REVIEW ARTICLE
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Operando studies of Mn oxide based electrocatalysts for the oxygen evolution reaction
Operando studies of Mn oxide based electrocatalysts for the oxygen evolution reaction

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Inspired by photosystem II (PS II), Mn oxide based electrocatalysts have been repeatedly investigated as catalysts for the electrochemical oxygen evolution reaction (OER), the anodic reaction in water electrolysis. However, a comparison of the conditions in biological OER catalysed by the water splitting complex CaMn4Ox with the requirements for an electrocatalyst for industrially relevant applications reveals fundamental differences. Thus, a systematic development of artificial Mn-based OER catalysts requires both a fundamental understanding of the catalytic mechanisms as well as an evaluation of the practicality of the system for industrial scale applications. Experimentally, both aspects can be approached using in situ and operando methods including spectroscopy. This paper highlights some of the major challenges common to different operando investigation methods and recent insights gained with them. To this end, vibrational spectroscopy, especially Raman spectroscopy, absorption techniques in the bandgap region and operando X-ray spectroelectrochemistry (SEC), both in the hard and soft X-ray regime are particularly focused on here. Technical challenges specific to each method are discussed first, followed by challenges that are specific to Mn oxide based systems. Finally, recent in situ and operando studies are reviewed. This analysis shows that despite the technical and Mn specific challenges, three specific key features are common to most of the studied systems with significant OER activity: structural disorder, Mn oxidation states between III and IV, and the appearance of layered birnessite phases in the active regime.

1. Introduction

The electrochemical oxygen evolution reaction (OER),

\[ \text{2H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \]  \hspace{1cm} (1)

or

\[ 4\text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \],  \hspace{1cm} (2)

is the anodic partial reaction of electrochemical water splitting. The cathodic partial reaction of water splitting, the hydrogen evolution reaction (HER), can be employed for the production of "green" hydrogen, when renewable electricity sources are used. However, the HER half-cell reaction is generally considered the bottleneck of the water splitting reaction because the involved transfer of 4 electrons is kinetically challenging. Currently, the most effective anode materials for water splitting rely on expensive noble metals such as Ru or Ir. Thus, lowering the OER overpotential by catalysts based on earth-abundant materials and support materials is a significant goal on the way towards more economical hydrogen based energy storage systems and a decarbonized economy.

Biological oxygen evolution occurring in photosystem (PS) II is catalysed in an active center containing a CaMn4Ox cluster as the oxygen evolving complex (OEC). Computational and spectroscopic investigations have contributed significantly to the understanding of the reaction mechanisms leading to the production of O2 during photosynthesis. Researchers have been tempted to ask whether simple synthetic Mn-based systems can take over the function of the PS II active complex in an electrochemical system, leading to a lot of interest in Mn-based OER electrocatalysts. These could act as alternatives to highly performing, but also rare and expensive systems based, e.g., on Ir or Ru. For biological oxygen evolution, manganese was considered the "natural" choice for a catalyst, due to the combination of several properties such as its availability as soluble Mn³⁺, its versatile redox chemistry with reachable oxidation states and its aqueous coordination chemistry. For industrial
applications, its high abundance on Earth makes it attractive, as Mn is available at a low price and with relatively low criticality. However, a fundamental difference between the requirements for OER catalysts in a biological system and in scenarios for the large-scale production of green hydrogen are the vastly varying current requirements. Biological O₂ production in the respiratory chain involves several transport steps. Thus, transport limitation will at some point limit the currents. At these rather low currents, a catalytic cycle has evolved that is made possible only by the high electronic and structural control of PSII as a supramolecular system.

Several technological approaches based on water splitting have been or are currently being developed, with very different requirements for the working conditions in which the required OER catalysts must persist. For instance, moderate currents in the range of 10–20 mA cm⁻² would be appropriate for solar water splitting applications, which however in most cases disallow extreme pH values and require specific optical or morphological properties. On the other side, industrial zero gap alkaline water electrolyzers can operate at currents up to 1 A cm⁻², in a 20–30 wt% KOH electrolyte and at temperatures of up to 100 °C, which differ significantly from the conditions in biological OERs. Yet, any economically useful catalyst should provide lifetimes in the range of years. Other aspects that require consideration for industrial applications are the costs and scalability of the catalyst preparation and electrode fabrication as well as robustness with respect to varying electrolyte compositions. Nevertheless, the high demand for affordable green energy storage technologies has triggered new research efforts towards Mn-based OER electrocatalysts.

The mechanism of the dioxygen formation via heterogeneous catalysis has been studied for decades (for a review see ref. 2). General schemes for metal oxide catalysts start from adsorbed OH at active surface (metal) sites, followed by single electron charge transfer steps to form M–O (terminal-oxo) species. The O–O bond formation may occur from adjacent M–O or M–OH sites or from a single site via peroxy intermediates. However, the nature of the intermediates and the intermediate steps remain controversial and likely depend on the exact conditions and the catalyst. Beside such atomic understanding, a knowledge driven catalyst development requires a detailed understanding of the processes occurring at application-relevant electrodes including the support and an evaluation of the practicality of the system in applications. Experimentally, these insights are obtained by characterisation of the catalyst using ‘in situ’ (i.e. in electrolyte “at the location” of the electrochemical process) and “operando” (i.e. “during the [electrochemical] process” itself) experiments.

The goal of electrochemical in situ and operando studies is the understanding of the chemical transformations taking place on the electrode surface (substrate and catalyst) as a function of potential or current. In spectroelectrochemical in situ experiments, the spectroscopic signature of a system is directly measured in a controlled environment, e.g., at an electrode in the electrolyte under potential control. Operando spectroelectrochemistry is a sub-type of the in situ experiment, which – for electrocatalytic applications – requires that a catalytic activity/selectivity is measured simultaneously to the spectroscopy. In OER electrocatalysis, the current density provided by the potentiostat is often used to monitor the catalytic activity. This article will discuss the potential of such operando studies to foster the understanding of Mn catalysed OERs. To that end, first, general and Mn specific challenges for such operando spectroelectrochemical methods are discussed, followed by a short review of selected recent in situ and operando studies.

2. Mn oxide-based systems pose special analytical challenges

2.1 General challenges for operando methods

Challenge 1: Operando data do not necessarily yield unique information on the reaction mechanism. In general all operando studies represent an “inverse” problem of an especially challenging nature. Predicting the answer given by an experiment is straightforward when the underlying mechanism or system is known. The opposite process, i.e. determining the unknown mechanism from the experimental result, is tedious and often does not yield unambiguous solutions.

Challenge 2: The necessity for reference data. Many spectroscopic or scattering techniques rely on an analysis that is based and established in ex situ measurements, such as a knowledge-base obtained e.g. on pure, well defined compounds. The potentially unstable species that occur as intermediates during chemical reactions are not necessarily covered by such reference data and might therefore yield signals which are hard to understand by bare comparison to intrinsically stable reference compounds.

Computational models can help to overcome the lack of reference data and also help to solve the inverse problem. However, for electrocatalytic systems, approaches to correctly describe the electrode potentials in computations with a relevant system size in interfacial systems are just emerging.

The fact that Mn-based systems likely require an appropriate description of the correct spin state make calculations computationally expensive. Thus, such systems are not necessarily the best early adoption systems for novel calculation techniques.

Challenge 3: Different coincident processes take place on multiple time scales in a catalyst system. When looking at OER catalysts, there are several factors which are worth investigating by operando experiments to enable the understanding and the evaluation of the whole catalytic system:

1. the metal (oxide) based active center, which can be inhomogeneous,
2. possible existence of inactive phases,
3. the support,
4. the intermediates and precursors for O₂ formation,
5. the O₂ gas bubbles which form, grow and detach from the electrode,
6. the solvent, here water, which is also a reactant,
7. the ions in solution,
Thus, model systems are usually studied which are designed to must be minimized or long time high currents must be avoided. sample must have certain optical or structural properties, relevant to an industrial environment. For instance, often the obtain meaningful results. These limitations usually do not in situ protocols – both with interleaved potential or current steps–, or electrochemical protocol. The nature e.g. of nucleation processes can lead to substantially different responses under these different protocols. To disentangle these processes different protocols must be applied and varied and analysed in detail. However, not all operando methods are compatible with the required different electrochemical protocols, potentially limiting the level of insight which can be obtained. Generally, the history of a system may affect its future behaviour, which must be considered in the choice of the electrochemical protocol.

Challenge 4: Observations depend on the electrochemical protocol, as time and potential-dependent processes may be intertwined. Typical operando spectroelectrochemical experiments employ chronoamperometric or chronopotentiometric protocols – both with interleaved potential or current steps–, or linear sweep experiments. Especially with linear sweep or other potentiodynamic protocols, time dependent processes, such as surface changes or diffusion processes, are probed entangled with the potential dependent processes. The nature e.g. of nucleation processes can lead to substantially different responses under these different protocols. To disentangle these processes different protocols must be applied and varied and analysed in detail. However, not all operando methods are compatible with the required different electrochemical protocols, potentially limiting the level of insight which can be obtained. Generally, the history of a system may affect its future behaviour, which must be considered in the choice of the electrochemical protocol.

Challenge 5: Sample requirements of operando setups. Each in situ or operando technique has specific sample requirements and methodical limitations that must be taken into account to obtain meaningful results. These limitations usually do not allow studying an electrocatalytic system under conditions relevant to an industrial environment. For instance, often the sample must have certain optical or structural properties, electrolyte concentrations must be moderate, gas formation must be minimized or long time high currents must be avoided. Thus, model systems are usually studied which are designed to still be sufficiently close in all aspects to an application-relevant electrocatalyst, but on the other hand simple enough to be accessible to a variety of techniques. Finally, the model should also allow a transfer of the results back to the more complex system for an advancement.

Challenge 6: Intense irradiation may damage the samples. The high energies or intensities used in some spectroscopic techniques may lead to irreversible changes in the sample structure, which are not always easily deduced or may lead to false conclusions. As discussed below, especially X-ray absorption and emission as well as laser based techniques such as Raman spectroscopy may cause sample damage. As a consequence, a critical analysis of the experimental results is required, considering the influence of possible sample modification.

Challenge 7: Many operando methods are not surface specific. Catalysis occurs at the interface between electrolyte and the catalyst where the active centers can access the reactants. In almost all practically relevant cases the surfaces are not ideally bulk terminated but rather transformed due to a variety of processes. Underneath the reconstructed surface a significant amount of non-active bulk material can be present. This bulk may give a signal much higher than the species of interest at the interface due to the lack of an intrinsic surface specificity of most operando techniques. This covering effect is further amplified by the naturally short life time of the catalytically active centers. In the worst case, the catalytically inactive bulk still shows redox behaviour that is not related to the catalytic activity but masks the changes of interest.

2.2 Specific challenges of Mn oxides

Challenge 8: The dissolution of Mn competes with the OER at practically relevant currents. The potential-pH diagram in Fig. 1 helps to illustrate some of the particular challenges of the Mn system. With reference to the active center in PSII it is worth noting that the presence of Ca$^{2+}$ for activities up to 1 does not change the diagram when neglecting mixed Ca Mn oxides and relying only on the intrinsic databases of the MEDUSA software used to calculate this diagram. Obviously, over a large pH-range MnO$_2$ is the stable phase around the line indicating the beginning of oxygen evolution. However, with increasing pH, the oxygen line approaches the line indicating oxidation of MnO$_2$ to MnO$_4$$^-$, i.e. the transpassive dissolution of Mn and its oxides. Taking into account the solubility of the formed oxides and hydroxides in water (coloured areas in Fig. 1), Pourbaix ranked metals by their “practical nobility” with Mn being placed 43rd of 43 ranked elements. Other metals with oxides catalyzing the OER would be for instance Ru and Ir which are among the top 10 and Ni and Co which rank at 29 and 30 in this scale. An interesting feature of MnO$_2$ is that a region of limited stability exists at lower pH above the OER potential. This region makes MnO$_2$ particularly interesting for applications as an OER catalyst in photoelectrochemical cell devices (aka ‘artificial leaves’) at low currents in acidic to neutral pH. However, the dissolution of Mn oxides at elevated pH and currents is a major challenge for the applicability of such systems in industrial alkaline water electrolyzers or PEM electrolysis cells.
The dissolution issue on the other hand implies that experimentally measured currents at elevated potentials often do not exclusively originate from oxygen evolution. In contrast, a purely thermodynamical reasoning is insufficient because the actual rate of dissolution is defined by the kinetics of the reactions which can be sluggish. Furthermore, the diagram in Fig. 1 may change in the presence of further ions or compounds which can significantly change the thermodynamics or kinetics of the dissolution.

**Challenge 9:** Even *ex situ* it can be difficult to determine the oxidation state of Mn unambiguously. The variety of stable Mn oxidation states and the possibility of their coexistence in one sample can make an unambiguous experimental determination difficult. Solid phases exist for at least three oxidation states: Mn$^{III}$, Mn$^{II}$, and Mn$^{IV}$ (Fig. 1). Mn$^{VII}$ exists as soluble species at high potentials. Especially in alkaline solution, Mn$^{III}$ and Mn$^{VI}$ also exist as intermediates, and there is no reason to exclude their existence in a solid phase.

**Challenge 10:** In addition to the variety of oxidation states, MnO$_2$ form many different polymorphic forms. Each of these polymorphs has its own intrinsic defect chemistry and in particular also the possibility to include Mn atoms in lower oxidation states. The latter is correlated with the amount and charge of metal ions in the tunnels or interlayer regions. More than 30 Mn oxide and hydroxide minerals exist. The ones mentioned in this paper are listed with their structural properties in Table 1. The structure of many of these oxides can be understood as chains of edge- or corner-sharing MnO$_6$ octahedra forming tunnel or layer structures as exemplified in Fig. 2.

On the one hand, this diversity makes MnO$_2$ interesting as potential catalysts. On the other hand, this heterogeneity makes fundamental studies, isolating individual aspects of a more complex problem, extremely difficult. An electrocatalyst prepared under certain conditions is likely to transform at elevated electrode potentials so that the actual catalytically active phase differs from the initially prepared material.

While all the features of the Mn oxide systems described above make a full interpretation of *operando* spectroscopic data challenging, they also highlight the strong need for studying such systems both “*in situ*” and “*operando*”. As one electrochemistry textbook puts it: “It cannot be over-emphasised how important it is to study any electrode process by as wide a variety of techniques as possible; only by this means can a reliable picture of the reaction be built up”.

In the following, the specific basics for several important experimental methods shall briefly be highlighted and their recent application to Mn-based electrocatalyst systems shall be described, together with a critical analysis of the obtained results.

### 3. Operando studies of Mn oxide based systems during the OER

#### 3.1 Vibrational spectroscopy

Vibrational spectroscopies, especially *operando* Raman spectroscopy, can yield information on the chemical identity of catalytically active materials. General introductions into the basic principles of these methods are available elsewhere. For an interpretation of the obtained spectra, thorough knowledge of the important vibrational modes of the bulk system is often required. To that end, several systematic studies of different common Mn oxides with X-ray diffraction based structural characterisation are available. Despite the many efforts to bring order into the vast variety of Mn oxide Raman spectra, the
reference spectra in the literature remain contradictory and confusing. A recent study provides an extensive and systematic collection of natural Mn oxides and addressed several contradictions and conflicts in the literature of recent years.\textsuperscript{41} Especially, the thermal instability of some MnO\textsubscript{x} may have led to contradicting results in the study of reference materials (Challenge 6).

The dominating Mn oxide vibrational modes are between 200 and 750 cm\textsuperscript{-1} (Fig. 3), which is easily accessible using standard lab-based Raman spectroscopy. Many Mn\textsuperscript{II,III,IV} oxides that may be of interest for OER catalysis, give rise to pronounced Raman modes above 500 cm\textsuperscript{-1}, which result from the symmetry of the structure. A mode around 510 cm\textsuperscript{-1} has strong contributions from Mn–O deformation, while the typically most intense modes around 580 and 630 cm\textsuperscript{-1} have strong contributions from Mn–O bond stretching.\textsuperscript{41,44} For the latter it was shown that the position of these prominent ‘marker modes’ depends on the average Mn–O distance and the polymerisation of the framework, \textit{i.e.}, the number of shared edges between the MnO\textsubscript{x} octahedra. This useful structural correlation was employed in the interpretation of Raman spectra of MnO\textsubscript{x} OER catalysts.\textsuperscript{32,49–51}

On the other hand, the strong similarities between spectra of different MnO\textsubscript{x} phases above 500 cm\textsuperscript{-1} can make a unique identification of a particular oxide extremely difficult, especially in mixed and dynamic systems as generally found for OER electrocatalysts. For instance, the patterns observed \textit{in situ} during electrochemical oxidation of metallic Mn have been identified as \textit{z}-MnO\textsubscript{2},\textsuperscript{32} based on the similarity to reference spectra.\textsuperscript{44} Very similar spectral features have otherwise been assigned to the birnessite like phase prepared by electrochemical deposition\textsuperscript{50} based on previous XAS results.\textsuperscript{52} Indeed, from a recent extensive analysis of spectra of well-defined compounds, it was concluded that it is virtually impossible to make a clear distinction between hollandite (\textit{z}-MnO\textsubscript{2}), birnessite (\textit{B}-MnO\textsubscript{2}) and romanechite on the basis of Raman data alone.\textsuperscript{41}

The OER performance of differently prepared hollandite \textit{z}-MnO\textsubscript{2} materials (aka cryptomelane) was studied.\textsuperscript{53} Differences in the electrochemical OER performances of the different materials were found to mainly be governed by differences in conductivity originating from morphological differences. However, the initially good electrochemical OER performance of the materials degraded quickly over time. Operando Raman spectroscopy yielded remarkably stable spectra during the OER revealing no significant transformations in the materials, thus the reasons for the activity loss remained indistinct. It appears unlikely that the materials do not change when simultaneously a deactivation is observed. This illustrates a specific challenge
for Raman spectroscopy, which is that the Raman cross-sections of different species differ significantly. Consequently, it is hard to get a representative picture of the surface species. Hence, quantitative information about the relative concentration of the species cannot be obtained and some species might even be virtually invisible in the Raman spectra. Furthermore, Raman spectroscopy is not per se surface specific (Challenge 7), however several strategies can be used to circumvent this problem.

Thin oxide layers of a few nm thickness on a Raman inactive substrate can be a workaround for the lack of surface specificity. To that end, electrochemically oxidized metals have been studied during the OER.\textsuperscript{32} The thicknesses of the formed oxide layers were below 10 nm, but Raman in situ measurements showed that the oxide layers remained intrinsically stable during voltammetric sweeps, down to relatively low potentials. During oxygen evolution the Raman spectra did not show similarities to any isolated stable oxide. Also, the spectrum shared some similarities with $\beta$-MnO$_2$, but also distinct differences. Very broad bands around 600 cm$^{-1}$, assigned to the Mn–O stretching vibrations showed that a strongly disordered MnO$_2$ was present during the OER. The occurrence of the stretching vibration at this position indicates that the disordered oxide is structurally based on the octahedral coordination of Mn.

For well characterised materials the specific synthesis of reference compounds for the assignment of Raman bands can be very helpful. For instance, operando Raman spectroscopy was used to study a selection of MnO$_2$ based catalysts, prepared by electrodeposition on ITO working electrodes.\textsuperscript{30} The oxide layers featured thicknesses up to 300 nm and the two (out of three) catalysts with the higher onset potentials underwent structural changes in the pre-OER region, attributed to a charging process. Comparison of the observed spectral changes with spectra of well defined birnessite structures led to the conclusion that charging includes a transformation from trioctahedra to hexagonal Birnessite and the formation of point defects. It was concluded that the formation of an amorphized birnessite structure and bixbyite-like Mn$^{III}$ centers facilitated the OER.\textsuperscript{50}

Alkali-metal manganese borophosphates were prepared using a mild-hydrothermal method and showed promising OER performances and stabilities.\textsuperscript{24} A thorough ex situ characterisation in combination with in situ Raman spectroscopy showed that these materials just served as pre-catalysts. Under OER conditions another active phase was formed which was termed a-\(\delta\)MnO$_2$. It was described as being amorphous with a short range order similar to birnessite which was concluded from comparison of the Raman spectra with literature. It was concluded that during the oxygen evolution, corrosion of the pre-catalysts took place, forming a-\(\delta\)MnO$_2$ while dissolving boron and phosphate species and incorporating potassium from the electrolyte. The leaching led to an increasing porosity of the materials which was assigned to the improved OER performance.

Using surface or tip enhanced Raman spectroscopy (SERS or TERS, respectively) can make Raman spectroscopy sensitive to sub-monolayer coverages. For instance the reduction of MnO$_2$ and reoxidation of Mn(OH)$_2$ was studied in an early application of in situ SERS.\textsuperscript{55}

Thin MnO$_2$ OER catalyst films were prepared on SERS active substrates by RF-magnetron sputtering.\textsuperscript{31,56} The variation in the oxygen content in the sputter gas allowed for control of the Mn/O ratio in the final film, yielding samples, which were mainly made up of MnO$_2$ in the main oxidation states II, III and IV. Here, only the samples in the main oxidation states II and IV are discussed, since they are the most representative. In the atmosphere, films with low O content (termed Mn(n)) were easily oxidized and readily decomposed under laser irradiation, while the stable, higher oxidized MnO$_2$ phases (termed Mn(nv)) consisted of mixtures of different Mn oxides with an average oxidation number of 3.7–3.8 which was also supported by XPS studies. The operando Raman spectra indicated that Mn(n) samples (Fig. 4a and b) were oxidized when approaching the OER, showing spectra similar to the Mn(nv) samples (Fig. 4c and d) which also indicated the formation of catalytically active Mn$^{IV}$. For the Mn(nv) phase a slight blue shift of the $\Delta_g(2)$ mode (from 667 to 681 cm$^{-1}$) and a red shift of the main Mn–O stretching band (from 599 to 568 cm$^{-1}$) was found during the OER as well as a signal appearing at 503 cm$^{-1}$ and shifting to 479 cm$^{-1}$ at higher potentials. This was interpreted as being due to the formation of additional Mn$^{IV}$ species and to an increase in the interplanar spacing between MnO$_6$ octahedra, which could allow additional inclusion of potassium ions and water in the formed tunnel and/or layer structures. The shape of the signals and their potential dependent behaviour was found to be very similar to the Raman results of mixed Birnessite/Bixbyite phases in ref. 50.
different peaks in the region close to and above 850 cm\(^{-1}\) that were observed in the OER active MnO\(_x\), ref. 32 and 51 (cf. Fig. 4) remain a matter of speculation. In fact, spectra of natural reference materials scarcely show peaks in this region, for instance a mode around 840–850 cm\(^{-1}\) was found only occasionally in reference spectra of \(\beta\)-MnO\(_2\).\(^{33,42,45,47}\) The formation of peroxo species maybe a possible origin of such peaks.\(^{37}\) An alternative explanation may be the excitation of multi-phonon modes or combination modes which significantly increase in intensity because of symmetry breaking in the presence of certain defects included in the defect rich films during the OER.

Note added in proof: During peer review, the question arose if the Raman spectra show any dependence on the excitation laser wavelength used. Such effects are indeed an important further aspect which could complicate \(\textit{operando}\) Raman analysis and data interpretation. In this system excitation wavelength dependence could arise from (a) heat-induced or photochemical damage, (b) selective resonance enhancement of certain features, or (c) complex solid state phenomena. Manganese oxides are very well known to show transformations upon intense illumination, as documented systematically, \textit{e.g.}, in ref. 41. Some earlier studies may have been affected by such transformation. As transformations are typically induced by local heating upon, heating is affected by light absorption, which is strongly wavelength dependent. Hence illumination thresholds are very likely different for different excitation wavelengths. Resonance enhancement of certain features may or may not account for differences observed when comparing spectra with UV excitation to spectra with 633 nm excitation.\(^{41}\) However, a systematic understanding of such effects is according to our knowledge lacking. Specific phenomena in solids can also lead, \textit{e.g.}, to wavelength dependence of peak positions. A prominent example is the D band in sp\(^2\) carbon systems, which shifts systematically with excitation wavelength because of a Kohn anomaly.\(^{38}\) Such shifts have to our knowledge not been reported in literature for relevant manganese oxides. The conditions during OER and the nature of transient species make it difficult to rule out such phenomena, and to study them systematically.

### 3.2 UV/Vis absorption and photoluminescence

Mn\(^{\text{III}}\) and Mn\(^{\text{IV}}\) containing oxides are typically brown to black in colour, \textit{i.e.} they have a strong light absorption in the visible spectrum. While on the one hand, black substances are difficult to characterise by absorption spectroscopy, their strong optical absorption also implies that absorption spectroscopy and possible photoluminescence (PL) as a follow up process is a sensitive tool to detect them. The use of UV/Vis absorption, but also PL spectroscopy, for \(\textit{operando}\) characterisation has been described by some of us recently.\(^{39}\)

Mn\(^{\text{IV}}\) oxides typically have a small bandgap of 1–2 eV.\(^{39}\) Consequently, UV/Vis absorption spectroscopy can be used to analyse the electronic structure around the band gap, and the presence of intragap states indicative of defects. For instance the local environment of Mn\(^{\text{III}}\) in a reduced, activated MnO\(_2\) catalyst was modeled by oxidizing Mn\(^{\text{II,III}}\) in a hausmannite like...
Interestingly, ex situ PL recorded with a confocal micro Raman setup indicated that the changes occurred in the material surface only, not in the bulk. The surface-only nature of the modification was explained by the structure of bixbyte α-Mn₁₂O₃₅ which, unlike many other MnOₓ with tunnel or layer structures, has no major voids allowing –OH ion insertion in the bulk material during the OER and ORR. The high and low valence states were proposed to act as the catalytic centers during the OER and ORR, enabled by the low defect formation potentials.

The pH dependency of the OER activity of δ-MnO₂ nanoparticles (potassium birnessite) was examined by operando UV/Vis absorption spectroscopy. In particular the OER onset with this catalyst had an increasing overpotential η in the pH range 4–8 and a decreasing η for pH > 9, indicating different mechanisms in these regions. A reversible absorption peak that showed a similar pH dependency was found at 510 nm but could not be assigned based on existing literature (cf. Challenge 2). Therefore, an assignment to Mn III was based on comparison experiments using pyrophosphate as a probe. The Mn III is assumed to be a precursor for O₂ evolution and the observed higher η at pH < 9 is thus a result of Mn III instability because of disproportionation. However at pH > 9, Mn III can be generated by conproportionation leading to a decreasing η. Following up on these results the authors were able to significantly reduce η at pH 8 by means of an amine containing polymer. Also here in situ UV/Vis spectroscopy substantiated that stabilisation of surface Mn III caused this effect. For the same catalyst an additional blue shifted absorption peak at 470 nm appeared under OER conditions at elevated pH was reported later. The shift was explained by deprotonation of surface specific Mn III species. Accumulation of protons was shown to vary the ratio of the two absorbance peaks and was correlated with the OER current. Due to missing reference spectra (Challenge 2) the exact Mn III species could not be determined unequivocally, but the authors argued for the formation of Mn III–O⁻ at basic and of Mn III–OH at neutral to acidic pH.

3.3 X-Ray spectroscopy

At higher photon energies, X-ray spectroscopy is a powerful tool to elucidate the core level electronic structure of a material on an atomic level. The theory of these methods and their applications to water oxidation catalysts in general have been extensively reviewed recently. Both X-ray absorption spectroscopy (XAS) and X-ray emission spectroscopy (XES) are frequently used techniques. Absorbance of X-ray photons leads to edge features in the spectra. Their position depends on the energy level of the excited core electrons. Therefore, 3d transition metal K-edges are located in the hard X-ray regime (5–10 keV), while oxygen K-edges and metal L-edges are observed in the soft X-ray regime (400–1200 eV).

XES experiments monitor the fluorescence relaxation process after ionization. They are greatly limited by the effective solid angle of detection imposed by the spectrometer. Therefore, these experiments remain very challenging for electrochemical operando studies and to the best of our knowledge to date there have been only a few examples of operando spectroelectrochemical XES on Mn, both in the soft and hard X-ray regime. For a non-ionizing excitation into an intermediate (previously unoccupied) electronic state, the emission experiment becomes resonant and is referred to as resonant XES (RXES) or resonant inelastic X-ray scattering (RIXS).

3.3.1 Hard X-ray absorption spectroscopy. An important aspect of hard X-ray spectroelectrochemistry is that, in contrast to XPS which is more surface sensitive, X-rays at typical transition metal K-edge energies penetrate several micrometers into the film (Challenge 7). In addition, in situ XAS can induce photoreduction or -oxidation, radiation damage, and solvent ionisation (Challenge 6) that might lead to incorrect interpretation of results. These two points as well as an XAS specific discussion on the difference between the experimental and the electron-transfer time scales (Challenge 3) have been discussed in great detail, earlier and exemplified using cobalt oxide OER catalysts.

One of the first operando SEC XAS studies at the Mn K-edge was performed on MnO₂ catalysts that have been developed to perform both ORRs and OERs at moderate overpotentials. XANES and EXAFS identified Mn₃⁵⁻,II,II,III,III O₄ (hausmannite) as the phase present during the ORR, and a mixture of a birnessite-like phase and a more reduced phase that probably corresponded to uncharged Mn₃,II,III,III,III O₄ under OER conditions (cf. Fig. 6). Since the reduced phase represented a small fraction of the sample, it was assumed that the porous structure of the electrocatalyst enabled good electrochemical control and electrolyte access to most of the sample and therefore increased activity.

Dissociation of a tetraneuclear Mn cluster into Mn III compounds upon immobilization in a Nafion matrix has been investigated in detail. These compounds became electrochemically re-oxidized to form nanoparticles of a disordered MnIVIVV (birnessite resembling) phase, which is catalytically active. Although the study was not exactly performed under operando conditions its results demonstrated that structures resembling that of the PSII water oxidation complex are not a requirement for catalytic performance and that complex structures in a non-biological environment may act only as precatalysts.

The effect of Ni addition to a bifunctional MnNiO₄ catalyst was studied by in situ XAS complemented by an XES method that allowed for simultaneous detection of signals from multiple metal centers, thereby disentangling the redox behaviour of Mn and Ni. The catalyst as prepared consisted of nano-phase separated crystalline Ni rich and Mn rich oxide phases. The presence of Ni resulted in a lower oxidation potential for Mn, facilitating the oxidation towards Mn IV during the OER as compared to the Ni-free catalyst. The MnNiO₄ was found to be bifunctional for the ORR and OER. While the oxidation states of Ni and Mn changed upon transition from the ORR to the OER regime, no major structural changes where observed.

Thin films of an MnO₂ co-catalyst on a SrTiO₃ photoelectrode were studied using in situ XAS. The results implied UV irradiation and potential dependent slow oxidation of the co-catalyst, from an average Mn oxidation number of +3.1 to...
+4 at an applied potential of 1.0 V (RHE) and to +3.3 at 0.5 V (RHE). The irradiation strongly influenced the rate of the oxidation, indicating that oxidation occurred by holes forming as a result of photoexcitation. The correlation found between hole transfer and OER activity was explained by a potential induced upward band bending in the semiconductor material that facilitates the charge separation and the hole transfer to the MnOx co-catalyst. Interestingly, the OER rate did not show strong dependence on the Mn oxidation state, thus it was concluded that both Mn^{III} and Mn^{IV} rich phases can be photo-electrochemically active to catalyse the OER.

In a combined quasi in situ and time-resolved in situ XAS study the redox behavior of the biological Mn_{4}Ca oxide cluster and three different birnessite type Mn oxides (with and without Ca) were analyzed. For the quasi in situ technique the samples were freeze-quenched after a potential was applied for 3 minutes and subsequently XAS was measured at 20 K. The low measuring temperature can help to minimize photoreduction by the beam and decreases thermal contributions to the EXAFS, which can greatly increase experimental resolution. For the time-resolved experiment, samples were studied at room temperature and the absorption signal was tracked over time at a fixed excitation energy when changing the potential. The results of catalytically active birnessite type MnO_{x} and Ca containing MnO_{x} were compared to an inactive MnO_{x} and the biological OEC of PSII.

It was found that the catalytically active birnessite type MnO_{x} undergoes oxidation and structural changes that share certain features with the OEC. The catalysts comprised metastable Mn^{III} centers at OER potentials which can accumulate oxidizing equivalents (holes) by Mn^{III} → Mn^{IV} oxidation coupled to changes in the μ-oxo bridging. Kinetic experiments implied that metal oxidation precedes the O^{2−} oxidation. The inactive MnO_{x} showed a significantly higher ordered structure than the active one, implying that non-crystalline materials promote the OER because they allow dynamic and flexible oxidation states and structural changes. This dynamic picture of the MnO_{x} OER catalyst instead of that of a static active center is quite akin to the mechanism of the biological oxygen evolution in the OEC.76

Another study at room temperature, also reported shifts in the Mn K-edge position as a function of applied potential. It was observed that electrodeposited δ-MnO_{2} birnessite films initially displayed very low electrocatalytic activity that increased upon cycling between −0.4 and +1.1 V vs. NHE (at pH 8.0).49 A continuous shift of the K-edge position towards lower energies with increasing number of cycles indicating an accumulation of Mn^{II} centers, and EXAFS analysis suggested that the activated material comprised a mixture of δ-MnO_{x} hausmannite-like and δ-MnO_{2} (birnessite) structures in a mixed oxidation state containing Mn^{III} and Mn^{IV}. The authors proposed that all octahedral (O_{6}) sites contain Mn^{IV} while Mn^{III} centers remain metastable, kinetically locked in tetrahedral (T_{4}) sites, unable to disproportionate. A computational model, describing the resulting electronic structure around these Mn^{III}(T_{4}) features a HOMO dominated by oxygen 2p valence states and a metal-based LUMO with a reduced energy gap as compared to pure δ-MnO_{2}. Oxidation would create oxygen holes leading to the formation of a very reactive oxyl radical that would explain the enhanced activity of these Mn^{II} containing materials.49

The co-deposition of gold particles (2–3 nm diameter) on MnO_{x} OER catalysis, studied by operando XAS, resulted in an increased oxidation state of the MnO_{x} catalyst under OER conditions compared to a MnO_{x} without Au particles.77 The increased oxidation state may have been related to the observed increase in OER activity caused by the gold particles.

An operando hard, tender, and soft XAS study was performed on a layered MnO_{x} catalyst with intercalated potassium ions in an KOH containing aqueous phosphate buffer solution (pH 8).78 In agreement with the previously discussed studies, the Mn K-edge position shifted to higher energies with increasing potential, indicating a reversible increase of the average oxidation state from ~+3.1 to ~+3.9. The shape of the Mn

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**Fig. 6** Example of a hard X-ray study undertaken by Gorlin et al. on a MnO_{x} film prepared on a Au coated Si_{3}N_{4} membrane.72 The Mn K-edge XANES undergoes clear changes with respect to the “as-prepared” state when ORR or OER conditions are applied indicating a reduction or oxidation of the catalyst, respectively (A). A comparison to spectra of reference samples additionally allows an estimation of the oxidation state and phase composition under the respective conditions (B and C). Reprinted with permission from ref. 72. Copyright 2013 American Chemical Society.
K-edge spectra and soft X-ray O K-edge spectra resembled δ-MnO₂. The catalytic activity of the MnOₓ film was attributed to the remaining Mn III species at high potentials. Complementary XAS with tender X-rays at the K K-edge suggested the formation of buserite – the hydrated form of birnessite – under in situ conditions.

3.3.2 Soft X-ray absorption spectroscopy and resonant inelastic X-ray scattering. Soft X-ray photon absorption excites 2p core electrons of the 3d-transition-metal centers and yields the L-edge spectra (Fig. 7). These excitations provide access to information about the valence electronic structure, which is involved in chemical bonding and is consequently critical for catalytic processes. Furthermore, with soft XAS, oxygen K-edge spectra can be obtained providing a second handle in the analysis of e.g. Mn oxides. The information accessible with soft X-ray comprises band/state energies, energies of electronic transitions, oxidation states, and information about the local coordination environment.

However, the operando application of soft X-ray spectroscopy comes with some additional challenges. In contrast to experiments in the visible or hard X-ray regime, the propagation of soft X-rays requires vacuum conditions and the penetration depth of the X-ray photons is limited to a few hundred nanometres. Its limited penetration makes the application of this technique rather challenging for operando experiments, in particular because the catalyst needs to be in contact with both the liquid electrolyte and an electrode support to apply a potential. This experimental challenge might be one reason why operando soft X-ray spectroscopy studies are still exceptional compared to hard X-ray experiments. In addition, the emission intensity of soft X-ray photons during the 3d2d-relaxation processes is rather low and photon yield experiments have to be conducted very thoroughly to avoid radiation induced changes of oxidation states or radiolysis of the electrolyte (Challenge 6). Nevertheless, during the past few years several in situ/operando studies with soft X-rays have demonstrated their value for the interpretation of Mn based water oxidation catalysts.

A combined absorption/emission study, complemented by operando total electron yield and combined with modeling,
was undertaken on an electrodeposited MnO₂ thin film for the OER applied in 0.1 M borate buffer (pH 9.2). It was shown that δ-MnO₂ (birnessite) is the main stable phase at OER conditions and no evidence for Mn in a higher oxidation state than +4 was found. Furthermore, RIXS experiments revealed an increase of a feature that is related to metal–ligand charge transfer (Fig. 7). This was associated with the evolution of the hybridization of Mn–O bonds with increasing potential leading to facilitation of metal–ligand electron transfer and the formation of O₂ species.

Mn valency and the role of Mn–O hybridization was studied in detail with a layered Mn oxide catalyst for the ORR and OER, by (inverse) partial fluorescence yield experiments at the Mn L-edges and the O K-edge. The catalyst was an electrodeposited birnessite type film applied in 0.1 M KOH. Upon cycling between ORR and OER conditions, the Mn valence varied between 2.4–2.6 for the ORR with tetrahedral Mn³⁺ identified in the sample, and 3.1–3.4 under OER conditions. Analysis of the O K-edge allowed an estimation of the maximum Mn–O hybridization for a Mn valence close to +3 (and an ε₀ occupancy of nearly one) and the presence of Mn³⁺ was suggested to be critical for the OER as well as ORR.

Soft XAS in transmission mode was carried out on an electrodeposited MnO₂ film, as a proof of principle to validate the function of a soft X-ray transmission flow cell. Although the authors point out that some of their data may have suffered from radiation-induced damage (Challenge 6) a clear transformation of the Mn L-edge absorption spectrum was observed when increasing the potential from 0.3 to 1.5 V vs. NHE. By using a linear combination fitting approach based on spectra taken on reference materials, the authors disentangle the spectra into contributions of individual MnO₂ phases. Decreasing the potential back to 0.3 V showed the hysteretic behavior of the phase transitions. Furthermore, the effect of radiation damage was demonstrated and related to the actual radiation dose during data collection.

The same setup was used to study the oxidation and reduction behavior of a MnO₂ thin film electrodeposited in a methylphosphate solution and applied for the OER at pH 7 in a KNO₃ containing 0.1 M phosphate buffer solution. Using a linear fitting approach it was found that the freshly prepared δ-MnO₂ (birnessite) is the main stable phase at OER conditions and no evidence for Mn in a higher oxidation state than +4 was found. Furthermore, RIXS experiments revealed an increase of a feature that is related to metal–ligand charge transfer (Fig. 7). This was associated with the evolution of the hybridization of Mn–O bonds with increasing potential leading to facilitation of metal–ligand electron transfer and the formation of O₂ species.

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A porous layer of MnO₂, deposited on a BiVO₄ photoanode following a similar deposition and analysis approach, was shown to also transform into a birnessite phase with increasing potential up to 1.91 V vs. RHE. The transformation was facilitated by illumination, attributed to the creation of photo-generated holes in the BiVO₄ and subsequent electron migration. In addition it was found that oxidation of Mn also occurred in this sample system with illumination only.

The influence of Mn loading on Ni catalysts was studied in a Ni L-edge XAS/2p3d-RIXS spectroelectrochemical study. The Mn loaded oxide, Ni₃MnO₄, was compared to pure NiO, and the structure–activity correlations were studied by tracking the changes of the Ni centers before and during the OER. It was found that Mn did not improve the catalytic activity of a pure NiO. Additionally, no significant changes in the electronic structure of the Ni could be identified as a result of adding Mn to the oxide. The study could identify γ-NIOOH as the active phase.

4. Summary and outlook

While the results from the different studies discussed are not free of contradictions, some important common interdependent key features have been extracted for several MnO₂.

I. Disordered structures and structural flexibility. Under working conditions MnO₂ are observed that are disordered, amorphous or mixed phases. Furthermore, phases based on octahedral Mn coordination are frequently observed. In this regard the operando results are consistent with many ex situ studies. Several positive influences of the disorder on the OER performance have been discussed. For instance structural defects may kinetically trap metastable intermediates or precursors as proposed for Mn³⁺. It was argued that non-crystalline materials comprise structural flexibility, allowing structural as well as oxidation state changes during the catalysis, and facilitate charge separation through electron–hole pair formation by reduced energy gaps. Also, the positive influence of flexible μ-oxo bridges in amorphous oxides has been proposed to facilitate redox-potential leveling by coupling μ-OH deprotonation to oxidation steps.

II. Influence of the oxidation number in the range III–IV. MnO₂ found under OER working conditions mostly featured oxidation numbers between +3 and +4. In this regard the MnO₂ resemble the biological OEC, where oxidation equivalents are accumulated by redox steps between Mn³⁺ and Mn⁴⁺. An enhancement of OER activity by the presence of Mn³⁺ in MnO₂ was also repeatedly reported. According to the assumptions these Mn³⁺ act as precursors or constitute the catalytic center. One mechanism was proposed that involved resting states of Mn³⁺ centers in acidic environments and mixed Mn³⁺⁴⁺ resting states in the alkaline regime. However, OER potentials largely exceed the oxidation of Mn³⁺ (cf. Fig. 1). Thus, the structural properties of the catalysts are thought to keep the Mn³⁺ centers locally in a metastable state.

III. Activity of birnessite like phases. MnO₂ catalysts with as prepared birnessite-like structure have been identified to have good OER activities and thus have been the focus of many studies that used operando methods. Moreover, the formation of additional birnessite phases from other materials under OER conditions or upon catalyst activation has also been observed by operando methods at various pH.

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Thus it is possible that other Mn-based materials also convert (partially) into birnessite like structures under OER conditions which can only be probed by operando studies. Birnessites, intrinsically unite the properties of the above points I & II. They comprise disordered, layered structures based on edge sharing MnO₆ octahedra, including Mn⁷⁺ and Mn⁴⁺ centers (Fig. 2b).³⁵,³⁶ The structural flexibility in birnessites is given by several features. In the interlayer space (distance ca. 7 Å) H₂O as well as metal ions can be incorporated and the latter can be easily exchanged.³⁶ For instance the incorporation of Ca²⁺, well as metal ions can be incorporated and the latter can be

(rixs) Resonant inelastic X-ray scattering

In contrast, recently the intrinsic OER activity of layered MnO₂ has been challenged by the discovery that traces of Ni and Fe ions significantly increase their activity and in the absence of these ions, birnessite’s intrinsic OER activity appears to be low.³⁷

Despite the challenges outlined in Section 2, in situ and operando spectroscopy has contributed a great deal to the understanding of reaction mechanisms of Mn-containing electrocatalysts for the OER. A wealth of studies has revealed key features that seem to determine whether a certain Mn material features efficient OER catalysis. Even though the challenges these methods face will not be overcome in the short term, it is hard to imagine progressing our understanding without operando spectroscopic analysis. Thus, there is plenty of room for ongoing method development with the existing methods, and also for the application of less widely available techniques. A number of questions remain open, and operando spectroscopy may be able to contribute to answering them. For example, the role of and need for the calcium in the biocatalyst, remains at least partly in the dark. Also, the stability issues generally observed at high current densities require further understanding. Stability is without any doubt important for their application, and solving stability issues is crucial for the application of Mn-based electrocatalysts in large scale water splitting applications.

**Conflicts of interest**

There are no conflicts to declare.

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**Notes and references**

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