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Extended Abstract

Gas Sensing Mechanism Investigation of $LaFeO_3$ Perovskite-Type Oxides via Operando Technique †

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1. Summary

Gas sensor based on perovskites, such as $LaFeO_3$ (LFO), have been used successfully to detect various target gases [1,2]. Despite the importance of understanding the underlying mechanism for future development of gas sensing materials, there is only little known on their gas sensing mechanism. Here, we investigated the gas sensing mechanism during ethylene and CO_2 exposure under operando conditions. The changes in the active sites at the surface, which are responsible for the gas response, have been observed. Our work has demonstrated a correlation between the gas sensing behaviour of LFO material and the changes in its surface chemistry during gas exposure in operando conditions. This work aims to gain more insight into the underlying mechanism.

2. Experimental Results

IR spectra of LFO sensor have been obtained through a series of Operando diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) experiments. This in operando technique combined with measurements of the resistance change of the sensor during the gas exposures which deliver significant information about the chemistry change on the surface and thus helps to interpret the gas sensing mechanism.

The DRIFTS spectra and DC resistance results of LFO sensor exposed to different ethylene concentration in dry condition at 200 °C are shown in Figure 1. The spectra were referenced to the spectra which were recorded in dry air. As the gas concentration is increasing, a systematic increase in the resistance can be observed in correlation with changes of some bands in the IR spectra. After the end of gas exposure, the change in the resistance and the spectra features started to decrease with time back to the original state, as shown in Figure 2. The recovery speed for the surface species is correlated to the changes of the resistance. Isotope labeling exchange experiments combined with experiments performed in N_2 backgrounds have been used for interpreting the spectra: The bands at 2953 and 2851 cm^{-1} together with 1580 and 1373 cm^{-1} could be assigned to formats. The highest intensity band at 1580 cm^{-1} is considered to have two components, one that refers to formates and another to carbonates. Spectra for the LFO sensor exposed to 500 ppm C_2H_4 and CO_2, separately, in dry conditions at 200 °C and 250 °C are shown in Figure 3 and 4 respectively. The sensor only showed a good response to ethylene at 200 °C whereas no responses have been observed to CO_2 at both temperatures.

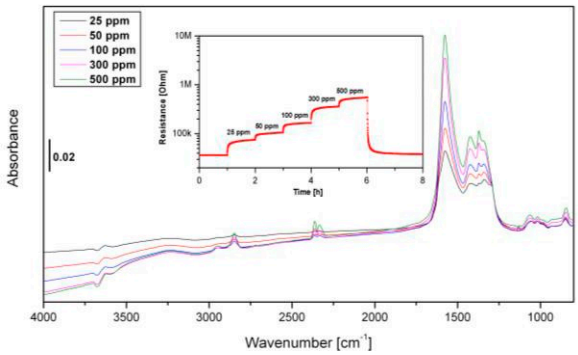

Figure 1. Drifts spectra of LFO sensor exposed to 25, 50, 100, 300 and 500 ppm C_2H_4 in dry air conditions at 200 °C. All spectra were referenced to the dry air spectrum measured prior to C_2H_4 exposure. Inset figure shows the DC resistance measurement.

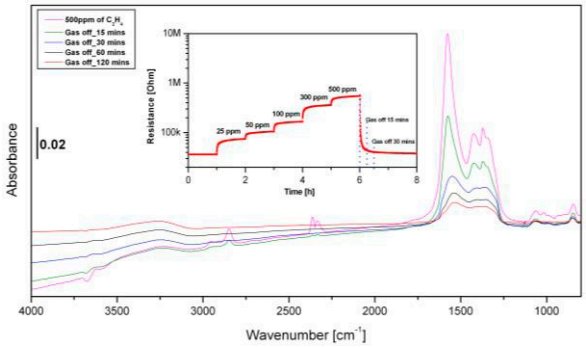

Figure 2. Drifts spectra of LFO sensor exposed to 500 ppm C_2H_4 in dry air followed by clean dry air for 15, 30, 60 and 120 min at 200 °C. All spectra were referenced to the dry air spectrum measured prior to C_2H_4 exposure. The inset figure shows the DC resistance.

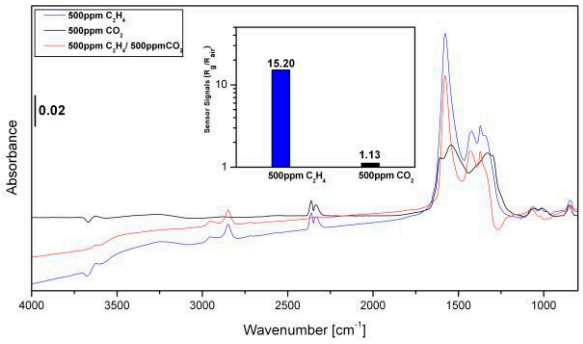

Figure 3. Drifts spectra of LFO sensor exposed to 500 ppm C_2H_4 (blue line) and CO_2 (black line) in dry conditions at 200 °C. All spectra were referenced to the dry air spectrum measured prior to C_2H_4 exposure, except for the C_2H_4 spectrum (red line) which was referenced to CO_2. The inset figure shows the sensor signals of C_2H_4 and CO_2 in same conditions.

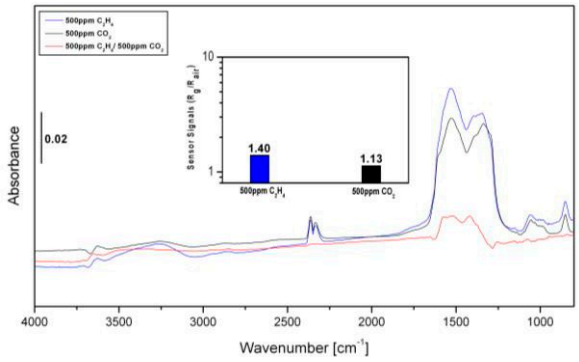

Figure 4. Drifts spectra of LFO sensor exposed to 500 ppm C_2H_4 (blue line) and CO_2 (black line) in dry conditions at 250 °C. All spectra were referenced to the dry air spectrum measured prior to C_2H_4 exposure, except for the C_2H_4 spectrum (red line) which was referenced to CO_2. The inset figure shows the sensor signals of C_2H_4 and CO_2 in same conditions.

The DRIFTS spectra reveal that the presence of formates on the surface during gas exposure results in determine the sensor signals. When the target gas exposure was stopped, a direct reduction of the resistance accompanied with the disappearance of formate bands was recorded, while corresponding to other surface species bands remained at the sensor surface. At 250 °C, ethylene preferred to form other types of carbonates on the surface of LFO rather than formates and that caused a huge reduction in the gas response from around 15 at 200 °C to only 1.5 at 250 °C. Therefore, we think that there is a correlation between the presence of formates on the surface and the gas response of LFO sensor.

Our findings indicate that the formation of formates at the surface of LFO sensor during gas exposure plays a key role in the gas sensing mechanism. This is a significant step in understanding the origin of gas response and helps the development of practical sensors.

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Conflicts of Interest: The authors declare no conflict of interest.

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