

Electrochimica Colloquia

6 Febbraio 2020 – Dipartimento di Scienze Chimiche
Aula A - Nasini, via Marzolo, 1 - Padova

Ore 14.30

Proton Relays and Local Concentration Effects in Molecular Catalysis

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Several examples of remarkably bidirectional or even reversible catalysis with small overpotentials have been recently described in the case of the electrochemical H₂ oxidation and production. This is the occasion to show that such challenging achievements are made possible by local concentration effects allowed by the installation of fast proton relays inside the catalyst molecule close to its metal center. A satisfactory kinetic model consists of two fast proton-coupled electron transfer square schemes linked together by means of two slower reactions involving changes in the metal coordination sphere. This leads to an equivalent description of the problem by means of a much more compact reaction scheme after definition of the connections with the parameters of electron and proton reactivity of the actual catalytic system. The treatment provides expressions for the catalytic cyclic voltammetric responses revealing the factors that govern the local concentration effects and the transition between bi-directionality and reversibility.

Ore 15.30

Molecular Gold Nanoclusters: Understanding the Properties of Hard-Heart, Soft-Skin Systems

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Thiolate-protected gold clusters are of continuously growing fundamental and applied interests. Several of these systems can be synthesized with atomic precision, allowing to assess their formula and often structure. This is the case of Au₂₅(SR)₁₈, which is the most studied thiolate-protected nanocluster displaying molecular properties, such as the presence of HOMO-LUMO gap and a rich electrochemical behavior. These complex systems can be defined as *hard* and *soft* molecules, *i.e.*, species where a hard gold core is protected by a soft interface of flexible ligands. Whereas the former controls the electronic energy levels, the latter provides a nanoenvironment that controls how the core interacts with the surrounding medium. Besides changing the core size, the properties of atomically precise nanoclusters can be modified by varying the core composition via metal doping and/or the type of ligands. Understanding the interplay between these factors is especially important from the viewpoint of electron-transfer reactions. This communication will primarily focus on how electrochemistry can provide information and often-unique insights into these and related aspects.

Ore 16.00

Ingenious nanomaterials for ultrasensitive ECL

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The impact of nanotechnology and nanosystems on analytical science is hardly overlooked. In the search for ever-increasing sensitivity in biomedical sensors, nanoparticles have been playing a unique role as, *e.g.*, ultrabright labels in clinical analysis (markers, tumor cells, and pharmaceuticals) and in the detection of pathogenic microorganisms, toxic agents, and pesticides in the environmental field and food products. Coupling such nanosystems with *electrochemiluminescence* (ECL), which naturally brings improved signal-to-noise ratio compared to photoluminescence, with minimized effects due to light scattering and luminescence background, has brought about new systems and strategies for analytes determination, even in very complex matrices, such as urine, blood or lysate.

Among the several nanosystems, dye-doped silica nanoparticles (DDSNs) have proved as very promising and versatile nanomaterials in ECL-based bioanalytical platforms. In the DDSNs, ECL generation occurs through the complex concurrence of several elementary processes, electron transfer and mass transport taking place within and at the boundary of the nanoparticles, influenced by coreactant-NP interactions. Unravelling the intimate mechanisms which govern the light generation in such nanosystems is mandatory for the design of ultrasensitive devices.

Ore 16.30

Electrochemical activation of carbon dioxide for the synthesis of chemicals

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To curb the negative effect of carbon dioxide as a greenhouse gas, an interesting approach is the utilization of Carbon Capture and Conversion (CCC) methodologies. These recycling technologies are focused on the use of CO₂ waste as a feedstock for the production of industrial relevant chemicals. In the last years, an increasing attention has been devoted to the electrochemical conversion of CO₂, which would combine the utilization of excess electric energy from intermittent renewable sources with the selective conversion of CO₂ into added value products. Furthermore, it would be possible, in order to reduce the costs, to use the excess of the daily produced electricity, not matching actual demand energy, that is usually lost or not properly used. Researches have shown that several products, including carbon monoxide, formic acid, methane, methanol, ethylene and oxalic acid, can be obtained by this process. Furthermore, it has been shown that carbon dioxide can be introduced in the backbone of other molecules, generating fine chemicals with high economic value, such as anti-inflammatory drugs, by cathodic reduction in aprotic solvents

In this work, various routes for the electrochemical conversion of carbon dioxide will be presented and discussed from both a scientific, technical and economic point of view, such as the synthesis of formic acid in water (in conventional and pressurized cells) or the electrocarboxylation of aromatic ketones and benzyl chlorides in organic solvents, in order to illustrate the current scenario.

Ore 17.00

Powerful, Versatile Inherent Chirality at Electrochemical Interphases

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Chirality can make electrochemistry even smarter, endowing it with a superior level of selectivity. In fact, chiral electrochemistry implies the ability to discriminate and possibly also quantify enantiomers of chiral molecules, *in situ* and with no preliminary separation steps, for analytical purposes; and to selectively activate or obtain the desired enantiomer of a chiral molecule, for synthetic purposes; moreover, a chiral electrochemical interphase can act as a spin filter, since electrons in rototranslational motion to/from the electrode surface are truly chiral objects.

Thus chiral electrochemistry represents an attractive area with a huge applicative potential, although mostly unexploited so far, in spite of many proposed approaches. [1]

In this context, the *inherent chirality* concept can provide the breakthrough. In fact, it implies chirality and key functional properties, like electroactivity, to originate from the same structural element, which can coincide with the whole backbone of the chiral selector, featuring a tailored torsion. Such unique threefold identity can endow the selector with extraordinary chirality manifestations.

Unprecedented enantioselectivity in terms of large potential differences was indeed recently observed in voltammetry experiments, implementing inherent chirality in electrochemical interphases in terms of either (a) enantiopure electrode surfaces consisting of inherently chiral heterocycle-based electroactive oligomer films [2-5] or (b) highly ordered enantiopure media based on inherently chiral molecular salts (either as bulk ionic liquids or as additives in achiral ionic liquids)[6,7] Attractively, a given selector looks effective with quite different chiral probes (in terms of structure, properties and stereogenic elements) and viceversa.

But such enantioselectivity has an even more wider character than that. In fact, the features of inherently chiral molecular materials can also make them outstandingly selective towards the two specular circular components of plane polarized light, resulting in outstanding chiroptical properties in both adsorption (circular dichroism) and emission (circularly polarized luminescence), even electrochemically modulable.[2,4,5] Furthermore, they could discriminate α vs β electrons in rototranslational motion to/from the electrode surface, which are truly chiral objects; and impressive features have been recently observed in magnetoelectrochemistry experiments.[8]

Such first thrilling evidences suggest fascinating correlations worthy to be explored among chiral electrochemistry, polarized light and spin magnetic moments.

Dedicated to professor Armando Gennaro, an outstanding teacher in science and in life

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Ore 17.30

Level 121

Armando Gennaro

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51 years of teaching, 51 years of attending Padua chemistry, two non-exclusive “loves”, but lived with passion. A chance to meet thousands of students, to whom I had to give always great attention, and hundreds of Colleagues Paduans, in Italy and abroad, some of them giving very important turning points to my scientific interest and to the development of my research, opening new frontiers of very gratifying work.

These have surely been my life, even if not all the life.