Using Cold Plasmas to Improve Electrochemical Sensorsand vice versa

Camille Colin, Vasilica Badets, Fanny Girard-Sahun, Pauline Lefrançois, U Botsos-Margerit, Dodzi Zigah, Sylvie Blanc, Neso Sojic, Franck Clement, Stéphane Arbault

K20. Using Cold Plasmas to Improve Electrochemical Sensors and *vice versa*

Colin Camille,[a] Badets Vasilica,[a] Girard Fanny,[a,b] Lefrançois Pauline,[a] Botsos-Margerit Ugo,[a] Zigah Dodzi,[a] Blanc Sylvie,[b] Sojic Neso,[a] Clément Franck,[b] Arbault Stéphane[a]

[a] *Univ. BORDEAUX, ISM, Bordeaux INP, CNRS UMR 5255, NSysA Group, Pessac, France*
[b] *UPPA, IPREM, CNRS UMR 5254, Pau, 64000, France*
stephane.arbault@u-bordeaux.fr

Cold plasmas are weakly ionized gases, generated by applying High-Voltage electrical discharges in a gaseous environment. They can be produced by sinusoidal or pulse power supplies, at either low pressures (ex. mTorr) or in ambient conditions depending on the electric field intensity as well as on the used gas (mixtures of N_2, O_2, Ar, He, methane etc.). Cold plasmas are complex mixtures of neutral species, electrons, ions, excited species (radiative and metastable states, radicals…) and emitted photons (UV, Vis, IR). In particular, when generated in oxygen-nitrogen mixtures (air), multiple reactive oxygen and nitrogen species (ROS, RNS) are present in the gas phase. Because of their diverse and intense reactivities, and relative ease for production, cold plasmas reveal themselves as excellent approaches to treat surfaces in order to modify their physical (cleaning, roughening) and chemical (functional groups) states.

In this context, we applied cold plasmas to modify the reactivity of metal and carbon electrode surfaces and studied the resulting effects on the detection of compounds involved by biosensors.[1,2] We first treated platinum and black platinum modified electrodes by 100 % Oxygen-plasmas produced by radio-frequency modulated electric fields (plasma cleaner setup) and observed lower capacitive currents, more stable faradaic responses, decreased standard potentials and improved sensitivity for H_2O_2 detection. These properties were related (XPS analyses) to a change of ratio between Pt oxides, which improve the surface hydrophilicity and initial adsorption of ROS. Similarly, the reactivity of glassy carbon electrodes could be homogenized and improved for the detection of both inner- or outer-sphere electron transfer species when treated by plasmas, allowing to prevent from polishing electrode surfaces for their cleaning or activation. Moreover, plasma effects were stable for periods longer than one week.

Reciprocally, such electrochemical sensors were involved to decipher on the nature of species produced by cold atmospheric pulsed plasmas when used to expose physiological fluids, cells or tissues.[3-5] Plasmas raise exponential interests for biomedical applications because of their strong reactivities. However, the true nature of reactive species involved in biocidal or oxidative bio-activation remains widely unsolved. To decipher on the *in situ* reactivity within solutions exposed to plasmas, we developed shielded microelectrodes to detect ROS and RNS appearing in solution, at millimetric distances from the plasma flow and electric source (nanosecond pulsed discharges). The concentration rises of hydrogen peroxide, nitrite as well as of superoxide anion were monitored with an unprecedented spatial and temporal resolutions.[6]

Consequently, we have demonstrated that electrochemical sensors can benefit from plasma treatments and *vice versa*.

References:

1 S. Ben-Amor, E. Vanhove, E. Suraniti, P. Temple-Boyer, N. Sojic, J. Launay and S. Arbault, *Electrochim. Acta*, **2014**, *126*, 171–178.
2 V. Badets, J. Pandard, N. Sojic and S. Arbault, *ChemElectroChem*, **2016**, *3*, 2288-2296.
3 F. Girard, V. Badets, S. Blanc, K. Gazeli, L. Marlin, L. Authier, P. Svarnas, N. Sojic, F. Clément and S. Arbault, *RSC Adv.*, **2016**, *6*, 78457–78467.
4 M. Dezest, A. L. Bulteau, D. Quinton, L. Chavatte, M. Le Béchec, S. Arbault, A. N. Salvayre, S. Cousty, F. Clément, *PLOS One*, **2017**, *12*, e0173618.
5 F. Girard, M. Peret, N. Dumont, V. Badets, S. Blanc, K. Gazeli, C. Noël, T. Belmonte, L. Marlin, J. P. Cambus, G. Simon, N. Sojic, B. Held, S. Arbault and F. Clément, *Phys. Chem. Chem. Phys.*, **2018**, *20*, 9198-9210.
6 F. Girard-Sahun, V. Badets, P. Lefrançois, N. Sojic, F. Clément and S. Arbault, *Anal. Chem.*, **2019**, *91*, 8002-8007.