AXAA

Australian X-ray Analytical Association

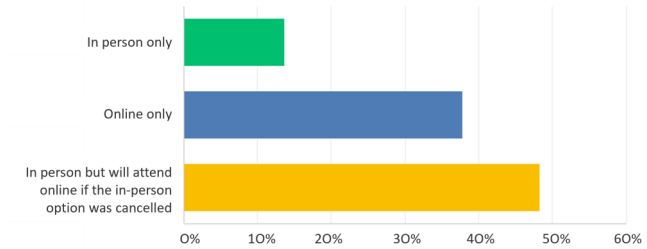
Newsletter Issue 1 2022

President's Address

Dear AXAA members and friends,

Our thoughts are with all those affected by the recent floods, and all of our members and their families who may have been impacted over the last few months as coronavirus waves swept through every state and territory across the country. While this year has granted us more freedom of mobility, the disruptions of the virus are still being felt acutely in many workplaces.

As we begin moving towards a new normal, AXAA is trying to identify the best ways to connect with and support our community. You may recall we ran a pulse survey in March to assess the viability of running an in-person conference at the end of this year. We approached the feasibility assessment with an abundance of caution given the financial risk of running large events in an ongoing pandemic. As a committee, we set a benchmark



for the number of on-site participants needed to meet financial targets and provide a good conference 'buzz'. Unfortunately, the survey results did not reach that benchmark, and we concluded that the risks of committing to an in-person event were too high for this year. As such, we will not run a national scale conference this year

More generally, the results were very positive in that they demonstrated a clear preference for in-person events (~60%) even if the location were in a regional area, which gives us confidence that the AXAA community remains engaged and keen to reconnect. Furthermore, most people (86%) remain open to online options if the need arises.

This information will allow us to plan state-based events with more confidence so stay tuned for announcements in the coming months!

As always, we are very interested in any feedback or ideas you may have – what would you like to see AXAA offer you in 2022?

Jessica Hamilton

AXAA President

Celebrating a humble research giant who studied tiny forces

By Natalie Chapman

Dr Ulrich Senff was many things: a German immigrant who loved cooking, soccer, poetry, music and beer, an early school leaver who acquired a PhD and my beloved stepfather. What I didn't discover until after he died earlier this month, aged 70, is that Ulrich's research in quantum chemistry is internationally renowned because it enabled a breakthrough after a decade-long impasse and is still key to cutting-edge technology.

I'm a trained chemist and while I knew he was proud of his PhD research I was unaware that his work was world-leading until I delved into online

records so I could write his eulogy. Clearly, he was also humble. My thanks go to Dr Meredith Jordan, Professor of Theoretical Chemistry at the University of Sydney, for helping me to better understand Ulrich's work. I regret that I didn't fully appreciate his achievements while he was alive, so I want to celebrate them now. Below is my summation of his remarkable life.

Derivation and Immigration

Ulrich was born in Borghorst, Germany, on 17th December 1951, his mother Rosel died from complications a few days later. His father Erich remarried and Ulrich was raised by his stepmother Heidel, along with his three younger siblings. Seeking greater opportunities, the family moved to Australia in 1960 and settled in Wollongong, on the southern coast of NSW.

Education and Admiration

Ulrich left school at 15 to work for BHP at Port Kembla, where he stayed for almost 30 years. While working full-time he also studied quantum chemistry at the University of Wollongong. In 1987, he won the University's award for PhD of the Year.

His ground-breaking research involved measuring the weak attractive forces between hydrogen, helium and lithium ions and dipoles: the smallest molecules, made from two atoms. The Cambridge University Professor who examined Ulrich's PhD thesis concluded that it was 'very high quality and certainly worthy of publication in reputable journals.'

Calculation and Citation

The Professor admired how cleverly and precisely Ulrich had calculated the tiny molecular interactions. 35 years later his results are still regularly cited by researchers. Amazingly, his results were accurate for the time and his interpretation of the chemical structures is a benchmark for modern calculations. Because the forces that Ulrich studied are fundamental to every chemical reaction, when he quantified them he enabled a myriad of scientific and technological advancements.

Ulrich's contribution is a foundation on which Australia is building new, safe methods to store hydrogen – the green fuel of the future – for domestic energy needs or export. His discoveries are also important in astrophysical studies of stars, space dust and cosmic rays.

Calibration and Commercialisation

As the head analytical chemist for what is now BHP Billiton, Ulrich applied his research to determine the chemical composition of primary materials (iron ore and coal) and the final product of the steel-making process, becoming an expert in X-ray fluorescence spectrometry. Over the course of his career, he travelled around the world calibrating XRF spectrometers and training people to use them more accurately for research and industrial purposes. He updated the Australian Standard for XRF Spectrometer Precision, which was adopted by the International Standards Association.

He helped an Australian start-up (now AXT Pty Ltd) to prototype, prove and produce commercial quality re-engineered XRF tubes. Ulrich was a Director of AXT from 1992 to 2009 and worked with the company until 2015. In 1995, he was headhunted by ANU for his outstanding expertise, and moved to Canberra with his partner Kay. He assisted another start-up called UniQuant to develop revolutionary software for XRF spectrometry that did not require reference samples, enabling creation of fast, portable spectrometers for field analysis.

Inspiration for the next generation

At home, Ulrich had a chemistry kit that would not have passed any test for child safety. It was about four times bigger than the kits stocked by toy stores, with contents that could blow your head off! My sister Karin and I loved assisting him with experiments on the dining room table.

With hindsight, I can clearly see the strong in-

fluence he had on my choice of studies and career direction. I am so proud of his achievements and legacy, which inspire me to continue my work with Australian researchers and innovators: people who are striving to make positive change in the world by developing new knowledge and technology – just like Ulrich.

A brief examination of the prevalence of erroneous XPS analysis in the scientific literature

Thomas Raeber, CSIRO

Introduction

X-ray photoelectron spectroscopy (XPS), or electron spectroscopy for chemical analysis (ESCA), is a soft x-ray-based materials characterisation method. The technique involves measuring the energy and number of x-ray-induced photoelectrons to probe the chemical structure and composition of materials. This nominally non-destructive method is a powerful tool that gives not only quantitative elemental information but also quite detailed information on chemical bonding states. When first introduced, XPS systems were single-purpose lab-built instruments that were technically complex to operate with users being required to write software to control the instrument and analyse data. By contrast, modern systems can contain numerous specialist chambers and significant hardware and software automation which has greatly improved throughput and ease of use. This has enabled ever-increasing uptake of the technique within commercial and academic settings.

As a result of improved access, researchers can now gain insight into the surface composition of their materials with increasing regularity. However, the growth in quantity of data has increased the potential of another problem: the quality of data and interpretation by the user. While automation in next-generation systems has made XPS relatively easy to use from an operation perspective, the difficulty involved in data interpretation has remained unchanged and, if anything, the increasing complexity of materials being studied makes it more challenging to extract reliable and accurate information from XPS data. It is becoming increasingly common to see XPS data interpretation in many non-surface science-related publications. The inclusion of XPS data in these journals has led to the expectation that reviewers with little to no experience in surface analysis verify the data and methods used. It is not surprising then that this has resulted in more and more examples of poor interpretation being accepted for publication. As additional erroneous XPS interpretation makes it to print, there is a higher probability this data is used as the standard to which new data is compared. This is a major issue among researchers who read about a particular result in the literature, and, without the necessary skill or experience with the technique, accept it as fact. Whole fields of research can end up heading down the wrong path if poor practices become accepted as mainstream. While this should be addressed at the review stage, non-experts will look at literature, see incorrect data presented as fact, and use this information to aid judgment during peer review.

XPS does not face these issues in isolation. In a 2016 *Nature* survey of 1576 researchers, 90% indicated there was a reproducibility problem in science and 50% identified it as a significant crisis.[1] Across the materials characterisation community, increasingly questions are raised as to the reproducibility and quality of data in the literature.[2] There are a number of driving factors for this issue. A significant contributing factor is the sheer volume of papers currently being published when compared to past years and sorting the quality from the questionable has never been harder. Another large contributor is the increasing importance of multidisciplinary science. Transition of established scientists into new, often 'hot', areas of research will require time to develop critical knowledge, and thus can contribute to the prob-

lem. Lack of supervision and training of graduate students and early career researchers (ECRs) further compounds the issue. Quite often, ECRs are expected to use a vast suite of techniques with little support as journals demand more and publication targets increase. If poor analysis and interpretation are perpetrated by a team that is highly regarded in a certain area, this can accelerate the uptake of poor practices as their work is typically highly cited and tends to garner greater respect from colleagues.

Identifying the problem

Over their years at CSIRO, the team — Thomas Gengenbach, Christopher Easton and, having started more recently, I — have observed numerous examples of poor XPS in the literature ranging from issues with the experimental methodology (e.g., incorrect sample preparation, experimental setup, analysis parameters, etc.) to data processing and presentation of data – with data processing and presentation proving to be the most common source of erroneous analysis. After correspondence with Don Baer, who has been a driving force behind various initiatives aimed at improving reproducibility, the team were invited to participate with an international group of experts on the broader issue of irreproducibility in surface science. The team at CSIRO discovered there was growing dissatisfaction among international XPS specialists with the frequency of erroneous XPS analysis not only in papers they reviewed but also in the wider literature.[3] Members of this group along with the team at CSIRO decided to examine the severity of this problem and generate hard metrics on the state of XPS in literature.

In 2020, a report by the aforementioned collaborators was published; it audited XPS data in 409 papers that had been published over a six month period in three major but unnamed journals.[4] The audit looked at the XPS analysis presented in those papers and evaluated its quality against a series of criteria deemed important for ensuring quality work. There were several key findings from this work that painted a sobering picture of the state of XPS in literature. The papers were ranked in coloured categories that represented the quality of the data ranging from green via yellow and orange to red. Green category papers contained no obvious errors and were deemed to be presented in a scientifically appropriate manner. Conversely, red category papers displayed significant examples of major errors that, in all likelihood, would compromise the validity of the work. These red errors typically demonstrate a complete lack of understanding of the physical and chemical processes occurring during analysis and the underlying surface chemistry of the material being analysed.

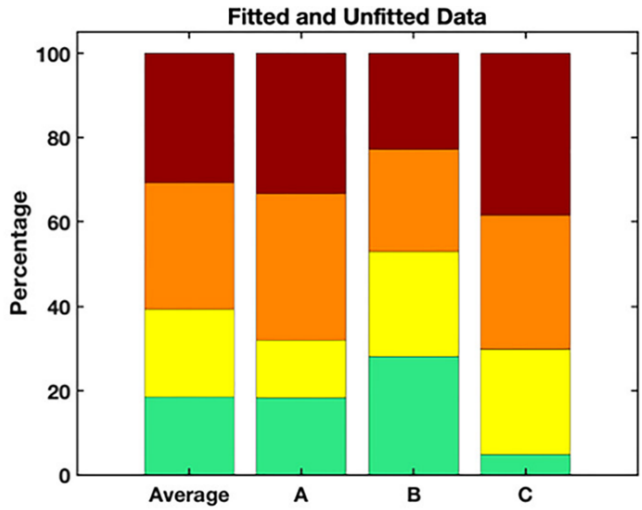


Fig. 1. Percentages of green, yellow, orange, and red rankings of the 409 papers the study considered. Journal A is energy and battery related, Journal B deals with surface and interface chemistry and Journal C is general science. Reprinted with permission from[4]. Copyright 2020, American Vacuum Society.

The main results of this study are summarised in Fig. 1. It was found that less than 20% of fitted and unfitted XPS data was correctly presented when averaged across the three journals. More alarming are the numbers when focussing on papers that fall into the red category. When averaged across the three journals, 30% of papers showing fitted and unfitted data fell into the red category with a further 30% in the orange category. Focussing on papers with fitted data averaged across the three journals (not shown here), less

than 10% of papers fall into the green category while more than 40% fall into the red category. The news is not all bad, however. Looking at the papers that presented unfitted data, the outlook is more positive with an average of 50% of papers falling into the green category and less than 10% in the red category.

So how do we fix it?

Identifying the problem is only one part of the solution. The CSIRO team have taken multiple steps to tackle different aspects of the issue. When problematic papers are discovered, the team will contact editors to highlight the specific problems. This can include requesting for the retraction of particularly troublesome papers, or, in one example, writing a rebuttal paper. The team have sought to raise awareness via letters and op-eds, and at conferences, through presentations and posters. Furthermore, an effort has been made to raise awareness within CSIRO Manufacturing. This includes education and also monitoring research outputs by the organisation. This ongoing effort has led to engagement with the task force implementing the Australian Code of Responsible Conduct of Research to further improve awareness of the organisation's research integrity.

Beyond the CSIRO team's individual efforts, there has been ongoing collaboration with other specialists in the international XPS community and journal editors to develop a roadmap on how to counter the growing issue. Developing a course of action has been the subject of debate among XPS specialists in informal and formal settings such as various American Vacuum Society (AVS) International Symposium and Exhibition events. In 2018, a survey by AVS distributed to the international XPS community concluded that a collection of guides was needed. In 2020, the Journal of Vacuum Science & Technology A published a Special Topic Collection presenting 32 articles acting as guides for different aspects of XPS with some targeting areas that have been identified as problematic or had a history of applying the technique.[5]

The guides are only one aspect, the discussion between researchers and XPS specialists also needs to improve, and researchers need to be better informed on the resources and knowledge available to them. XPS specialists need to engage with researchers to offer expertise and ensure a high standard of work. Further to this, better education on the complexity of the technique is required. As mentioned earlier, the increasing automation of XPS has made the technique deceptively simple from an experimental point of view. This becomes an issue when researchers carry this impression over to data processing. Users need to be better informed about the fact that XPS is much more than just the push of a button and that thought, and nuance is required to extract meaningful and reliable information from XPS data. Information needs to be disseminated among graduate students and ECRs early during their careers as they are developing their understanding of analytical techniques. Providing adequate training from the beginning will go a long way to mitigating the prevalence of poor XPS in the future. This approach will also ensure that the upcoming generation of researchers does not perpetuate the mistakes published by others.

What's next?

While the current guides are a good start, further work is required in improving XPS analysis in the literature. Given their success, members of the international committee are developing a second set of guides with a greatly expanded scope and a whole host of other surface characterisation techniques being considered. Expect to see a call for submissions from AVS for guides and explainers on techniques such as auger electron spectroscopy (AES), secondary ion mass spectrometry (SIMS), low-energy ion scattering spectroscopy (LEIS), ellipsometry, and various scanning probe methods as well as XPS topics not fully covered in the first collection including high energy XPS (HAXPES) and near ambient pressure XPS (NAP-XPS). As awareness continues to grow, other fields are actively

pursuing improvements. One example is a recent seminar that was held by the North American Catalysis Society on "Addressing Rigor and Reproducibility in Heterogeneous, Thermal Catalysis". The organiser's aim is to start a dialogue in the greater catalysis community to help raise awareness on the issues facing the field and to begin the search for solutions to the problem. As awareness spreads among these communities, hopefully, the culture will begin to change. Understandably, this problem is not expected to be fixed in the short term. However, through a concerted effort by researchers and the greater XPS community, the outlook for XPS and other characterisation techniques is positive.

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Characterisation of Energy materials with X-ray Absorption Spectroscopy – Advantages, Challenges, and Opportunities

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Introduction

When it comes to energy materials, such as electrocatalysts and batteries, there are a number of challenges that present themselves in the characterisation of these materials. Often, these materials possess some degree of structural disorder that makes many traditional methods of structural characterisation difficult or impossible, due to the near or complete lack of discernible diffraction patterns. Furthermore, some of the most active energy materials are composed of two or more elements where each elemental component plays a unique and equally interesting role in the operation of the overall material.

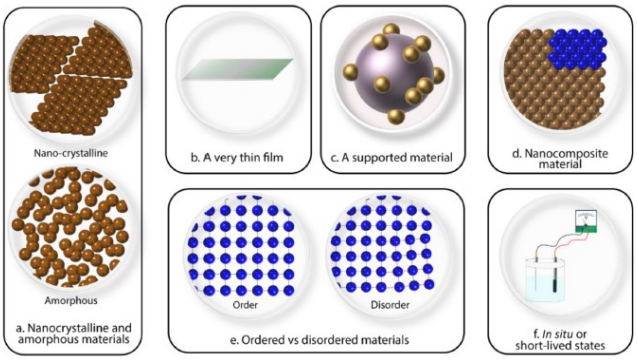


Figure 1. Sample types that are commonly studied by XAS as a result of the elemental specificity of the technique include (a) nanocrystalline and amorphous materials, (b) very thin films, (c) supported materials, (d) multicomponent materials (like composites), (e) ordered versus disordered materials, and (f) in situ experiments. Reprinted with permission from Kerr et al (2022). Copyright 2022 American Chemical Society.

X-ray absorption spectroscopy (XAS) is a powerful tool used in the characterisation of energy materials owing to its ability to extract data from disordered materials. Beyond that, the element selective nature of XAS means that each elemental component of a material can be investigated individually. The benefit of this is being able to isolate elements and extract relevant information about their electronic and geometric structure – an important feature when studying materials under operation. XAS is particularly well-suited to amorphous and nanocrystalline materials (Figure 1a), thin films, such as thin film catalysts (Figure 1b),

supported nanomaterials (Figure 1c), nanocomposites or multicomponent materials (Figure 1d), ordered *vs* disordered materials (Figure 1e), and *in situ* experiments.

'Ideal' XAS samples produce the best data with few sample-based distortions, yet, many energy materials – and in fact, many materials in general – cannot be reasonably considered 'ideal' XAS samples. The reality of experimental materials is that often they are inhomogeneous, too concentrated, not concentrated enough, or have mixed species present.

Given that these non-ideal circumstances can produce distorted data, which has the potential to lead to incorrect data and/or conclusions about key aspects such as oxidation state changes, there is a significant need to consider and investigate the technical aspects of XAS and the challenges involved in analysing materials. Given that the circumstances under which this data is collected can affect our spectral observations, it is imperative that they form an integral part of the planning *and* analysis stages of an XAS experiment. Furthermore, while XAS is excellent at providing local structural information, where larger structural effects are a key component of the material (e.g. pore sizes, stacking) XAS should be paired with other analytical observations including transmission electron microscopy (TEM) and/or X-ray diffraction (XRD).

What is XAS, and why is it useful?

XAS spectra contain two key interpretable regions, the X-ray absorption near edge structure (XANES), which can tell us about both the electronic structure and, indirectly, the geometric structure; and the extended X-ray absorption fine structure (EXAFS) which directly provides local structural information up to about 7 Å from the absorbing atom. The hard XAS beamline at the Australian Synchrotron is able to detect K or $L_{2,3}$-edges of most transition metals. K-edges are higher energy edges as they involve electron transitions originating from 1s orbitals while L-edges are lower energy edges that arise from 2p electron transitions. Example of K and L-edges for two low-spin iron samples are given in Figure 2.

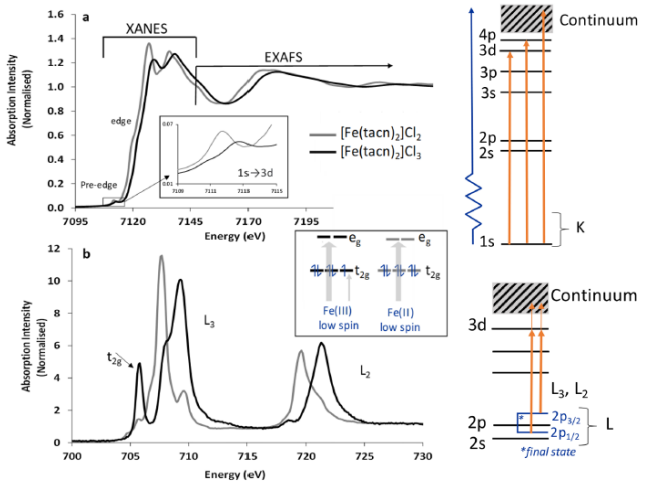


Figure 2. XAS data collected at the (a) Fe K-edge and (b) Fe $L_{2,3}$-edges of $[Fe(tacn)_2]Cl_2$ (black trace) and $[Fe(tacn)_2]Cl_3$ (gray trace). Transitions responsible for K- and L-edges are presented on the right-hand side of the respective XAS data. Key regions of the spectra of each type are labelled. Reprinted with permission from Kerr et al (2022). Copyright 2022 American Chemical Society.

The XANES region contains two key features, the pre-edge and the edge. While the pre-edge is the result of weak 1s→3d electron transitions, the edge arises from a convolution of 1s→4p and 1s→continuum transitions. It is common for analysis of XANES to involve the comparison of experimental data to standard spectra in a 'fingerprint' analysis, however, in-depth analysis of XANES shape, energy position, and transition selection rules that govern XANES features can be applied to gain deeper insights into the electronic structure.

EXAFS of K-edges

The EXAFS region is highly valuable in providing local structure information. Figure 3 displays an example of how EXAFS data presents itself based on the bonding within a MnO cubic lattice. MnO was chosen in this instance due to its simple structure and significant long-range structural order. Furthermore, cubic lattice structures possess similar bond distances in every direction and are less prone to contributions destructively interfering

with one another and cancelling out. Demonstrating how the bonding of MnO contributes to EXAFS shape and intensity, experimental MnO data were fit from a known crystal structure of MnO. Figure 3a demonstrates how the EXAFS of experimental and theoretical MnO compare, and separates the contribution from each "group" of bonds within the EXAFS fit to show their individual contributions.

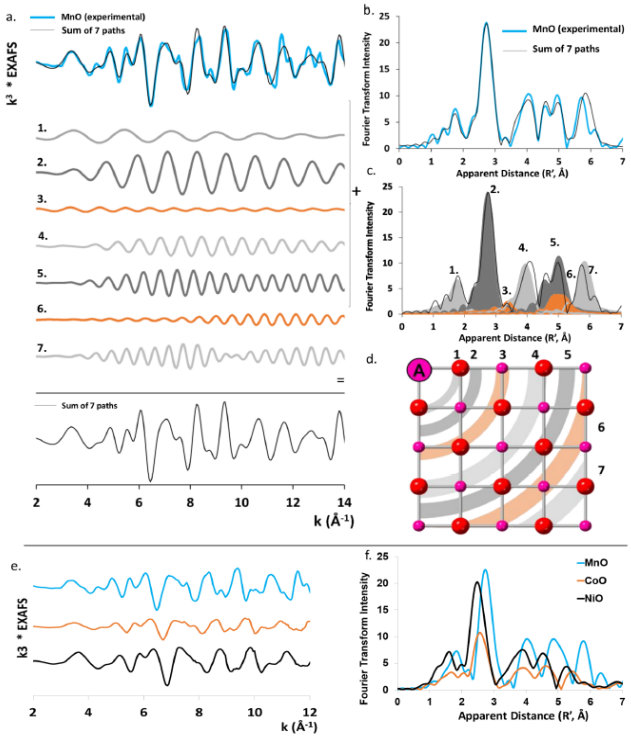


Figure 3. EXAFS analysis of MnO experimental data using a seven path fit based on the crystal structure and EXAFS spectra of MnO, CoO, and NiO. Reprinted with permission from Kerr et al (2022). Copyright 2022 American Chemical Society.

Figure 3c visualises Fourier transform of each individual EXAFS contribution, while Figure 3d depicts each coordination sphere within the structure of MnO and how they correspond to the EXAFS fit groups. Understanding that EXAFS, at its core, is the sum of constructive and destructive wave interferences from electrons in the continuum, is highly beneficial to understanding many more complex EXAFS scenarios. Furthermore, since EXAFS arises from interferences, it is possible for multiple similar materials to possess nearly indistinguishable EXAFS, as can be seen in Figure 3e and f which compare the EXAFS and Fourier transforms of MnO, CoO, and NiO. Further detail about how EXAFS interpretations may be confounded by structural characteristics (*e.g.* disorder) can be found in the associated paper.

Combining XAS with other analytical techniques

While XAS is excellent for characterising geometric structure on atomic scales, it is key to understand the limitations of XAS and know that XAS should be paired with other characterization techniques. EXAFS can probe the structure around absorbing atoms to a distance of approximately 5-7 Å, this is known as the "EXAFS window". Figure 4 graphically depicts the EXAFS window as a circle and indicates the limitations of probing structures that exceed the area of the EXAFS window. Architecture that is larger than this window (nano- and macroscale structures) requires alternative techniques, such as TEM or XRD, to fill in the gaps.

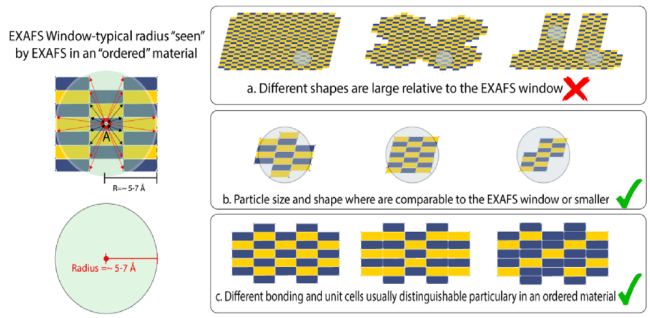


Figure 4. Schematic illustration of the EXAFS window (depicted as a circle with a diameter of 10–14 Å), with the scale of the EXAFS window.

In situ XAS analysis

Another benefit of XAS is that it can be used on complex materials *while* they are operating in their active state, allowing us to understand a material's mechanism of action, how it changes over time or in response to different environmental stimuli (*e.g.* changing potentials during electrocatalysis), and why a material loses function. *In situ* experiments are much more complex than *ex situ* experiments, as samples must be optimised to allow for good detection by XAS under appropriate

reaction conditions whilst considering other issues that can be seen in *ex situ* experiments as well (*e.g.* self-absorbance). In addition, *in situ* experiments come with their own set of unique challenges such as thickness effects, beam damage effects, and bubble formation. Despite these challenges, embarking on an *in situ* experiment is well worth the effort as the insights it provides can be unparalleled, such as being able to determine the reformation mechanism of self-healing catalysts. Furthermore, the ability for catalysts to restructure under operational conditions makes *in situ* characterisation essential for these systems

Conclusion

XAS plays an important role in the characterization of energy materials, and it is anticipated that innovation will happen alongside analytical technique development. However, the nature of the XAS experiment needs to be carefully planned to optimize any compromise between the material and spectroscopy, understanding how the technique works, what it can tell us, and equally what it *cannot* tell us, ensures that the most appropriate and useful conclusions are made.

Author's comment

This paper was written to introduce readers to the principles of XAS and guide them through some of the challenges, and benefits, of XAS – particularly those readers who are seeking to use XAS but are not intimately familiar with the technique. For further information on the fundamentals of the XAS experiment, issues with data distortion, how certain phenomena can lead to data misinterpretations, and differentiating different bonding scenarios with XAS please see the full paper:

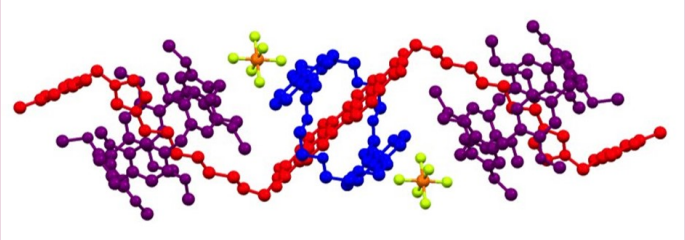
Kerr, B. V; King, H. J.; Garibello, C. F.; Dissanayake, P. R.; Simonov, A. N.; Johannessen, B.; Eldridge, D. S.; Hocking, R. K. Characterization of Energy Materials with X-Ray Absorption Spectroscopy–Advantages, Challenges, and Opportunities. Energy & Fuels 2022, 36 (5), 2369–2389. https://doi.org/10.1021/acs.energyfuels.1c04072.

Technical Article

First Crystallographic Structures Determined Using a Turnkey Electron Diffractometer Published in Nature Communications

Cameron Chai, AXT

Electron diffraction (ED) is an emerging technique for determining crystallographic structures of single crystals that are too small and beyond the detection limits for XRD. Researchers from the University of Birmingham and the University of Nottingham have published the first crystal structures in the high-profile journal Nature Communications, using the first commercially available turnkey ED system the Rigaku XtaLAB Synergy-ED.



Rotaxane structure determined using electron diffraction.

The research team, led by Professor Neil Champness, attempted to use more conventional SC-XRD on a synchrotron beamline. Unfortunately, poorly diffracting rotaxane crystals meant structure determination was extremely difficult, resulting in poor quality structure refinement. As a result they were unable to locate or identify anions in the structure.

When the same samples were examined using ED, the researchers were pleasantly surprised at the quality of the data the new technique generated, which was significantly better than the synchrotron data.

In a world first, using ED they were able to successfully determine the structure of a heterorotaxane by merging 9 datasets from 10 crystallites, approximately 100nm thick. Using multiple datasets,

they were able to achieve a higher-quality refinement, which even allowed identification and refinement of the anions.

Rotaxanes are notoriously difficult to crystallise but possess interesting photochemical properties. Understanding of the precise structure and organization of the molecular components is key to understanding their properties and hence, ED is enabling better insights into these materials.

Read the full paper at https://www.nature.com/articles/s41467-022-28022-3

Water cluster structure in the MOF CAU-10-X (X = H, OH): a powder diffraction perspective

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Introduction

Several metal-organic frameworks (MOF) excel in harvesting water from the air or as heat pumps as they show a high water uptake, a steep step in the water isotherm at 10-30 RH% with a small hysteresis, which helps to minimize heat loss[1]. However, only a few of those compounds can resist the harsh conditions imposed by the repeated adsorption/desorption cycling, which is the prerequisite for their applicability[2,3]. Aluminium isophthalate CAU-10-H is one of these resilient MOFs. It adsorbs up to 0.34 g g^{-1} of water, shows a small reversible structural change from hydrated (non-centrosymmetric structure) to dry (centrosymmetric structure), and withstands up to 10,000 cycles under working conditions[4,5]. Deeper understanding of the water network within the confined space of CAU-10-H is essential for the optimization of the synthesis process and successful utilization of the material. Here we report the structural properties of CAU-10-H under various water content, studied by means of powder X-ray diffraction (XRD).

Methods

Two samples of CAU-10-H were synthesized following two different synthesis procedures. Hereafter the two samples are referred to as synthesis path 1 and 2.

To study the MOF framework without the guest molecule, prior the loading sample was dried at 105 ºC and loaded and sealed in a capillary at 75 ºC. Capillaries with the outer diameters of 0.5 and 0.7 mm were used.

Powder XRD measurements in transmission geometry at ambient conditions were performed on Malvern Panalytical Empyrean diffractometer equipped with a Cu X-ray anode, focusing mirror and PIXcel[1D] detector. A series of scans in the 2Theta range between 5 and 120-135 º2Theta.

Results and discussion

The XRD pattern of dried CAU-10-H (synthesis path 1) and its Rietveld refinement are shown in Figure 1a. The pattern is fitted with $I4_1/amd$ space group, which is the symmetry previously reported for dry CAU-10-H[4]. The refined lattice parameters are a = 21.5131(3) Å, c = 10.33369(15) Å. Low reported Rwp value of the fit (Figure 1a) suggests good agreement with the literature[4.] The corresponding structure of dry CAU-10-H is shown in Figure 2a.

The same reference[4] documented the transition to $I4_1$ symmetry during water adsorption. However, the data presented here point to the higher symmetry of the hydrated CAU-10-H.

Indexing of the XRD pattern of hydrated CAU-10-H (Figure 1b) suggests the $I4_1md$ symmetry, rather than previously reported $I4_1$[4]. Both symmetries are non-centrosymmetric and therefore neither contradicts the result of the second harmonic generation measurement study of the structural

transition of CAU-10-H, which showed that the hydrated phase has non-centrosymmetric structure. However, the $I4_1md$ is a higher symmetry, compared to $I4_1$, which makes it a more likely candidate.

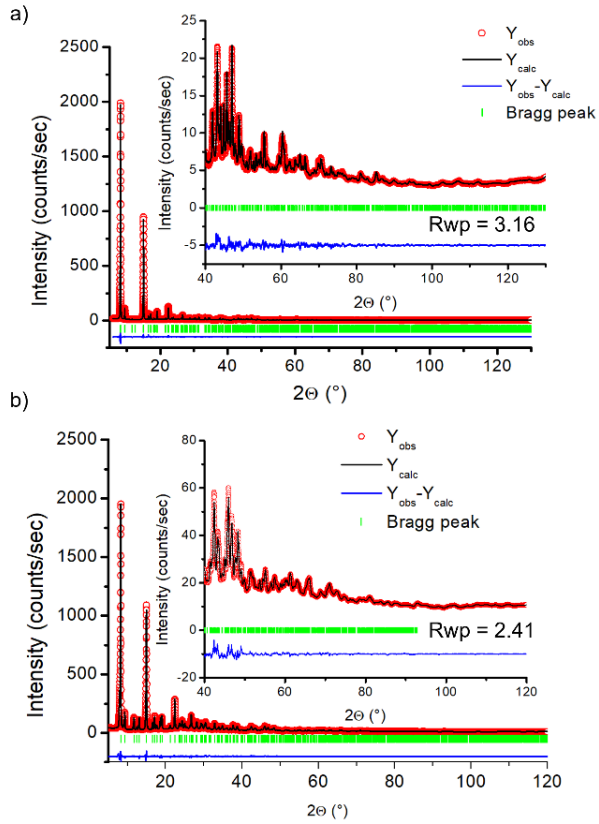

Figure 1. Rietveld refinement of (a) dry and (b) hydrated CAU -10-H (synthesis path 1)

To further investigate the discrepancy, we performed a pseudosymmetry search using PSEUDO program[6]. The hydrated CAU-10-H structure with the $I4_1$ symmetry reported elsewhere[4] was used as the input. The test showed that as low as 0.15 Å atoms shift is sufficient to describe the same structure with $I4_1md$ symmetry. Thus, both indexing of the XRD data presented in this case study and the pseudosymmetry test performed using the literature data[4] suggest that hydrated CAU-10-H is likely to have $I4_1md$ symmetry.

We used $I4_1md$ symmetry for the Rietveld refinement of XRD pattern of hydrated CAU-10-H (synthesis path 1). The result is presented in Figure 1b. A very good fit with the low Rwp value of 2.41

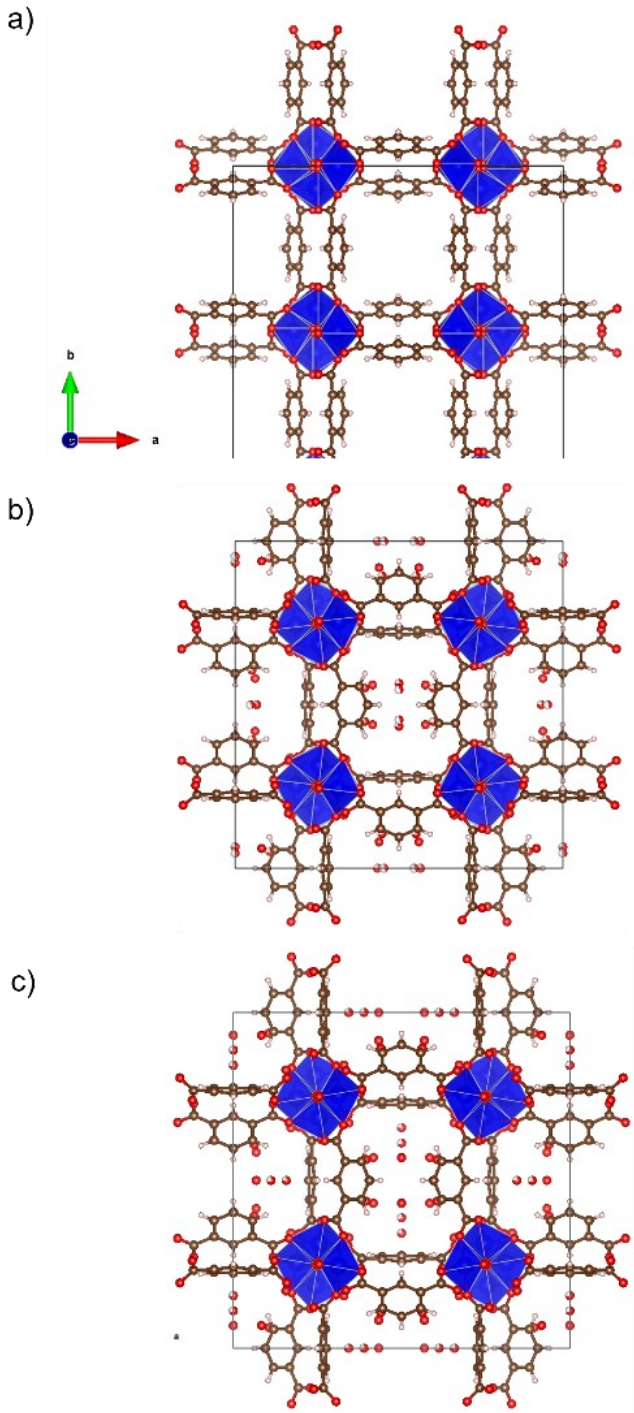

Figure 2. Crystal structure of dry CAU-10-H (a) and two hydrated modifications synthesized using path 1 (b) and path 2 (c).

was achieved; the refined lattice parameters are a = 21.3813(2) Å, c = 10.6162(3) Å; the water content was determined to be 3.87(1) water molecules per formular unit, which is higher than previously reported 2.8(2) molecules per formular unit[4]. The same model was applied to refine the XRD pattern of the hydrated CAU-10-H (synthesis

path 2, data are not shown here). The refinement revealed even higher water content: 4.22(1) water molecules per formular unit.

The same powder diffraction dataset (Figure 1b) was used to locate the water molecules in the hydrated CAU-10-H. Figure 2 compares the crystal structure of dry CAU-10-H and two hydrated modifications and highlights the differences in the water network between the two CAU-10-H samples, synthesized via different routes (Figure 2b and 2c). Closer inspection of the water network reveals the presence of the "central water cluster", which is nearly identical between the two modifications. Away from the "central water cluster" more differences can be seen between CAU-10-H synthesis path 1 and 2. Namely, positions, which are occupied by the two water molecules in hydrated CAU-10-H (synthesis path 1, Figure 2c) hosting 3 water molecules in hydrated CAU-10-H (synthesis path 2, Figure 2c).

Conclusions

Two samples of CAU-10-H synthesized using two different procedures were investigated using powder XRD. Analysis of the XRD pattern of CAU-10-H confirms its previously reported centrosymmetric structure with $I4_1/amd$ symmetry[4]. The previously documented transition to a non-centrosymmetric structure during water adsorption[4] is also confirmed. However, the XRD pattern of the hydrated CAU-10-H suggests a higher symmetry than was previously reported: $I4_1md$ vs. $I4_1$[4]. This finding is also confirmed by the pseudosymmetry search. Rietveld refinement of XRD patterns of the two hydrated CAU-10-H samples (synthesis path 1 and 2) using corrected $I4_1md$ space group shows higher water content than was previously reported for the hydrated CAU-10-H[4]. Furthermore, it was shown that CAU-10-H (synthesis path 2) can accommodate more water molecules, compared to the modification, synthesized via the path 1. Apart from the total water content the water network of the two CAU-10-H hydrated modifications were compared.

Thus, the case study revealed that the water uptake of CAU-10-H can be tuned not only by using the relative humidity and temperature, but also by the synthesis procedure.

Besides bringing further insights into the water clusters present in the MOF the study demonstrates the powerfulness of powder diffraction in the analysis of MOF materials in general. The findings described in this report as well as the additional in situ XRD study of CAU-10-H at varying temperature and relative humidity conditions will be presented at the Royal Australian National Congress 2022.

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