Shining light on metal oxide based gas sensor: Operando synchrotron radiation experiments

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State of the art semiconducting metal oxide based gas sensors for reducing gases are mainly based on porous SnO_2 as sensor material [1]. In order to improve their performance, especially in terms of increase sensitivity and stability and decrease of the operation temperature, the SnO_2 is "doped" with noble metals. Despite Pd, Pt or even Au additives are already considered the most relevant ones since several decades, the understanding of their role and structure under operating conditions is still a matter of strong discussion [2]. Up to now, most spectroscopic studies were obtained in idealized conditions or the concentrations of the noble metal were much higher than in real gas sensors. Thus both a gap in structure and in gas sensing conditions have to be overcome. In the last years operando studies have gained a lot of attention (e.g. in catalysis [3]). However, little has been reported in the field of gas sensors, especially on the chemical state of the noble metals or their structural changes during sensing. X-ray absorption spectroscopy is an excellent technique for deriving structure-function relationships [3]. Here, the challenge is that the structure of a noble metal in low concentration (0.5 wt. % and lower) in a heavily absorbing SnO_2 matrix has to be identified. Moreover, the sensing layer is highly porous and only 50 µm in thickness.

Recently, we gained new insight into the structure of the Pd, Pt and Au constituents of SnO_2-based sensors by high energy resolved fluorescence detected (HERFD) X-ray absorption spectroscopy at dopant levels down to 0.2 wt % Pt and Pd in a highly porous 50 µm film layer using the high-flux beamline ID26 at ESRF [4,5]. Since platinum is used both present as dopant and in the heater/electrodes, additionally, the sensor was modified in a way that platinum was only present in the sensing layer [5]. Secondly, the gold fluorescence was efficiently eliminated by using the HERFD mode. Under operating conditions both platinum and palladium are in oxidized state. These results are surprising because in previous studies with model gases or samples metallic particles or clusters were found and have been ascribed in some of the models to the improved properties. In case of platinum, Pt in a highly oxidized state seems to be incorporated in the lattice of SnO_2. These studies demonstrate the importance of studying the materials as close as possible to the operating conditions (similar sample, similar sensing conditions), the strength of novel X-ray absorption spectroscopic techniques and in general the importance of operando studies in the field of sensors.

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