

Australian X-ray Analytical Association

Newsletter Issue 2 2021

President's Address

Dear AXAA members,

With much of the country in various states of lockdown, it's a good time to reflect introspectively. For some, lockdown provides time to slow down and focus on the little things. It can give a sense of clarity about what's truly important in life, and an appreciation for things we took for granted or overlooked. Working from home can recover valuable hours in the day previously lost to transit, which may be put to use in pursuing other interests or new projects. How many of us have upskilled in vegetable growing, sourdough baking, crochet mastery and more? Personally I have not managed to learn or improve on any new skills, I have only consumed an abundance of streamed TV and movies, and comfort food. But I'm ok with that.

Lockdowns can also be a stressful and sometimes scary time. Although we've all undoubtedly been through more than one by now, there's always a flutter of anxiety as we wait for the numbers of the day, and check the latest exposure sites. At the same time, the impacts on the research and education sectors are being felt around the country, and for many, that has meant drastic changes to workloads, adapting at short notice to changes in on site and off site learning, and job security has become more perilous for all. For many of our colleagues, long term heightened stress and uncertainty can creep up and take a toll. It's up to all of us to support each other, remember to reach out and maintain connections with our colleagues, be generous, kind, and accommodating. We are all in different situations and even the brightest stars may be suffering in ways we can't see.

For an organisation like AXAA, we are learning to navigate the challenges of the last year and find ways to connect our community. A few weeks ago, we successfully launched a new AXAA Speaker Series with an event hosted by Matthew Rowles. While we had hoped to hold an in-person event in WA, even the west is no stranger to lockdowns and we quickly pivoted to an online event, which allowed the rest of the country to attend online. Fantastic science talks were presented by Dr. Terry Humphries of Curtin University on X-rays: Empowering Energy Research, and PhD student Gemma Turner of UWA on Post -synthetic modification of a metal-organic framework at high pressure. The event was well attended, reflecting AXAA's strong and active community. The Seminar Series will continue to hold online events throughout the rest of the year, so if you would be interested in presenting, or know someone with a great story, please let us know!

Jessica Hamilton

AXAA President

Golden Jubilee of Research Publications

In 1972 Ian Grey and Gus Mumme co-authored a paper titled "The structure of CrFeTi₂O₇" in the Journal of Solid State Chemistry. This work was the start of a long and ongoing collaboration between Ian and Gus who have both gone on to have long and highly distinguished careers with CSIRO. They have both focused on structural and chemical analysis problems often relating to commercial processing of minerals. Ian focused on the Australian mineral sands industry and solving associated problems while Gus focused on sulphide/sulphate mineralogy and other industrially applied problems. Both maintained links with mineralogists around the world and this has led to their involve-



ment in solving numerous new mineral crystal structures. This year Gus and Ian co-authored a paper entitled "Galeaclolusite, $[Al_6(AsO_4)_3(OH)_9(H_2O)_4]\cdot 8H_2O$, a new bulachite-related mineral from Cap Garonne, France" making 50 years of joint publications a truly remarkable achievement.

Both have minerals named after them iangreyite $(Ca_2AI_7(PO_4)_2(PO_3OH)_2(OH,F)_{15}\cdot 8H_2O)$ a phosphate mineral located in the Silver Coin Mine in Nevada, USA and Gus has mummeite $(Cu_{0.58}Ag_{3.11}\ Pb_{1.10}\ Bi_{6.65}S_{13})$ a sulphide mineral from Alaska Mine, Colorado, USA.



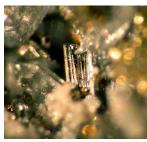


Figure 1. Left, langreyite (Silver Coin Mine, Nevada USA) and right, Mummeite (Alaska Mine, Colorado USA)

Gus and Ian also both worked closely with the recently departed Joy Bear in solving various sulphate structures. Joy and Ian worked on the structures of zinc sulfates publishing in Acta Crystallographica (B) in 1969 (https://doi.org/10.1107/S0108768186098622), while Joy and Gus went on to work on the crystal chemistry of zirconium sulfates publishing in Acta Crystallographica (B) in 1969 (https://doi.org/10.1107/S0567740869004341).



Figure 2. Gus Mumme (left) and Ian Grey (right) at home in the CSIRO Mineral Resources Diffraction Laboratory

New Mail-In Program for Powder Diffraction beamline at the Australian Synchrotron

Anita D'Angelo

Beamline Scientist (PD), Australian Synchrotron, (ANSTO) Melbourne

The Powder Diffraction (PD) beamline at the Australian Synchrotron is pleased to announce a new mail-in program for powder samples in capillaries at ambient conditions. This program is aimed at researchers with only a few samples and those that have been unsuccessful in accessing merit based beamtime in the past. Commercial users cannot use the mail-in service and need to contact the beamline staff directly.

Groups can select one of two energies: 21 or 16 keV, and there is a maximum of 20 samples or a 3 hour shift, per group per round. Researchers are invited to submit a standard merit proposal if they require more time or have more than the maximum number of samples. All proposals are reviewed for technical feasibility and reviewed by the PD program advisory committee.

Researchers with successful proposals will receive a "sample box kit" that contains sample mounts and materials, excluding capillaries, which are needed to prepare and send their samples to the Australian Synchrotron. The boxes are 3D printed onsite at the Australian Synchrotron, and were initially designed by Australian Synchrotron staff with modifications made based on the valued input from Dr Matilde Saura-Múzquiz (USYD) and Prof. Brendan Kennedy (USYD).

This new capability has been realised through our sample changing robot and new capillary auto spinner. The robot is an Epson C4 6-axis robot that has a gripper designed in-house specifically for capillary 'pin' mounts, and image processing is used by the auto spinner to align the capillary with the rotation axis. The overall measurement time is reduced with the new spinner, as samples can be aligned in approximately 15 seconds, compared to



2-3 minutes using the previous version. All capillaries will be run using the Mythen II detector and researchers will receive their data within ~2 weeks of the scheduled beamtime.

We invite those interested in the mail-in program to visit the PD teams <u>Wiki page</u> or email staff directly at: as-pd@ansto.gov.au for more information.



Figure 3. Sample box kit provided for mail-in experiments

The Toroidal Electron Analyser at the Australian Synchrotron – A Unique Tool For Angle Resolved Photoelectron Spectroscopy

Anton Tadich
Senior Beamline Scientist (SXR), Australian Synchrotron, ANSTO Melbourne

Alex Schenk Lecturer (Physics), La Trobe University, Victoria

Angle Resolved Photoelectron Spectroscopy (ARPES)

Within the condensed matter and materials science communities there is a strong drive to understand the electronic structure of highly ordered low dimensional crystalline solids. The unique properties of these "quantum materials" promise advancement in next generation technologies such as room temperature quantum computing, dissi-

pation-less charge transport, spintronics and storage media. Examples include high temperature superconductors, 2D materials (e.g graphene, boron nitride), topological materials and many more. Building a complete picture of the interplay between physical and electronic/chemical structure requires applying a combination of different experimental techniques.

One property of fundamental importance is the "electronic band structure" which is the allowed energy and momentum values of propagating (delocalised) electron states in the crystalline lattice. The band structure controls a variety of material properties including optical absorption and electrical transport, superconductivity and spin transport. The most direct method for determining the electronic bandstructure of a crystal is Photoelectron Spectroscopy Angle Resolved (ARPES). In conventional photoelectron spectroscopy the energy distribution of occupied electron states is measured using the photoelectric effect (Figure 4a). A source of monochromatic photons excites electrons from the sample, with the resultant kinetic energy measured using a photoelectron spectrometer. This yields the initial state binding energy E_B of the electron via $E_B = \hbar \omega - E_K - \varphi$.

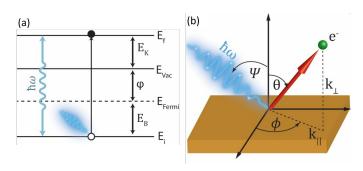


Figure 4: (a) Energy level diagram of the photoemission process. A photon with energy $\hbar\omega$ excites an electron from an initial state E_i to a final state E_f resulting in the electron having kinetic energy E_K . E_{Fermi} is the Fermi energy of the sample, which is treated as the zero point of the energy scale (b) The electron wavevector \mathbf{k} of the photoelectron is determined in an ARPES measurement through measurement of the photoelectron emission angles θ and ϕ with respect to the crystal axes.



The most common use of the technique which the reader may be familiar with is X-ray Photoelectron Spectroscopy or XPS. In an ARPES experiment however, the emission angle of the emitted electrons is additionally measured (Figure 4b), which yields the photoelectron's momentum, or wavevector "k". Importantly, due to conservation of momentum this allows one to calculate the electron momentum vector *inside* the solid, and yields the bandstructure E(K) in addition to the electron binding energy. This makes ARPES one of the most powerful techniques in the condensed matter physicist's toolkit and popular in laboratories and synchrotron facilities worldwide.

The La Trobe University Toroidal Analyser for ARPES

In an ARPES experiment the photoelectron spectrometer must be capable of measuring the electron kinetic energy and emission angle from the surface of a sample. Rather than measure a single angle at a time using, for example, a goniometer stage, ARPES spectrometers typically accept a band pass of emission angles from the surface using a 2D detector in order to reduce experiment time. Since the early 1970's La Trobe University in Melbourne Australia has conducted a research and development program in electron spectrometer design for wide angular acceptance instruments. From this research effort a unique "toroidal" design of ARPES spectrometer was born. The latest 3rd generation instrument was completed in 2017 and now resides at the Australian Synchrotron to cater to local demand for ARP-ES from the condensed matter physics community. Figure 5 shows a photo of the system on the experimental floor at the synchrotron, as well as a cross section through the main spectrometer chamber illustrating the key components which are discussed below.

When not performing synchrotron experiments, the toroidal analyser is used for offline ARPES studies with a vacuum ultra-violet (VUV)



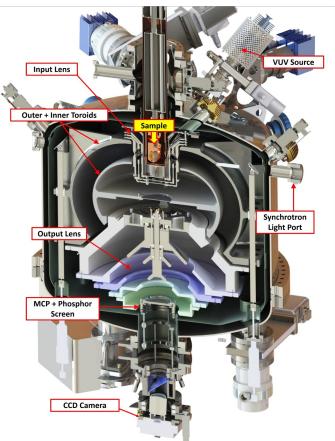
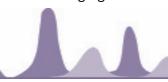


Figure 5. The toroidal analyser system on the experimental floor at the Australian Synchrotron (top) and a schematic cross section through the toroidal electrode spectrometer chamber with the key elements indicated (bottom)

helium plasma discharge lamp. A monochromator allows selection between two main energies (He $I\alpha$ = 21.2 eV and He $II\alpha$ = 40.8 eV). For beamtime the system is moved from its offline staging area





using a three element "omni wheel" setup. The omni wheels allow for complex translation and rotation movements on the experimental floor. Once positioned at the beamline a secondary alignment frame is used to precisely align the spectrometer with a precision of 50 microns; this is remarkable given the overall weight is ~ 1.5 tonnes! Ultra-high vacuum (UHV, < 10-9 mbar) is maintained in all of the chambers of the system. A suite of surface science tools enables the user to prepare a single crystal sample under UHV; argon bombardment, cleaving, and thin film growth via molecular beam epitaxy techniques are possible. The measurement stage features a cryostat for liquid nitrogen cooling and in the future, liquid helium cooling, for improved energy resolution and exploration of electronic phase changes. For most experiments, low energy soft X-rays (hv = 85 - 120eV) are used for valence band ARPES studies, however the instrument is also capable of angleresolved core level photoemission at higher X-ray energies, which allows the technique of photoelectron diffraction to be performed, discussed in the next section.

As with all photoelectron spectrometers, the toroidal analyser uses a series of electrostatic fields to image photoelectrons from the sample through to a detector. In the toroidal analyser, an input lens accepts a 180° "fan" of emission angles from the surface (Figure 6a) at some nominal electron kinetic energy before the electrons enter the toroidal deflection sector. A negative (positive) voltage is applied to the outer (inner) toroids, causing an inward deflection of the electrons around the sector and chromatic dispersion; electrons with higher kinetic energy take a larger radius trajectory than those with lower energies, resulting in a linear spread in energy at the toroidal sector output (Figure 6b). Finally, a three-element accelerating output lens re-images this energy window onto the detector itself, which is a microchannel plate/phosphor screen module in vacuum which is imaged by a low noise CCD camera (Figure 6c).

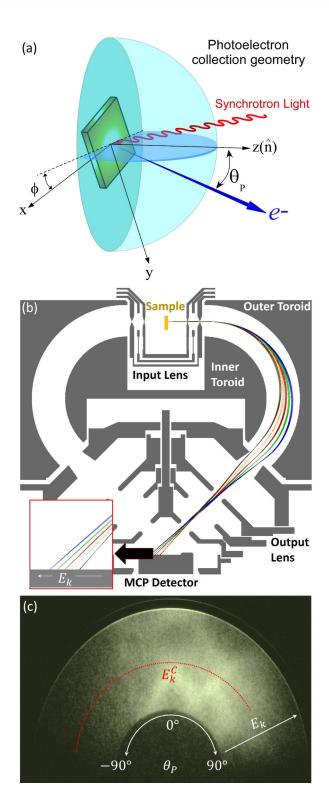


Figure 6 (a) Angular acceptance geometry; for fixed azimuthal ϕ relative to crystalline axes, all polar emission angles θ_P are measured (blue fan) (b) Electron optics simulation (SIMIONTM) for five equi-spaced energies, illustrating the linear energy dispersion (c) MCP detector image, displaying the band-pass of kinetic energy and 180° of polar angle from the sample



This unique detection geometry enables rather straightforward measurement of the entire emission hemisphere of photoelectrons compared with conventional instruments. One simply chooses an electron energy to be detected, and then steps the sample azimuthal angle through 180° to map the emission distribution. This leads to some unique measurements not possible with conventional spectrometer designs.

Example Measurements

As mentioned above, in addition to being able to perform conventional ARPES measurements, the toroidal analyser is able to measure the entire emission hemisphere of photoelectrons being emitted from the surface of a sample. This "full -hemisphere" photoemission measurement capability is unique within Australia. A powerful application of this acquisition modality is Fermi Surface (FS) mapping. The FS is the constant energy surface in momentum space separating the occupied electron states from the unoccupied states. Its topology governs many microscopic and macroscopic properties, such as charge carrier transport, optical and magnetic response, heat capacity, phase transitions and structural instabilities. When using ARPES for FS mapping one obtains a direct "cut" through the FS in momentum space, which depends on the photon energy used. Being able to measure a wide angular range provides a number of advantages, primarily that the entire FS can be captured in one measurement. To illustrate the concept, Figure 7a shows the well known FS of Copper, with its characteristic "neck" and "belly" features in the first Brillioun Zone. Figures 7b and 7c show full hemisphere photoemission maps from the (111) low index face, taken at the Fermi Energy using the VUV source energy of $h\nu =$ 21.2eV and synchrotron light at 90eV respectively. The data is presented as a 2D projection of the emission hemisphere in the sample plane. In Figure 7b one can clearly see the FS outline projected in three-fold symmetry, illustrating the characteristic "neck" and "belly" features. In the centre, the

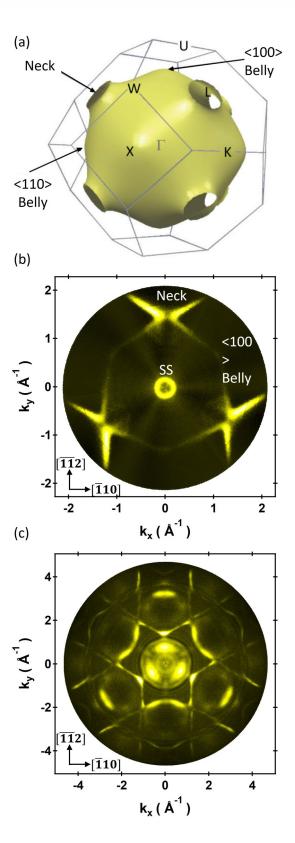


Figure 7: (a) The Fermi Surface of Copper. Brillouin zone boundaries, symmetry points of the face centred cubic lattice, and key FS features, are indicated (http://www.phys.ufl.edu/fermisurface) (b,c) Fermi Surface of Cu(111) measured using hv = 21.2 eV and 90 eV respectively



Shockley surface state (SS) is observed, which is a well-known 2D electron state existing at the surface of Cu, Ag and Au(111) surfaces. At the higher photon energy in Figure 7c, one can see that the cut through the FS extends over many adjacent Brillioun zones. Although a simple example, this shows how ARPES can directly yield an important detail of the electronic structure of a crystalline material.

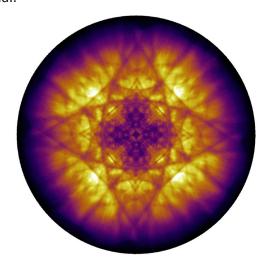


Figure 8: Full hemisphere XPD pattern of Carbon 1s excited from a (100) single crystal of hydrogenterminated diamond (hv = 675 eV)

A second technique which takes advantage of the full hemisphere mapping capability of the toroidal analyser is full hemisphere X-ray photoelectron diffraction or XPD. This is a unique tool for surface characterisation, combining the chemical specificity of XPS with structural information about that chemistry at the surface. Briefly, X-rays are used to excite core-level photoelectrons from a material. The propagating (wave-like) photoelectron state in the material is capable of partially scattering from nearby atoms in the crystal. The primary photoelectron wave and the scattered photoelectron waves undergo interference in a manner which is strongly sensitive to the kinetic energy of the photoelectrons and the atomic environment surrounding the emitter. An example data set is shown in Figure 8; here, X-rays of energy 675 eV are used to excited carbon 1s electrons

from a hydrogen terminated (100) diamond surface. The four-fold symmetry of the surface is clearly seen, with a number of detailed interference structures and intense regions from low index atomic planes in the bulk. The data can be compared with multiple scattering calculations, with structural refinement performed iteratively.

Conclusion

The toroidal analyser is a unique instrument in Australia for performing ARPES. Not only is it capable of revealing details of the electronic bandstructure through angle resolved valence band photoemission at low photon energies, it is also powerful for investigating structural information of surfaces using photoelectron diffraction at higher X-ray energies.

Author Biographies

Dr Anton Tadich (antont@ansto.gov.au) is a Senior Scientist at the Soft X-ray Spectroscopy beamline at the Australian Synchrotron, and system manager of the toroidal analyser. Dr Alex Schenk (a.schenk@latrobe.edu.au) is a lecturer and researcher in physics at La Trobe University. His research expertise focuses on atomic-scale modification of diamond surfaces and 2D materials for low-dimensional quantum electronics and quantum computing.

The application of synchrotron X-ray powder diffraction in determining the crystal chemistry and structure of natural jarosite

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Introduction

Jarosite [KFe₃(SO₄)₂(OH)₆] is a yellow-brown miner-





al commonly found in acid sulphate soils and acid mine drainages [e.g., 1,2]. It is a member of the alunite supergroup, which has the general formula $DG_3(TO_4)_2(OH)_6$ [3], and the most common naturally occurring variant of jarosite is natrojarosite $[NaFe_3(SO_4)_2(OH)_6]$, with Na+ substituting for K+ in the D site of the jarosite structure [4]. Significant differences exist between natural and synthetic jarosites. For example, complete solid solutions have been observed in synthetic jarosites whereas only limited solid solutions have been observed in natural jarosites [e.g., 4,5]. Further, natural jarosites have only been observed with rhombohedral symmetry (R-3m), whereas synthetic jarosite minerals have been formed with rhombohedral and monoclinic (C2/m) symmetries [4,6]. These differences likely effect the behaviour of the mineral and therefore make studying natural jarosites important in the context of managing them in the environment.

Extensive jarosite outcrops occur in sulphurrich coastal sediments in Victoria, Australia, providing an opportunity to better understand their crystal chemistry and structure. Synchrotron powder X-ray diffraction (PXRD) was employed as high-resolution XRD data is required to resolve subtle differences in peak shape due to incorporation of different ions and structural changes in the jarosite.

Method

Hand ground samples of jarosite collected from two beaches in Victoria, Australia, were loaded into borosilicate glass capillaries and analysed on the Powder Diffraction (PD) beamline at the Australian Synchrotron. Diffraction patterns were collected over several beamtime allocations using the MYTHEN–II microstrip detector. Two patterns, each of 300 s, were collected for each sample with the detector set 5° apart. The two patterns were merged using the PDViPeR software available at the beamline. DIFFRAC. EVA was used to identify the minerals present in the samples. DIFFRAC. TOPAS 5 was used to model the structure of the

jarosite through Rietveld refinement. To support PXRD, elemental chemistry of the samples was determined using inductively coupled plasma-mass spectrometry (ICP-MS).

Results and Discussion

PXRD and ICP-MS results showed that most of the samples are K-rich natrojarosite, with a smaller number being natrojarosite or Na-rich jarosite. Asymmetric peak-broadening was identified in the (00l) peaks (Figure 9) in most samples and appears similar to asymmetric microstrain broadening. This can be the result of asymmetric compositional variation in a phase consisting of a solid solution [7]. The presence of asymmetry in the (00l) peak indicates that substitution was occurring in the D site and suggests that most of the jarosite samples fall along the solid solution between natrojarosite and jarosite. This observation suggests that like synthetic jarosites, extensive solid solutions can occur in natural jarosites.

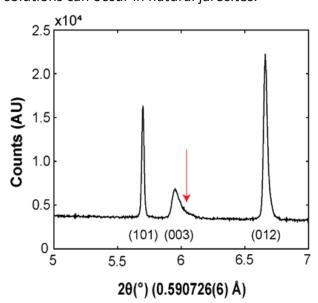


Figure 9. PXRD pattern of Js-SB-32A, a Na-rich jarosite sample, with only the first three peaks shown. The red arrow shows log-normal asymmetric peak broadening of the (003) peak. Image from Whitworth et al [9].

Rietveld refinement of sub-samples collected from sample Js-SB-35, a natrojarosite, showed peak shouldering suggestive of monoclinic sym-



metry (Figure 10). Rietveld refinement of the samples also showed an ordering of iron-site vacancies onto the Fe(1) site of the natrojarosite, which is consistent with the synthetic monoclinic natrojarosite sample described by Scarlett et al. [6], and a β' angle <90 ° when the monoclinic unit cell was converted into a pseudohexagonal lattice, consistent with the synthetic monoclinic jarosites described by Grey et al. [8]. These findings therefore suggest that monoclinic symmetry can occur in natural jarosites.

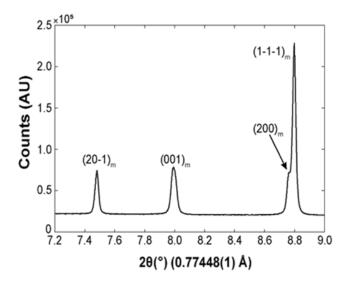


Figure 10. PXRD pattern of Js-SB-35A, a natrojarosite sample, with only the first three peaks shown. A characteristic peak shoulder associated with monoclinic symmetry is indicated by the black arrow. Image from Whitworth [10].

Conclusions

This investigation demonstrated that (1) extensive solid solutions can exist in natural jarosites, and (2) that natural jarosites can have monoclinic symmetry. These findings demonstrate that natural jarosites are chemically and structurally complex and highlights the importance of characterising natural jarosites when developing management strategies. High-resolution PXRD can aid in accomplishing this.

Readers are referred to Whitworth et al. [9] and Whitworth [10] for more information.

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Footnote: Anne J Whitworth is now at the University of Queensland.



AXAA Community News

DECTRIS detecting the future

DECTRIS webinars on structural biology and high X-ray energy XRD

•	Structural Biology and Crystal Healing: <u>Dr. Sam Horrell</u> presents the I24 beamline
	(DLS) and a collaborative research of SARS-CoV-2

Upcoming

- Macromolecular Crystallography in a LAB?! <u>Dr. Daniel Kneller</u> collects XRD data suitable for structure determination
- <u>Dr. Kunio Hirata</u> presents research at RIKEN macromolecular crystallography beamlines (SPring-8).

• <u>Dr. Catherine Dejoie</u> explains the novel setup used for collecting high-resolution PXRD and PDF data at the ID22 beamline (ESRF).

Recordings

- <u>Dr. Jens Meyer</u> (STOE) tackles high-energy lab setups and their use in charge density and non-ambient measurements
- At the GSECARS, APS, <u>Dr. Vitali Prakapenka</u> collects high-pressure XRD data on samples of varying crystallinity
 Postdoctoral Fellowship

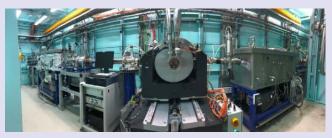
CSIRO Postdoctoral Fellowship in Characterization & Modelling of Fluid Rock Interactions in Sediment

CSIRO, Perth, WA

CSIRO seeks an outstanding ECR specialising in the analytical characterization and geochemical modelling of fluid rock interactions to join the Deep Earth Imaging Future Science Platform.

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XAS and MEX Workshop Australian Synchrotron, ANSTO 26-27 August

Are you a new or current user of the XAS beamline? Would you like to know what the new MEX beamline (coming 2022) could do for you? We have the workshop for you!

This free two day online workshop will feature talks from beamline scientist and experts in the field as well as a hands-on tutorial in XANES data analysis. Click the link below to check out the line-up and register your attendance!

Register here





AXAA Community News



Good Things Come in Small(er) Packages

The EIGER2 R 250K detector, the newest addition to Bruker's detector family for X-ray diffraction, is fully integrated into D8 ADVANCE and D8 DISCOVER diffractometers.

Watch our recorded Q&A event here to gain insight to the new EIGER2 R 250K detector's development at DECTRIS and hear from our Bruker application scientists why they like the EIGER2 detector for thin film analysis and powder diffraction applications

Featured webinars

Images & Analysis of Geomaterials with X-ray Microscopy Speaker: Norman Schott, Senior Sales Representative, XRM

Bruker AXS GmbH, Karlsruhe, Germany

The non-destructive characteristic of 3D X-ray Microscopy allows for quantitative analysis of structural parameters, monitoring dynamic processes and more. The correlation between structure and mechanical properties can also be investigated in high detail. This upcoming 1-hr webinar will focus on geological materials.

Register here to get recording.





X-ray Microscopy (XRM) Techniques, Systems & Application Examples

Speaker: Norman Schott, Senior Sales Representative, XRM, Bruker AXS GmbH, Karlsruhe, Germany

Nondestructive <u>3D X-ray computer tomography (XRM)</u> analysis is critical for the success in industrial production, research and development. 3D dimensional results bring about crucial advantages in industrial process and quality control. The best analytical techniques help to achieve knowledge about inner structure such as void calculation, fiber orientation or CAD comparison of the sample. Analytical strength is key to fast progress in product development and fundamental research.

Register here to get the recording.





AXAA Community News

Featured Training Courses

Malvern Panalytical is proud to offer a mix of online and in-person trainings to help you improve your XRD & XRF data collection & analysis.

(In-person training) XRF in the Workplace

Serving to provide high-quality training for industry and research professionals, this 5-day course will focus on most facets of XRF spectrometry. This course is suitable for all users of XRF, regardless of the brand of your instrumentation. Register here: 8th - 12th November

(On-line training) Super Q Hands-on Training For WDXRF users

The SuperQ Software Training course is aimed at personnel interested in learning the step-by-step procedure of using the software for various aspects of running their XRF system. It is a 3-day course, with handson experience in using the software. Register here: 13th - 15th October

(On-line training) XRD data analysis

Master Rietveld analysis to amorphous quantification, crystallite size calculations to managing large data sets and more! More one-to-one opportunities with our XRD scientists. Learn also how to optimize HighScore including shortcuts and smart batch analysis.

30 Aug - 3 Sep, 12.30pm - 4pm Sydney Academia rates \$400 (UP \$2,000).

Quote MPAXAA for promo rate.

More details here

FREE 1-year XRD software for academia

With many researchers working from home, we recognize that you may not have access to shared software licenses in the laboratory. Ask for either HighScore Plus version 5.1 (for PXRD research) or AMASS (for thin film research). Did you know? HighScore Plus is compatible with data collected from any brand of XRD instrumentation! More details here

Featured webinars

Look out for the "Ask-an-expert" webinar series that answers your frequently asked questions on experimental set up, data collection and analysis. Register for the recording



- •11 Aug, 4pm SYD: Even more superior data resolution with fantastic background noise cancellation. And all in record speed. Stay up to date with the newest XRD detectors and optics for your cutting-edge research. Register here
- •MOF research: Going beyond PXRD to uncover hidden properties with insitu studies. View here
- •Battery, nanomaterials and thin film applications & analysis discussed in this workshop by renowned professors. View here
- •Thin layer analysis best practices. View here





CONDUCTING ADVANCED BATTERY RESEARCH

Expand your knowledge on in-situ in-operando XRD on lithium-ion batteries

Consumer expectations on lithium-ion batteries have become more demanding. Batteries need to charge faster, weigh less, be smaller, store for longer yet perform better and safer. Scientists rely on in-operando in-situ X-ray diffraction to study the aging process and durability of battery materials. Such experiments can be complex and do take time to conduct. Especially with restricted access to synchrotrons and labs, lab time is precious and it's important to your data collection done correctly. Here are some tips to get you going on such advanced experiments.

Tips on the experimental set up

Measurement	Experimental set up on the intelligent Empyrean XRD with these perimeters
Radiation	Μο Κα
Incident beam optics	Focusing mirror with ¼ Ta divergence slit, ¼ Ta anti-scatter slit, 0.02 rad Soller slit, 10 mm
Sample stage	XYZ stage in combination with custom-designed sample holder
Diffracted beam optics	Anti-scatter slit, 0.02 rad Soller slits
Detector	1Der or GaliPIX ^{3D}
Scan parameters	5° - 55° 2θ scans, 16 min scan time

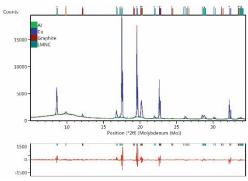


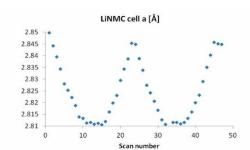


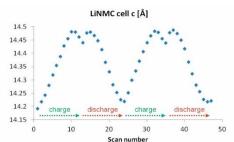
For this *in situ* and *in operando* study of lithium-ion pouch cell batteries, we analyse the charge /discharge cycles using hard X-rays in transmission geometry on the **Empyrean floorstanding XRD**. Variations in the crystallographic structure of the elements in the pouch cell were correlated directly with the amount of Li incorporated in the electrodes.

- The cell was cycled twice between discharged and charged states following a sequential CCCV (constant current constant voltage) procedure.
- First the cell is charged incrementally in 10 steps with a C/10 rate and 2 h stops in the current flow. Then the cell is charged further until it reaches a certain cut-off voltage potential, and the current flow drops below the cut-off threshold.
- The *in situ* XRD measurements were performed continuously over several hours consisting of two complete charge/ discharge cycles of the battery cell
- Subsequently, scans measured during the ramping of the current were discarded, and the scans performed at constant or zero current value were analysed.

Results and discussion





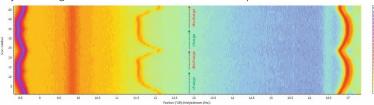


A script was written in Malvern Panalytical' HighScore Plus XRD software to automatically merge all the scans measured at the same conditions. Automatic Rietveld and Pawley mixed fits were performed on every scan, to obtain the cell parameters for the LiNMC and the graphite phases (example - above left). From the automated

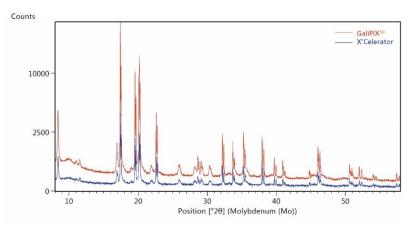


fits (above center and right scans), changes in the lattice parameters can be observed, which relate directly to the structural evolution of the electrode materials during the intercalation/ deintercalation process. The most striking feature is the different behaviour of the "a-" and "c-axis" of the LiNMC cathode. During the charge process, which corresponds to removal of lithium ions from the structure of the cathode, the "a cell" parameter first shows a decrease followed by a shorter region where it is nearly constant. On the other hand, the "c-axis" shows first a strong increase and then switches to a decrease just before the cell is fully charged. Both these trends are reversible upon discharge of the battery.

By measuring the linear correlation between the lattice parameter ratio c/a and the lithium content x(Li) during the 1st and 2nd cycle of the cell with in situ XRD it is also

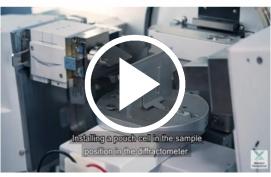


possible to obtain a value for the amount of active lithium in the cathode. It is important to highlight that this value can then be compared to the electrically observable capacity. Deviations of these two values from each other give valuable insights towards the aging process. By using the isolines plot available in HighScore (left), it is possible to observe the variation of the cell parameters directly by following the shifting of the Bragg peaks for LiNMC as well as for graphite. The peaks at about 8.5° and 17° 2theta belong to the LiNMC phase, (003) and (101) reflections respectively. The peak at about 12° 2theta is the (002) reflection of graphite.



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The data presented is from the work of Malvern Panalytical's application specialists in our supply center in the Netherlands as well as the MLZ neutron research facility members. We'd like to thank the MLZ researchers, namely Dr. Stefan Seidlmayer (TU München) and Armin Kriele (Helmholtz Zentrum Geesthacht).

- Read the full application note here
- Watch how our XRD scientists conduct in-operando research on our pouch cell here
- On-demand workshop access: Tune into lectures from renowned professors on batteries, nanomaterials and thin film applications & analysis here
- Live webinar, 11 Aug, 4pm SYD: Interested to know how to collect even more superior data resolution with fantastic background noise cancellation? And all in record speed? Register for the recording here



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All registered participants of the AXAA-2017 conference are automatically granted AXAA membership for 3 years. Alternatively, new memberships can be obtained free of charge, by making an application to the National Council.

Candidates should send the membership form from the <u>AXAA website</u>, and a short statement about how they intend to contribute to the organisation, to the National Council Secretary Anita D'Angelo.

AXAA Resource Centre

There are a range of resources available on the <u>AXAA website</u>, including video recordings of the two Public Lectures at AXAA-2017, tips for Rietveld Analysis, Clay Analysis, XRF tips, and more. We welcome further contributions to our Resource Centre.

Next AXAA Newsletter

The next issue of the AXAA Newsletter will be distributed in December 2021. Please feel free to send contributions for the newsletter to Valerie Mitchell at *ausxray@gmail.com*. Any comments or feedback about the Newsletter are welcome.

A Day in the Life of an X-ray / Neutron Scientist

We are seeking posts for our 'Day in the Life' series. If you'd like to contribute, or know someone who might be interested, please contact National Council

