Olga Kasian has received her PhD in Electrochemistry from Ukrainian State University of Chemical Technology in 2013. After that she worked as a postdoc at the Brandenburg University of Technology Cottbus-Senftenberg. In 2015 she received fellowship from the Alexander von Humboldt Foundation and joined Max-Planck-Institute für Eisenforschung in Düsseldorf. In 2019 Olga Kasian received funding from the Helmholtz Association and since then has been leading the Helmholtz Young Investigator Group at the Helmholtz Center Berlin (HZB) focused on dynamic changes in materials during electrocatalytic reactions. In 2021 she has joined Friedrich-Alexander-Universität Erlangen-Nürnberg as a Professor of Materials for Electrochemical Energy Conversion. The research of Olga Kasian aims at providing mechanistic understanding of chemical processes at complex electrochemical interfaces, with a special focus on electrocatalysis for energy storage and conversion, aiming to overcome stability limitations in catalyst materials.

Electrocatalysis for long-term Energy Conversion Performance

Olga Kasian
Electrocatalysis For Long-Term Energy Conversion Performance

I. Introduction

Renewable energy sources are expected to eventually replace traditional fossil fuels. Due to the intermittent nature of sustainable energy sources like wind and solar, their increased installation will result in fluctuating power generation. A large variety of concepts for utilization of this dynamic power supply is currently under development. The environmentally-safe power storing technologies are based on interconversion of chemical and electrical energy [1]. The most promising among them are the storage of renewable energy through the electrochemical reduction of carbon dioxide (power-to-value), electrical storage using battery electric vehicles (power-to-mobility), or production of hydrogen by water electrolysis (power-to-fuel) [2]. Hydrogen can be further used in several ways, schematically illustrated in *Figure 1*, including direct conversion into heat (fuel-to-heat), reconversion to power in fuels cells (fuel-to-power, fuel-to-mobility) or as a reactant in the synthesis of hydrocarbons and ammonia (fuel-as-chemical). Possibility of hydrogen utilization in such various applications makes water electrolysis technology an attractive solution for the conversion and storage of excess electricity into hydrogen and oxygen.

The large scale application of electrochemical systems used for energy conversion and storage including water electrolysis is chal-lenging due to low efficiency and instability of catalyst materials during long term and dynamic operation [3]. For example, in proton-exchange membrane water electrolyzers for hydrogen production, reactions are catalyzed by noble metals based alloys and oxides making the issues related to efficiency of catalyst utilization and durability even more critical. In this connection the main requirements for catalysts in water electrolysis are stability over time and low energy consumption to split water into hydrogen at the cathode and to oxygen at the anode of the electrolyzer. If these requirements are met, the electrolyzer is expected to exhibit

Resume:

With increasing environmental concerns and transition of energy sector towards renewables the importance of electrochemical technologies for energy conversion and storage is constantly growing. Such technologies are based on interconversion between chemical and electrical energy and rely on performance of electrocatalyst materials. The efficiency and service life of these materials are intrinsically related to their chemistry, electronic state, microstructure and interaction with their environment. The development of improved catalysts thus requires deep understanding of the reactivity of single atoms involved in the catalysis and the mechanisms that lead to their degradation or deactivation. To tackle this challenge we developed an approach to tracking the chemical transformations of catalytically active layers, with atomic resolution, which reveals the most crucial processes that cause deactivation and structural degradation of the catalysts. Gained insights guide development of the strategies to hinder unwanted reactions and drive the rational design of advanced catalyst materials for energy conversion and storage applications.

high performance at a reduced cost. However, development of catalyst materials that fulfill these strict requirements demands a deep understanding of catalytic reactions of hydrogen and oxygen evolution themselves as well as mechanisms of other reactions that lead to electrocatalysts degradation.

These reactions take place at solid-liquid interfaces and include multiple steps of adsorption/desorption, electron transferring and chemical interactions. The composition of the catalyst surface and its gradual transformation play a crucial role in both, activity and stability behavior. Resolving which of the surface species serve as the active sites for the catalytic reactions and the role of the individual atoms of the topmost layers in the degradation processes, however, still remains challenging. The resulting knowledge gap regarding the nature of the active species in catalysts which might undergo transformation during the catalytic process hinders the further development of high-performance commercial systems such as water electrolyzers.

》 Electrochemical energy conversion is a key technology for the future sustainable energy scenario. 《
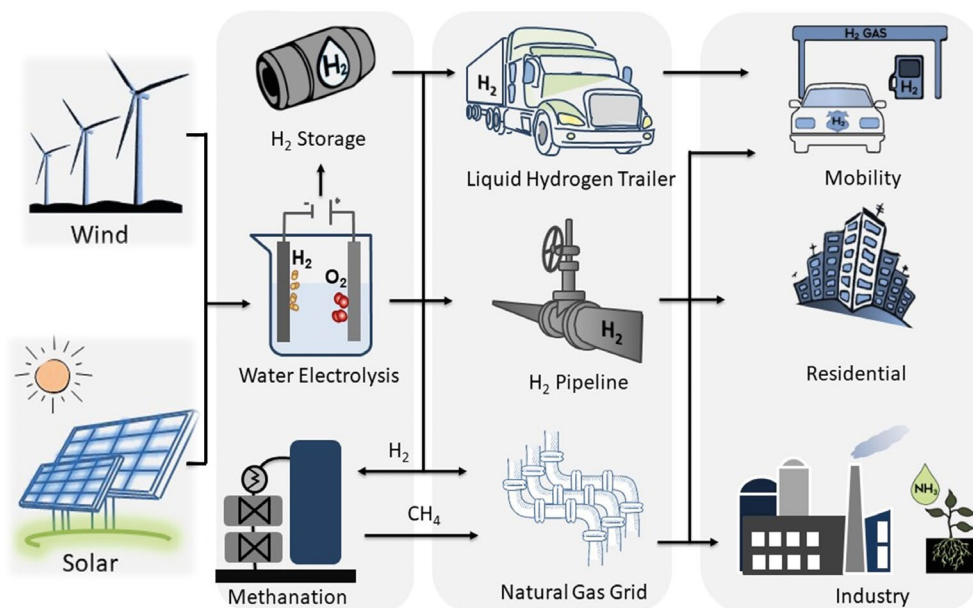
Olga Kasian

II. Resolving the reaction mechanisms in electrocatalysis

The main challenges in resolving mechanisms of the reactions can be showcased on the example of electrochemical water splitting to hydrogen and oxygen. As was mentioned above, high activity and stability are the main requirements for electrodes in water splitting devices. In catalysis research activity of materials towards desired reaction is often evaluated based on Sabatier's principle. It is a qualitative concept which states that the catalyst exhibits high activity when reaction intermediates adsorbed to its surface neither too strongly nor too weakly. If the interaction is too weak, the intermediate will fail to bind to the catalyst and no further reaction steps will take place. If the interaction is too strong, the intermediate fails to dissociate, or the product will not desorb blocking the surface for further interactions. This principle provides predictive basis for the catalytic activity using so-called "volcano" relationships, where measured reaction rate (in electrochemistry exchange current densities) are plotted versus the various properties (descriptors) correlated with adsorption energy [4, 5]. The descriptors can be experimentally defined (e.g. the enthalpy change of the transition from a lower to higher oxide for oxygen evolution; the metal-hydrogen bond strength for hydrogen evolution) or derived from the density functional theory (calculated adsorption energies). Although the volcano plots may provide insight into the optimum catalyst with desired activity, they are not applicable to stability predictions and have other limitations, since the simple descriptor-based model does not consider additional factors affecting the reaction kinetics. To derive fundamental understanding of

the composition-activity/stability relationship the reaction kinetics, mechanisms and, ideally, intermediates must be known.

The electrochemical reaction of hydrogen evolution is one of the simplest reactions in electrochemistry, yet, it typically occurs via several elementary steps including (i) formation of hydrogen atoms on free active sites (Volmer step); followed by (ii) formation of hydrogen molecule by electrochemical desorption (Heyrovsky step); or (iii) recombination of adsorbed H atoms (Tafel step) [2].

The generalized hydrogen evolution mechanism in acidic media is schematically presented in *Figure 2a*. In alkaline electrolyte the pathway is similar, with the only difference of formation of adsorbed hydrogen atoms from water. Even though the reaction is simple and was extensively studied, the understanding of the mechanism is incomplete. Apart from these commonly accepted three steps other unresolved alternative pathways are taking place. The mechanism becomes even more complex when reaction is catalyzed by alloys, hydroxides, metal sulfides

and phosphides [6]. In parallel to hydrogen formation the electrochemically induced dissolution of the catalyst may take place [6]. In conditions of intermittent electrolysis the stability problem may become even more crucial if the potential is pushed into the region of free dissolution (corrosion) during the shutdown of an electrolyzer [6, 7].

The mechanism of the oxygen formation during electrolysis of water is even more complex and less understood, as it involves transferring of 4 e– and occurs through many intermediate steps. The reaction initiates from adsorption of OH radicals formed from water molecules (acidic media) or OH-ions (alkaline solutions). The multiplicity of further possible elementary steps is schematically shown in *Figure 2b*. Though a large number of possible oxygen evolution mechanisms has been proposed [4, 8], the topic remains a subject of intensive debates in literature, since the intermediates and their possible interrelations are in most of the cases unknown. The mechanism of the oxygen evolution is commonly derived using conventional electrochemical me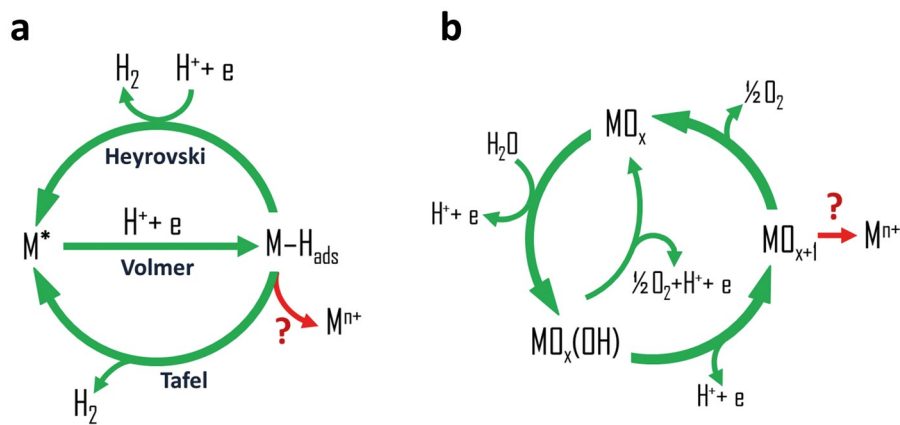thods (determination of the Tafel slopes in conditions of steady-state and reaction orders with respect to protons). However, deep understanding of the reaction mechanism requires knowledge on possible reaction intermediates. Resolving the intermedi-

" Success of large scale application of electrochemical power storing technologies relies on efficiency and stability of catalyst materials during long term and dynamic operation. "

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ates is a very challenging task, considering their low concentration and limited lifetime, which requires application of highly sensitive analytics. In particular volatile intermediates with sufficient lifetime can be detected in situ using mass spectrometry in combination with electrochemistry. The commonly used methods are differential and online electrochemical mass spectrometries. The understanding of oxygen evolution mechanism can be advanced by using a method of isotope-labelling. This method helps to distinguish between oxygen molecules formed from the atoms in the oxide lattice and water and justify participation/consumption of oxide catalyst lattice in the reaction mechanism [9, 10]. Another approach to reveal the intermediates in the oxygen evolution reaction includes synchrotron based techniques [11, 12], which enable detection of the surface species and tracking possible changes in the oxidation state of the catalytic centers.

Resolving the mechanism of catalysts degradation/dissolution during the oxygen evolution reaction is another challenging topic. Though the existence of experimental correlation between the activity of oxygen evolution catalyst and its dissolution was numerously reported and discussed [13, 14], only a few works addressed the mechanistic aspects of these two reactions in one study [13, 15]. The main bottleneck in simultaneous resolving mechanisms of the oxygen formation and catalyst degradation is constant evolution of the surface. As a result
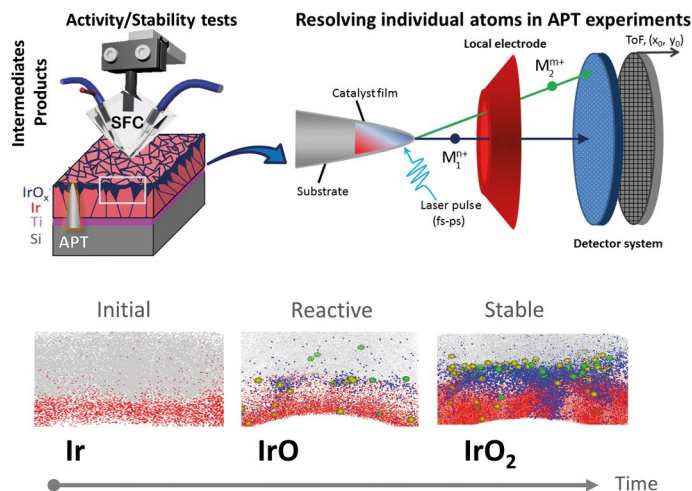
each single moment of the reaction takes place on a newly formed surface having different chemistry, physics and structure.

III. Atomic scale and mechanistic insights

Electrocatalytic interactions are too complex for a single technique to deliver all the necessary information. Correlative assessments must be developed to build upon the strength of each individual technique and complement the data on the reactivity and formed intermediates by the atomic scale insights. Our approach to tackling this challenge is displayed by the oxygen electrocatalysis on iridium catalyst. The comprehension of oxygen evolution mechanism on iridium has significant importance, considering its utilization in the state-of-the-art proton exchange membrane water

electrolyzers for hydrogen production. We have addressed this question and suggested the possible pathways of the oxygen evolution reaction and iridium dissolution in acidic media *(Figure 3)*[16]. Comparison of the schemes in *Figure 2b* and *Figure 3* shows that the mechanism taking place on a 'real' catalyst material is much more complex. To unveil possible intermediate steps of the reaction we combine electrochemistry with inductively coupled plasma mass spectrometry (ICP-MS) and online mass spectrometry in order to detect soluble and volatile intermediates or products of the reactions. In particular our approach proves that reactions of oxygen formation and degradation of the catalyst undergo via a common intermediate, namely volatile IrO_3. This intermediate is thermodynamically unstable and can be formed only at high applied potentials. In parallel the concentration of dissolved species is monitored using

Figure 2:

Schematic presentation of the mechanisms of a) electrochemical hydrogen evolution on metallic electrodes and b) oxygen evolution on metal oxide catalyst. The red arrows indicate reaction steps leading to catalyst dissolution/degradation.

Figure 3:

Scheme illustrating the oxygen evolution mechanisms on iridium based catalysts. The red arrows indicate steps leading to degradation.

ICP-MS, suggesting another pathway at lower applied potentials where the oxidation state of Ir should be lower than (VI). Since this method cannot provide the information on the oxidation states of the dissolved species, the alternative pathway presented in *Figure 3* is suggested based on the data from in situ synchrotron based spectroscopy on possible oxidation states of iridium during the oxygen evolution. Independently another group of researchers has shown formation of Ir(VI)-intermediate on the surface of iridium-based perovskite during the oxygen formation in X-ray absorption experiments [17]. This indicates that the mechanism proposed in *Figure 3* may have universal character and can be applicable to various Ir-based catalysts at certain conditions. Existence of common intermediates for the oxygen formation and catalyst degradation denotes that more active catalyst materials

are less stable. In order to hinder the degradation reactions, it is, therefore, crucial to identify these intermediates and develop the strategy how to stabilize them on the surface.

As was stated above challenges in mechanistic studies are often related to the constantly changing composition of the catalytic surfaces that affects the kinetics and further path of the reaction. Since only surface layers contribute to the electrocatalysis, such compositional changes are predominantly ongoing with the topmost atoms and require utilization of techniques providing sensitivity in resolution on the atomic level to be tracked. Resolving such transformations is vital for the understanding the reaction mechanisms. To identify the individual atoms within the near surface regions of the electrodes we propose to em-

ploy atom probe tomography (APT). APT is a mass spectrometry based method that allows mapping a distribution of individual atoms in three dimensions (3D). *Figure 4* shows working principle of the method. Applying this approach, we resolve gradual transformation of the Ir surface during the oxygen evolution catalysis [18, 19]. A view of the 3D elemental distribution *(Figure 4)* provides unique experimental evidence of formation of highly reactive non-stoichiometric metastable species Ir-O residing at the near surface of iridium oxides at the beginning of oxygen formation. Presence of these metastable species is correlated with electrocatalytic activity and stability. In time these species gradually transform to stoichiometric iridium dioxide, yielding durability improvement, but deterioration of activity. In addition stability drops when the oxygen atoms in the catalyst are replaced by those from water. In case of extremely reactive oxide catalysts, the oxygen molecule can be released directly from the oxide lattice, without water contribution [17]. Iridium dioxide, which is the most stable oxygen evolution catalyst known, also ongoing structural changes during water splitting. Using isotope labelling method in combination with atom probe tomography we observe surface restructuring that affects two nanometers of the oxide due to a constant exchange between oxygen atoms in the catalyst and water [20]. Spectroscopy data suggests that water-lattice oxygen exchange leading to degradation becomes even more pronounced if $-Ir^{III}OOH$ species are present in the structure of the catalyst [10]. Thus, if dissolution has to be eliminated the structure of the catalyst should be free of above mentioned species which become the origin of instability.

Figure 4:

Schematic illustration of single atoms detection by atom probe tomography (top) in combination with electrochemical analysis and gradual transformation of catalytic surface of iridium during the oxygen evolution by water splitting (bottom). Each red spot corresponds to a single iridium atom detected by the atom probe tomography. Blue spots represent single oxygen atoms. Water molecules and hydroxyl species are shown in green and yellow respectively. The stoichiometry derived based on the average ratio between the atoms of oxygen and iridium in the topmost surface layer.

In summary, with the insight on the reaction mechanism obtained from mass spectrometry the correlative APT measurements can resolve special structural features that are responsible for high reactivity and/or instability of other catalytic systems guiding the development of materials with superior electrocatalytic performance [21]. Applying this advanced characterization approach to resolve surface species of other catalytic systems [22] will advance the understanding of reactions mechanisms on constantly evolving surfaces.

"Our unique approach allows tracking the compositional changes in catalysts with atomic resolution and reveals which of them lead to deactivation and degradation."

Olga Kasian

Conclusion and Outlook

In summary, the current understanding of the reactions mechanisms occurring in energy conversion and storage devices has several fundamental shortcomings, such as unknown interplay between the nature of the active sites and their reactivity and stability at the atomic scale; difficulties in resolving the reaction mechanism on constantly evolving surfaces. This outlines that detection of reaction intermediates and products by means of mass spectrometry should be complemented by spectroscopy insight from operando synchrotron based experiments and characterization techniques with atomic scale resolution to draw the full picture of the reaction mechanism. This will guide rational design of high-performance catalyst materials for long-term energy conversion and storage.

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