## Intermetallic compounds for electrocatalysis

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The catalytic properties are governed by the state of the catalyst surface under reaction conditions. The well-defined crystal structure and foreseen chemical bonding features of intermetallic compounds provide the plausible background for an understanding of chemical changes under dynamic reaction conditions and their relation to the investigated catalytic performance.

The global demand for (partial) transition towards renewable energy sources and consideration of hydrogen as one of the future energy carrier molecules calls for the improvement and scalability of the hydrogen production techniques. The "bottleneck" for large-scale application of water electrolysis (and particularly, PEM electrolysis) is the limited efficiency due to sluggish kinetics of the anode oxygen evolution reaction (OER), which requires very active electrocatalysts. Furthermore, the extreme oxidative conditions (acid electrolyte, applied potentials, chemically active intermediate species, etc.) restricted the choice of OER electrocatalysts to noble metals and their oxides, among which  $IrO_x$  compromises activity and stability criteria. However, reduction of Ir amount or its replacement is of enormous importance.

One of the implemented approaches is to dilute the Ir in the form of well-defined intermetallic compounds, simultaneously providing a chemically robust environment for Ir atoms. As an example, the ternary compound  $Hf_2B_2Ir_5$  was investigated as OER electrocatalyst [1]. From chemical bonding point of view,  $Hf_2B_2Ir_5$  is a cage-like compound with Ir-B polyanionic framework, built of  $B_2Ir_8$  structural units, and Hf cations located in the cages [2]. Due to significant electron transfer, Hf atoms possess high positive charge (+1.83), whereas B and Ir are negatively charged (B: -0.19; Ir: -0.63-0.66). The OER activity of  $Hf_2B_2Ir_5$  is comparable with the *fcc* Ir (Fig. 1). However, the amount of dissolved Ir using the IMC as anode material is two orders of magnitude lower than that using fcc Ir, pointing out the noticeable influence of the atomic interactions in Hf<sub>2</sub>B<sub>2</sub>Ir<sub>5</sub> on its stability. The long-term operation at current density (*j*) of 100 mA cm<sup>-2</sup> reveals the continuous activation of the investigated material. Metallography in combination with XPS analysis show that OER activity can be related to the Ir-terminated surface of Hf<sub>2</sub>B<sub>2</sub>Ir<sub>5</sub>, supported by activity of in situ-formed particles of  $IrO_x(OH)_y(SO_4)_z$ . The particles are mainly formed due to the oxidation of a negligible amount of HfB<sub>4</sub>Ir<sub>3</sub> admixture in the specimen and near-surface oxidation of Hf<sub>2</sub>B<sub>2</sub>Ir<sub>5</sub> itself. The covalent interactions between Ir and B atoms in the polyanionic framework hinder the deep Ir leaching, allowing the bulk stability of Hf<sub>2</sub>B<sub>2</sub>Ir<sub>5</sub> over 240 h of anodic operation.

Looking for Ir-free OER electrocatalysts and considering the outstanding stability of *fcc* Pt against dissolution under OER, the intermetallic compound Al<sub>2</sub>Pt was studied as anode material [3]. The poor OER activity of *fcc* Pt was assumed to be enhanced as a result of atomic interactions between Al and Pt in Al<sub>2</sub>Pt. The QTAIM calculations reveal significant charge transfer from Al atoms to Pt ones, leading to negatively charged Pt (- 3.52) in the Al<sub>2</sub>Pt. The chemical bonding analysis shows the strongly polar



Fig. 1: OER activity of  $Hf_2B_2Ir_5$  anode material compared to elemental Ir (left, inset: long-term chronopotentiometry at 100 mA cm<sup>-2</sup>) and its microstructure after long-term electrochemical experiment (right).



Fig. 2:  $Al_2Pt$  under OER conditions: long-term CP at current density of 90 mA cm<sup>-2</sup> (left), variation of Pt 4f core levels position at different time of CP (middle), morphological changes of  $Al_2Pt$  during long-term OER (right).

interaction between Al and Pt, making the latter nonequivalent with Pt atoms in fcc Pt. During the longterm electrochemical experiment, a few steps were observed: (i) initial activation of the material during 48 h, (ii) stable activity over the next 30 h with (iii) subsequent continuous suppression of the OER activity for the rest of long-term CP (Fig. 2). Such changes in the electrochemical features are related to the continuous leaching of the Al from the specimen, which is accompanied by formation of a Pt-rich phase (presumably solid solution of Al in fcc Pt) on the surface and in the near-surface region. The formation of a Pt-rich phase with an electronic structure similar to that of the *fcc* Pt was confirmed by the shift of Pt 4*f* core levels in the XPS spectra (Fig. 2). Additionally, the contribution of PtO<sub>2</sub> was detected. As a result, the active OER material is a composite of Al<sub>2</sub>Pt, Pt-rich phase and PtO<sub>2</sub>. Its OER activity is considerably higher compared to fcc Pt. The formation of the surface oxide layers leads to reduced electrical conductivity and is responsible for the loss of OER activity during the last period of the long-term OER experiment. From a metallographic point of view, the bulk material retains its structural and compositional integrity during 19 days of OER at enhanced j = 90 mA cm<sup>-2</sup>. The depth of material restructuring reaches ca. 400 µm (Fig. 2).

To extend the chemistry of  $M_2$ Pt materials, the isostructural compounds  $M_2$ Pt (M = Ga, In, Sn) were also studied as OER electrocatalysts. The activity follows the trend In<sub>2</sub>Pt > Ga<sub>2</sub>Pt > Al<sub>2</sub>Pt and is governed by the chemical nature of the counterpart elements Mand their leaching rates under OER conditions. The leaching of M into the electrolyte creates a dynamic material, composed of remaining intermetallic  $M_2$ Pt and Pt-rich phase in the near-surface region. For Sn<sub>2</sub>Pt, the passivation layer of SnO<sub>2</sub> hinders electron transfer and leads to a poor OER performance. The presented examples clearly highlight the importance of the chemical bonding features for our understanding of chemical behavior of intermetallic compounds, leading to the appropriate interpretation of the catalytic results. Further exploration of the material library for the oxidation reactions will be helpful for a development of new concepts in catalysis and following competence for focused catalyst search.

## **External Cooperation Partners**

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