European Fuel Cell Car Workshop | March, 1st - 3rd 2017, Orléans, France

New methods and new catalysts for the ORR: Surface science applied to CoO_x/Pd(100) ultrathin films.

T. Kosmala, L. Calvillo, S. Agnoli, G. Granozzi
Dipartimento di Scienze Chimiche, Università di Padova, Via Marzolo 1, 35131 Padova, Italia

gaetano.granozzi@unipd.it

Keywords: CoO_x, Pd@CoO_x, electron tunneling, oxygen reduction, methanol, catalytic species

A great deal of efforts is currently taken for the development of innovative electroactive materials. A little travelled road to reach the target envisages the used of ultrathin metal oxide thin films supported on metal substrate. As a matter of fact, these hybrid systems exhibit unprecedented structural and chemical properties and a wide gamut of special phenomena such as interfacial electronic hybridization and easy electron tunneling that can be exploited for a rational design of highly active catalysts. However, the subtle physics and chemistry ruling these systems require a sophisticated methodological approach for their study. With this aim, a rather unique home-lab set-up (see Fig.1), which allows combining X-ray photoelectron spectroscopy (XPS) and electrochemical measurements, has been used. We have prepared highly controlled CoO_x/Pd(100) model systems in UHV conditions, with atomic scale precision in order to study the activity of different prototypical cobalt oxide nanometric films (CoO and Co_3O_4 from nm to bulk dimension) and the influence of the Pd substrate on their chemical properties. Composition/structure/activity relationships have been established through a systematic study of their electrochemical behavior and the chemical/structural changes induced under working conditions. The combination of cobalt oxide with palladium allowed to obtain a very active material, with an activity comparable to pure palladium, but maintaining a higher poisoning tolerance due to the presence of the oxide. Moreover, thanks to the exploitation of an *in situ* technique we were able to identify the real active phase involved in ORR conditions. Such study demonstrates how the use of ultrathin hybrid films and *in situ* techniques can pave the way toward the development and comprehension of radically new electrode materials.

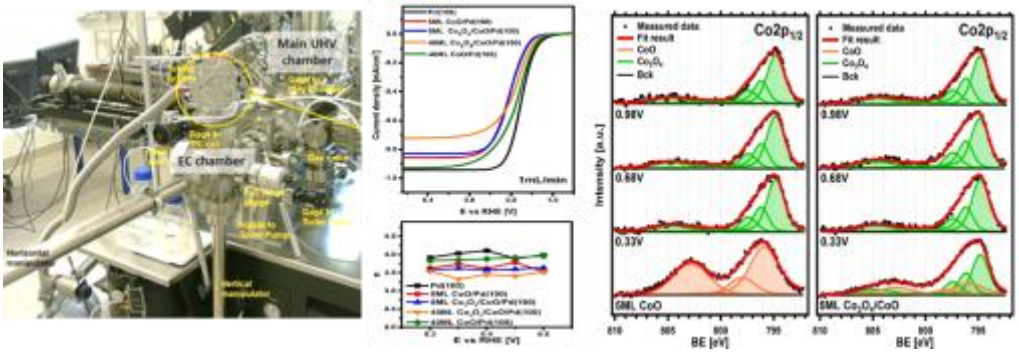

Figure 1: Experimental set-up for the in situ combined XPS and electrochemical measurements (left); LSV in O_2-saturated 0.1M KOH and number of transferred electrons for the CoOx/Pd(100) systems studied (middle); and Co $2p_{1/2}$ region for the CoO and Co_3O_4 systems at different potentials in O_2-saturated 0.1M KOH.

REFERENCES

1. L. Gragnaniello, S. Agnoli, G. Parteder, A. Barolo, F. Bondino, F. Allegretti, S. Surnev, G. Granozzi, F. P. Netzer, "Cobalt Oxide Nanolayers on Pd(100): The Thickness-Dependent Structural Evolution, *Surf. Sci.*, **604**, 2002–2011 (2010)