Determining the state of Pt in SnO_2-based gas sensors under working conditions

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State of the art semiconducting metal oxide based gas sensors for the detection of reducing gases are mainly based on porous SnO_2 as a sensor material.[1] In order to improve their performance, especially in terms of increased sensitivity and stability and a decreasing of the operation temperature, the SnO_2 is generally “doped” with noble metals like Pd, Pt and Au. Although they are 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 50 µm in thickness.

Recently, we gained new insight into the structure of the Pd constituent of SnO_2-based sensors by applying high energy resolved fluorescence detected (HERFD) X-ray absorption spectroscopy at dopant levels down to 0.2 wt % Pd in a highly porous 50 µm film layer using the high-flux beamline ID26 at ESRF.[4] Since Pt was used for the heater/electrodes in the former sensor device, it had to be modified in such a way that platinum was only present in the sensing layer in order to determine the state of Pt in SnO_2-based gas sensors.[5] Secondly, the gold fluorescence from the new electrode material was efficiently eliminated by using the HERFD mode. Under operating conditions – exposure towards CO and H_2 at an operation temperature of 300°C - platinum is in oxidized state. This results is surprising because in previous studies dealing with model samples or conditions metallic particles or clusters were found and have been ascribed in some of the models to the improved properties. Further, platinum being in a highly oxidized state seems to be also 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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