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

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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 CoOx/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 Co3O4 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 O2-saturated 0.1M KOH and number of transferred electrons for the CoOx/Pd(100) systems studied (middle); and Co 2p1/2 region for the CoO and Co3O4 systems at different potentials in O2-saturated 0.1M KOH.

REFERENCES