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New strategies for interrogation of redox flow batteries via Synchrotron radiation

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Operando and *in situ* characterisation studies with the assistance of high energy light produced by synchrotrons are becoming increasingly attractive in the energy storage area, allowing for nondestructive investigations of material properties and device behaviour in realistic working environments, and with high temporal resolution afforded by the latest generation of high-flux beamlines. Many operando synchrotron techniques are well suited to redox flow batteries, which undergo redox changes of the active species in their electrolytes when flowed through porous electrodes. There is a large variety of redox flow battery designs and chemistries, spanning transition metal solutions, hybrid gas-liquid devices, plating and stripping mechanisms and organic redox species. This review presents an overview of recent progress and preponderance of synchrotron techniques in investigating the current issues of redox flow batteries. For each synchrotron X-ray analytical approach, practical examples and breakthrough findings are outlined and the potential applications on the newly developed redox flow batteries are discussed.

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Introduction

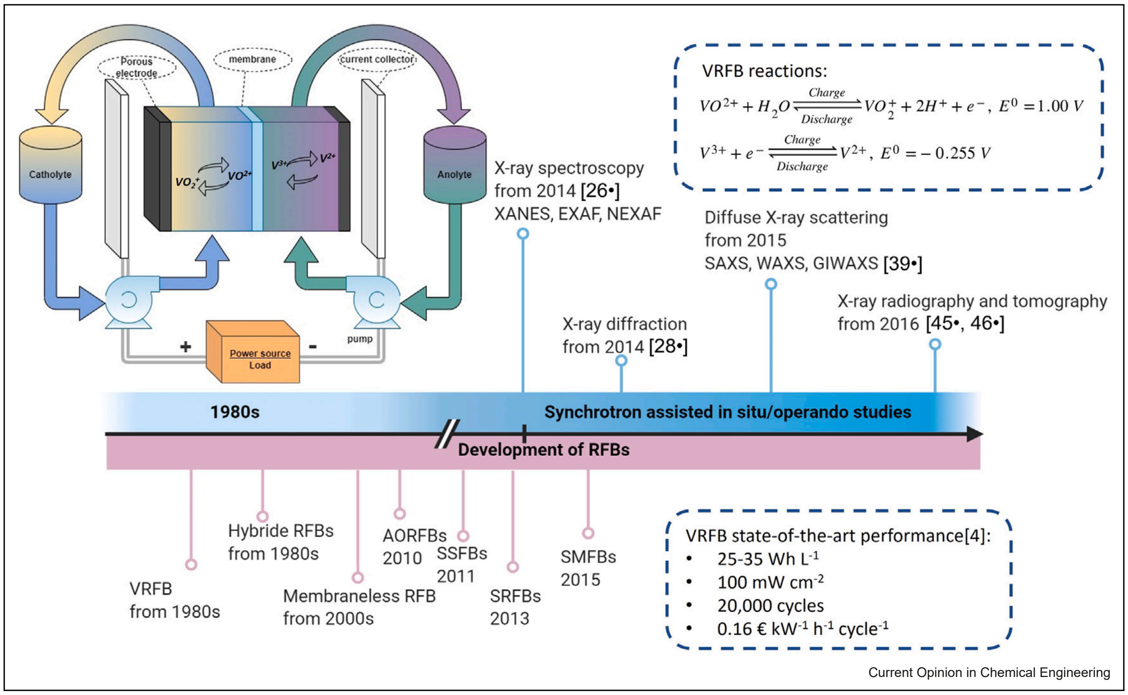
Clean and renewable energy sources have been gradually replacing traditional energy sources with the aim of a more sustainable society [1]. The intermittent nature of renewables means that cost-effective stationary energy storage is urgently required on the grid. Redox flow batteries (RFBs) are a prime candidate for grid-scale storage due to their ability to decouple energy density and power output. Though the technology was demonstrated in the 1970s [2], there are still barriers to commercialisation related to electrolyte cost, energy and power density, efficiency, and cycle life [3,4].

To achieve the goals and address existing and emerging issues of RFBs, advanced techniques for *in situ* or operando studies are required to better understand phenomena under a dynamic working environment. Many operando or in-line lab characterisation techniques have been successfully applied to monitor the state of charge, such as UV–Vis [5] and fluorescence [6], or chemical states and the distribution of electrolyte redox couples, via bulk magnetisation [7], nuclear magnetic resonance [8] and electron paramagnetic resonance [9] for organic RFBs. However, lab-based X-ray characterisation techniques suffer from low temporal and (often) spatial resolution and restrictive working environments, limitations that can be overcome via the use of synchrotron radiation sources (SRSs) [10]. Synchrotron accelerators produce millions of times brighter light, predominantly in the X-ray region, which is useful for many material characterisation including imaging (2D radiography and 3D tomography), spectroscopy, and diffraction/scattering techniques. Since the 1960s, SRSs have evolved through first, second and third generations with the largest SRSs located in Europe (ESRF), USA (APS) and Japan (Spring-8) and have been recognised as a powerful research tool in many research areas [10–12]. With growing attention on energy storage systems, a vast range of experiments using synchrotron radiation have been carried out on batteries [12,13], fuel cells [14] and other electrochemical materials and devices [15,16]; the first experiment at an SRS on RFBs used X-ray absorption near-edge spectroscopy (XANES) to monitor vanadium oxidation state for all-vanadium redox flow batteries (VRFBs) in 2014 [17]. This comparatively late example highlights the underutilisation of SRSs for RFB research.

Redox flow batteries

RFBs are one of the most promising solutions for grid-scale storage due to their capability of decoupling power and energy. Their unique architecture separates the external energy storage tanks from the stacked electrochemical cells, where the electrolytes (catholyte and anolyte) containing the active redox species are pumped through the electrodes to activate the electrochemical reactions during charge/discharge. The basic principle of

Figure 1



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Scheme of the state-of-the-art VRFB with detailed reactions and performance. The abbreviations are aqueous organic redox flow batteries (AORFBs), semi-solid redox flow batteries (SSFBs), solar redox flow batteries (SRFBs), solid mediated redox flow batteries (SMFBs).
Timelines of the historical development (information reproduced with permission from ref.[4]) and synchrotron assisted *in situ*/operando studies of RFBs.

RFBs is illustrated in Figure 1 with the state-of-the-art VRFB as an example. VRFBs stand out for its resilience to crossover of reactants, as both sides contain vanadium and protons. However, there are still limitations including low voltage efficiency due to poor electrocatalytic activity and low active surface area of the electrode, low energy density constrained by material solubility, small voltage window restricted by hydrogen evolution and cost of vanadium.

Multiple types of RFBs have been developed through alterations of the electrolyte, electrode, and separator (Figure 1 [4]). The emerging chemistry or design of RFBs requires advanced characterisation of a variety of phenomena such as redox mechanisms, gas generation, flow characteristics and heterogeneity of reaction in the electrodes. The beneficial properties of synchrotron radiation make it an attractive option for interrogation of RFBs across a range of techniques.

Synchrotron X-ray studies on redox flow batteries

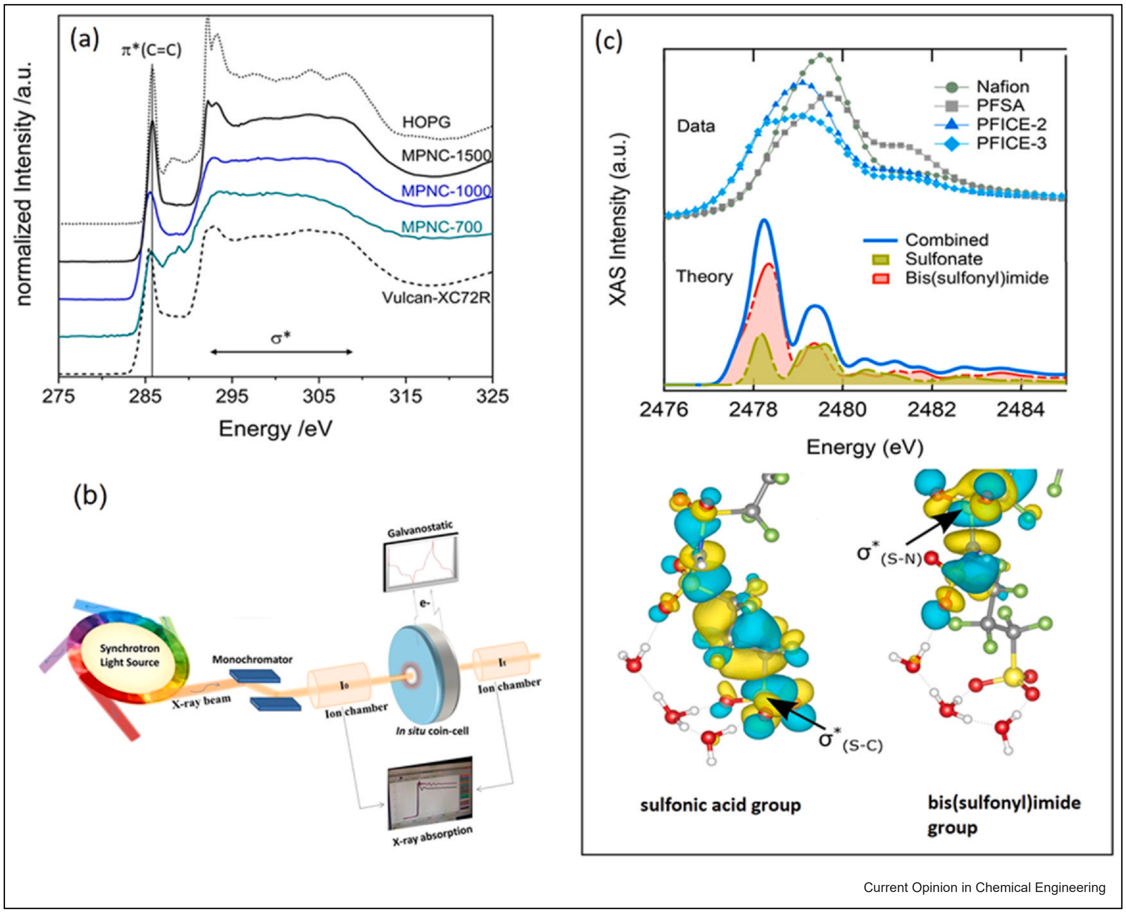
Overview of synchrotron X-ray techniques

Synchrotrons use magnetic fields to accelerate charged particles (electrons) to generate high-energy electromagnetic radiation (X-ray), and have been powerful tools for many research areas over decades of their existence. Depending on the interaction of the radiation with the sample, synchrotron X-ray techniques can be categorised into three broad areas: (1) spectroscopy, where X-rays are spectrally separated before absorbing and emitting by the sample to obtain information on the samples' electronic states; (2) diffraction or scattering experiments, probing long range order (diffraction) or noncrystalline local structure (scattering); and (3) imaging experiments, where the X-rays penetrate samples and are absorbed, based on atomic mass and sample density, producing 2D images (radiography) or 3D images (tomography) to reveal internal structure. With the high flux synchrotron beam, acquisition time is minimised to achieve operando experiment conditions, where the dynamic variations of electron and chemical states, molecular structures and phase separation under RFBs' operational conditions could be analysed.

X-ray spectroscopy

Spectroscopic experiments analyse the wavelength of absorbed or emitted X-rays by the studied specimen as shown in Figure 2. X-ray absorption spectroscopy (XAS) is a powerful and informative tool to investigate the oxidation state and electronic local structure of elements. Most XAS studies are performed at an SRS due to the

Figure 2



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(a) C K-edge NEXAFS spectra of different carbon materials. **(b)** Schematic diagram of X-ray spectroscopy. **(c)** Experimental and simulated S K-edge NEXAFS spectra of the PFSA and PFICE ionomers and density distributions of the electronic component for a sulphur atom.
(a) Adapted with permission from [24]. Copyright 2022 American Chemical Society. **(b)** Adapted with permission from [25]. ©2022 John Wiley and Sons, Inc. **(c)** Reproduced with permission from [26*] . Copyright 2022 American Chemical Society.

intense monochromatic radiation produced and lack of available lab-based XAS technology until recently [18]. The very first of RFBs studied at a synchrotron used *in situ* XANES to monitor the valence state variation of vanadium during one battery charge-discharging cycle [17]. An 82% battery state of charge (SOC) was calculated under a traditional cycling profile, prompting the proposal of an additional constant voltage charge to achieve 100% SOC [17].

Lutz and Fittschen [19] also studied the vanadium species gradient inside the electrolyte but with lab-based XANES, where 2–5 h was required for a single measurement with around 1% relative uncertainty on edge jump when correcting based on synchrotron data. Though the lab XANES can be helpful to understand the electrochemistry, it is not sufficient for operando studies, which require higher time resolution and more accurate measurements. Following this work, they conducted synchrotron experiments with just 5 ms for a single scan and micro-size probe, enabling sufficient spatiotemporal resolution to unravel the vanadium redox variation during the diffusion through the membrane at different points in the flow field [20]. The experimental procedures were carefully designed and proved to limit vanadium oxidisation by radiation damage (e.g. photo-oxidation and water radiolysis) and confirm the chemical formation of V(IV) inside the membrane after exposing to V(III) on one side and V(V) on the other [20,21].

Christopher et al. [22] studied the iron centre ionic liquid (ILs), where the solvent itself contains redox-active anions and cations, unlike the solvated salt systems (e.g. VRFB). To evaluate the electron transfer barrier into and from the active site during a redox reaction, Fe K-edge XANES and extended X-ray absorption fine structure (EXAFS) on ligand structures of the Fe centre were applied, showing a mixed $Fe^{+2/+3}$ oxidation state during oxidation (XANES) and no expected extension of nearest neighbour Fe-O distances during reduction (EXAFS). This work shows the great potential of XAS in addressing intrinsic mechanisms in the polarisation process, and XAS has also been used in many catalytic studies of metal catalysts and functional groups for RFB. Sheeraz et al. [23] applied XAS combined with other material analytical techniques to study the post-cycling performance of their electrocatalyst, SnO_2 nanoparticles on carbon felt. With the near edge X-ray absorption fine spectroscopy (NEXAFS) results at the C K-edge of carbon felt, they analysed the extent of oxygen functional groups on the surface, which has catalysing activity and was found to increase with cycling. The NEXAFS result of the O K-edge spectrum and XANES of Sn K-edge confirmed a consistent Sn^{4+} state and stable adherence of SnO_2 electrocatalyst on the carbon felt during cycling. NEXAFS measured at C K-edge was also used to study sp^2 carbon extent (graphitisation degree) by comparing the peak intensities at 285.6 eV photon energy, which is the typical C-C π^* resonance in the graphite C-ring shown in Figure 2a [24].

Except for electrolyte and electrode studies discussed above, XAS was also found to be a potent tool for unravelling the molecular structure of ion-conducting polymer membranes that provide insights into water uptake and conductivity performance, assisting with the design of membrane chemistry for different energy devices. Gregory et al. [26•] reported NEXAFS studies at S K-edge of perfluorosulfonic acid (PFSA) and perfuoro ionene chain extended (PFICE) ionomers, which contains a sulphonic acid group and additional one or two bis(sulfonyl)imide groups on the side-chain terminal. The molecular structure and chemistry of the hydrophobic backbone of polytetrafluoroethylene and hydrophilic sidechains of sulphonate groups determine the nanoscale phase separation by hydrophilicity force, where the hydrophilic phase separations could be studied by combining NEXAFS with energy-dependent X-ray scattering to increase contrast with low electron transfer variation. Another highlight of this work is the ab initio calculation and theoretical simulation (Figure 2c), which revealed the beneficial PFICE chemistry of well-ordered phase-separated structure with short-range order and enhanced water uptake through hydrogen-bonding. To conclude, XAS is an effective technique for understanding chemical states and electronic density distribution of electrodes, electrolytes, and separators in RFBs.

X-ray diffraction

Synchrotron X-ray diffraction (SXRD) probes the crystallographic structure of ordered material by measuring the diffracted X-ray intensity at different angles. In comparison with lab XRD, SXRD provides higher resolution and sensitivity of the diffraction peaks, which can detect trace phases or minor variations of crystallographic structure, and higher penetration allowing for *in situ* studies. Zhao et al. [27] proved the stability of Li-ion conductive ceramic separators for lithium-iodine hybrid RFBs with the unnoticeable variation of SXRD results before and after cycling.

A recent highlight studied redox targeting VRFBs [28•], which are conventional VRFBs with a homemade Prussian blue analogue powder (PBA), $(VO)_6[Fe(CN)_6]_3$ stored in the catholyte tank. When charging and discharging, the PBA was thermodynamically favoured to be chemically oxidised or reduced by vanadium. This design is benefited by the increased cathodic volumetric capacity given by PBA, which had uncertain crystal structure, solved by SXRD. Jisu et al. [29] also carried out SXRD to measure the crystal structures of different redox-active organic molecules for all-organic RFBs. The precise peak position and intensity of the scanning diffraction pattern makes SXRD attractive to determine the synthesised unknown crystal structures, which is advantageous for novel RFBs with complex chemistry.

Diffuse X-ray scattering

Diffuse X-ray scattering is mainly used to characterise the structure of noncrystalline materials such as polymers (e.g. the separators in RFB) [30], and is particularly effective in detecting the *in situ* structural variations as the long-period relaxation nature of polymers and rapid data acquisition afforded by the high X-ray luminance of synchrotron radiation. Depending on the scattering angle, small-angle X-ray scattering (SAXS) and wide-angle X-ray scattering are applied to analysis of large structure and small features, respectively [31].

With a broad variety of hydrophobic backbones and hydrophilic sidechains, the properties of polymer separators can be highly diverse [32]. The most important property of RFB separators, ionic conductivity [33] was reported to be mainly affected by the size and distribution of hydrophilic phase separation as the hydrophilic sidechains containing functional groups provide the ionic pathway. SAXS, as a nondestructive quantitative approach, is favourable to analyse the morphology, hydrophilic channel length, size and distribution of phase separation caused by intrinsic chemistry or external perturbation effects [34–36]. Si et al. [35] improved the ionic conductivity of anion-exchange membrane for VRFBs through forming 3D ionic channels with microscopic hydrophobic-hydrophilic segregated phases like cation-exchange membranes (e.g.

Nafion), where the target morphology and chemistry was verified by SAXS. Chen et al. [36] designed a copolymer membrane with controllable morphology, where the morphology variation and swelling effects were studied by SAXS.

Other than application as membranes, conductive polymers have also been studied as RFB electrodes [37,38]. Bharati et al. [39•] addressed the importance of polymer microstructure and polymer/liquid interface on the redox kinetics. The varied micro-crystalline structures of conductive polymers with different fabrication methods were compared and investigated by grazing-incidence wide-angle X-ray scattering (GIWAXS), correlating the microstructure to the electronic properties, and characterising the molecular aggregation state (molecular orientation) at the interface [40]. They found the changing of polymer microstructure resulted in different polymer density of states, which is directly linked to the symmetry of redox reactions. Therefore, they proposed the possibility of kinetic selectivity by altering the microstructure and nanostructure of the conductive polymer electrode.

X-ray radiography and computed tomography

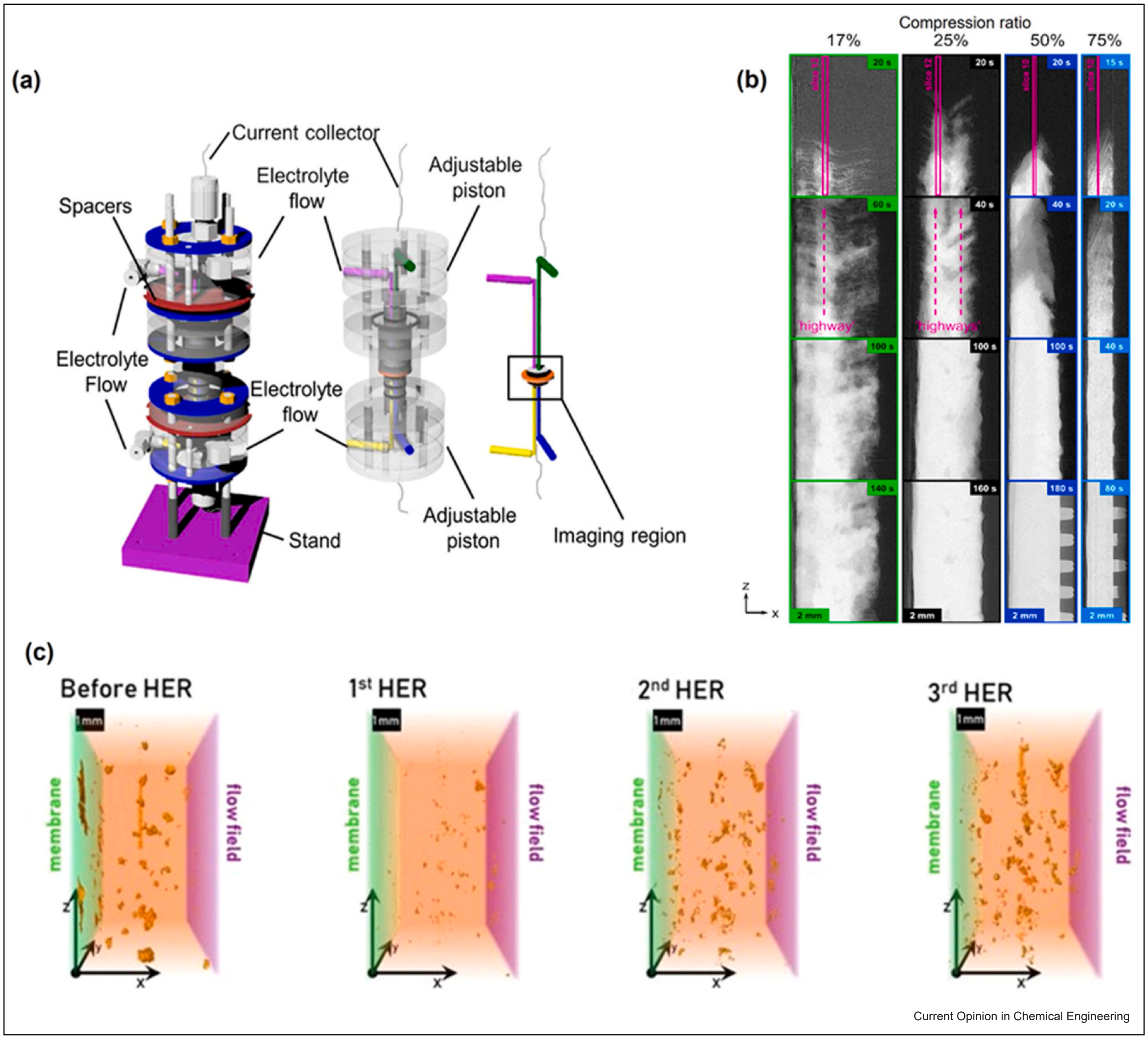
X-ray imaging techniques are invaluable for non-destructive monitoring of the internal structure of energy devices [41]. Computed tomography (CT) produces a virtual 3D volume of electrode microstructures which can be used as the basis of image-based modelling [42]. For RFBs, electrode microstructural properties are vital in influencing the pressure drop, mass transport phenomena, electrolyte flow patterns and the wetting properties, which all affect battery efficiencies and performance [43,44]. Furthermore, electrolyte flow patterns can be simulated based on the 3D microstructure of the electrode and verified with 2D radiography [45*,46*]. However, to realise a high image quality with lab-based CT, compensation of long acquisition time-limits the *in situ* and operando capabilities. SRSs provide steady high photon flux and hence high spatio-temporal resolution, and so the structure modelling parameters of energy devices under a dynamic environment and the transient phenomena under operating conditions can be obtained and captured.

In 2016, Jervis et al. designed a miniature flow cell to conduct *in situ* imaging of RFB electrodes with synchrotron X-ray CT [47]. This work proved the capability of synchrotron CT to image electrode structure and electrolyte variation under an operating environment. The cell was built in a rotational symmetry as shown in Figure 3a, where the attenuation of the beam at all angles was kept constant to reduce the artefacts from the reconstructions. This work compared CT images by SRS and lab-based CT systems, showing that the former achieved higher signal-to-noise ratio and better segmentation of electrode fibres from the electrolyte phase in a significantly reduced time frame, which enables imaging of RFBs with *in situ*/operando X-ray CT [47].

Real-time imaging electrolytes and electrode structures is desirable because of the direct impacts on the electrochemically active surface area leading to a significant variation of battery efficiency. The focus was on electrode compression which has a large influence on the performance of RFBs [43,48]; studies indicated reduced porosity, permeability, and diffusion [43,49], increased electrolyte resistance and pressure drop with compression [50]. Apart from the *in situ* compression studies, electrolyte species [51], electrode thermal treatment [49], operation potential [45•] and flow field-electrode interface [46•] were found to be closely related to electrolyte flow patterns, where synchrotron X-ray radiography and tomography interrogated temporal variations. Bevilacqua et al. [51] traced the initial invasion and flow-through behaviours of electrolytes with radiography and tomography, where the effect of different electrolyte species, varied compression and thermal activation were studied. They concluded improved wetting and reduced pressure drop were observed in activated electrodes with a flow-through configuration. In terms of electrode saturation, electrode activation was the determining factor, which also improved with increasing compression ratio until 50%. Banerjee et al.[49] reported the negative impacts of compression: reduced permeability and single-phase diffusion, and increased breakthrough pressure with compression up to 67%, where they modelled the electrolyte invasion and transport patterns based on electrode 3D structure from tomography and compared this with the experimental visualised flow with radiography.

Roswitha's group [46•] also studied compression ratio up to 75% and different flow fields; synchrotron X-ray radiography combined with quantitative analysis presented a time and spatially resolved saturation of electrolyte, where higher compression ratio improved the saturation ratio, and more than 97% utilisation of electrode was achieved when compression reached 50%. The highlight of this study was the electrolyte invasion pattern at lower compressions (25% and 17%), which breaks in and followed a 'highway' path till reaching the other side, then spreads through the tilted fibre alignment shown in Figure 3b and gradually filled the electrode over time. However, at higher compression, the invasion steps were time-scale unresolvable due to a faster process, attributed to a steeper tilt angle of fibres

Figure 3



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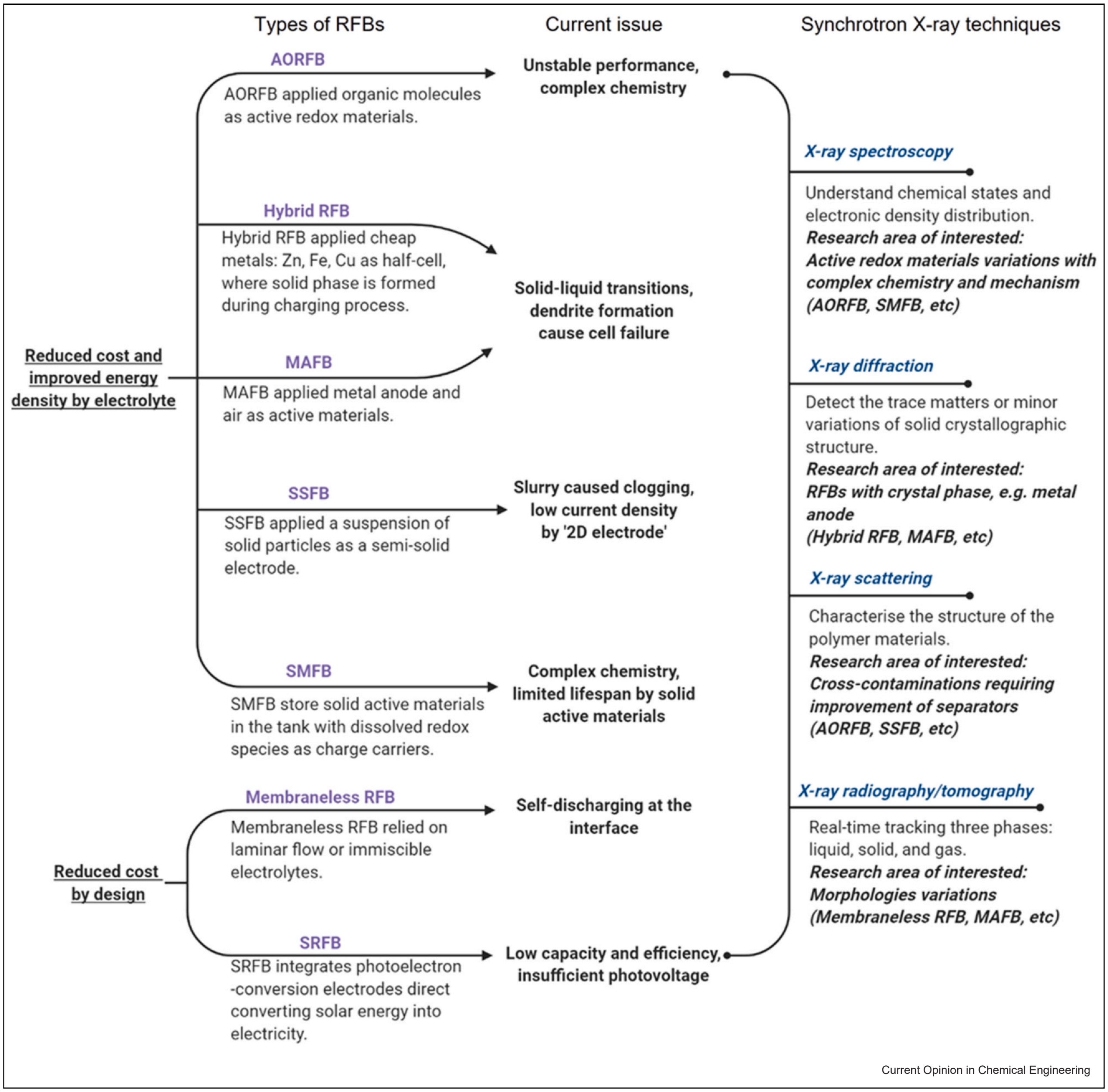
(a) Design of a miniature flow cell with a transparent view of internal structure and electrolyte flow, **(b)** radiograms of the vanadium electrolytes in time-spatial scales with different compression ratios, **(c)** tomograms of gas-phase evaluation before and after continuously hydrogen evolution periods. **(a)** Adapted with permission from [47], **(b)** Reproduced with permission from [46•], **(c)** Reproduced with permission from [45•] ©2022 John Wiley and Sons, Inc.

caused by compression, altering the wetting behaviour. Another work by Roswitha's group [45•] investigated the side reaction of hydrogen production through visualisation of gas-phase variation by tomography, where electrolyte flow dynamics by radiography with three different flow geometries were monitored and related to the potential-current response and hydrogen gas formation. This study found flow-through configuration achieved the highest saturation (96.56%), and interdigitated flow field has a slightly higher saturation ratio (90.99%) than serpentine (90.29%). With a time-resolved 3D gas detection, the hydrogen gas was discovered to be mainly retained by pre-existing air bubbles (Figure 3c), which result in decreased saturation at 1.09% per redox cycle. It is worth noting that the combination of radiography and tomography realised the real-time tracking of all existing phases: liquid-solid-gas in the VRFB electrochemical cell, which allows the relationships between

Figure 4



AORFB applied organic molecules as active redox materials.

Hybrid RFB applied cheap metals: Zn, Fe, Cu as half-cell, where solid phase is formed during charging process.

MAFB applied metal anode and air as active materials.

SSFB applied a suspension of solid particles as a semi-solid electrode.

SMFB store solid active materials in the tank with dissolved redox species as charge carriers.

Membraneless RFB relied on laminar flow or immiscible electrolytes.

SRFB integrates photoelectron -conversion electrodes direct converting solar energy into electricity.

Understand chemical states and electronic density distribution. ***Research area of interested: Active redox materials variations with complex chemistry and mechanism (AORFB, SMFB, etc)***

Detect the trace matters or minor variations of solid crystallographic structure. ***Research area of interested: RFBs with crystal phase, e.g. metal anode (Hybrid RFB, MAFB, etc)***

Characterise the structure of the polymer materials. ***Research area of interested: Cross-contaminations requiring improvement of separators (AORFB, SSFB, etc)***

Real-time tracking three phases: liquid, solid, and gas. ***Research area of interested: Morphologies variations (Membraneless RFB, MAFB, etc)***

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Conclusion diagram of emerging types of RFBs and their current issues linked with the potential solutions by synchrotron X-ray techniques.

variables and aqueous electrolyte intake to be analysed in detail.

Conclusion and perspective

With the assistance of synchrotron radiation, an additional dimension of time is realised to capture the variations under dynamic or operating conditions of RFBs. The development of new RFBs with advanced electrolyte materials or battery design will require increasing use of synchrotron techniques that are now almost routinely used in related fields of Li ion batteries and fuel cells; similar studies are far less ubiquitous in RFBs. Figure 4 summarises the current issues of RFBs and proposes the great potential of applying synchrotron techniques to addressing the problems.

Although it is a powerful tool, there are a few points that need attention when designing an experiment at SRSs: (i) Synchrotron experimental protocols for RFBs, as to monitor dynamic changes, should avoid any possible errors caused by the characterisation itself (e.g. radiation damage); (ii) Design of operando cells to eliminate artefacts caused by attenuation or X-ray interaction of the cell and peripheral parts; (iii) Environment and scale differences between the synchrotron testing cell and real RFBs, where assumptions could be considered to reduce the undesired impacts by the differences; (iv) the interplay between resolution and region of interest, and data quality and time resolution. There is an obvious opportunity for SRSs to play a larger role in RFB research with the correct approach to such experiments and new insights could be gained into this exciting family of storage technologies.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References and recommended reading

Papers of particular interest, published within the period of review, have been highlighted as:

- of special interest

1. McCollum DL, Zhou W, Bertram C, de Boer HS, Bosetti V, Busch S, Després J, Drouet L, Emmerling J, Fay M, Fricko O, Fujimori S, Gidden M, Harmsen M, Huppmann D, Iyer G, Krey V, Kriegler E, Nicolas C, Pachauri S, Parkinson S, Poblete-Cazenave M, Rafaj P, Rao N, Rozenberg J, Schmitz A, Schoepp W, van Vuuren D, Riahi K: **Energy investment needs for fulfilling the Paris Agreement and achieving the Sustainable Development Goals**. *Nat Energy* 2018, **3**:589-599, https://doi.org/10.1038/s41560-018-0179-z (2018 3:7).
2. L.H. Thaller: **Electrically rechargeable redox flow cells - NASA/ADS**. In *Intersociety Energy Conversion Engineering Conference*; 1974.
3. Soloveichik GL: **Flow batteries: current status and trends**. *Chem Rev* 2015, **115**:11533-11558, https://doi.org/10.1021/CR500720T
4. Sánchez-Díez E, Ventosa E, Guarnieri M, Trovò A, Flox C, Marcilla R, Soavi F, Mazur P, Aranzabe E, Ferret R: **Redox flow batteries: status and perspective towards sustainable stationary energy storage**. *J Power Sources* 2021, **481**:228804, https://doi.org/10.1016/J.JPOWSOUR.2020.228804
5. Skyllas-Kazacos M, Kazacos M: **State of charge monitoring methods for vanadium redox flow battery control**. *J Power Sources* (20) 2011, **196**:8822-8827, https://doi.org/10.1016/J.JPOWSOUR.2011.06.080
6. Wong AA, Rubinstein SM, Aziz MJ: **Direct visualization of electrochemical reactions and heterogeneous transport within porous electrodes in operando by fluorescence microscopy**. *Cell Rep Phys Sci* 2021, **2**:100388, https://doi.org/10.1016/j.xcrp.2021.100388
7. Zhao EW, Shellard EJK, Klusener PAA, Grey CP: **In situ bulk magnetization measurements reveal the state of charge of redox flow batteries**. *Chem Commun* 2022, **58**:1342-1345, https://doi.org/10.1039/D1CC01895G
8. Zhao EW, Liu T, Jónsson E, Lee J, Temprano I, Jethwa RB, Wang A, Smith H, Carretero-González J, Song Q, Grey CP: **In situ NMR metrology reveals reaction mechanisms in redox flow batteries**. *Nature* 2020, **579**:224-228, https://doi.org/10.1038/S41586-020-2081-7
9. Zhao EW, Jónsson E, Jethwa RB, Hey D, Lyu D, Brookfield A, Klusener PAA, Collison D, Grey CP: **Coupled in situ NMR and EPR studies reveal the electron transfer rate and electrolyte decomposition in redox flow batteries**. *J Am Chem Soc* 2021, **143**:1885-1895, https://doi.org/10.1021/JACS.0C10650/SUPPL_FILE/JA0C10650_SI_001.PDF
10. Ezquerra TA, Garcia-Gutierrez MC, Nogales A, Gomez M: **Applications of Synchrotron light to scattering and diffraction in materials and life sciences**. *Lect Notes Phys* 2009, **776**:18-20, https://doi.org/10.1007/978-3-540-95968-7
11. Blaustein R: **Biology and Light Sources: Synchrotrons allow researchers a deep look into life**. *BioScience* 2017, **67**:201-207, https://doi.org/10.1093/BIOSCI/BIW183
12. Llewellyn A v, Matruglio A, Brett DJL, Jervis R, Shearing PR: **Using in-situ laboratory and Synchrotron-based X-ray diffraction for lithium-ion batteries characterization: a review on recent developments**. *Condens Matter* 2020, **5**, https://doi.org/10.3390/CONDMAT5040075
13. Leach AS, Llewellyn A v, Xu C, Tan C, Heenan TMM, Dimitrijevic A, Kleiner K, Grey CP, Brett DJL, Tang CC, Shearing PR, Jervis R: **Spatially resolved operando Synchrotron-based X-ray diffraction measurements of Ni-rich cathodes for Li-ion batteries**. *Front Chem Eng* 2022, **3**:76-85, https://doi.org/10.3389/FCENG.2021.794194
14. Leach AS, Hack J, Amboage M, Diaz-Moreno S, Huang H, Cullen PL, Wilding M, Magliocca E, Miller TS, Howard CA, Brett DJL, Shearing PR, McMillan PF, Russell AE, Jervis R: **A novel fuel cell design for operando energy-dispersive x-ray absorption measurements**. *J Phys Condens Matter* 2021, **33**:314002, https://doi.org/10.1088/1361-648X/AC0476
15. Bak SM, Shadike Z, Lin R, Yu X, Yang XQ: **In situ/operando synchrotron-based X-ray techniques for lithium-ion battery research**. *NPG Asia Mater* 2018, **10**:563-580, https://doi.org/10.1038/s41427-018-0056-z
16. Lin F, Liu Y, Yu X, Cheng L, Singer A, Shpyrko OG, Xin HL, Tamura N, Tian C, Weng TC, Yang XQ, Meng YS, Nordlund D, Yang W, Doeff MM: **Synchrotron X-ray analytical techniques for studying materials electrochemistry in rechargeable batteries**. *Chem Rev* 2017, **117**:13123-13186, https://doi.org/10.1021/ACS.CHEMREV.7B00007
17. Jia C, Liu Q, Sun CJ, Yang F, Ren Y, Heald SM, Liu Y, Li ZF, Lu W, Xie J: **In situ X-ray near-edge absorption spectroscopy investigation of the state of charge of all-vanadium redox flow batteries**. *ACS Appl Mater Interfaces* 2014, **6**:17920-17925, https://doi.org/10.1021/am5046422
18. Seidler GT, Mortensen DR, Remesnik AJ, Pacold JI, Ball NA, Barry N, Styczinski M, Hoidn OR: **A laboratory-based hard x-ray monochromator for high-resolution x-ray emission spectroscopy and x-ray absorption near edge structure measurements**. *Rev Sci Instrum* 2014, **85**:113906, https://doi.org/10.1063/1.4901599
19. Lutz C, Fittschen UEA: **Laboratory XANES to study vanadium species in vanadium redox flow batteries**. Cambridge University Press; 2020:S24-S28, https://doi.org/10.1017/S0885715620000226
20. Lutz C, Hampel S, Beuermann S, Turek T, Kunz U, Garrevoet J, Falkenberg G, Fittschen U: **Determination of the through-plane profile of vanadium species in hydrated Nafion studied with micro X-ray absorption near-edge structure spectroscopy – proof of concept**. *J Synchrotron Radiat* 2021, **28**:1865-1873, https://doi.org/10.1107/S160057752100905X (Urn:Issn:1600-5775).
21. Lutz C, Hampel S, Ke X, Beuermann S, Turek T, Kunz U, Guilherme Buzanich A, Radtke M, Fittschen UEA: **Evidence for redox reactions during vanadium crossover inside the nanoscopic water-body of Nafion 117 using X-ray absorption near edge structure spectroscopy**. *J Power Sources* 2021, **483**:229176, https://doi.org/10.1016/J.JPOWSOUR.2020.229176
22. Apblett CA, Stewart DM, Fryer RT, Sell JC, Pratt HDI, Anderson TM, Meulenberg RW: **In situ XANES and EXAFS analysis of redox**

active Fe center ionic liquids. *Electrochim Acta* 2015, **185**:156-161, https://doi.org/10.1016/J.ELECTACTA.2015.09.093

23. Mehboob S, Ali G, Shin HJ, Hwang J, Abbas S, Chung KY, Ha HY: **Enhancing the performance of all-vanadium redox flow batteries by decorating carbon felt electrodes with SnO2 nanoparticles**. *Appl Energy* 2018, **229**:910-921, https://doi.org/10.1016/J.APENERGY.2018.08.047

24. Melke J, Martin J, Bruns M, Hügenell P, Schökel A, Montoya Isaza S, Fink F, Elsässer P, Fischer A: **Investigating the effect of microstructure and surface functionalization of mesoporous N-doped carbons on V4+/V5+ kinetics**. *ACS Appl Energy Mater* 2020, **3**:11627-11640, https://doi.org/10.1021/ACSAEM.0C01489

25. Wu Z, Kong Pang W, Chen L, Johannessen B, Guo Z: **In situ Synchrotron X-ray absorption spectroscopy studies of anode materials for rechargeable batteries**. *Batter Supercaps* 2021, **4**:1547-1566, https://doi.org/10.1002/BATT.202100006

26. • Su GM, Cordova IA, Yandrasits MA, Lindell M, Feng J, Wang C, Kusoglu A: **Chemical and morphological origins of improved ion conductivity in perfluoro ionene chain extended ionomers**. *J Am Chem Soc* 2019, **141**:13547-13561, https://doi.org/10.1021/jacs.9b05322.

This work advised the applications of EXAFS combined with *ab initio* calculation and theoretical simulation, which provides electronic level variations and pointed a direction on understanding the intrinsic mechanisms with EXAFS.

27. Zhao Y, Hong M, Bonnet Mercier N, Yu G, Choi HC, Byon HR: **A 3.5 v lithium-iodine hybrid redox battery with vertically aligned carbon nanotube current collector**. *Nano Lett* 2014, **14**:1085-1092, https://doi.org/10.1021/nl404784d

28. • Cheng Y, Wang X, Huang S, Samarakoon W, Xi S, Ji Y, Zhang H, Zhang F, Du Y, Feng Z, Adams S, Wang Q: **Redox targeting-based vanadium redox-flow battery**. *ACS Energy Lett* 2019, **4**:3028-3035, https://doi.org/10.1021/acsenergylett.9b01939.

This study made great progress on redox targeting flow batteries and characterised the synthesised uncertain crystal structure with SXRD.

29. Back J, Kwon G, Byeon JE, Song H, Kang K, Lee E: **Tunable redox-active triazenyl-carbene platforms: a new class of anolytes for non-aqueous organic redox flow batteries**. *ACS Appl Mater Interfaces* 2020, **12**:37338-37345, https://doi.org/10.1021/acsami.0c09400

30. Takahara A, Higaki Y, Hirai T, Ishige R: **Application of Synchrotron radiation X-ray scattering and spectroscopy to soft matter**. *Polymers* 2020, **12**:1624, https://doi.org/10.3390/POLYM12071624

31. García-Gutiérrez MC, Rueda DR: **Bases of synchrotron radiation, light sources, and features of X-ray scattering beamlines**. *Lect Notes Phys* 2009, **776**:1-22, https://doi.org/10.1007/978-3-540-95968-7_1

32. Pan Y, Chou S, Kun Liu H, Xue Dou S: **Functional membrane separators for next-generation high-energy rechargeable batteries**. *Natl Sci Rev* 2017, **4**:917-933, https://doi.org/10.1093/nsr/nwx037

33. Gubler L: **Membranes and separators for redox flow batteries**. *Curr Opin Electrochem* 2019, **18**:31-36, https://doi.org/10.1016/J.COELEC.2019.08.007

34. Titvinidze G, Kreuer KD, Schuster M, de Araujo CC, Melchior JP, Meyer WH: **Proton conducting phase-separated multiblock copolymers with sulfonated poly(phenylene sulfone) blocks for electrochemical applications: preparation, morphology, hydration behavior, and transport**. *Adv Funct Mater* 2012, **22**:4456-4470, https://doi.org/10.1002/ADFM.201200811

35. Si J, Lv Y, Lu S, Xiang Y: **Microscopic phase-segregated quaternary ammonia polysulfone membrane for vanadium redox flow batteries**. *J Power Sources* 2019, **428**:88-92, https://doi.org/10.1016/J.JPOWSOUR.2019.04.100

36. Chen XC, Jiang X, Balsara NP: **Swelling of individual nanodomains in hydrated block copolymer electrolyte membranes**. *J Chem Phys* 2018, **149**:163325, https://doi.org/10.1063/1.5029452

37. Winsberg J, Hagemann T, Muench S, Friebe C, Häupler B, Janoschka T, Morgenstern S, Hager MD, Schubert US: **Poly (boron-dipyrromethene)-a redox-active polymer class for polymer redox-flow batteries**. *Chem Mater* 2016, **28**:3401-3405, https://doi.org/10.1021/ACS.CHEMMATER.6B00640/SUPPL_FILE/CM6B00640_SI_001.PDF

38. Janoschka T, Martin N, Martin U, Friebe C, Morgenstern S, Hiller H, Hager MD, Schubert US: **An aqueous, polymer-based redox-flow battery using non-corrosive, safe, and low-cost materials**. *Nature* 2015, **527**:78-81, https://doi.org/10.1038/nature15746 (2015 527:7576).

39. • Neelamraju B, Rudolph M, Ratcliff EL: **Controlling the kinetics of charge transfer at conductive polymer/ liquid interfaces through microstructure**. *J Phys Chem C* 2018, **122**:21210-21215, https://doi.org/10.1021/acs.jpcc.8b06861.

The authors addressed the importance of polymer microstructure and polymer/liquid interface on the redox kinetics, where GIWAXS was proved a useful tool to study the polymer structure.

40. Hexemer A, Müller-Buschbaum P: **Advanced grazing-incidence techniques for modern soft-matter materials analysis**. *IUCrJ* 2015, **2**:106-125, https://doi.org/10.1107/S2052252514024178

41. Wood V: **X-ray tomography for battery research and development**. *Nat Rev Mater* 2018, **3**:293-295, https://doi.org/10.1038/s41578-018-0053-4 (2018 3:9).

42. Heenan TMM, Finegan DP, Tjaden B, Lu X, Iacoviello F, Millichamp J, Brett DJL, Shearing PR: **4D nano-tomography of electrochemical energy devices using lab-based X-ray imaging**. *Nano Energy* 2018, **47**:556-565, https://doi.org/10.1016/J.NANOEN.2018.03.001

43. Jervis R, Kok MDR, Neville TP, Meyer Q, Brown LD, Iacoviello F, Gostick JT, Brett DJL, Shearing PR: **In situ compression and X-ray computed tomography of flow battery electrodes**. *J Energy Chem* 2018, **27**:1353-1361, https://doi.org/10.1016/J.JECHEM.2018.03.022

44. Kok MDR, Jervis R, Brett D, Shearing PR, Gostick JT: **Insights into the effect of structural heterogeneity in carbonized electrospun fibrous mats for flow battery electrodes by X-ray tomography**. *Nano-Micro Small* 2018, **14**:1-15, https://doi.org/10.1002/smll.201703616 (1703616).

45. • Eifert L, Bevilacqua N, Köble K, Fahy K, Xiao L, Li M, Duan K, Bazylak A, Sui PC, Zeis R: **Synchrotron X-ray radiography and tomography of vanadium redox flow batteries—cell design, electrolyte flow geometry, and gas bubble formation**. *ChemSusChem.* 2020, **13**:3154-3165, https://doi.org/10.1002/CSSC.202000541.

This study succeeds in monitoring the gas evolution under the impact of side reaction (hydrogen evolution reaction) with the assistance of time-resolved radiography.

46. • Köble K, Eifert L, Bevilacqua N, Fahy KF, Bazylak A, Zeis R: **Synchrotron X-Ray radiography of vanadium redox flow batteries – time and spatial resolved electrolyte flow in porous carbon electrodes**. *J Power Sources* 2021, **492**:229660, https://doi.org/10.1016/J.JPOWSOUR.2021.229660.

The highlight of this work is utilising the time-resolved X-ray radiography and tomography, which enabled the picturing the invasion patterns of electrolyte flow.

47. Jervis R, Brown LD, Neville TP, Millichamp J, Finegan DP, Heenan TMM, Brett DJL, Shearing PR: **Design of a miniature flow cell for in situ x-ray imaging of redox flow batteries**. *J Phys D Appl Phys* 2016, **49**:434002, https://doi.org/10.1088/0022-3727/49/43/434002

48. Brown LD, Neville TP, Jervis R, Mason TJ, Shearing PR, Brett DJL: **The effect of felt compression on the performance and pressure drop of all-vanadium redox flow batteries**. *J Energy Storage* 2016, **8**:91-98, https://doi.org/10.1016/J.EST.2016.10.003

49. Banerjee R, Bevilacqua N, Mohseninia A, Wiedemann B, Wilhelm F, Scholta J, Zeis R: **Carbon felt electrodes for redox flow battery: impact of compression on transport properties**. *J Energy Storage* 2019, **26**:100997, https://doi.org/10.1016/j.est.2019.100997

50. Ghimire PC, Bhattarai A, Schweiss R, Scherer GG, Wai N, Yan Q: **A comprehensive study of electrode compression effects in all vanadium redox flow batteries including locally resolved measurements**. *Appl Energy* 2018, **230**:974-982, https://doi.org/10.1016/J.APENERGY.2018.09.049

51. Bevilacqua N, Eifert L, Banerjee R, Köble K, Faragó T, Zuber M, Bazylak A, Zeis R: **Visualization of electrolyte flow in vanadium redox flow batteries using synchrotron X-ray radiography and tomography – Impact of electrolyte species and electrode compression**. *J Power Sources* 2019, **439**:227071, https://doi.org/10.1016/J.JPOWSOUR.2019.227071