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EQCM (Electrochemical Quartz Crystal Microbalance): Basic principle and pertinent examples in the environmental and energy fields.

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Interactions between acoustic waves and materials have led to the development of a wide range of sensors. The most well-known is called QCM (Quartz Crystal Microbalance) where a bulk acoustic wave, generated in the MHz frequency range, can interact with films in contact with the QCM surface. When a mass change occurs in them, the resonant frequency responds proportionally to this mass change. Typically, when working at 10MHz, the sensitivity is in the nanogram range which corresponds to an oxygen monolayer adsorbed on the quartz surface. By increasing the resonant frequency, up to 100 MHz, this sensitivity can reach values in the picogramme range. Various commercial devices are now available and various applications have been developed in diverse fields.

Since the last twenty years, our group develops QCM with specific performances. For example, QCM devices associated with (micro)fluidic cells are developed with enhanced sensitivity, mainly for environmental applications. In this case, the gravimetric tool is particularly pertinent to follow the quantity of biomolecules (DNA probes, antigens...) adsorbed on functionalized/appropriate surfaces. It appears as a unique tool for this purpose due to its high sensitivity, the possibility of in-situ measurements and also, for the kinetics parameters which can be directly determined. All the steps, when a biosensor is fabricated, can be easily followed during a reasonable time of measurement.¹

Another application of these tools in our group, may be the most attractive, is related to the energy field. These methods indeed can be employed to more precisely characterize various materials which are of interest for the energy storage. It appears very challenging to examine in detail the mechanism of ion/solvent transfer/diffusion and by this way to improve the performances of these dedicated materials. A first possibility is to use a classical QCM coupled with cyclic voltammetry. Unfortunately, even though interesting responses are obtained, the deconvolution of the mass and current changes, after a potential step, is quite complicated. Our group has developed an original approach based on the association between a fast QCM and EIS technique (Electrochemical Impedance Spectroscopy). This coupled method, named *ac*-electrogravimetry, has the ability to detect the contribution of the charged or uncharged species transferred at the electrode/electrolyte interfaces and able to separate/identify the anionic, cationic, and the free solvent contributions during electrochemical processes occurring in charge storage films. During this talk, charge storage behavior of carbon based materials (nanotubes, reduced graphene oxides) and metal oxides (birnessite type MnO₂, WO₃, or RuO₂ electrodes) will be discussed, constituting examples for electrode materials in supercapacitors and pseudocapacitors, respectively.^{2,3} The dynamics of ion transfer at the electrode/electrolyte interfaces, the effect of solvent and solvation/desolvation of the transferred ions will be discussed based on the *ac*-electrogravimetry responses.

References:

- 1) H. Perrot, "Chemical Sensors and Biosensors", edited by R. Lalauze, ISTE, Wiley 2012.
- 2) C. Ridruejo Arias, C. Debiemme-Chouvy, C. Gabrielli, C. Laberty-Robert, A. Pailleret, H. Perrot, O. Sel, New insights into pseudocapacitive charge storage mechanisms in Li birnessite type MnO₂ monitored by fast quartz-crystal microbalance methods, *J. Phys. Chem. C*, **2014**, *118*, 26551-26559.
- 3) F. Razzaghi, C. Deviemme-Chouvy, F. Pillier, H. Perrot, O. Sel, Ion intercalation dynamics of electrosynthesized mesoporous WO₃ thin films studied by multi-scale coupled electrogravimetric methods, *Phys. Chem. Chem. Phys.* **2015**, *17*(22), 14773-87.