Spectroscopic View onto the Catalyst's States

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Catalysis studies require an exhaustive analysis of the catalyst material in the pristine state as well as after (electro)catalysis to be able to track the possible changes of the material and to interpret the catalytic data correctly. An extension of the library of systematically studied catalysts allows to elucidate the nature of catalytically active sites or specific steps of the reaction mechanisms. Powerful X-ray diffraction and metallography methods shed light on the phase and composition changes, morphological alterations, segregation effects, etc. However, these data do not provide any insight into the electronic state of the elements on the surface of the catalyst, where the actual catalytic reaction takes place. Here, a few examples of fruitful collaborations between the *Department of Chemical Metal Science* and the *Department of Physics of Correlated Matter*, illustrating the power of combined catalytic studies, spectroscopy, and quantum chemical calculations, are presented.

Spectroscopy and quantum chemical calculations

Searching for Ir-free electrocatalysts for the anodic half-reaction (oxygen evolution reaction, OER) of water electrolysis, elemental Pt, possessing an outstanding stability under harsh oxidative conditions, was combined with Al to form different Al-Pt intermetallic compounds. In terms of the OER activities, notable ones were seen for Al_2Pt and Al_3Pt_2 compounds [1, 2]. At the same time, independently of their composition, Al-Pt compounds do not maintain their structural and electronic properties on the surface and near-surface region as a result of the Al leaching and surface rearrangement under OER. The depth of such changes depends on the composition and structure of the Al-Pt compound. *In situ*-formed catalytically active and dynamic surfaces, containing the remnants of Al-Pt intermetallic compounds, Pt-rich Al_xPt_{1-x} phase and Pt oxides, possess comparable or better OER activity (w.r.t. *fcc* Pt).

In order to facilitate this study, other main group elements (M = Ga, In, Sn) were used as counterpart elements, keeping the crystal structure of M_2Pt (*anti*-CaF_2 type) unchanged [3]. As expected, the electronic state of Pt changes, leading to shifts of the Pt 4*f* core levels compared to Pt. However, the shift to higher binding energies in M_2Pt (usually associated with a positive valence state of the Pt atom) occurs together with a charge transfer from the M atoms to Pt (i.e. negatively charged Pt). Similar positive core level shifts accompanied with negatively charged atoms were also observed for Be_5Pt and Ga-Pd compounds. However, at that time no detailed study was carried out. For the first time, careful analysis using the electron localizability indicator (ELI-D) approach provides an alternative explanation for the case of M_2Pt compounds based on the number of electrons in the 5*d* subshell. A total of 68 electrons (54 up to Xe configuration plus 14 for the 4*f*) always belong to the core. Therefore, the difference between the total number of core electrons and 68 gives the number of 5*d* electrons, n_{5d}, of the Pt atom. A linear trend between the shifts of the Pt 4*f* core levels experimentally observed by X-ray photoelectron spectroscopy (XPS) and the number of 5*d* electrons (n_{5d}) computed for the M_2Pt compounds (M is a group 13 element, Al, Ga and In) was found (Figure 1). Tin, belonging to group 14 with a formal valence of 4+, causes Sn_2Pt to be an outlier. The more electrons are in the 5*d* subshell, the smaller is the 4*f* core level shift. This implies that 5*d* electrons play a crucial role in screening the core hole and providing the relaxation of the electronic structure after the 4*f* electron is ejected from the 4*f* subshell.

To study such an effect in a systematic way, Al-Pt compounds were synthesized in a single-phase state and consistently analyzed by hard X-ray photoelectron spectroscopy (HAXPES) at the Max-Planck-NSRRC end station at the Taiwan undulator beamline BL12XU at the synchrotron Spring-8 in Japan [4]. The samples were cleaved *in situ* under ultra-high vacuum conditions at base pressures in the low 10^{-10} mbar range. The purity of the investigated sample area was verified by

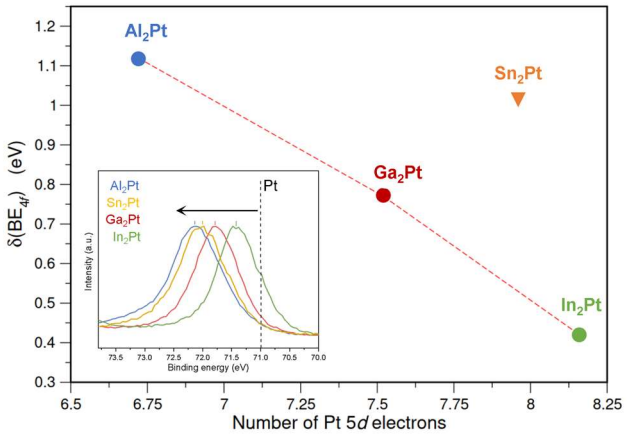

Fig. 1: Correlation between experimental Pt 4f XPS core level shifts and computed number of 5d electrons for M_2Pt compounds. Inset: Pt 4f core level spectra.

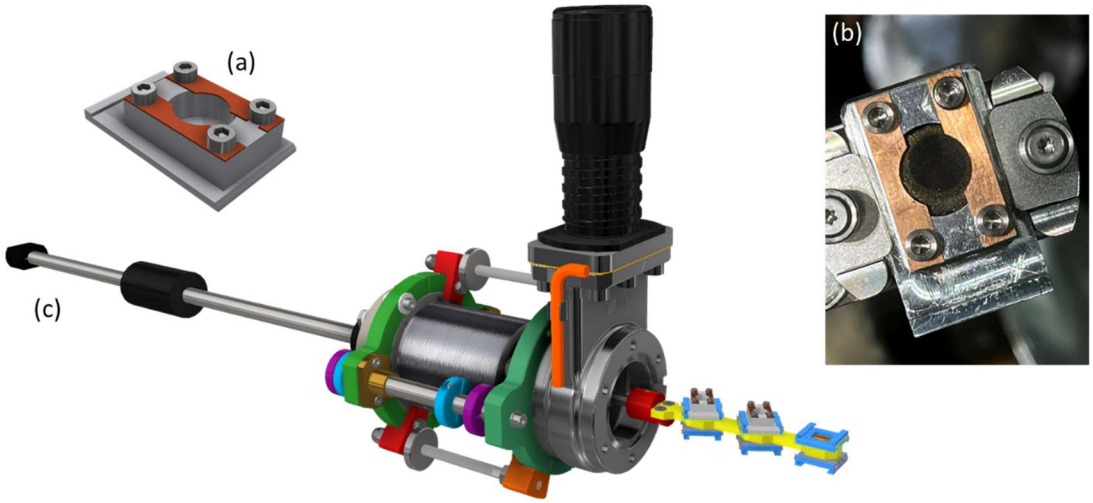

Fig. 2: (a,b) Special sample holder for the characterization of the electrodes which is compatible with the in situ transfer inside the spectroscopy chamber. (c) Vacuum suitcase for transfer of the samples from the Argon glove box to the ultra-high vacuum system without exposure to air.

measuring a wide scan prior to the core level measurements. The use of hard X-rays with larger probing depth compared to standard laboratory XPS sources allows to minimize the contributions from the surface, thus supporting reliable studies of the intrinsic properties of the intermetallic compounds, here in particular of the Pt 4*f* peak positions for the different Al-Pt compounds. An extensive computational analysis points toward higher negative charges of Pt atoms being accompanied by a reduced occupancy of the Pt 5*d* orbitals, leading to the restricted screening of the 4*f* core hole by these electrons, which can explain the experimentally observed shifts of the Pt 4*f* core levels towards higher binding energies. To the best of our knowledge, this is the first systematic case study on correlations between the experimental spectroscopic data (HAXPES) and computational data on electronic structure and chemical bonding [4] and **CMS_04_Wagner**.

Spectroscopy and catalysis

In addition to the insight into the specific features of XPS core level shifts in the case of Al-Pt compounds, very useful results were obtained by analyzing the electrocatalysts before and after electrochemical experiments under various conditions. In order to allow a systematic characterization after each step of the reaction, in-house XPS was employed. For this purpose, a special sample holder for electrodes in cylindrical shape was designed and manufactured at the MPI CPfS (Figure 2a and 2b). The electrodes are clamped with copper stripes onto the aluminum holder, compatible with the ultra-high vacuum environment and the *in situ* transfer inside the spectroscopy chamber.

Electrodes made of isostructural intermetallic compounds M_2Pt (M = Al, Ga, In, Sn) were studied for the OER. From electrochemical data, the OER activity decreases in the sequence $In_2Pt > Ga_2Pt > Al_2Pt$, whereas Sn_2Pt is inactive. Different bulk- and surface-sensitive techniques were applied to study this behavior. These studies revealed that the OER activity is governed by the chemical nature of the counterpart elements M and their leaching rates under OER conditions. The improved OER activity is due to the roughening of the surface as well as a result of the enhanced reactivity of modified Pt. This modification of the electronic structure of Pt can easily be inferred from the Pt 4*f* core level shifts towards lower binding energies (Figure 3). Another interesting feature of the XPS spectra after the OER experiment is the presence of PtO_x in case of Al_2Pt and Ga_2Pt, and its absence in case of In_2Pt. The inactivity of Sn_2Pt is due to the formation of passivating PtO_2 and SnO_2 layers with poor electrical conductivity. At the same time, the signal corresponding to the (inter)metallic Pt is noticeably reduced. This insight from XPS data is in line with the elemental analysis of the electrolyte, revealing quantitatively the M leaching, and metallographic studies, clearly showing the consumption of In_2Pt. This results in a continuous refreshment of the surface, hindering the coverage by PtO_x and making it the most OER-active among M_2Pt.

Another example of the guiding role of XPS for the understanding of the active state of the electrocatalyst is our work on the ternary $Hf_2B_{2-2\delta}Ir_{5+\delta}$ compound [5]. The short- and long-term OER experiments at moderate (10 mA cm^{-2}) and elevated (100 mA cm^{-2}) current

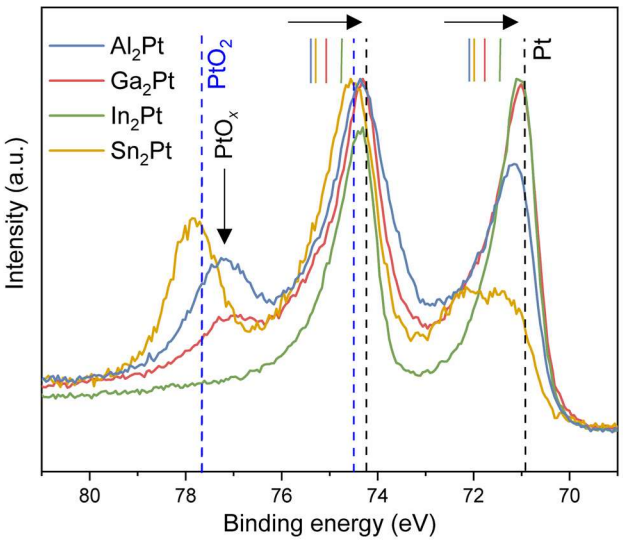

Fig. 3: Normalized Pt 4f XP core level spectra of M_2Pt (M = Al, Ga, In, Sn) after standard OER. Vertical colored ticks represent core levels in pristine M_2Pt.

densities reveal the continuous improvement of the OER activity with time. Neither any changes of the powder X-ray diffraction pattern nor a noticeable modification in the morphology of the electrode (based on standard scanning electron microscopy analysis) were observed. However, systematic XPS analyses after short- and long-term OER clearly highlight the increasing additional contributions of IrO_x and HfO_2 to the Ir 4*f* and Hf 4*f* XPS core levels. This prompted more precise scanning electron microscopy analysis at reduced acceleration voltages (to be more surface-sensitive) and looking for more details in the porous electrode surface. Nicely shaped HfO_2 crystallites as well as agglomerates of IrO_x were identified on the surface and in the electrode pores. Furthermore, a detailed analysis of the crystal structure and chemical bonding strongly supports the controlled oxidation of $Hf_2B_{2-2\delta}Ir_{5+\delta}$ and its long-term bulk stability.

In order to perform a spectroscopic investigation of such changes at the surface, contact with air has to be avoided and therefore, a special transfer routine was established. The OER experiments were performed in an argon glove box. A dedicated vacuum suitcase, which can be introduced into the glove box and can accommodate up to six sample holders, was designed (Figure 2c). After the OER experiments, the electrodes are mounted in the suitcase, which is then tightly sealed and transported to the ultra-high vacuum system. Here, the suitcase is connected to the load lock chamber to pump out the argon gas prior to the transfer of the samples to the spectroscopy chamber.

These prominent examples clearly illustrate the huge potential of collaborative work, combining catalytic experiments, insight from spectroscopy and quantum chemical calculations. The possibility to exclude the exposure to air using our dedicated vacuum suitcase will allow for even more detailed insights into the intrinsic electronic properties of the compounds and avoid their coverage by oxide layers. In future, such concerted studies will be explored not only towards other compounds or variations of OER conditions, but also their use in other electrocatalytic processes and comprehensive characterization afterwards.

External Cooperation Partners

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