In Situ/Operando Investigation of Catalytic and Electrocatalytic Interfaces

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Abstract

In situ and *operando* spectroscopic methods play a fundamental role in a variety of different fields of modern science. Especially, as the energy and environmental science have become increasingly important nowadays, the need of *in situ* and *operando* spectroscopic methods has also increased significantly. Therefore, we felt it was time to have a Special Issue focused on such techniques and whose aim was "*to merge the research communities investigating catalytic and (photo)electrochemical interfaces with different in situ/operando spectroscopic techniques, to share recent results, experimental methods, and future perspectives*", as we reported in the scope of this special issue. With its 23 original research papers and 2 topical reviews, spanning from heterogeneous catalysis to photoelectrochemistry, we believe that the outcome of this Special Issue fulfills the aforementioned aim.

In situ and *operando* spectroscopic methods play a fundamental role in a variety of different fields of modern science. Especially, as the energy and environmental science have become increasingly important nowadays, the need of *in situ* and *operando* spectroscopic methods has also increased significantly. This is well-documented by **Figure 1**, reporting a search performed by the authors of this editorial on Web of Science where the keywords were "*in situ/operando* spectroscopy". As reported by **Figure 1a**, the research fields that mostly take advantage of these new experimental capabilities are materials science, physical chemistry, applied physics and chemistry, and electrochemistry. Furthermore, as shown by **Figure 1b**, over the last two decades the number of articles published per year and employing *in situ*/*operando* spectroscopic methods has increased by more than four times.

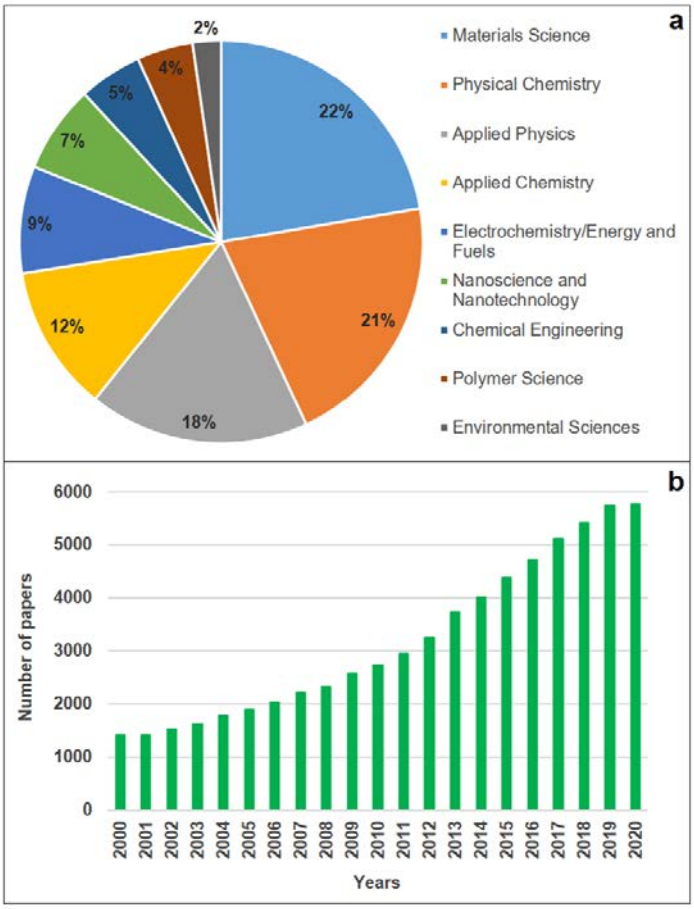

Figure 1. Results of a search on Web of Science using "*in situ/operando spectroscopy*" as search keywords. The total number of publications found was 78954. **a**: Distribution of the articles among the first 9 research fields identified by Web of Science; **b**: Number of articles published each year, between 2000 and 2020.

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scope of this special issue. With its 23 original research papers and 2 topical reviews, spanning from heterogeneous catalysis to photoelectrochemistry, we believe that the outcome of this Special Issue fulfills the aforementioned aim.

Several contributions focused on the *in situ* characterization of model and actual heterogeneous catalysts. Large et al. [1] and Pacholik et al. [2] made use of ambient pressure X-ray photoelectron spectroscopy (APXPS) to characterize actual catalysts. While the former group successfully demonstrated the effect of platinum doping of palladium to mitigate water poisoning during methane combustion [1], the latter investigated the effect of metal doping of MoS_2 applied to carbon dioxide hydrogenation [2]. The work of Pacholik, as well as that of Byrne [3], demonstrate the relevant technological improvements of laboratory based APXPS setups. The latter study describes in detail the “offset droplet method”, used to create and investigate *in situ* the solid/liquid interface, which is relevant in several research fields (e.g. photocatalysis and electrochemistry) [3]. Diulus et al. [4] and Simonovis et al. [5] focused their studies on model systems, using APXPS to understand fundamental aspects of surface chemistry and catalytic reactions. The thermal oxidation mechanism of Ru(0001) to RuO_2(110) can be divided into subsequent steps, involving the formation of a metastable phase precursor [4]. Simonovis and co-workers showed that the reaction environment strongly influences the reactivity of platinum atoms on Cu(111): CO_2 is activated on platinum in presence of hydrogen, whereas oxygen creates a Cu_2O overlayer during CO oxidation [5]. The dissociation of CO_2 (and its hydrogenation) was also the focus of the work of Lin et al. [6]. The authors observed a complex interplay between surface reactivity and evolving chemical makeup when exploring the aforementioned process at elevated temperatures on NiGa thin film alloys. A different approach was instead taken by Ye et al., who investigated the adsorption/dissociation of CO_2 on GaP surfaces induced by solar light simulation at room temperature, proposing a CO_2 dissociation pathway that could be used to rationalize the early stages of CO_2 reduction reaction at the semiconductor/electrolyte interface [7]. In another contribution, Toyoshima et al. [8] examined the oxidation states of oxidized rhodium catalysts under CO exposure and explored how the reduction of oxidized Rh nano-particles evolved during catalytic reaction conditions in the presence of oxygen and NO. Similarly, Jeong et al. determined the chemical states of palladium in palladium hydroxide ($Pd(OH)_2$) when exposed to water and oxygen environments, providing critical insights on hydrous Pd oxide catalyst under reaction conditions [9].

X-ray absorption spectroscopy (XAS), as stand-alone technique or in combination with APXPS, was also employed in several contributions to characterize catalytic processes in an *in situ/operando* fashion. For instance, Yao et al. [10] monitored the formation mechanism of monodispersed palladium nanoparticles in an ionic liquid matrix. Karagoz et al. provided

instead a comprehensive picture of the surface chemical behavior on $Cu_2O(111)$ surface as a function of NO_2 gas pressure [11].

Recent developments of ambient pressure photoelectron spectro-microscopy allow imaging and spectroscopy of the solid/gas interface under realistic working conditions, as reported by Amati et al. in their manuscript [12].

The *in situ/operando* investigation of solid/liquid interfaces is also tackled by several contributions to this Special Issue. The challenge of creating stable solid/liquid electrified interfaces whose characterization can be performed with APXPS was the primary focus of the work of Velasco-Vélez et al. [13]. Leidinger and co-workers provided an extensive report about the optimized conditions for obtaining high quality, large area graphene membranes that can be used to seal off high pressure *in situ/operando* cells [14]. Su et al. [15] and Favaro et al. [16] coupled instead the "Dip-and-Pull" method with APXPS to investigate corrosion phenomena on nickel in alkaline electrolytes and the surface reactivity of different bismuth vanadate photoanodes at the open circuit potential under illumination conditions, respectively. Using the same approach, Carvalho et al. probed the surface adsorbates on a series of $La_{1-x}Sr_xNiO_{3-\delta}$ epitaxial thin films exposed during oxygen evolution reaction (OER) and interpreted the role of Sr in OER with oxygen vacancies-mediated OER mechanism [17].

The role of metallic nanoparticles in electrocatalytic processes was explored by two contributions. In their work, Yang and co-workers linked the size of Pt nanoparticles deposited on $Co_3O_4(111)$ to the reactivity toward the electrooxidation of 2-propanol, employing electrochemical infrared reflection absorption spectroscopy (EC-IRRAS) [18]. Pt nanoparticles (deposited on carbon substrates) were also investigated by Schröder et al. during fuel cell accelerated stress operation by means of small-angle X-ray scattering (SAXS) performed with a laboratory instrument [19]. Different *in situ/operando* experimental techniques and methods dedicated to investigating solid/liquid interfaces and reaction intermediates have been summarized in two comprehensive topical reviews, by Bieberle-Hütter et al. [20] and Yoo et al. [21].

The investigation of catalytic and (photo)electrocatalytic processes under *in situ/operando* conditions is challenging due to complex chemical processes occurring at the working interfaces over multiple orders of magnitude in both length- (angstrom to millimeter) and timescales (femtoseconds to seconds). Hence, such an investigation requires complementary analytical techniques used in a rational multi-modal approach, supported by advanced data analysis/mining and simulations (both in terms of *ab-initio* calculations of structural and electronic properties and *Monte Carlo* analysis of reaction kinetics). For instance, combining *in situ* STM and APXPS, Li et al. [22] observed the structural dynamics of 2-dimensional FeO nanostructures on Au(111) under oxidation condition, monitoring the transition process from the FeO bilayer to the FeO_2 tri-layer. Jiang et al. developed a model system for all-solid-state

Na_2O_2 battery and performed *operando* analysis of the formation and decomposition of Na_2O_2 in Na–O_2 batteries using both Raman spectroscopy and APXPS [23]. Finally, Martins et al. presented a new methodology of using APXPS under near total reflection regime for probing buried interfaces with extreme depth resolution, which can be highly valuable for solid/liquid interface study [24].

In conclusion, understanding how a catalyst or (photo)electrocatalyst behaves under reaction conditions helps identifying what are the active phases/sites involved and, finally, to sketch reaction mechanisms. Furthermore, *in situ* and *operando* spectroscopic methods allow investigating degradation mechanisms and poisoning processes occurring at the working interfaces. This knowledge is therefore crucial to tailor stable catalytic functionalities in novel materials, and to develop fabrication methods that optimize them.

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