line has a main line M (ascribed to $3d^9 4f^0$) and a satellite line S (ascribed to a charge transfer $3d^9 4f^1 L$, here L represents the hole in a ligand site) at higher binding energy. The corresponding binding energy of La3d_{5/2} is 834.1 eV [13]. Energy difference between the 3d_{3/2} and 3d_{5/2} levels is approximately equal to 17 eV. The binding energies and the multiplet splitting agree well with reported values for La³⁺ compounds [13–15]. It is noted the binding energies of La3d do not also change before and after heating treatment in UHV chamber.

Fig. 5 shows the Mn2p XP spectra of LSM. They display a broad emission line with a maximum near at 642.4 eV for Mn2p_{3/2} emission. The interpretation of the Mn2p spectrum is complicated due to the multiple splitting of the Mn2p spectra of Mn⁴⁺, Mn³⁺, and Mn²⁺ ions [16]. Gupta and Sen [17] calculated the multiplet structure of Mn⁴⁺, Mn³⁺, and Mn²⁺ free ions and demonstrated that the Mn2p_{3/2} spectrum of the each single oxidation state consists of four or five multiplet emission lines separated from each other by 0.7–1.2 eV. For this reason, the Mn2p XP spectrum cannot be easily analyzed by a simple fitting procedure concerning the contribution of Mn²⁺, Mn³⁺, and Mn⁴⁺ compounds [16], so that the exact oxidation state of Mn ions is difficult to calculate from Mn2p spectra. But according to the binding energy of Mn2p_{3/2}, the oxidation state of Mn ions is

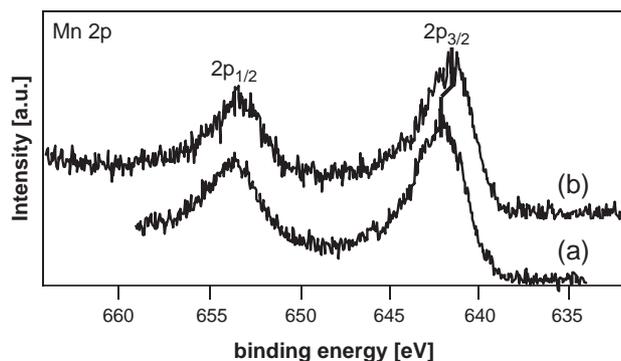


Fig. 5. The Mn2p core level XP spectra of LSM, (a) as prepared, (b) after heating treatment.

between +3 and +4. A slight lower binding energy shift is found for Mn2p after heating treatment (see Fig. 5b). The decrease in the binding energy of the core level (chemical shift) usually indicates a decrease in the positive charge of the transition metal ions. The cation ratio among La, Sr, and Mn is calculated from the background corrected La3d, Sr3d, and Mn2p core level XP spectra according to Eq. (1). A value of 1/1.1/2 is obtained for as prepared LSM, and 1/1.2/2 is obtained for the LSM after heating treatment. The results support that the surface is a little bit Sr rich due to the formation of SrO after heating treatment.

The 3s core levels of the 3d transition metals are known to exhibit exchange splitting due to the interaction between the 3s core hole created in a XPS process and 3d electrons [18]. The splitting magnitude of Mn3s XP spectra strongly depends on the valence state of the Mn ions. There is almost 0.8–1.0 eV difference between the binding energy of the 3s level of Mn²⁺ and that of Mn³⁺ and also about 0.8–1.0 eV between Mn³⁺ and that of Mn⁴⁺ [19,20]. The multiple splitting is larger for Mn³⁺ than for Mn⁴⁺. This results from the different energies of the charge transfer processes. The expected splitting of the 3s level is about 6.5 for Mn²⁺, 5.5 for Mn³⁺ and 4.5 for Mn⁴⁺ [21]. From the spectra in Fig. 6a, the binding energy of the 3s level is determined to be 84.2 eV and the 3s(1)–3s(2) splitting is about 5.0 eV, which is on the middle between that of Mn³⁺ (5.5eV) and Mn⁴⁺ (4.5eV). Thus a formal oxidation state of +3.5 for the Mn ions in LSM is found. After the sample was heated in UHV chamber, the Mn3s is observed to shift to lower binding energy, and the splitting energy increases from 5.0 to 5.2 eV, which implies that general oxidation state of Mn ions decreases from +3.5 to +3.3. The result is consistent with that found on Mn2p lines. The Mn ions are slightly reduced after heated in UHV chamber probably due to the formation of oxygen vacancy on the surface, which is similar to that of iron ions in LSF [22]. The removal of the originally

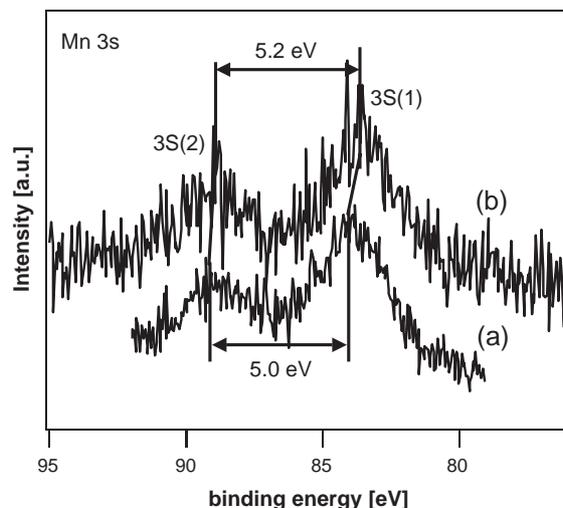
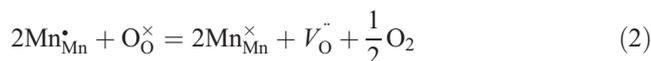


Fig. 6. The Mn3s core level XP spectra of LSM, (a) as prepared, (b) after heating treatment.

negatively charged oxygen ion as neutral species leads to the reduction of the nearest neighbour transition metal ions,



4. Conclusions

The LSM cathode electrode for SOFC prepared by a modified sol–gel process has been studied by XPS. XPS results show that Mn ions are in +3.5, Sr ions are in +2, and La ions are in +3 oxidation state for as prepared LSM. A small amount of SrO was found on the LSM surface after heating treatment in UHV chamber at 600 °C. Simultaneously, Mn ions are slightly reduced from +3.5 to +3.3 probably due to the generation of oxygen vacancy on the surface during heating treatment in UHV chamber. These results suggest that surface transition metal (Mn) ions are the active sites for oxygen reactions.

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