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Towards comprehensive understanding of proton-exchange membrane fuel cells using high energy x-rays

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Abstract

For a future hydrogen economy, the development of cost effective energy conversion devices is a key issue. In this perspective, we discuss the use of high energy x-rays for obtaining comprehensive insights into the complex processes which occur inside such devices, focusing on proton exchange membrane fuel cells. This probe enables structural characterisation under operating conditions on all relevant length scales, from the atomic-scale interfaces to complete stacks. This opens up possibilities to go beyond characterisation of the isolated components, towards an understanding of their interactions in the full system which determine the power output, efficiency and degradation pathways in operational devices.

Acronyms

BCDI	Bragg coherent diffraction imaging
CCL	coated catalyst layer
CTR	crystal truncation rod
DFXM	dark field x-ray microscopy
EXAFS	extended x-ray absorption fine structure
GDL	gas diffusion layer
HESXRD	high energy surface x-ray diffraction
MEA	membrane electrode assembly
ORR	oxygen reduction reaction
PDF	pair distribution function
PEMFC	proton exchange membrane fuel cell
PEMWE	proton exchange membrane water electrolyser
PGM	platinum group metals
SAXS	small angle x-ray scattering
SOFC	solid oxide fuel cell
SXRD	surface x-ray diffraction
TSD	transmission surface diffraction
WAXS	wide angle x-ray scattering

1. Introduction: the need for advanced *operando*, multiscale characterisation techniques

In the face of climate change caused by ever increasing emission of greenhouse gases, electrochemical energy conversion and storage technologies provide an efficient path for decarbonisation of the energy sector. Rapid progress has been made in the commercialisation of these technologies but the high price tag, limited specific power density in fuel cells, limited specific energy density in batteries, limited access to key materials,

insufficient lifetime, and lack of H₂ distribution networks still prohibit wider proliferation needed to tackle the climate change challenge. For proton exchange membrane fuel cells (PEMFC) and water electrolyzers (PEMWE), the most promising hydrogen conversion devices, much of the research is focused towards decreasing the content of platinum group metals (PGMs), and increasing the lifetime of the devices [1–5]. The latter can be achieved by limiting the degradation of the constituent materials through material engineering and optimisation of the operation modes.

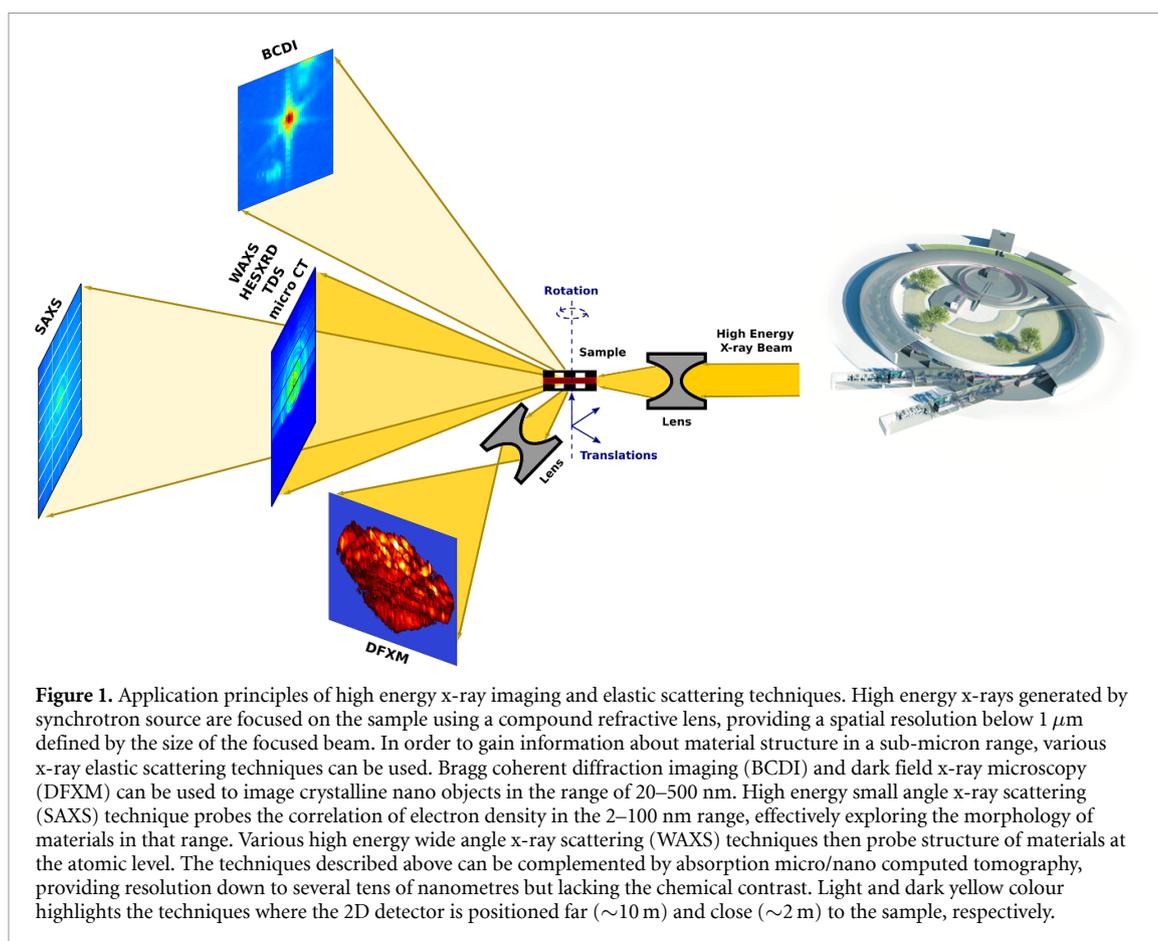
Lowering the amount of PGM in the catalyst layers without compromising the performance of the PEMFC is essential, as this leads to significant resource savings, especially for applications in transportation [6]. Currently the most practical and most used catalyst in commercial PEMFC devices is still Pt, but this is being slowly replaced by alloy catalysts and with a moderate decrease in loading inside membrane electrode assemblies (MEA) [2]. Currently a guiding principle for designing the next generation of catalysts is fine tuning the active site geometry and altering its chemical properties, through electronic and steric means [7–11]. The catalyst optimisation relies heavily on advanced characterisation by electron microscopy and spectroscopy as well as elastic and inelastic x-ray scattering.

Interestingly, even the most advanced catalysts suitable for low PGM loading MEAs show disappointing beginning-of-life performance in PEMFC devices [2, 12], even while in the laboratory rotating disc electrode tests they present activities greatly exceeding the targets. It is believed that the problem is mainly complexity driven [2]. The materials in the coated catalyst layer (CCL) (catalyst nanoparticles, carbon support and ionomer binder), and their exact distribution, need to be tailored to a given catalyst. They have to work synergetically to provide free active sites, sufficient flux of reactants to these sites, removal of reaction products and ideal water distribution at high power densities. This is a challenging task and requires careful design not only of the active site's turnover frequency but also its local environment [13]. Furthermore, at the MEA level, the reactants and products need to be efficiently transported into and out of the CCL to avoid unnecessary diffusion barriers that negatively affect the device performance. This is achieved by sandwiching the CCL between proton exchange ionomer membranes (PEMs) and gas diffusion layers (GDLs) with carefully designed porosity. Finally, the reactant and product streams are removed from the GDLs mainly through macroscopic flow fields. The diffusion of water across the PEM is also important, under some operating conditions.

Advanced analytical characterisation is necessary at each step of optimising catalyst's activity, CCL composition, MEA properties, GDL pore structure and flowfield design. Virtually every available analytical technique has been utilised for PEMFC characterisation. However, techniques which provide the most detailed structural information and surface sensitivity have significant shortcomings as they are typically limited to ex-situ characterisation or are only suitable for probing a single component inside the cell. The ideal analytical probe should be able to probe the complicated hierarchical structures of the materials at all relevant length-scales during device operation in a single experiment. In this perspective we argue that high energy x-rays meet these criteria and allow multiscale correlative analysis. We will give various examples of state-of-the-art high energy x-ray techniques tailored particularly for PEMFC characterisation (figure 1) and discuss the expected possibilities of new 4th generation synchrotron sources in this respect. Aspects of catalyst, MEA and device development are examined, starting from the fundamentals of single crystal surfaces and finishing with *operando* characterisation of PEMFC devices.

2. Investigations of model catalysts in *operando* conditions using high energy x-rays

Surface science plays an important role in the development of electrocatalysts for electrochemical devices, such as PEMFCs, PEMWEs or CO₂ converters. The standard approach in surface science is to simplify the complexity of the problem by studying well-defined or well-ordered model surfaces, such as single crystal interfaces. These interfaces provide well defined reaction sites to investigate the reaction mechanisms and to explore relationships between structure (electronic and geometric), activity and degradation. Both elastic and inelastic x-ray scattering have been historically employed to study the model surfaces in electrochemical environments [14, 15]. The advent of 3rd generation synchrotrons further enabled high energy x-rays to probe these systems. Only the heaviest elements have spectroscopic features in the high energy x-ray range (>25 keV), and these transitions are both weak and insensitive to the chemical environment. However, these photon energies are advantageous for *in-situ* structural studies of surfaces using surface x-ray diffraction (SXRD) [16, 17]. These technique can be easily coupled with grazing incidence small angle scattering measurements, which allow in parallel investigation of the morphology of the model catalyst surface [18, 19]. In the case of Pt single crystal surfaces, the model catalyst for oxygen reduction and hydrogen evolution reactions, this coupled characterisation approach has been very successful in improving our understanding of fundamental processes. Understanding the enhanced catalytic activity of Pt(111) surfaces [20–22] and the



basic principles behind Pt surface oxidation and dissolution, are critical in rationally designing catalysts with higher performance and durability in devices [19, 23–25].

In the previous studies, researchers used point detectors or small area detectors, together with x-ray energies around 20 keV, to measure crystal truncation rods (CTR) reflections. While this approach is well established, it limits the speed of measurements and the maximum obtainable momentum transfer \mathbf{q} of the diffracted photons. It has been shown recently that there are significant advantages to using high energy x-rays ($>50\ \text{keV}$) and large 2D detectors for SXRD experiments [26], because a larger portion of reciprocal space can be observed in a single detector frame [27]. This significantly speeds up the measurement and allow more precise determination of the surface structure. The above reasons, coupled with the high penetration of high energy x-rays makes this technique ideal for *in-situ* and *operando* investigation of model catalyst surfaces in electrochemical environments. We expect that this strategy will become the gold standard for SXRD measurements in the near future.

High energy surface x-ray diffraction (HESXRD) was recently used to correlate the mechanism of Pt oxidation with the dissolution behaviour (figure 2) [28]. In this work, two different surface orientations, Pt(111) and Pt(100), were investigated during surface oxidation in an electrochemical cell. By elucidating the atomistic picture of the surface at different stages of the oxidation, the authors were able to distinguish the key differences in the transient surface atom positions, which lead to enhanced dissolution of the Pt(100) surface. This analysis was only possible by exploiting the superior time resolution of the HESXRD technique, which made it possible to resolve the transient oxide structure.

Our group has recently developed transmission surface diffraction (TSD) [29], as an alternative to conventional grazing incidence (HE)SXRD geometry. The surface structure is determined with a focused x-ray beam hitting the surface of a thin single crystal at normal incidence. High energy photons are necessary to transit even relatively thin single crystals of Pt (ca. $100\ \mu\text{m}$). This geometry allows large in-plane snapshots of reciprocal space, where the diffraction patterns resemble low energy electron diffraction patterns. The main advantage is that the spatial resolution of this technique is only limited by the size of the incident x-ray beam, permitting surface diffraction studies with unprecedented spatial resolution [30]. Another convenience is that the qualitative data analysis and interpretation is familiar for many surface scientists, making this approach accessible for non-expert users. In addition, the experimental setup and measurement is less sensitive to sample misalignment. While this approach has certain advantages, the information is for

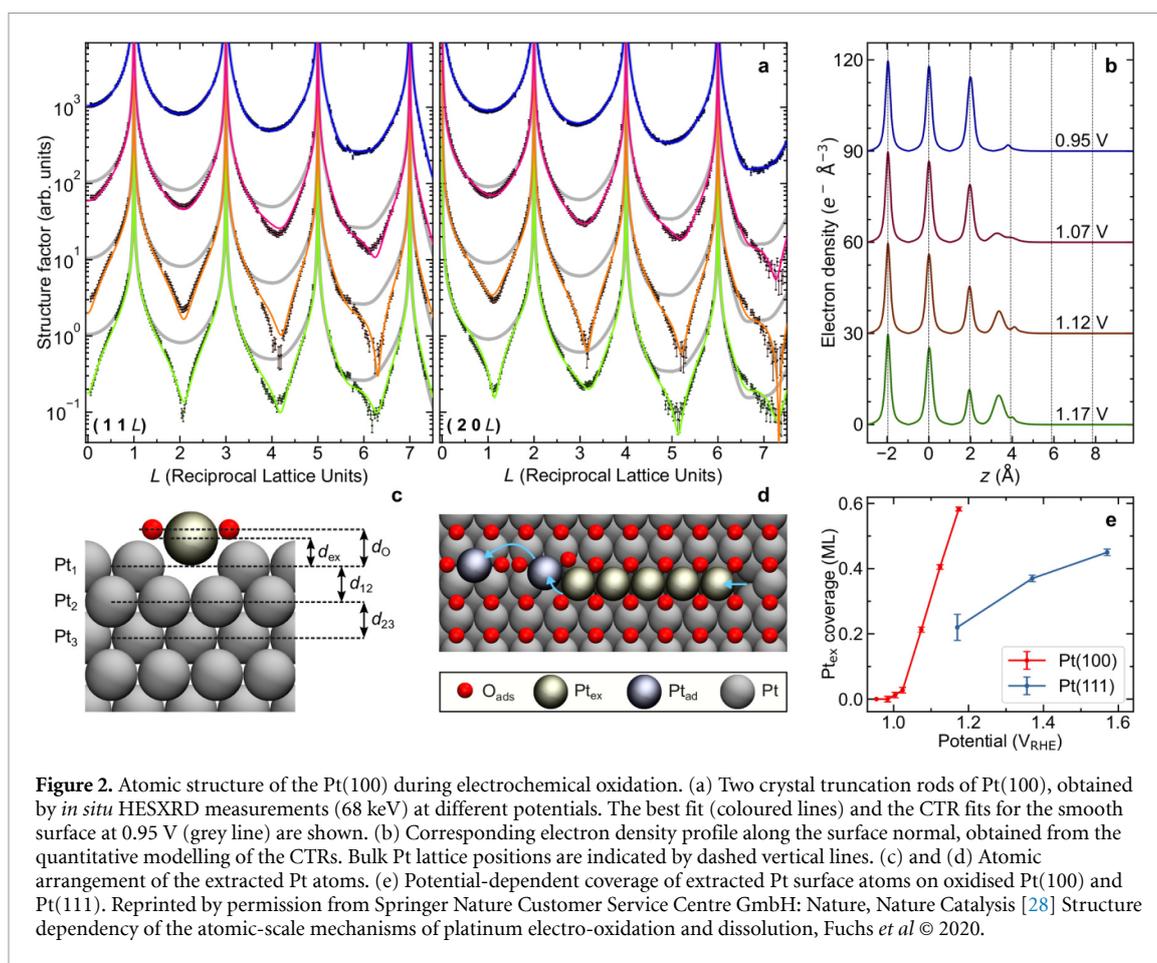


Figure 2. Atomic structure of the Pt(100) during electrochemical oxidation. (a) Two crystal truncation rods of Pt(100), obtained by *in situ* HESXRD measurements (68 keV) at different potentials. The best fit (coloured lines) and the CTR fits for the smooth surface at 0.95 V (grey line) are shown. (b) Corresponding electron density profile along the surface normal, obtained from the quantitative modelling of the CTRs. Bulk Pt lattice positions are indicated by dashed vertical lines. (c) and (d) Atomic arrangement of the extracted Pt atoms. (e) Potential-dependent coverage of extracted Pt surface atoms on oxidised Pt(100) and Pt(111). Reprinted by permission from Springer Nature Customer Service Centre GmbH: Nature, Nature Catalysis [28] Structure dependency of the atomic-scale mechanisms of platinum electro-oxidation and dissolution, Fuchs *et al* © 2020.

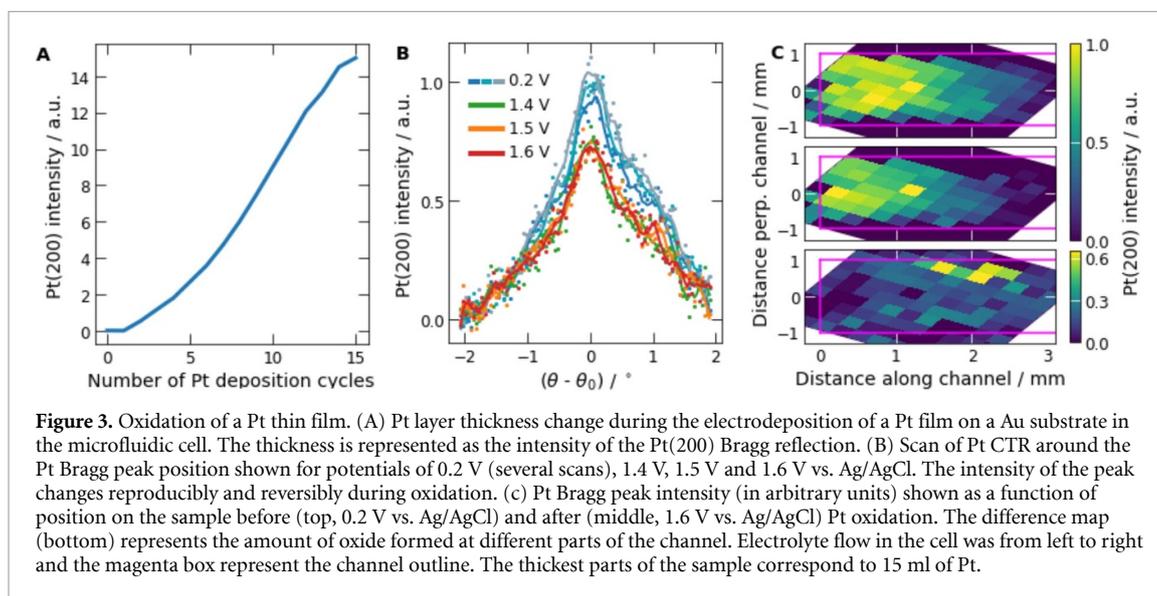


Figure 3. Oxidation of a Pt thin film. (A) Pt layer thickness change during the electrodeposition of a Pt film on a Au substrate in the microfluidic cell. The thickness is represented as the intensity of the Pt(200) Bragg reflection. (B) Scan of Pt CTR around the Pt Bragg peak position shown for potentials of 0.2 V (several scans), 1.4 V, 1.5 V and 1.6 V vs. Ag/AgCl. The intensity of the peak changes reproducibly and reversibly during oxidation. (c) Pt Bragg peak intensity (in arbitrary units) shown as a function of position on the sample before (top, 0.2 V vs. Ag/AgCl) and after (middle, 1.6 V vs. Ag/AgCl) Pt oxidation. The difference map (bottom) represents the amount of oxide formed at different parts of the channel. Electrolyte flow in the cell was from left to right and the magenta box represent the channel outline. The thickest parts of the sample correspond to 15 ml of Pt.

practical reasons limited to the in-plane surface structure. Furthermore, due to the lack of surface enhancement effects associated with evanescent waves, TSD is much less sensitive than grazing incidence geometry. Regardless, we have shown that submonolayer thickness resolution is possible, and that TSD opens exciting opportunities towards characterisation of model electrocatalysts for energy conversion devices.

Figure 3 shows an example of TSD measurements. A Pt layer of various thickness is electrodeposited in a microfluidic channel onto a Au/Si substrate, and characterised during electrooxidation and electroreduction by TSD. The growth of the Pt layer can be followed *in-situ* during the deposition (figure 3(A)), and its oxidation/reduction behaviour assessed using measuring the intensity of the Pt(200) reflection (figure 3(B)). The spatial map of the thickness deposit (figure 3(C) top) shows uneven deposition rates along the

electrolyte flow in the microfluidic channel. The thickest Pt layer is deposited close to the channel inlet and almost no Pt is deposited close to the outlet. The difference in spatial maps of Pt Bragg intensity (figure 3(C) bottom) suggests that the oxidation behaviour is not the same in all parts of the cell and depends on the thickness of the film and/or its morphology. The spatial resolution of this technique opens up possibilities for *in-situ/operando* characterisation of highly heterogeneous electrodes and measurements of spatio-temporal oscillations of various electrochemical reactions (including reactions relevant for electrochemical conversion and storage) on model surfaces.

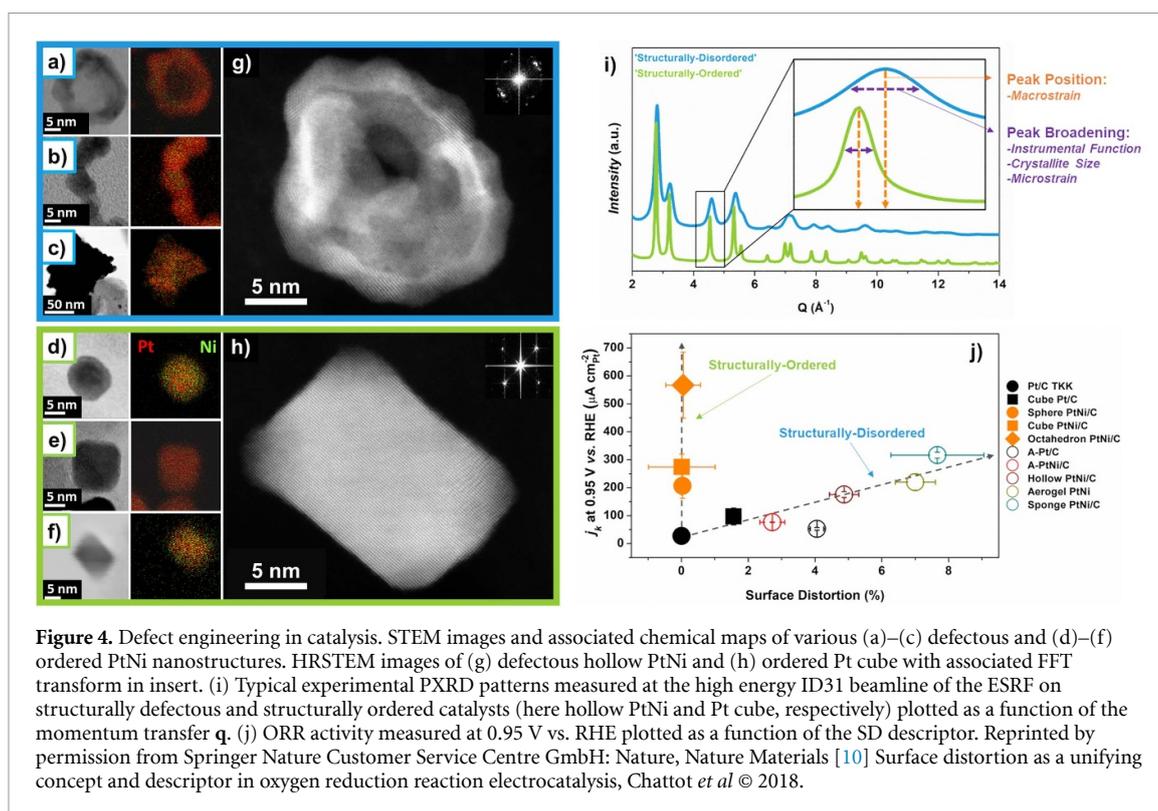
3. Local structure, defects and nanostructure interfaces

The ability to probe the surface chemistry of electrified interfaces using diffraction is not only limited to single crystals [31, 32]. The surfaces of nanoparticles can be measured by exploiting their large surface area to volume ratio. For example, monolayer surface oxidation of commercial Pt nanoparticle PEMFC catalysts (2–3 nm in diameter) decreases the volume of the coherently diffracting crystallite by 40%–60%. Bulk sensitive techniques such as powder diffraction can therefore be used to directly measure the surface chemistry in these systems, as a significant portion of the atoms are located on the surface of the nanoparticle. Synchrotron diffraction measurements routinely achieve signal to noise ratios of greater than 10^3 , which allows for submonolayer quantification at low electrocatalyst loadings and imperfect particle utilisation. With increasing size of the crystalline particle the surface sensitivity decreases, but remains up to 5% for 30 nm spheres. Because practical electrocatalysts are typically optimised for maximum surface area, a broad range of different nanocatalysts are accessible within this range.

Unlike competing microscopy techniques, x-ray scattering measurements analyse the structure in reciprocal space. This has certain advantages as small spatial dimensions in real space produce large distances in reciprocal space, providing facile and precise access to atomic scale information with strain resolution far superior to real space techniques. This can be used to detect surface adsorption processes and local strain fields, as will be discussed later. Furthermore, high energy photons allow measurements large momentum transfers \mathbf{q} , which allows: (1) lower scattering backgrounds at high \mathbf{q} , (2) precise lineshape analysis, and (3) total scattering experiments, where a large portion of reciprocal space is measured in one acquisition.

First, reflections at high \mathbf{q} are significantly less contaminated by background scattering of low- Z elements, as high- Z atoms elastically scatter more intensely at high \mathbf{q} due to larger atomic form factors. Because many electrocatalysts are based on heavy metals, strong diffraction signals from the active material can be discriminated from the background signal originating from the sample environment, electrode binders, catalyst support particles, etc. The second advantage is that the fine structure of diffractograms contains significant nanostructural information regarding the crystal (dis)ordering. The peak widths in a diffractogram reflect the coherence length of the crystal, and the reflection peak profiles from a large number of reflections allow quantitative deconvolution of the size and microstrain of nanocrystallites. The size of the crystals is useful for studying the stability of electrocatalyst materials, while the microstrain reflects the local lattice distortion and defect content in the crystal. The third advantage is that total scattering can be used to probe amorphous and highly disordered materials which do not yield sharp diffraction peaks. This is because the 1D powder diffractogram measured at sufficiently high \mathbf{q} can be Fourier transformed to yield the pair distribution function (PDF) [33]. This radial distribution function of all scattering atoms in the material is a measurement of local structure. PDF analysis does not require long range order, merely an understanding of the sample's elemental composition. It is a complementary approach to spectroscopic techniques such as extended x-ray absorption fine structure (EXAFS) and is often used in cases where EXAFS measurements are not practical, such as when the high penetration power of x-rays is necessary to probe materials inside electrochemical cells and devices [34–36].

The advantages of high energy x-rays have been exploited in the search of active, stable and high surface area Pt based nanocatalysts for PEMFCs. The high penetration power of the x-ray beam is utilised to study the structural changes of the catalyst during accelerated stress tests in liquid half-cells [37]. The surface sensitivity for small nanoparticles can be used to dynamically study the oxidation behaviour of the electrocatalysts during potential cycling, which is the main phenomena leading to the catalyst dissolution and shape degradation [32]. This is an extension from single crystal studies and allows a direct comparison between model surfaces and practical nanoparticle catalysts, effectively bridging the size gap of the surface science approach. One of the most interesting applications of high energy x-rays is the determination of defect density in nanocatalysts and its effect on catalytic activity. Recently, we showed that surface defects play a major role in the performance of oxygen reduction reaction (ORR) catalysis. Careful design of such defects can lead to more stable and more active catalysts [10, 38, 39]. This paradigm shift was allowed by careful line shape analysis of the measured diffractograms and subtraction of the bulk microstrain



determined by *ab-initio* calculations. Based on the direct microstrains measurements we defined a new Surface Distortion structural descriptor, which can be used to rationalise the activity of various ORR catalyst structures and guide the development of a new family of highly defective catalytic nanomaterials (figure 4).

Fourth generation synchrotrons, such as the extremely bright source upgrade of ESRF, have opened new opportunities for the characterisation of practical nanocatalysts and surface defects due to the significant increase in the coherent fraction of the x-ray beam at high energies. Coherent scattering offers a chance to combine high resolution in reciprocal space with excellent real space resolution. Bragg coherent diffraction imaging (BCDI) exploits the coherent properties of nanofocused beams to produce 3D images of individual nanocrystals by oversampling their diffraction pattern. These images are exceptionally sensitive to phase shifts caused by lattice distortion, anisotropic strain, and dislocations/defects. While strain mapping at atomic resolution can be reliably performed in electron microscopes, the limited penetration depth of electrons severely limits *in situ* capabilities. BCDI can be performed with arbitrarily high energy photons, opening the door to *in situ* electrochemical strain mapping at the single particle scale. This has not been previously feasible as the minimum practical size of single nanoparticle which could be easily studied by BCDI was in the range of hundreds of nanometres, 1–2 orders of magnitude above the practical size of the electrocatalysts. However, in battery research, where the individual particles are often up to several microns in size, BCDI has already been very successfully applied for studying strain changes and dislocation movement during battery charging and discharging [40].

Another emerging high energy x-ray imaging technique suitable for the research of PEMFC materials, and other energy materials, is dark field x-ray microscopy (DFXM), which is conceptually similar to dark field transmission electron microscopy [41, 42]. In DFXM the image of the material is formed using objective lens, overcoming the phase problem of the reciprocal space methods such as BCDI while taking advantage of the high penetration power. This gives an opportunity to bring real space imaging to the *operando* studies of nanomaterials used in PEMFC, as discussed below. The resolution of the technique mainly depends on the numerical aperture of the objective lens, which is the major bottleneck. Currently the typical resolution using refractive lenses is on the order of hundred of nanometres [43], which is not yet suitable for imaging nanocatalysts in PEMFC and other energy conversion devices. However this imaging technique can be already used in solid oxide fuel cells (SOFCs) [44] and battery research where the crystalline domains of the relevant materials are in micrometre range. Due to the fast progress in multilayer Laue lens technology we expect that the instrument resolution will reach nanometre scale in the near future for high x-ray energies [45].

4. Multiscale device *operando* characterisation with high energy x-rays

In the sections above we discussed the use of high energy x-rays for investigations of model catalysts and nanocatalysts. In both cases, the main focus was to utilise the compressed reciprocal space together with large 2D detector to either speed up the measurement and increase the precision of structure determination or to perform advanced line shape analysis and microstrain refinement. In this section we discuss the utilisation of high penetration of high energy x-rays to study the materials in actual electrochemical energy conversion and storage devices, in particular PEMFCs. The high transmission at high x-ray energies (above 40 keV), particularly for low Z elements, allow penetration of large samples and cell housings while still fully exploiting all the advantages to study the materials at the atomic/molecular level. This is an important feature, as scattering studies at low x-ray energies typically require electrochemical cells that are adapted to low penetration depths of the probe, which comes at the expense of electrochemical performance. Furthermore, liquid cells often used to simplify the electrochemical environment do not completely mimic the triple phase boundary (gas, liquid, solid) surrounding the catalyst inside functional devices [46]. These severely limit the electrochemical performance and often do not allow to cell operation at high currents, potential ranges, and environments typical for real PEMFCs. On top of the advantage given by high penetration, the full diffraction pattern at high x-ray energies can be also obtained at millisecond time resolution using synchrotron sources, which is characteristic for the diffusion limited phenomena happening at the micron scale. Because the diffusion fluxes define the local environments of the materials within the electrochemical device, the ability to monitor structural changes on this time scale is important for understanding the final performance and degradation of nanocatalysts.

Apart from the wide angle x-ray scattering (WAXS) discussed in the previous section, various other high energy x-ray scattering techniques can be used to characterise the electrochemical devices. X-ray micro/nano computed tomography and imaging are the most advanced and used at all stages of PEMFC development. Tomography gives a good estimate of the porosity of GDLs, as well as the morphology of the catalyst layer, at multiple lengthscales ranging from nanometres to hundreds of micrometres [47–54]. This information is important as an input for physico-chemical models predicting the device performance and used in the optimisation [55–57]. Imaging techniques can be used to track water formation inside the GDL and channel structure and its removal at high current operation (figure 5) [58–61]. The imaging of fast acquisition rates (ca. 2000 frames per second) provide superb time resolution, which has been used to study the failure modes of functioning Li-ion batteries during thermal runaway [62, 63]. Even though this approach has not yet been reported for PEMFC research, we foresee that fast imaging experiments can be utilised to study the transient processes happening between the operation modes and during the start-up and shut-down of the cell. The development of 4th generation synchrotron sources will significantly increase the coherent fraction of the beam at high energies, which will boost phase contrast imaging simplifying and speeding up the measurements. Therefore we foresee that fast phase contrast imaging and micro/nano tomography will play an increased role in the development of materials for PEMFC.

An interesting approach to study PEMFC devices is to couple elastic scattering x-ray techniques with tomographic reconstruction (XRD-CT and small angle x-ray scattering (SAXS)-CT), giving access to the molecular level information with device level spatial resolution. Such an approach has been successfully used to image batteries [64], gas phase catalytic reactors [65] and SOFCs [66]. So far those experiments were performed in simplified sample environments and in quasi-*operando* conditions. The reason for this is that there is an interplay between the measurement speed, the resolution and the amount of reconstruction artefacts when full size electrochemical devices are characterised. XRD-CT on small, but reasonably sized (5 cm²) PEMFC devices has now been demonstrated, and in principle can be scaled towards industrially relevant full stacks [67, 68]. This diffraction-contrast imaging allows various nanocrystalline phases to be accurately mapped throughout operating cells based on the unique diffraction pattern for different materials, as seen in figure 6. Equivalently, the phase composition of specific locations buried deep inside the sampled volume can be extracted and analysed, independent of the surrounding environment.

For the XRD-CT technique, one significant limitation is the parallax error for large samples. This effect broadens the diffraction peaks as a function of \mathbf{q} , making peak shape analysis on the reconstructed data very difficult. A possible solution to address this problem, termed direct least-squares reconstruction algorithm, combines the reconstruction and Rietveld fitting steps into a single step [68, 69]. This approach is computationally heavy, but with advancements in algorithm development, deployment of supercomputers and machine learning approaches, 4D diffraction-contrast reconstructions of large electrochemical devices during operation are viable within the next few years. Such characterisation is necessary to fully understand the role of the working environment on performance and materials degradation as will be discussed in the next section. The SAXS-CT technique does not suffer from parallax error because the data are collected at low

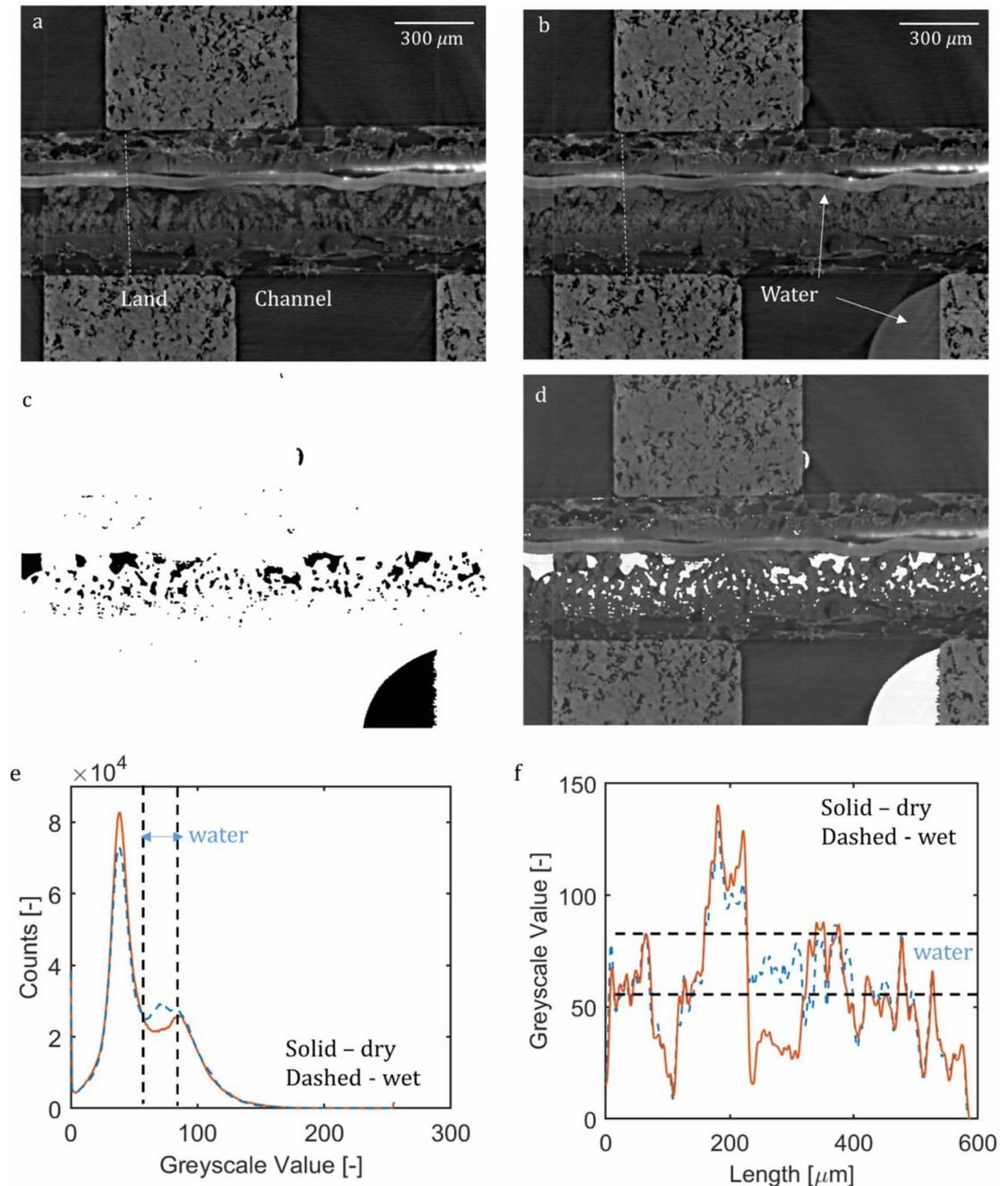


Figure 5. X-ray micro computed tomography. Cross-section tomographs of the assembled fuel cell having a PGM-free cathode at 30°C under (a) OCV (dry), (b) with a current density of 40 mA cm⁻² drawn from the cell (wet), (c) thresholded water clusters and (d) overlay of thresholded water and image from plot (b). (e) A histogram of greyscale dry and wet images, with the region belonging to water, (f) the greyscale values along the dashed line shown in (a and b), where the window for greyscale values for water is shown too. Gen 3 cell. 1.3 μm resolution. Data is collected at 8.3.2 beamline at ALS. Reproduced from [61]. © IOP Publishing Ltd. [CC BY 3.0](https://creativecommons.org/licenses/by/3.0/).

diffraction angles, the data analysis in this case is straight forward and standard approaches yield accurate reconstructions. The use of high energies for SAXS require positioning the detector far away from the sample (5–10 m). Currently, there are only few high energy beamlines equipped for this setup. Nevertheless, we expect to see more combined XRD/SAXS-CT studies of PEMFC in the near future, as the increased flux and decreased source size at high energies at 4th generation synchrotron sources will be beneficial for both the small and the wide angle scattering regime. Specifically, it will allow better spatial resolution while significantly increasing the measurement throughput due to faster acquisition times. Currently XRD-CT measurements of one slice of 5 cm² PEMFC, with resolution of 200 μm and 0.05 s acquisition time for one frame, require about 30 min [68]. The expected increase of the photon flux at 4th generation sources will

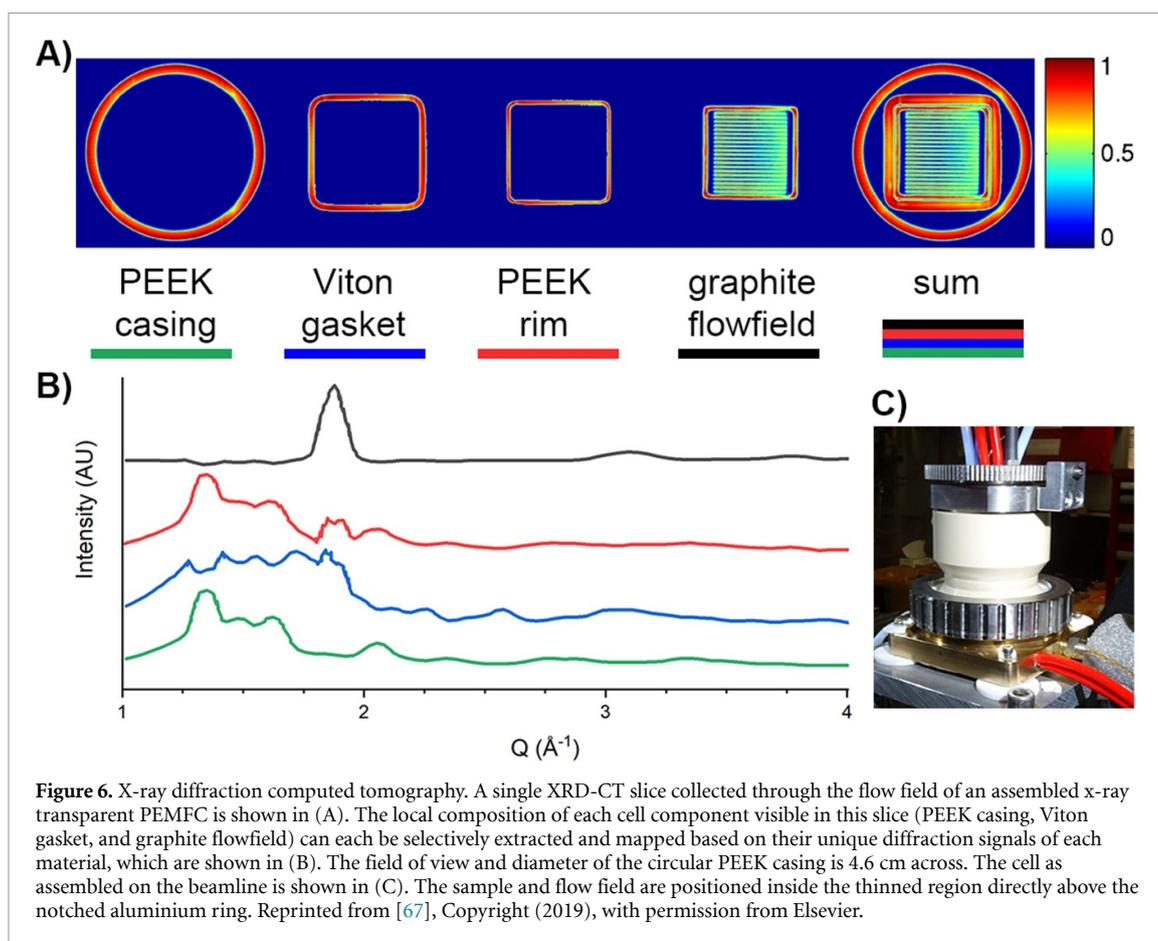


Figure 6. X-ray diffraction computed tomography. A single XRD-CT slice collected through the flow field of an assembled x-ray transparent PEMFC is shown in (A). The local composition of each cell component visible in this slice (PEEK casing, Viton gasket, and graphite flowfield) can each be selectively extracted and mapped based on their unique diffraction signals of each material, which are shown in (B). The field of view and diameter of the circular PEEK casing is 4.6 cm across. The cell as assembled on the beamline is shown in (C). The sample and flow field are positioned inside the thinned region directly above the notched aluminium ring. Reprinted from [67], Copyright (2019), with permission from Elsevier.

reach the detector high speed exposure limits for the modern high energy x-ray detectors and speed up the measurements by a factor of 10, without compromising the quality of the data and the signal to noise ratio.

5. Perspective towards holistic understanding of electrochemical devices

As discussed above, high energy x-rays provide means to study all parts of electrochemical devices at all relevant length scales with a single probe in a single experiment. This provides an opportunity to combine all the information obtained by various imaging and scattering techniques into a comprehensive picture of the material's atomic structure, morphology and chemical composition in native environment and during the operation of the device. Even though this requires flexible setups and technological advancements, modern beamlines currently in operation (or are being built at 4th generation synchrotrons) are made with this in mind, and SAXS, WAXS, x-ray imaging and tomography can be combined in one experiment.

Holistic characterisation using these new instruments will allow us to reassess and fully understand the processes leading to materials degradation and performance fade. As an example of such approach, the flowfield design and dynamics of water movement in the PEMFC can be linked to the degradation of the catalyst [68]. This kind of information will allow engineers to refine the best flowfield structure optimised not only for the power output, but to also for ageing phenomena. Related to the above example, the transient oxidation processes responsible for the catalyst degradation and dissolution can be tracked at the atomic level on both model and nanoparticle surfaces in PEMFC operating conditions. This can be used to find optimal operation parameters (including potential, total allowed oxidation charge, etc) for each catalyst and thus help mitigating catalyst degradation.

One of the most exciting opportunities, albeit the most challenging one, is the ability to probe local structure inside the operating PEMFC. This will require utilisation of all scattering and imaging techniques in one experiment, as well as the most advanced WAXS and SAXS data analysis approaches. WAXS, coupled with differential PDF analysis can provide information about the local environment near the catalyst interface. Such an approach has previously been used to understand the restructuring of polar and nonpolar solvents around colloidal nanoparticles [70], serving as a template for how this might be utilised in PEMFCs. Complementary SAXS can provide information about the CCL morphology and its evolution during operation. Recently, we showed that an extension of SAXS Gaussian-field models can be effectively used

towards this class of nanostructured materials, allowing us to analyse a wide range of different nanoparticles and CCL morphologies [71].

One of the advantages of high energy x-rays is that local mapping of structural properties by CT is not limited to small, experimental devices, but is in principle applicable also for large size industrial devices. The main challenges are in this case amplified: the parallax effect for XRD-CT and the scattering background signals associated with the PEMFC housing, and other parts of the sample environment. The first challenge can be overcome by improving the reconstruction algorithms, which is in our opinion feasible, and rapidly progressing. As for the second challenge, multiple approaches can be utilised at the software and hardware levels: (1) The diffraction patterns from all cell components can be measured and then deconvoluted from the diffraction patterns of interest [67], (2) principal component analysis can be deployed on a series of patterns measured during *operando* experiments [72] and (3) advanced Soller slits can be used, which effectively suppress the cell background during the measurement [73].

One of the remaining questions in using high energy x-rays for the characterisation of electrochemical systems is the influence of the measurement itself. Intense x-ray beams are well-known to induce pronounced structural modifications, but a precise quantitative assessment of these beam damage effects remains absent for complex systems [32, 74]. Determining the maximum reasonable x-ray dose for a particular investigation, and designing low-dose measurement and data analysis strategies are necessary for robust, reliable characterisation. Neglecting beam damage can have dire consequences, and can lead to wrong conclusions when studying delicate nanostructured material. Especially for the 4th generation bright sources this question is of utmost importance. This issue needs to be thoroughly assessed and needs to be addressed in detail in the future.

In conclusion, recent progress in using high energy x-ray probes for studies of electrochemical systems was discussed, with a focus on PEMFC technologies. We argue that this probe allows in-depth characterisation of all parts of the system, at all relevant length scales, from model systems to operating devices. This enables correlative experiments which will lead to much better holistic understanding of the operation and degradation phenomena at the device level. The latter may be a game changer for PEMFC technologies where the lack of understanding at the device level leads to difficulties in incorporation of new materials into current technology. Fourth generation synchrotron sources will boost the coherence of the beam at high energies and improve the data collection speed, allowing single particle *in-situ* studies and more efficient use of advanced scattering tomography techniques.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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