

Substrate Effect on Cluster-like Electrocatalyst Materials Probed via Scanning Tunneling Spectroscopy (STS)

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Investigation of multi-electron charge transfer mechanisms, such as, the oxygen reduction reaction (ORR), or methanol oxidation reaction (MOR) is of relevance for both fundamental electrochemistry and material science. Both approaches are the basis for the development of energy converting systems (fuel cells). Therefore, from a fundamental point of view, it is interesting to learn about the density of states (DOS) of the resulting cluster-like material surface systems used for such a purpose. In catalysis or electrocatalysis, materials in the nanodivided form (particles) are frequently used. These materials are supported on substrates with defined physical-chemical properties (conductivity, acidity, basicity, etc.). However, interfaces between dissimilar materials may exhibit size dependent properties that affect electrical, mechanical and electrocatalytic responses, and further the thermodynamic stability. This communication is aimed at probing the interface between cluster and the substrates, as near as possible to the condition employed in real world, using the scanning tunneling microscopy (STM) and spectroscopy (STS).

The catalyst materials were prepared via the low temperature synthetic procedure to obtain $\text{Pt}_{0.7}\text{Ru}_{0.3}$ (from Pt and Ru)¹ and Ru_xSe_y ² colloidal solutions. Fluor-doped tin oxide layer (FTO, $10\Omega\text{cm}^{-1}$), glassy carbon (GC) and highly oriented pyrolytic graphite (HOPG) were used as substrates. The materials were deposited by dipping the substrate in the colloidal solution, thereafter annealed in air for Pt-Ru (300°C) and under Ar for Ru_xSe_y (230°C). This treatment provided the formation of ultra-thin layers. In fact, as revealed by STM the morphology of such layer, in the nanometer scale range, is essentially based on a network of interconnected nanoparticles.

The collection of local $I_T(V)$ curves was of special interest to probe the interface properties. All curves were measured with the feedback loop off, at a preselected voltage set point by STM operated in air, with the tip ($\text{Pt}_{0.8}\text{Ir}_{0.2}$) placed on various places in a surface of $50\text{nm} \times 50\text{nm}$. STM images were obtained before and after spectroscopy to verify the spatial region.

All tunneling spectra were acquired with an averaging during acquisition at a tip bias voltages of 0.2, and -0.2V with a set point current of 0.5nA. Differential conductivity (proportional to local density of states (LDOS)) was determined from a 15-points smoothing routine of $I_T(V)$ followed by a numerical differentiation. Figure 1 shows the spectra of substrates FTO, GC and HOPG (sample bias = -0.2V). Above the Fermi level (E_F) the conduction band of FTO can be identified. Slightly filled levels below E_F is observed, as expected for a degenerate n-type semiconductor. GC and HOPG the conduction and valence band can be identified. GC, a variety of graphitic electrodes, has a higher conductivity

below and above E_F . The situation looks different when such substrates are modified by the deposition of $\text{Ru}_{0.7}\text{Pt}_{0.3}$ (Figure 2) and Ru_xSe_y (Figure 3). A preliminary evaluation of these spectra shows: (i) that the local density of states at the Fermi level increases by a factor of 2 on HOPG and 0.3 on GC. (ii) the conduction and valence bands of carbon materials are affected by the electronic properties of the catalysts. This is more evident on the semiconducting substrate (valence side).

The lack of sensitive of such measurements to local variations on these substrates (in a range of $50\text{nm} \times 50\text{nm}$) puts in evidence that an homogeneous surface conductivity exists among the nanoparticles. Furthermore, since STS is sensitive to surface properties, apparently a strong interaction with the substrate may exist in the case of HOPG, but the metal-substrate surface interaction on this substrate is known to be small. In fact, the nanoparticles were preferentially deposited on edges (defects) of HOPG. This might explain these results. Therefore, these investigated substrates constitute a model to understand electrocatalysis of nanodivided materials.

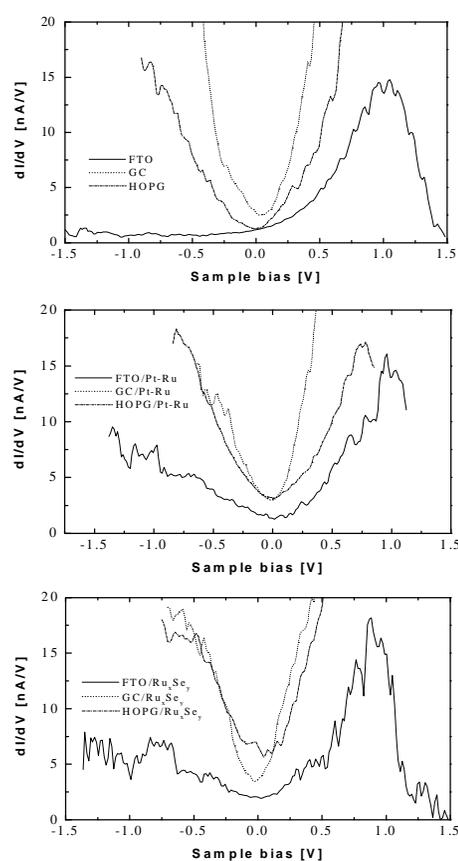


Figure 1. Tunneling spectra of substrates (top); **Figure 2.** Tunneling spectra of surface modified substrates by $\text{Ru}_{0.7}\text{Pt}_{0.3}$ (middle); and **Figure 3.** Tunneling spectra of surface modified substrates by Ru_xSe_y (bottom). All data were collected under similar conditions.

1. Bönnehan, H., Braun, G., Brijoux, W., Brinkmann, R., Schulze-Tilling, A., Seevogel, K., Siepen, K., *Organometallic Chem.*, **1996**, 520, 465.
2. Alonso-Vante, N., German Patent DE 196 44 628 A1.

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