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RARE-EARTH BASED CHEMORESISTIVE CO2 SENSORS AND THEIR OPERANDO INVETIGATIONS

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Summary

Obtaining low cost, simple, compact and good performance chemoresistive CO2 gas sensors has the potential to be a game changer in the field of indoor air quality monitoring as well as the agricultural and food businesses. Rare-earth oxycarbonates Ln2O2CO3 (Ln = La and Nd) have been proposed as promising chemoresistive materials for CO2 sensors 1 2. In this contribution we present the results of a broad investigation focused on selecting the best candidates in the rare-earth compounds and, in the case of the best performing material, preliminary results dealing with the understanding of sensing by the operando methods 3.

Material synthesis and Sensor Fabrication

Rare-earth oxycarbonates and rare-earth oxides (rare-earth element = La, Nd, Sm, Gd, Dy, Er, Yb) were produced by the heat treatments of the oxalate hydrate or the acetate hydrate in a flow of ambient air at temperatures between 450℃ and 550℃ for 18 or 72 hours. The powders after the heat treatment were mixed with propane-1,2-diol. The resulting pastes were screen printed onto alumina sensor substrates (provided with Pt interdigitated electrodes and Pt heater). The substrates were dried and then heated at the same temperature as its heat treatment.

Results and Discussion

DC resistance measurements

Figure 1 shows the comparison of sensor signals to 1,000ppm CO2 under standard humidity and operation temperature conditions (20℃50%rh, 300℃) for all (11) sensors. The sensor signal is defined as the relative change of the resistance with respect to the resistance in air (CO2=0ppm). Every sensor, excepting the CeO2 and Nd2O3 based, was sensitive to CO2.
Additional investigations of selectivity and stability indicated that hexagonal La2O2CO3 possesses the best properties for a CO2 sensor so far. The detailed performance is shown in Figure 2.

Operando Investigations

To reveal the sensing mechanism, we started by investigating the transduction by focusing on the conduction through the sensitive layer, with the help of operando AC impedance spectroscopy, and the effect of humidity, with the help of operando work function changes measurements; these investigations will be complemented by operando DRIFTS (Diffuse reflectance infrared Fourier transform spectroscopy) experiments; the operando stands for actual gas sensing conditions (e.g. at an
operation temperature of 300℃, with or without gas exposure, humid or dry atmosphere).
Out of the results of AC impedance spectroscopy, presented in Figure 3 as Cole-Cole plots, one can derive an equivalent circuit, see Figure 4. In it, there are two contributions that describe space charge regions – comprising parallel resistive and capacitive contributions. They can either describe electrode contact and intergranular contributions or heterogeneous intergranular contributions. In series, one finds an additional resistive contribution, which could describe the grains bulk. In DC conditions, the resistive contributions that are describing space charge regions, dominate and will show an exponential dependency on the surface barriers, which vary with ambient conditions. The changes of resistive contributions (Rc + Rgb) are correlated with the changes in the surface barrier height ΔVs as in equation (1).
$(Rc + Rgb)0 / (Rc + Rgb)gas = \exp(-q\Delta Vs/kT)$ (1)
where (Rc + Rgb)0 and (Rc + Rgb)gas are the values at 0 ppm and at a certain concentration of CO2, and q is elementary charge respectively.
The inputs from the AC impedance spectroscopy are allowing to separate the contribution of electron affinity Δχ and band bending qΔVs to the work function changes ΔΦ as in (2).
$\Delta\Phi = q\Delta Vs + \Delta\chi$ (2)

Figure 5 show the preliminary results in the case of the hexagonal La2O2CO3 based sensor operated at 300℃ in 20℃10%rh. In this case, the work function changes more than 0.6 eV at 4,000ppm CO2 and the contribution of electron affinity Δχ is larger than that of band bending qΔVs.
The electron affinity mainly depends on the surface dipoles which are caused by surface adsorbents such as hydroxyl groups. We will identify the surface adsorbents by operando DRIFTS experiments.

References

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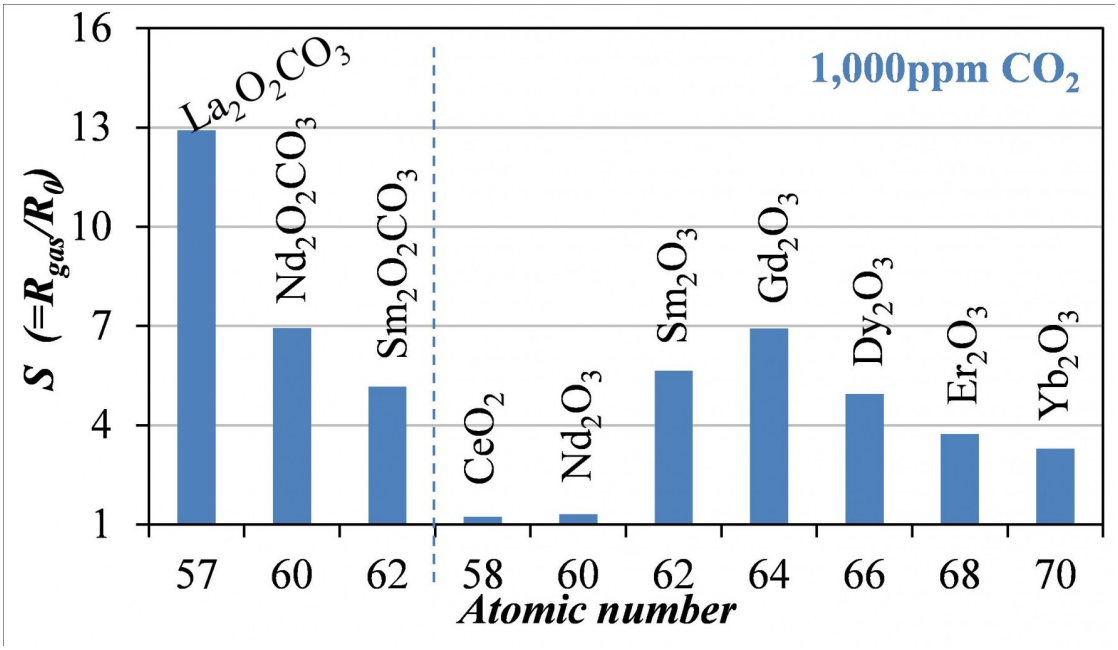

Figure 1: Comparison of sensor signal to CO2

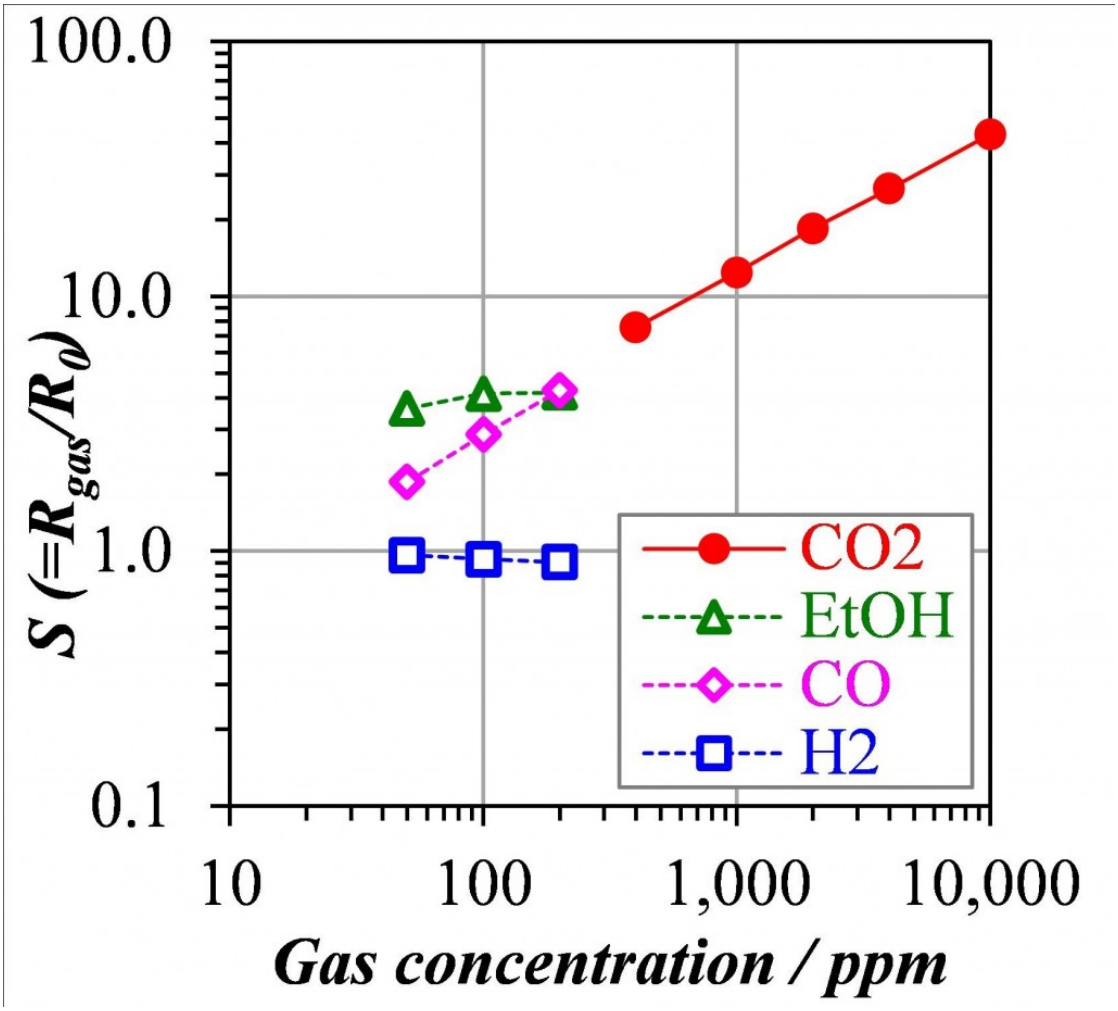

Figure 2: Sensing performance of hexagonal La2O2CO3

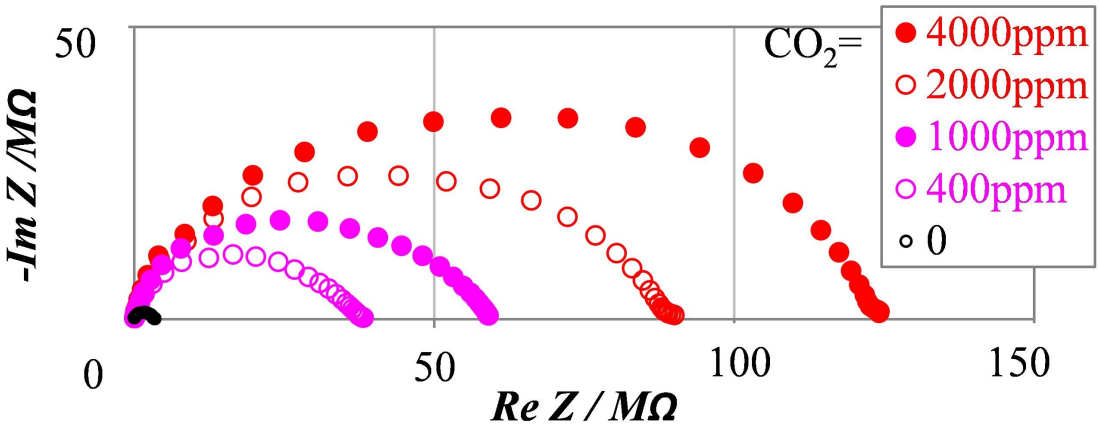

Figure 3: Cole-Cole plots from AC impedance spectroscopy of hexagonal La2O2CO3

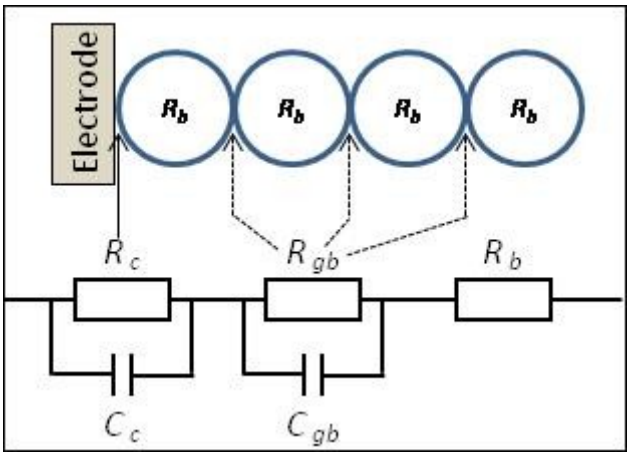

Figure 4: Equivalent circuit

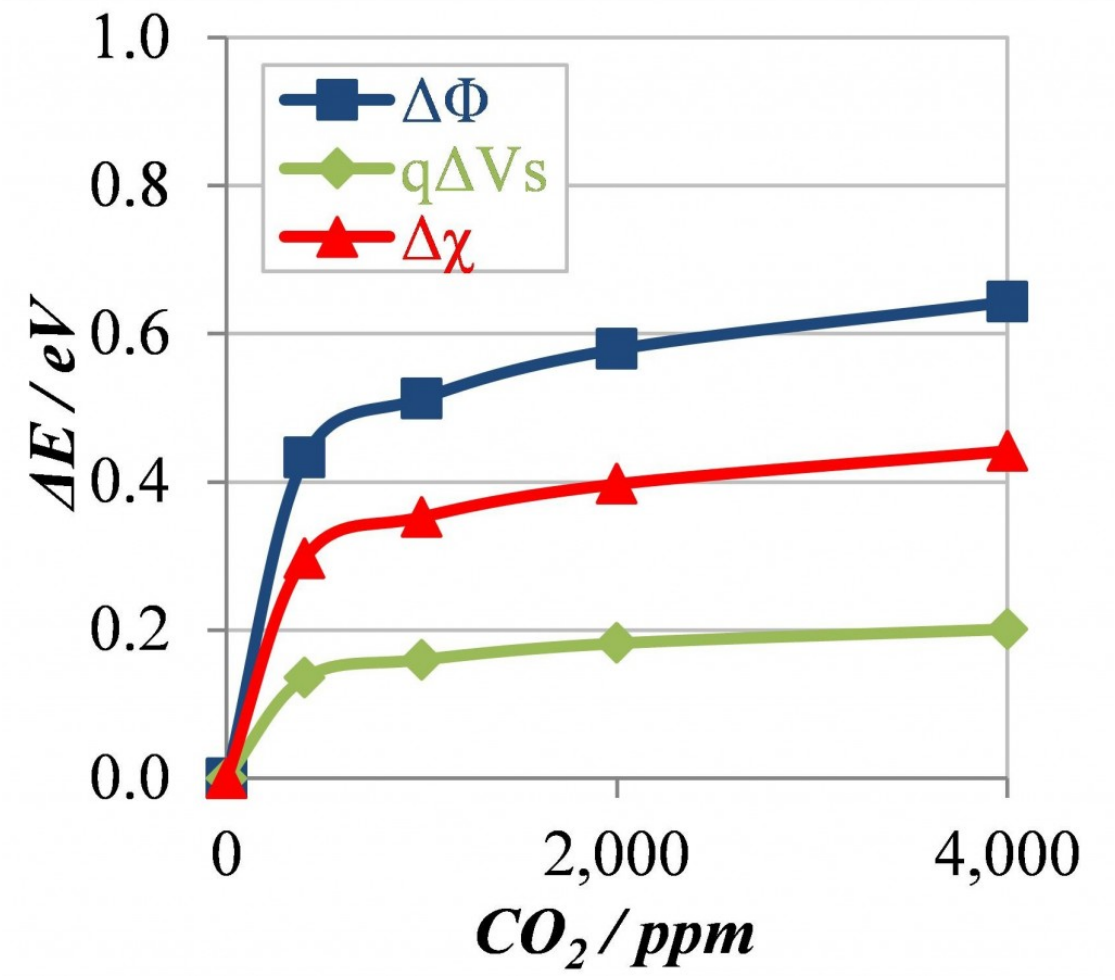

Figure 5: Variation of work function, band bending, and electron affinity with CO2 concentration

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