Electrochimica Colloquia

In memory of Sergio Trasatti:

“From the Volcano plot to the Electrocatalysis of small molecules."

February 25th 2022
Dipartimento di Scienze
Chimiche, UNIPD
Aula A, via Marzolo, 1 – Padova

h 14.30: Prof Marc Koper
(Leiden University)
h 15.30: Prof. Alessandro Minguzzi
(Università degli Studi di Milano)
h 16.00: Prof. ssa Sabrina Antonello
(Università degli Studi di Padova)
h 16.30: Prof. Josè H. Zagal
(University of Santiago de Chile)
H 17.15 Prof. Giovanni Valenti
(Università degli Studi di Bologna)
h 17.45: Prof. Achille De Battisti
(Università degli Studi di Ferrara)

Società Chimica Italiana
Divisione di Elettrochimica

Zoom Virtual Room: 812 6011 2114

https://unipd.zoom.us/j/81260112114?pwd=eTVBRWhEQ0hNMUhuN2VlQ1Azak40Zz09

Double layer and electrolyte effects in electrocatalysis

Prof. Marc Koper

(Leiden University)

Abstract: In my talk, I will discuss new results on the double layer structure of the Pt(111) electrode, showing significant deviations with Gouy-Chapman-Stern theory, also (in fact especially) at low electrolyte concentrations. A new theory will be introduced, specifically taking into account an additional attraction between ions and the surface, as well as the interaction of water with the Pt(111) surface. I will also show how the composition of the double layer, mainly the presence of cations, has a crucial influence on the electrocatalysis of hydrogen evolution and CO2 reduction. This then leads to the concept of cation-coupled electron transfer.

Electron Transfers through 2D and 3D self-assembled monolayers on gold

Prof. Sabrina Antonello

(Università degli Studi di Padova)

Abstract: Modification of 2D metal surfaces by controlled chemisorption of an organic monolayer is a well-established procedure with relevant gains in different applications as sensoring and electronics. In the last years, the need for a fully understanding of how this interface between solid material and solution behaves in different conditions has become even more urgent due to the relevance that nanomaterials gained in both scientific research and everyday life. Metal nanoparticles are indeed usually stabilized by an organic surfactant forming a 3D monolayer that represents the communication port between the metal core and the surroundings. In this context, electrochemistry could be extremely beneficial to investigate the electron transfer properties of 2D and 3D monolayers. In this talk, some of the relevant achievements of our research on thiolate modified gold electrodes and on monolayer-protected gold nanoclusters will be illustrated.

X-ray absorption spectroscopy in electrochemistry: a journey from electrocatalysis to the emergence of life

Prof. Alessandro Minguzzi

(Università degli studi di Milano)

Alessandro Minguzzi,[a,b] *Martina Fracchia,*[c] *Xiufang He,*[a] *Francesco Panico,*[a] *Sandra Rondinini,*[a,b] *Michael J. Russell,*[d] *Alberto Vertova,*[a,b] *Paolo Ghigna*[b,c]

[a] *Dipartimento di Chimica, Università degli Studi di Milano, via Golgi 19, 20133, Milano, Italy;* [b] *Consorzio Interuniversitario di Scienze e Tecnologia dei Materiali, Via San Giusti 9, 50121, Firenze, Italy* [c] *Dipartimento di Chimica, Università degli Studi di Pavia, Viale Taramelli 13, 27100, Pavia, Italy* [d] *Dipartimento di Chimica, Università degli Studi di Torino, 10125 Torino, Italy;*

Abstract: The use of large facilities in chemistry is gaining attention thanks to the increasing variety of techniques that have been under development in recent years. Among these, synchrotron-based X-ray absorption spectroscopies allow the study of several types of samples – liquid, solid (amorphous or crystalline), gas – over a wide range of temperatures and pressures. Moreover, they are element selective.

The technique allows the study of the local structure and charge state of the addressed element for what concerns an electrochemical system, in any of the sample's "actors" (i.e., electrolyte, electrode material, catalyst, etc.).

We have been using and developing electrochemical XAS for the last 10 years and we want here to discuss the most interesting cases in electrocatalysis, photoelectrochemistry, corrosion, photochemistry, before going on to show how the conclusions stimulated our interests in new (and unexpected) journeys, including research into the emergence of life on Earth.

Selected publications

1. Minguzzi, A., Ghigna, P. in *Electroanalytical Chemistry: A Series of Advances*, **2017,** *Vol 27.*
2. Malara, F. et al *ACS Catal*. **2020**, *10*, 10476−10487,
3. Spanu, D. et al *ACS Catal*. **2020**, 10, 8293–8302,
4. Minguzzi, A. et al *Chem. Sci*. **2014,** *5*, 3591.,
5. Minguzzi, A. et al *ACS Catal*. **2015,** *5*, 5104,
6. Rondinini, S. et al *Electrochim. Acta*, **2016**, *212*, 247.
7. Fracchia, M. et al *Surfaces*, **2018**, *1*, 138,
8. Minguzzi, A. et al *Phys. Chem. Chem. Phys*., **2017,** *19*, 5715.
9. Fracchia, M. et al *Electrochim. Acta*, **2019**, *320*, 134561,
10. Nitschke, W. et al *Electrochem. Sci. Adv.* Under review

Reactivity descriptors for MN4 molecular catalysts catalysts compared to those for metallic electrodes.

Prof. José H. Zagal
(University of Santiago de Chile)

A classical reactivity descriptor in electrocatalysis is the binding energy of key intermediates to the catalyst active sites. The activity at constant potential plotted versus these descriptors has the shape of a volcano. The maximum of the volcano is generally associated to a thermoneutral condition. Professor Sergio Trasatti was indeed a pioneer in volcano correlations in electrocatalysts. In contrast to metal electrodes, molecular catalysts of the MN4 type have well defined reversible fast redox processes centered on the metal. The active site is usually M(II) for planar MN4 macrocyclics and M(I) for MN4 tetrahedral Cu complexes for the ORR reduction. The M-O_2 binding energy correlates linearly with the M(III)/(II) redox potential, which becomes a reactivity descriptor for MN4 catalysts and this is observed for several reactions. The maximum in a volcano correlation of $(\log i)E$ versus $E^{\circ\prime}_{M(III)(II)}$ is associated with a partial coverage of the surface by M(II) species, usually close to 0.5 at the potential.

So for some reactions the maximum in the volcano occurs at $E = E^{\circ\prime}_{M(III)(II)}$ potential, where E is the potential used for comparing the activities. I will discuss several theoretical and semiempiric descriptors for several reactions and compared them with those for metals. I will also discuss the different ways the redox potential of the catalysts can be “tailored” or “tuned” to a certain value by changing the 3D coordination environment around the metal.

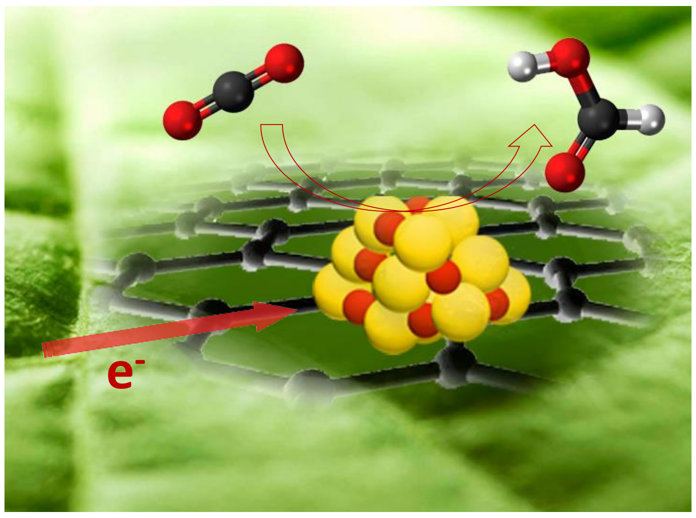
Hierarchical nanostructures in multi-functional electrocatalysts for CO_2 conversion

Prof. Giovanni Valenti
Department of Chemistry "G. Ciamician" University of Bologna, via Selmi 2, 40126 Bologna, Italy
https://site.unibo.it/emfm/en

Abstract: The growing need for energy on global scale and the realization that the so called oil-based economy cannot sustain our world anymore, prompted researchers to find new ways to "power" the planet.[1] In particular a lot of efforts have been done in the field of chemical energy conversion, that remains very challenging because of the requirement for higher efficiencies.[2] The electrocatalytic reduction of CO_2 is a captivating strategy for the conversion of CO_2 into fuels, to realize a close loop for carbon footprinting.

The research has focused on the development of new materials and technology capable of capturing and converting CO_2 into useful products.[3] Among all reduction products, formic acid is particularly attractive for its high volumetric hydrogen density, low toxicity, and liquid state, that make it a valuable hydrogen storage vector. In this context nanomaterials are nowadays at the forefront of materials science research. The design and realization of hierarchical nanoarchitectures, in which selected components are arranged to leverage their expected mechanistic functions are obtaining a wide range of applications, from the aerospace industry to bio-medicine, and as benchmarks for many catalytic reactions. Carbon-based nanomaterials have been the main actors of nanotechnology since their very first discovery, and their unique morphological/electronic properties are particularly suited to be used in electrocatalytic applications. CNTs and graphene are indeed ideal supports in catalysis as they have an optimal electronic conductivity and provide percolation routes for charge transfer reactions to occur. The integration of nanocarbons into hierarchical materials is an effective strategy to further boost the potentiality of nanostructured catalysts. The generation of multiple interfaces in such hierarchical assemblies is responsible for their exceptional activity, whose origin is however only rarely understood.

Our last efforts have been done in the development of new C-based nanocomposites that combine the unique properties of multiwall carbon nanotubes (MWCNTs) or graphene and metal oxides (TiO_2, BiO_2, CeO_2 and Fe_2O_3).[4-8] The nanocomposites have been designed and evaluated as electrocatalyst for the reaction of CO_2 reduction. We will show that in our nanoarchitectures the synergic participation of all the building blocks are involved in the mechanism resulting in better electrocatalytic activities.



References

[1] Armaroli N., Balzani V., *Angew. Chem. Int. Ed.*, **2007**, *46*, 52-66.
[2] Centi G., Perathoner S., *ChemSusChem*, **2010**, *3*, 195-208.
[3] Kumar B., et al., *Catalysis Today,* **2016**, 270, 19-30
[4] Toma F.M., et al., *Nature Chem.* **2010**, *2*, 826.
[5] Varlato E., et al., *J. Mater. Chem. A,* **2019**,7, 17896-17905
[6] Liu M., et al., *Nanoscale* **2020**, *12*, 20165
[7] Valenti G., et al., *ACS Appl. Energy Mater.*, **2020**, *3*, 8509-8518
[8] Valenti G., et al., *Nature Commun.* **2016**, *7*, 13549

Sergio Trasatti, a Scientific and Human Profile.
Memories of a Lifelong Friendship and Collaboration

Prof. Achille De Battisti
(University of Ferrara)

The scientific activity of SergioTrasatti extends, without solution of continuity, between the middle of 60s and June 2021, when he left us. It covers a quite wide area of Electrochemical Science, from the study of electrified interfaces at equilibrium, to electrochemical kinetics and electrocatalysis. A mighty interdisciplinary approach was already a main feature of his early papers. In a relatively short period, still quite close to his thesis discussion, a number of papers appeared on Pt and Pd electrodes (e.g. [*Ric. Sci . **35**(1965)1012*], [*Electrochimica Acta **15**(1970)729*]). In the late 60’s, early 70’s, the research on adsorption at the Hg/solution interface was undertaken ([*Trans. Faraday Soc. **65**(1969)3314*], [*J. Electroanal. Chem. **27**(1970) App.7-9*], [*J. Electroanal. Chem. **28**(1970)257*] together with the works on RuO_2-film-electrode properties (e.g.[*J. Electroanal. Chem., **29** (1971) App.I-5*]]). In the same restricted time range, the first studies on the correlations between electron work function and electrochemical properties of metals were published ([*Chimica e Industria **53**(1971)364*], [*J. Electroanal. Chem. **33**(1971)351*]). Within each theme, frontier aspects were originally discussed and readily obtained international recognition. In early Trasatti’s production we can easily recognize the extreme efficiency and creativity, leading features, not only scientific, of his personality, a constant throughout his scientific career.

The context in which Sergio Trasatti got his first scientific education and started his scientific path, was also quite interesting. The level of electrochemical research in Milano State University and Milano Polytechnic University during the first half of XX century, and during fifties and sixties, in particular, was certainly quite high, pivoted on Professor Roberto Piontelli, one of the founders of CITCE (Comité International de Thermodynamique et de Cinétique Electrochimiques) (the future ISE), and on his coworkers, among them Professor Giuseppe Bianchi, head of the laboratory of electrochemistry, then of the *Istituto di Elettrochimica dell’Università Statale di Milano*. Connections with industry were further strengthened in those times, and in the new seat of the Institute, in via Venezian 21, the basement floor was entirely occupied by researchers of De Nora Company, carrying out their work in a frame of effective collaboration with Institute staff. No doubt, this international atmosphere and the high level of electrochemical education, contributed to the formation of the scientific profile of Sergio Trasatti and prompted him to research in the field of electrochemical science. Yet, I think that his experience in Bristol at the end of the sixties, at the school of Professor Roger Parsons had a major role in this sense. The duration of the stage was not very long, but very intensive and it allowed him to practise the methods of investigation of the properties of the Hg/solution interface and to become familiar with the theories of double layer structure. This is evident, for instance, in [*J. Electroanal. Chem. 28(1970)257*], a quite prompt fruits of the Bristol experience. Another source of inspiration certainly was part of the work of Professor Alexander Naumovich Frumkin, head of the Institute of Electro-chemistry of the AS URSS, with special reference to the studies of the properties of the Ga/ and In-Ga/solution interface. Sergio Trasatti never met Frumkin personally, but maintained an active correspondence exchange with him, till the death of the Russian Electrochemist in 1976.

The capacity to develop different research lines in parallel, and, together with them, to carry out the organization of national and international events, maintaining an outstanding level in his university courses, highly appreciated by his students, were a constant in the further development of Trasatti’s professional action during the next almost four decades. The exceptional international acknowledgement he achieved, is certainly the best witness of a quite outstanding performance.

Beyond, somewhat foregone, comments on Sergio’s scientific profile and scientific production, basing on my personal experience of the collaboration with him, I feel important to conclude mentioning his open-minded, friendly, attitude toward colleagues, and toward coworkers at different levels. Very active in meeting discussions, his comments were always non polemic and respectful of others’ positions.

Electrochimica Colloquia

February 25th 2022
Dipartimento di Scienze
Chimiche, UNIPD
Aula A, via Marzolo, 1 – Padova

DiSC

Società Chimica Italiana
Divisione di Elettrochimica

INTERNATIONAL SOCIETY OF ELECTROCHEMISTRY
ISE