

# Gas sensors based on metal oxides: what one can learn about the surface reactions from *in-situ* electrical and spectroscopic techniques

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On the surface of a metal oxide one can find sites (defects, additives, etc.) that can play a role in different processes, namely: gas reaction, charge transfer with the bulk and both. They can be useful for the catalytic or sensor function or just kind of interference. The understanding of their role is, in all cases, useful for both catalysts and sensors. The characterisation of charge transfer between the catalyst and adsorbed species at the surface of the catalyst in working conditions provides important information about the mechanism of the catalytic reaction, it allows to distinguish between: (i) delocalised and localised chemisorption, (ii) donor and acceptor type of the interaction as well as to study electron transfer effects and electron affinity changes and dipole contributions.

We use a portfolio of specially adapted *in-situ* (“operando” [1]) electrical and spectroscopic techniques [2] to characterise the sensors in normal working conditions (total pressure: 1 bar, total flow: 10-1000 ml; relative humidity: 0-90%, operating temperature of sensors: 300-700 K; dosing system for gases: few ppb – 100%):

- DC resistance measurements give information about electronic n- or p-conductivity as well as about delocalised phenomena which accompanies the electron transfer between the solid and adsorbed species.
- AC impedance spectroscopy provides knowledge on the different contributions (surface, bulk) to catalytic reactions and gives an additional information about adsorbed surface species (due to the dependence of the capacitance  $C$  on the dielectric constant  $\epsilon$ :  $C \sim (\epsilon\epsilon_0/V_S)$ , which is influenced by adsorption of molecules with different dipoles).
- Work function change measurements provide insight about surface reactions (oxygen species, donor-acceptor interaction); it happens because the work function changes induced by gas exposure follow the change in band bending and electron affinity:  $\Delta\Phi = q\Delta V_S + \Delta\chi$  ( $q$  denotes elementary charge, due to the definition,  $V_S = E_{C,S} - E_{C,B}$ , where S – surface, B - bulk).
- Simultaneous conductance and work function change measurements additionally provide insight about surface reactions where free charge carriers are not involved and surface species that are not carrying a net charge, such as dipoles. The different contributions to the work function change  $\Delta\Phi$  can be determined according to:  $\Phi_{I,F} = -kT\ln(G_{I,F}/G_0) + \chi_{I,F}$  hence  $\Delta\Phi = \Phi_F - \Phi_I = kT\ln(G_I/G_F) + \chi_F - \chi_I = kT\ln(R_I/R_F) + \Delta\chi$  whereby  $\Phi_I$ ,  $R_I$  and  $\chi_I$  are the work function, the resistance and the electron affinity in the initial gas atmosphere and  $\Phi_F$ ,  $R_F$  and  $\chi_F$  the corresponding values in the final gas atmosphere.
- On line gas analysis (paramagnetic oxygen analyser, IR gas monitors (CO, CO<sub>2</sub> etc.), chemiluminescence NO<sub>x</sub> analyser, IR ozone analyser, on-line MS) and catalytic conversion measurements give additional information about the reaction paths.
- Infrared spectroscopy and especially DRIFT measurements are allowing for the identification of surface species involved in the processes in normal operation conditions.

The description of the theory, experimental techniques and results of the case studies (CO and propane sensing (accompanied with catalytic oxidation) on Pd-doped SnO<sub>2</sub>) will be given in the presentation.

[1] B.M.Weckhuysen. Phys. Chem. Chem. Phys., **5**, 4351-4360 (2003).

[2] N.Bársan, U.Weimar. J.Phys.: Condens. Matter., **15**, R183-R839 (2003).