Bridging X-ray Computed Tomography and Computational Modeling for Electrochemical Energy-Conversion and –Storage

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X-ray imaging techniques are powerful tools for understanding morphology, transport and even reactions within the electrochemical energy systems. Transmission X-ray microscopy (TXM) and X-ray computed tomography (CT) have been widely used in *ex-situ* studies to probe morphology of electrochemical energy materials. Emerging *operando* studies highlight the possibility of imaging energy materials and devices under realistic operating conditions. We present an overview of recent advances in the X-ray CT methods with application to fuel cells, batteries and other energy technologies, and describe how the information obtained with multimodal imaging is used within the multi-scale computational models. Overall, the progress in imaging outran the modeling progress, and current models are limited in their utility to incorporate vast amount of multimodal image data.

Keywords: X-ray CT; multimodal imaging; multi-scale modeling; batteries; fuel-cells.

1. Introduction

Sustainable energy infrastructure requires broader incorporation of intermittent energy sources. Scientific advances in battery, redox flow-battery, electrolyzer and fuel cell technologies for grid-based, transportation and portable applications, as well, as cost-reduction are needed to meet the future targets of clean, affordable net-zero emissions energy infrastructure [1]. The electrochemical energy-conversion and –storage technologies rely on porous, heterogeneous, multi-scale materials for charge storage and transfer. Structure-property relations of these materials strongly depend on knowledge of three-dimensional morphologies. Overall, performance of electrochemical energy-conversion and storage devices depends on species transport through the porous materials, as well as, the materials response to thermal, electrochemical and mechanical inputs.

Three-dimensional imaging techniques, such as X-ray computed tomography (CT) offer unprecedented insight into the internal workings of these devices and corresponding material morphologies [2-12]. X-ray beam focused by a condenser or zone-plate onto a sample, is transmitted through the sample to reach the scintillator, with resulting image to be captured with charge-coupled device (CCD). The sample has to rotate at least 180 degrees to achieve sufficient information for 3D reconstruction. Synchrotron radiation transmitted with bright X-ray sources allows for nanometer spatial resolution [10, 13, 14], sub-second dynamic CT imaging [5, 15], and/or chemical information [14, 16] (Figure 1). As shown by Figure 1, chemical mapping is possible during CT imaging by using X-ray absorption spectroscopy (XAS). In this technique the X-ray energy of incident beam is scanned across an absorption edge of element of interest to understand its oxidation sate and other chemical properties. Optimization of spatial, temporal and chemical imaging dimensions is critical for electrochemical energy systems, as generally only two out of three can be sufficiently satisfied for a given experiment (Figure 1). For example, X-ray absorption near edge structure (XANES) technique requires longer times for imaging as one scans over fine energy resolution near absorption edge of an element limiting temporal resolution. With the current advances in X-ray imaging with micro-CT one is able to achieve ~1 μm resolution with sub-second scan [15]. To achieve nano-scale resolution specialized optics in form of either Fresnel zone plates or multilayer coated Si mirrors in Kirkpatrick-Baez (KB) configuration are needed to focus X-ray beam into a nanometer spot size [17]. Generally, additional optical elements on the beam's path reduce its intensity, what results in longer scan-time. To reach 30 nm resolution with Fresnel zone-plates configuration the scan-time is approximately 20 minutes. However, Yang et al. [18] have shown that with deep convolutional neural networks it is possible to reduce scan-time by an order of magnitude. Villanova et al. demonstrated break-through in pixel size vs. scan time with resolution <100 nm obtained in less than 10 s scan with KB mirrors set-up [17]. These developments happened in the last year and are extremely important for electrochemical energy-conversion and –storage systems, as they pave the way to *operando* experiments.

Less effort was put forward to develop modeling frameworks that interpret and complement imaging data to engineer better energy materials, components and devices. To date, most of the effort is focused on using 3D models to extract morphology-dependent effective transport properties from the X-ray CT data. These are effective diffusivity, thermal, electric and ionic conductivity, gas and liquid permeability. Current challenges are in bridging the scales from nano- to micro- and synergistic use of morphologies from nano and micro X-ray CT imaging. Building higher-fidelity models that are able to couple information from multiple imaging sources, or combine chemical, mechanical and morphological inputs is an additional challenge. [5, 19, 20, 21]. In this paper we provide an overview of integration of X-ray CT imaging data and models to synergistically correlate structure-property relations of energy materials and their behavior within energy devices. The main focus of the review is the literature data from the period of 2016 to 2018 with several key works prior to that.

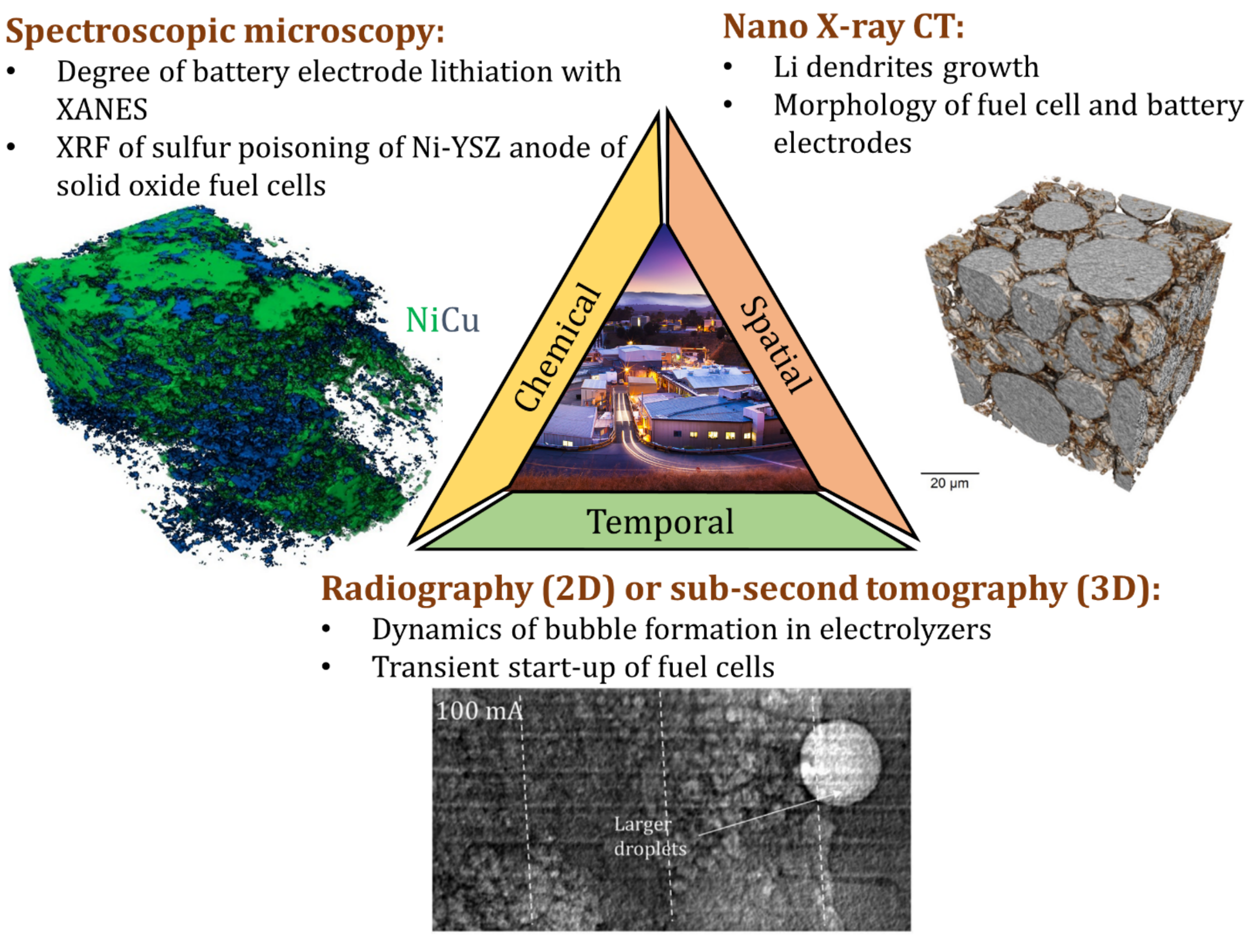

Figure 1. X-ray CT technique optimized along three parameters: chemical, spatial and temporal. The goal of the TXM to optimize these three parameters for a given experiment. Spectroscopic microscopy aims at quantifying chemical state of material in addition to 3D imaging. XANES and X-ray fluorescence (XRF) are two most commonly used techniques for spectroscopic imaging. Spatial dimension optimization enables visualizing <100 nm features, such as morphology of battery electrodes [11]. Reprinted with permission from [11], copyright 2017, Elsevier. Temporal dimension enables fast imaging to capture dynamic phenomena, such as oxygen bubbles evolution in electrolyzer with 100 ms exposure radiography-mode [5]. Reprinted with permission from [5], copyright 2018, Elsevier.

2. X-ray CT Imaging Studies for Electrochemical Energy Systems

One of the advantages of the X-ray CT is that it is an ambient technique and it enables studying *in-situ* and *operando* processes in electrochemical energy devices [2]. Wide spectrum of time and length scales can be accessed with hard X-rays from nano to millimeters and on temporal scale from hours to subseconds depending on the lab-scale or synchrotron beamline capabilities. *In-situ* observations of electrochemical system subjected to various driving forces, such as thermal, electrochemical, mechanical are extremely valuable as they can guide the design of energy materials [17]. *Operando* systems require complex sample holder designs to accommodate various inputs, such as electric fields, temperature, mechanical forces, gasses, relative humidity [12]. Table 1 outlines the advantages and disadvantages of *ex-situ*, *in-situ* and *operando* techniques. Broadly, X-ray CT studies of electrochemical energy systems can be quantified into four categories depending on experiment complexity and the target data acquisition:

(a) Quantifying materials morphology with *ex-situ* studies [4, 22-25]

(b) *In-situ* single or multiple driving forces to understand transport and degradation of materials (e.g. compression [7, 8, 26], thermal [27], water activity gradient [28],)

(c) *In-situ* simulated actual process of energy-conversion or –storage device with either limited other components or half-cell. [24, 29-33]

(d) *Operando* study of device behavior under electrochemical, thermal, mechanical stimuli. [5, 34-39]

Here we highlight each category with a representative study. Kok et al. used *ex-situ* nano X-ray CT to characterize the morphology of electrospun carbon fiber mats for redox flow-batteries [22]. Shum et al. studied the effect of thermal gradients on water distribution within porous carbon layers for fuel cells applications with *in-situ* setup [27]. Harry et al. used symmetric Li-metal battery to observe subsurface Li structures forming as the cell is cycled [32]. Finegan et al. used *operando* high-speed, micro X-ray CT to capture thermal runaway of batteries. [34]

Table 1. Pros and cons for ex-situ, in-situ and operando techniques in terms of the final information obtained and difficulty of the technique.

Technique	**Ex situ**	**In situ**	**Operando**

Nano and micro X-ray CT Chemical mapping	Pros: Ease to handle the sample; finite dimensions of sample; can extract morphology	Pros: Well-defined driving force; can extract morphology and additional dimension; sample holders are relatively easy to handle	Pros: Physics phenomena and material behavior under operating condition; multiple stimuli
	Cons: Limited information as no stimuli	Cons: One or two driving forces; not actual conditions; sample can fall outside FOV if holder is large	Cons: Beam damage as more components present; sample holders are very difficult to make; sample stability
Dynamic imaging	Pros: Ease to mount and handle sample; can rotate fast and multiple revolutions	Pros: Well-defined driving force; sample holders without tubing; fast rotation possible	Pros: Multiple stimuli; dynamic behavior of full systems under study
	Cons: dynamic studies are generally not useful for ex-situ samples	Cons: One or two driving forces	Cons: Need for slip-ring as tubing and electric contacts need to rotate multiple revolutions and as fast as the rotating stage does; challenging sample-holder design to accommodate high signal to noise ratio.

Combined chemical information (via XAS or XRF) with X-ray CT or X-ray radiography is a new paradigm in energy-conversion and –storage characterization. During electrochemical experiment chemical mapping can be used to differentiate elements within fuel cell catalyst layer, Li intercalation into active material, degradation phenomena, batteries state-of-charge, oxidation state of active material and many more. For electrochemical energy-conversion and –storage a combination of TXM and XAS, and XRF proved to be useful to understand:

(a) Batteries: over-lithiation in cathode materials, where particles undergo significant cracking [16]; difference in micrometer cathode particles state-of-charge [40, 41]; salt distribution in electrolyte [19].

(b) Fuel cells: Pt migration during degradation in polymer electrolyte fuel cells (PEFCs) with operando CT and XANES [42]; distinction of Ni phase in solid oxide fuel cell [43].

Outside XAS and XRF, *in situ* Bragg coherent diffractive imaging (CDI) is a promising technique to be coupled to TXM to map three-dimensional strain in metal oxide particles within operating battery [44].

3. Model inputs from imaging data

In electrochemical energy-conversion and –storage X-ray CT serves mostly as a tool to extract morphological information from the *ex-situ* studies [45, 46]. As shown by Figure 2 image stack obtained with X-ray CT is thresholded (with Otsu or other algorithms) to obtain morphologically separate phases, such as solid and void. This procedure is possible because of different grey-scale values of solid and void, and the separation of phases is achieved by selecting a threshold value on grey-scale histogram. Further, as shown by Figure 2 computational meshes are generated on the representative elementary volumes (REV) to couple the morphology with species transport and current densities [47]. The following type of data is commonly extracted from images that can be used as an input to various types of models:

(a) Morphological parameters such as porosity, tortuosity, size-distributions, connectivity, surface area etc. Effective geometrical transport properties based on morphological information [7, 48-52].

(b) Transport properties that are not directly extracted from morphological data [5, 19, 20].

(c) Chemical or mechanical information [53] [54-56].

Currently, the first category is the most dominant in terms of model inputs.

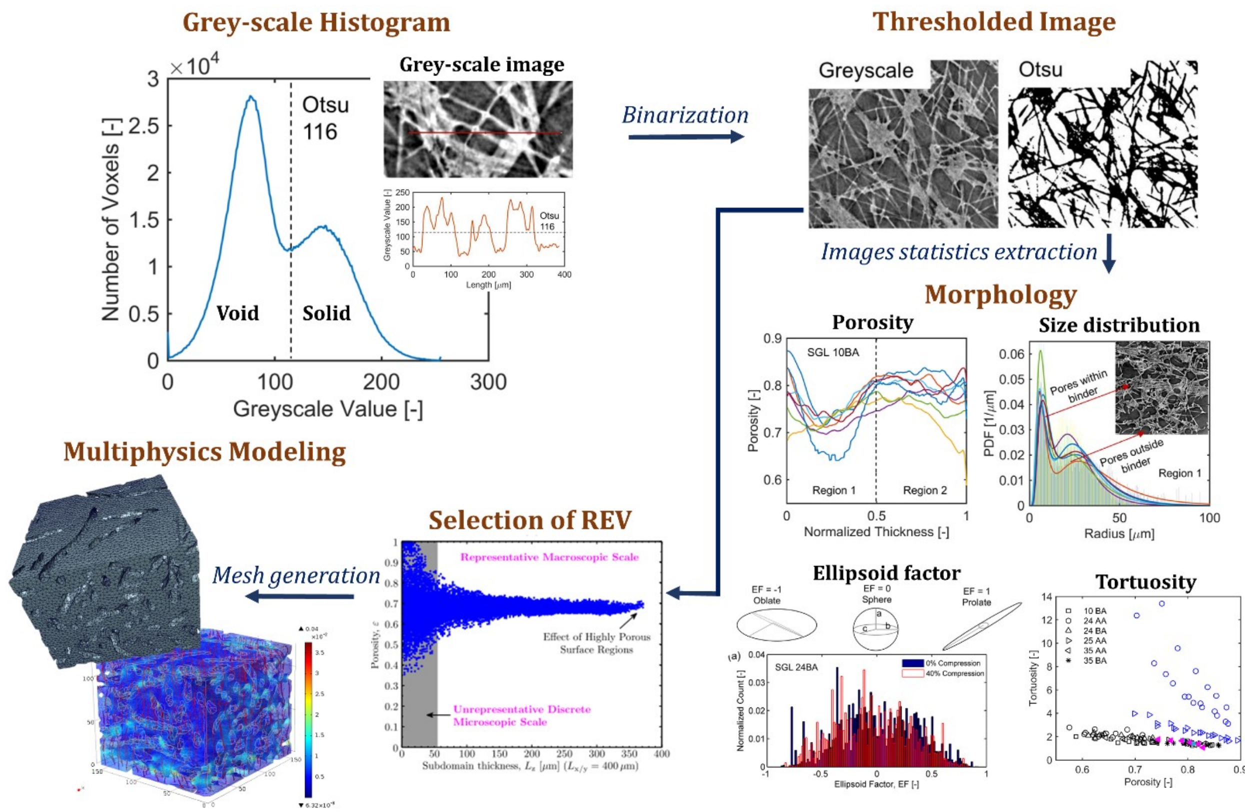

Figure 2. X-ray CT image analysis and data extraction flow-chart. Grey-scale histogram is used to convert grey-scale images into thresholded image-stack. From this binarized image-stack morphological information is extracted, such as porosity, tortuosity, size distribution and ellipsoid factor [7]. Reprinted with permission from [7], copyright 2016 Elsevier. Representative elementary volume (REV) is also selected from the thresholded image to perform computational modeling [57]. Reprinted with permission from [57], copyright 2016 Elsevier. For modeling a geometric surface or volumetric mesh over the computational domain is created.

4. Modeling frameworks for electrochemical energy technologies

X-ray CT images are used as direct numerical domains for computational simulations. Through using X-ray CT data as modeling computational domains understanding of morphological properties on multiphysics can be obtained. Most of the electrochemical porous materials are of hierarchical nature [58], requiring scale-bridging frameworks and imaging data inputs from both micro and nano-scales. For transport simulations through the porous domains obtained through the X-ray CT, direct numerical simulation methods include: computational fluid dynamics (CFD) [59, 60], Lattice-Boltzmann (LB) [48, 61] or pore-network models (PNM). As shown in Figure 2 it is critical to select a modeling domain that is representative of the overall porous media studied. Studies aimed at identifying the minimum volume of the REV are necessary and serve as intermediate step between imaging and actual multiphysics simulations. [48, 57, 62, 63].

Here, several of the critical modeling frameworks are outlined. Cetinbas et al. [64] used inputs from multi-modal imaging techniques (X-ray CT and transmission electron microscopy) to create multi-scale domain and studied transport in PEFC catalyst layers using CFD method. Landesfeind et al. used battery electrode tortuosity values form the X-ray CT data to compare those from electrochemical impedance spectroscopy method [23]. Torayev et al. used PNM to understand interconnectivity of pores for Li-oxygen cathode and electrochemical performance (galvanostatic discharge profiles) dependence on cathode morphology [65]. Kashkooli et al. performed mechanical simulations on $LiMn_2O_4$ electrodes obtained with nano X-ray CT. [47] Kashkooli et al. also used X-ray absorption and phase-contrast imaging to extract active domain and carbon binder of $Li_4Ti_5O_{12}$ cathode and performed CFD simulations for both transport and electrochemistry. Latz and Zausch [66] coupled microscale and cell scale levels for studying thermal behavior of lithium ion batteries, where localized heat distribution is solved with 3D microstructure-resolved simulations, and overall continuum-scale model resolves heat distribution.

5. Conclusions and Future Outlook

Currently, imaging data generation in electrochemical energy systems outruns data utilization. Historically, analytical tools and CFD volume-averaged models provided sufficient information for engineering energy-conversion and –storage materials and devices. However, as durability, stability, safety concerns became more pronounced, a need emerged for complex models that capture micro- and nano-scales phenomena in a holistic way. Industrial deployment of energy technologies requires most optimal and cost-effective designs that can no longer be predicted with analytic or volume-averaged CFD models. Over the next several years we will witness the rise of multi-scale modeling frameworks that feed of multi-modal images. Critical to the development of these frameworks are upscaling algorithms to convey information from nano- to macro-scales. These algorithms are widely available in geo-sciences community [67], where transport coupled reactions in porous rocks is studied. The tremendous progress of multi-scale modeling in geo-sciences community is due to their samples complex morphology and chemical composition, where conventional analytical and numerical tools are not easily applicable. Figure 3 summarizes the existing frameworks in electrochemical energy community that are developed to incorporate X-ray CT information. Figure 3a shows thermal transport resolved with direct numerical simulations (DNSs) on microstructure obtained with X-ray CT and upscaled to continuum-level model. To resolve fine water transport in porous domains of fuel cells PNM is used and the results are upscaled into continuum-level cell model (Figure 3b). Alternatively, two length-scales can be bridged within the either PNMs or DNSs by incorporating finer meshes in sub computational cells (Figure 3c and d). With improved computational tools, high fidelity models can be developed with plurality of inputs from imaging sources to guide the design of materials for energy technologies. The models will have to accommodate not only the morphological information but also various chemical and mechanical inputs, a field of modeling that is still at its infancy.

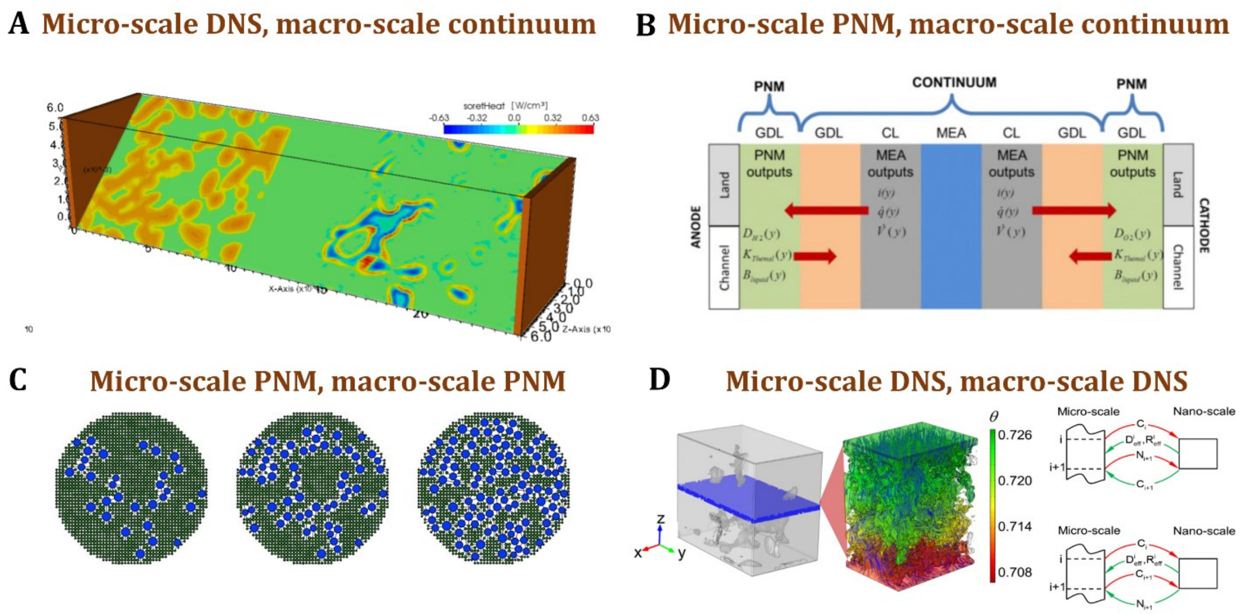

Figure 3. Examples of upscaling frameworks in electrochemical energy systems. A) Micro-scale DNS coupled to continuum cell-level model for batteries thermal distribution [66] (open source). B) PNM coupled to continuum-level model [69], (Reprinted with permission from [69], copyright 2015 Elsevier). C) PNM with two levels of meshing [68], (Reprinted with permission from [68], copyright 2017 Elsevier) D) and DNS on both scales (Unpublished data).

Acknowledgments

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References and recommended reading

*Paper of special interest
**Paper of outstanding interest

[1] S.J. Davis, N.S. Lewis, M. Shaner, S. Aggarwal, D. Arent, I.L. Azevedo, S.M. Benson, T. Bradley, J. Brouwer, Y.-M. Chiang, Net-zero emissions energy systems, Science 360 (2018) eaas9793.
[2] G.J. Nelson, Z.K. van Zandt, P.D. Jibhakate, Direct X-Ray Imaging as a Tool for Understanding Multiphysics Phenomena in Energy Storage, Journal of Electrochemical Energy Conversion and Storage 13 (2016) 030802-030802-030805.
[3] R.W. Atkinson, Y. Garsany, B.D. Gould, K.E. Swider-Lyons, I.V. Zenyuk, The Role of Compressive Stress on Gas Diffusion Media Morphology and Fuel Cell Performance, ACS Applied Energy Materials 1 (2018) 191-201.
[4] R. Carter, B. Huhman, C.T. Love, I.V. Zenyuk, X-ray computed tomography comparison of individual and parallel assembled commercial lithium iron phosphate batteries at end of life after high rate cycling, Journal of Power Sources 381 (2018) 46-55.

[5] E. Leonard, A.D. Shum, S. Normile, D.C. Sabarirajan, D.G. Yared, X. Xiao, I.V. Zenyuk, Operando X-ray tomography and sub-second radiography for characterizing transport in polymer electrolyte membrane electrolyzer, Electrochimica Acta 276 (2018) 424-433.
[6] I.V. Zenyuk, A. Lamibrac, J. Eller, D.Y. Parkinson, F. Marone, F.N. Büchi, A.Z. Weber, Investigating Evaporation in Gas Diffusion Layers for Fuel Cells with X-ray Computed Tomography, The Journal of Physical Chemistry C 120 (2016) 28701-28711.
[7] I.V. Zenyuk, D.Y. Parkinson, L.G. Connolly, A.Z. Weber, Gas-diffusion-layer structural properties under compression via X-ray tomography, Journal of Power Sources 328 (2016) 364-376.
[8] I.V. Zenyuk, D.Y. Parkinson, G. Hwang, A.Z. Weber, Probing water distribution in compressed fuel-cell gas-diffusion layers using X-ray computed tomography, Electrochemistry Communications 53 (2015) 24-28.
[9] I.V. Zenyuk, A.Z. Weber, Understanding Liquid-Water Management in PEFCs Using X-Ray Computed Tomography and Modeling, ECS Transactions 69 (2015) 1253-1265.
[10] D.S. Eastwood, P.M. Bayley, H.J. Chang, O.O. Taiwo, J. Vila-Comamala, D.J.L. Brett, C. Rau, P.J. Withers, P.R. Shearing, C.P. Grey, P.D. Lee, Three-dimensional characterization of electrodeposited lithium microstructures using synchrotron X-ray phase contrast imaging, Chemical Communications 51 (2015) 266-268.
[11] J. Gelb, D.P. Finegan, D.J. Brett, P.R. Shearing, Multi-scale 3D investigations of a commercial 18650 Li-ion battery with correlative electron-and X-ray microscopy, Journal of Power Sources 357 (2017) 77-86.
[12] R. Jervis, L.D. Brown, T.P. Neville, J. Millichamp, D.P. Finegan, T.M. Heenan, D.J. Brett, P.R. Shearing, Design of a miniature flow cell for in situ x-ray imaging of redox flow batteries, Journal of Physics D: Applied Physics 49 (2016) 434002.
[13] P. Pietsch, V. Wood, X-Ray Tomography for Lithium Ion Battery Research: A Practical Guide, Annual Review of Materials Research 47 (2017) 451-479.
[14] W.M. Harris, J.J. Lombardo, G.J. Nelson, B. Lai, S. Wang, J. Vila-Comamala, M. Liu, M. Liu, W.K. Chiu, Three-dimensional microstructural imaging of sulfur poisoning-induced degradation in a Ni-YSZ anode of solid oxide fuel cells, Scientific reports 4 (2014) 5246.
[15] J. Eller, F. Marone, F.N. Büchi, Operando sub-second tomographic imaging of water in pefc gas diffusion layers, ECS Transactions 69 (2015) 523-531.

*[16] J.N. Weker, A.M. Wise, K. Lim, B. Shyam, M.F. Toney, Operando Spectroscopic Microscopy of LiCoO2 Cathodes Outside Standard Operating Potentials, Electrochimica Acta 247 (2017) 977-982.
Combination of X-ray radiography and XANES was used to study Li intercalation into batteries cathode particle during process of overlithiation. Significant cracking is observed during overlithiation.

**[17] J. Villanova, R. Daudin, P. Lhuissier, D. Jauffrès, S. Lou, C.L. Martin, S. Labouré, R. Tucoulou, G. Martínez-Criado, L. Salvo, Fast in situ 3D nanoimaging: a new tool for dynamic characterization in materials science, Materials Today 20 (2017) 354-359.
Using specialized KB mirrors optics at the synchrotron beamline the authors were able to achieve nanometer X-ray CT resolution imaging with ultra-fast scan-time of seconds for in-situ setups. This study enables nanoscale dynamic imaging of electrochemical systems under realistic conditions

**[18] X. Yang, V. De Andrade, W. Scullin, E.L. Dyer, N. Kasthuri, F. De Carlo, D. Gürsoy, Low-dose x-ray tomography through a deep convolutional neural network, Scientific reports 8 (2018) 2575.
Using standard Fresnel zone plates synchrotron nano X-ray CT beamline the authors were able to achieve a ten fold reduction in imaging time with convolutional neural networks and lower number of projections. Lower imaging time reduces X-ray dose onto electrochemical materials and enables quasi-dyanmic studies.

**[19] D. Takamatsu, A. Yoneyama, Y. Asari, T. Hirano, Quantitative Visualization of Salt Concentration Distributions in Lithium-Ion Battery Electrolytes during Battery Operation Using X-ray Phase Imaging, Journal of the American Chemical Society 140 (2018) 1608-1611.
First-time ever X-ray radiography is used to quantify salt distribution in electrolyte in lithium-ion battery under operating conditions. Because electrolyte material is soft, X-ray phase-contrast imaging is used. This technique opens opportunities for evaluating electrolytes with hard X-rays of many electrochemical systems.

[20] S.J. Normile, D.C. Sabarirajan, O. Calzada, V. De Andrade, X. Xiao, P. Mandal, D.Y. Parkinson, A. Serov, P. Atanassov, I.V. Zenyuk, Direct observations of liquid water formation at nano- and micro-scale in platinum group metal-free electrodes by operando X-ray computed tomography, Materials Today Energy 9 (2018) 187-197.
[21] M. Wolf, B.M. May, J. Cabana, Visualization of Electrochemical Reactions in Battery Materials with X-ray Microscopy and Mapping, Chemistry of Materials 29 (2017) 3347-3362.
[22] M.D. Kok, R. Jervis, D. Brett, P.R. Shearing, J.T. Gostick, Insights into the Effect of Structural Heterogeneity in Carbonized Electrospun Fibrous Mats for Flow Battery Electrodes by X-Ray Tomography, Small 14 (2018) 1703616.
[23] J. Landesfeind, M. Ebner, A. Eldiven, V. Wood, H.A. Gasteiger, Tortuosity of Battery Electrodes: Validation of Impedance-Derived Values and Critical Comparison with 3D Tomography, Journal of The Electrochemical Society 165 (2018) A469-A476.
[24] O.O. Taiwo, M. Loveridge, S.D. Beattie, D.P. Finegan, R. Bhagat, D.J.L. Brett, P.R. Shearing, Investigation of cycling-induced microstructural degradation in silicon-based electrodes in lithium-ion batteries using X-ray nanotomography, Electrochimica Acta 253 (2017) 85-92.
[25] F. Shen, M.B. Dixit, X. Xiao, K.B. Hatzell, Effect of Pore Connectivity on Li Dendrite Propagation within LLZO Electrolytes Observed with Synchrotron X-ray Tomography, ACS Energy Letters 3 (2018) 1056-1061.
[26] R. Jervis, M.D. Kok, T.P. Neville, Q. Meyer, L.D. Brown, F. Iacoviello, J.T. Gostick, D.J. Brett, P.R. Shearing, In situ compression and X-ray computed tomography of flow battery electrodes, Journal of Energy Chemistry (2018).

*[27] A.D. Shum, D.Y. Parkinson, X. Xiao, A.Z. Weber, O.S. Burheim, I.V. Zenyuk, Investigating Phase-Change-Induced Flow in Gas Diffusion Layers in Fuel Cells with X-ray Computed Tomography, Electrochimica Acta 256 (2017) 279-290.
The authors used X-ray CT to observe water distribution within carbon materials used in fuel cells. Simultaneous 3D morphology, water distribution and measuremetns of thermal conductivity and compression were obtained in this single experimental set-up.

[28] G.S. Hwang, D.Y. Parkinson, A. Kusoglu, A.A. MacDowell, A.Z. Weber, Understanding water uptake and transport in nafion using x-ray microtomography, ACS Macro Letters 2 (2013) 288-291.
[29] S. Frisco, D.X. Liu, A. Kumar, J.F. Whitacre, C.T. Love, K.E. Swider-Lyons, S. Litster, Internal Morphologies of Cycled Li-Metal Electrodes Investigated by Nano-Scale Resolution X-ray Computed Tomography, ACS applied materials & interfaces 9 (2017) 18748-18757.
[30] O.O. Taiwo, D.P. Finegan, J. Paz-Garcia, D.S. Eastwood, A. Bodey, C. Rau, S. Hall, D.J. Brett, P.D. Lee, P.R. Shearing, Investigating the evolving microstructure of lithium metal electrodes in 3D using X-ray computed tomography, Physical Chemistry Chemical Physics 19 (2017) 22111-22120.
[31] D. Devaux, K.J. Harry, D.Y. Parkinson, R. Yuan, D.T. Hallinan, A.A. MacDowell, N.P. Balsara, Failure Mode of Lithium Metal Batteries with a Block Copolymer Electrolyte Analyzed by X-Ray Microtomography, Journal of The Electrochemical Society 162 (2015) A1301-A1309.
[32] K.J. Harry, D.T. Hallinan, D.Y. Parkinson, A.A. MacDowell, N.P. Balsara, Detection of subsurface structures underneath dendrites formed on cycled lithium metal electrodes, Nat Mater 13 (2014) 69-73.
[33] K.J. Harry, X. Liao, D.Y. Parkinson, A.M. Minor, N.P. Balsara, Electrochemical Deposition and Stripping Behavior of Lithium Metal across a Rigid Block Copolymer Electrolyte Membrane, Journal of The Electrochemical Society 162 (2015) A2699-A2706.

*[34] D.P. Finegan, M. Scheel, J.B. Robinson, B. Tjaden, I. Hunt, T.J. Mason, J. Millichamp, M. Di Michiel, G.J. Offer, G. Hinds, D.J.L. Brett, P.R. Shearing, In-operando high-speed tomography of lithium-ion batteries during thermal runaway, Nature Communications 6 (2015) 6924.
The authors used operando dynamic X-ray CT imaging of actual battery to capture thermal runaway. This study combines dynamic studies with morphological information and also information on betteries degradation, generating possible mulitple inputs into models.

[35] S.J. Normile, D.C. Sabarirajan, O. Calzada, V. De Andrade, X. Xiao, P. Mandal, D.Y. Parkinson, A. Serov, P. Atanassov, I.V. Zenyuk, Direct observations of liquid water formation at nano-and micro-scale in platinum group metal-free electrodes by operando X-ray computed tomography, Materials Today Energy 9 (2018) 187-197.
[36] J. Eller, J. Roth, F. Marone, M. Stampanoni, F.N. Büchi, Operando Properties of Gas Diffusion Layers: Saturation and Liquid Permeability, Journal of The Electrochemical Society 164 (2017) F115-F126.
[37] F. Sun, M. Osenberg, K. Dong, D. Zhou, A. Hilger, C.J. Jafta, S. Risse, Y. Lu, H. Markötter, I. Manke, Correlating Morphological Evolution of Li Electrodes with Degrading Electrochemical Performance of Li/LiCoO2 and Li/S Battery Systems: Investigated by Synchrotron X-ray Phase Contrast Tomography, ACS Energy Letters 3 (2018) 356-365.
[38] F. Sun, R. Moroni, K. Dong, H. Markötter, D. Zhou, A. Hilger, L. Zielke, R. Zengerle, S. Thiele, J. Banhart, Study of the Mechanisms of Internal Short Circuit in a Li/Li Cell by Synchrotron X-ray Phase Contrast Tomography, ACS Energy Letters 2 (2016) 94-104.
[39] P. Pietsch, D. Westhoff, J. Feinauer, J. Eller, F. Marone, M. Stampanoni, V. Schmidt, V. Wood, Quantifying microstructural dynamics and electrochemical activity of graphite and silicon-graphite lithium ion battery anodes, Nature Communications 7 (2016) 12909.

[40] W.E. Gent, Y. Li, S. Ahn, J. Lim, Y. Liu, A.M. Wise, C.B. Gopal, D.N. Mueller, R. Davis, J.N. Weker, Persistent State-of-Charge Heterogeneity in Relaxed, Partially Charged Li1−xNi1/3Co1/3Mn1/3O2 Secondary Particles, Advanced Materials 28 (2016) 6631-6638.
[41] J. Nelson Weker, Y. Li, R. Shanmugam, W. Lai, W.C. Chueh, Tracking Non-Uniform Mesoscale Transport in LiFePO4 Agglomerates During Electrochemical Cycling, ChemElectroChem 2 (2015) 1576-1581.
[42] H. Matsui, N. Ishiguro, T. Uruga, O. Sekizawa, K. Higashi, N. Maejima, M. Tada, Operando 3D Visualization of Migration and Degradation of a Platinum Cathode Catalyst in a Polymer Electrolyte Fuel Cell, Angewandte Chemie International Edition 56 (2017) 9371-9375.
[43] Y.-c. Karen Chen-Wiegart, W.M. Harris, J.J. Lombardo, W.K. Chiu, J. Wang, Oxidation states study of nickel in solid oxide fuel cell anode using x-ray full-field spectroscopic nano-tomography, Applied Physics Letters 101 (2012) 253901.

*[44] A. Ulvestad, A. Singer, J. Clark, H. Cho, J. Kim, R. Harder, J. Maser, Y. Meng, O. Shpyrko, Topological defect dynamics in operando battery nanoparticles, Science 348 (2015) 1344-1347.
Novel imaging techniques that provide additional physics are especially useful. In this study, in situ Bragg coherent diffractive imaging (CDI) was used with 3D imaging to map three-dimensional strain in metal oxide particles within operating battery.

[45] Z. Liu, K. Han, Y.-c.K. Chen-Wiegart, J. Wang, H.H. Kung, J. Wang, S.A. Barnett, K.T. Faber, X-ray nanotomography analysis of the microstructural evolution of LiMn2O4 electrodes, Journal of Power Sources 360 (2017) 460-469.
[46] C. Zhao, T. Wada, V. De Andrade, D. Gürsoy, H. Kato, Y.-c.K. Chen-Wiegart, Imaging of 3D morphological evolution of nanoporous silicon anode in lithium ion battery by X-ray nano-tomography, Nano Energy 52 (2018) 381-390.
[47] A.G. Kashkooli, E. Foreman, S. Farhad, D.U. Lee, K. Feng, G. Lui, V. De Andrade, Z. Chen, Morphological and Electrochemical Characterization of Nanostructured Li4Ti5O12 Electrodes Using Multiple Imaging Mode Synchrotron X-ray Computed Tomography, Journal of The Electrochemical Society 164 (2017) A2861-A2871.

*[48] P.A. García-Salaberri, I.V. Zenyuk, A.D. Shum, G. Hwang, M. Vera, A.Z. Weber, J.T. Gostick, Analysis of representative elementary volume and through-plane regional characteristics of carbon-fiber papers: diffusivity, permeability and electrical/thermal conductivity, International Journal of Heat and Mass Transfer 127 (2018) 687-703.
A study dedicated to identifying REV of inhomogeneous, thin porous media (gas diffusion layer) commonly used in polymer electrolyte fuel cell community. Various effective property metrics were used to correctly identify the REV.

[49] T. Li, H. Kang, X. Zhou, C. Lim, B. Yan, V. De Andrade, F. De Carlo, L. Zhu, Three-Dimensional Reconstruction and Analysis of All-Solid Li-Ion Battery Electrode Using Synchrotron Transmission X-ray Microscopy Tomography, ACS Applied Materials & Interfaces 10 (2018) 16927-16931.
[50] A. Roy, M.R. Talarposhti, S.J. Normile, I.V. Zenyuk, V. De Andrade, K. Artyushkova, A. Serov, P. Atanassov, Nickel–copper supported on a carbon black hydrogen oxidation catalyst integrated into an anion-exchange membrane fuel cell, Sustainable Energy & Fuels (2018).

[51] S. Kabir, K. Lemire, K. Artyushkova, A. Roy, M. Odgaard, D. Schlueter, A. Oshchepkov, A. Bonnefont, E. Savinova, D.C. Sabarirajan, Platinum group metal-free NiMo hydrogen oxidation catalysts: high performance and durability in alkaline exchange membrane fuel cells, Journal of Materials Chemistry A 5 (2017) 24433-24443.
[52] W.K. Epting, J. Gelb, S. Litster, Resolving the Three-Dimensional Microstructure of Polymer Electrolyte Fuel Cell Electrodes using Nanometer-Scale X-ray Computed Tomography, Advanced Functional Materials 22 (2012) 555-560.
[53] S. Müller, P. Pietsch, B.-E. Brandt, P. Baade, V. De Andrade, F. De Carlo, V. Wood, Quantification and modeling of mechanical degradation in lithium-ion batteries based on nanoscale imaging, Nature Communications 9 (2018) 2340.
[54] J. Lim, Y. Li, D.H. Alsem, H. So, S.C. Lee, P. Bai, D.A. Cogswell, X. Liu, N. Jin, Y.-s. Yu, Origin and hysteresis of lithium compositional spatiodynamics within battery primary particles, Science 353 (2016) 566-571.
[55] R.T. White, A. Wu, M. Najm, F.P. Orfino, M. Dutta, E. Kjeang, 4D in situ visualization of electrode morphology changes during accelerated degradation in fuel cells by X-ray computed tomography, Journal of Power Sources 350 (2017) 94-102.
[56] P. Mandal, B.K. Hong, J.-G. Oh, S. Litster, Understanding the voltage reversal behavior of automotive fuel cells, Journal of Power Sources 397 (2018) 397-404.
[57] P.A. García-Salaberri, J.T. Gostick, G. Hwang, A.Z. Weber, M. Vera, Effective diffusivity in partially-saturated carbon-fiber gas diffusion layers: Effect of local saturation and application to macroscopic continuum models, Journal of Power Sources 296 (2015) 440-453.
[58] A. Serov, A.D. Shum, X. Xiao, V. De Andrade, K. Artyushkova, I.V. Zenyuk, P. Atanassov, Nano-structured platinum group metal-free catalysts and their integration in fuel cell electrode architectures, Applied Catalysis B: Environmental (2017).
[59] M. Sabharwal, L. Pant, A. Putz, D. Susac, J. Jankovic, M. Secanell, Analysis of catalyst layer microstructures: From imaging to performance, Fuel Cells 16 (2016) 734-753.
[60] S.M. Moosavi, M. Niffeler, J. Gostick, S. Haussener, Transport characteristics of saturated gas diffusion layers treated with hydrophobic coatings, Chemical Engineering Science 176 (2018) 503-514.
[61] P. Satjaritanun, J. Weidner, S. Hirano, Z. Lu, Y. Khunatorn, S. Ogawa, S. Litster, A. Shum, I. Zenyuk, S. Shimpalee, Micro-scale analysis of liquid water breakthrough inside gas diffusion layer for PEMFC using X-ray computed tomography and Lattice Boltzmann Method, Journal of The Electrochemical Society 164 (2017) E3359-E3371.
[62] P.A. García-Salaberri, G. Hwang, M. Vera, A.Z. Weber, J.T. Gostick, Effective diffusivity in partially-saturated carbon-fiber gas diffusion layers: Effect of through-plane saturation distribution, International Journal of Heat and Mass Transfer 86 (2015) 319-333.
[63] A.G. Kashkooli, A. Amirfazli, S. Farhad, D.U. Lee, S. Felicelli, H.W. Park, K. Feng, V. De Andrade, Z. Chen, Representative volume element model of lithium-ion battery electrodes based on X-ray nano-tomography, Journal of Applied Electrochemistry 47 (2017) 281-293.

**[64] F.C. Cetinbas, R.K. Ahluwalia, N. Kariuki, V. De Andrade, D. Fongalland, L. Smith, J. Sharman, P. Ferreira, S. Rasouli, D.J. Myers, Hybrid approach combining multiple characterization techniques and simulations for microstructural analysis of proton exchange membrane fuel cell electrodes, Journal of Power Sources 344 (2017) 62-73.
The authors used multi-modal imaging as inputs to generale stoichastic catalyst layer of the polymer electrolyte fuel cells. This is one of the first attempts in fuel cell community to use scale-

bridging to create multi-scale morphology of the computational domain. CFD calculations were run on the meshed domain to obtain effective properties.

[65] A. Torayev, A. Rucci, P.C.M.M. Magusin, A. Demortière, V. De Andrade, C.P. Grey, C. Merlet, A.A. Franco, Stochasticity of Pores Interconnectivity in Li–O2 Batteries and its Impact on the Variations in Electrochemical Performance, The Journal of Physical Chemistry Letters 9 (2018) 791-797.

**[66] A. Latz, J. Zausch, Multiscale modeling of lithium ion batteries: thermal aspects, Beilstein Journal of Nanotechnology 6 (2015) 987-1007.
One of the first multi-scale modelign attempts to incorporate micro-structure into cell-level model. The authors studied thermal behavior of lithium ion batteries by resolving localized heat distribution with 3D microstructure simulations, and overall heat distribution with continuum model.

[67] A.Q. Raeini, M.J. Blunt, B. Bijeljic, Direct simulations of two-phase flow on micro-CT images of porous media and upscaling of pore-scale forces, Advances in Water Resources 74 (2014) 116-126.
[68] M.A. Sadeghi, M. Aghighi, J. Barralet, J.T. Gostick, Pore network modeling of reaction-diffusion in hierarchical porous particles: The effects of microstructure, Chemical Engineering Journal 330 (2017) 1002-1011.

*[69] I.V. Zenyuk, E. Medici, J. Allen, A.Z. Weber, Coupling continuum and pore-network models for polymer-electrolyte fuel cells, International Journal of Hydrogen Energy 40 (2015) 16831-16845.
One of the first attempts in fuel cell community to bridge cell-level continuum model and discrete PNM, which resolved only one porous media component within the cell. The PNM was effective at predicting water distribution in the gas diffusion layer.