Bridging length scales in organic mixed ionic-electronic conductors through internal strain and mesoscale dynamics

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Abstract

Understanding structural and dynamic properties of disordered systems at the mesoscale is crucial. This is particularly important in organic mixed ionic-electronic conductors (OMIECs), which undergo significant and complex structural changes when operated in electrolyte. In this study, we investigate the mesoscale strain, reversibility, and dynamics of a model OMIEC material under external electrochemical potential using operando X-ray photon correlation spectroscopy. Our results reveal strain and structural hysteresis depend on the sample's cycling history, establishing a comprehensive kinetic sequence bridging the macroscopic and microscopic behaviors of OMIECs. Furthermore, we uncover equilibrium and non-equilibrium dynamics of charge carriers and material doping states, highlighting the unexpected coupling between charge carrier dynamics and mesoscale order. These findings advance our understanding of the structure-dynamics-

function relationships in OMIECs, opening pathways for designing and engineering materials with improved performance and functionality in non-equilibrium states during device operation.

Main

Organic mixed ionic-electronic conductors (OMIECs) show promise in broad application areas, including energy storage, generation, and power electronics[1], neuromorphic computing[2-4], and biosensors and bioelectronics[5-7]. Even with remarkable progress in materials, the underlying structure-function relationships that promote efficient conduction of both ionic and electronic charge species are poorly understood. Often operating in aqueous electrolytes, OMIEC materials typically undergo large structural changes that depend on the electrochemical potential and device history, but the lack of compatible operando structural techniques across the relevant length and time scales has limited overall understanding of the physical processes of mixed conduction[8,9]. Recent work highlighted the unexpected and history-dependent molecular level structural changes in operando along with the associated limitations of ex-situ characterization[10-17]; however, the macroscopic film swelling/contraction[18,19] do not directly translate to changes in the intermolecular spacings in the crystalline domains[13,20]. These works suggested the mesoscale plays an important role in the functional properties[12,13,15]. Bridging this gap between macroscale and microscale would provide valuable insights into the fundamental properties, potential failure sites, and defects during electrochemical cycling that could ultimately contribute to the optimization of molecular and device design and long-term stability.

A widely used polymeric OMIEC material is poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS). Under operational conditions in aqueous electrolytes, there are fixed anionic species on the polyelectrolyte PSS, holes on the conjugated polymer PEDOT and extra mobile salt ions to maintain charge neutrality. The compositional control and commercial availability of PEDOT:PSS make it an ideal model system and a variety of methods exist to modify the mesostructure and performance of PEDOT:PSS. Notably, PEDOT:PSS can be post-treated with ethylene glycol (EG) to induce multi scale rearrangement[21,22] and treatment with strong acids will partially dissolve excess PSS and crystallize PEDOT to produce a highly conductive 3D fibral network[23-25], leading to a marked increase in electronic mobility and capacitance.

Here, we investigate the mesoscale structure-function relationships driving both equilibrium and non-equilibrium properties of acid-treated PEDOT:PSS in aqueous electrolytes using operando X-ray photon correlation spectroscopy (XPCS). XPCS uses coherent scattering patterns as a fingerprint of the system microstate, allowing a direct and quantitative measure of how a system evolves in both time and length scale[26,27]. Using these data, the estimated strain, dynamics, and the reversibility of devices during operation are combined with our previously reported multimodal characterization and kinetic sequences. This kinetic model includes a fast response portion associated with polarization, macroscale electronic charge transport, and slower mass transport/rheology relaxation[13,19]. By self-consistently combining these components, we demonstrate the unexpected coupling of charge carrier dynamics with mesoscale order. Strain and structural hysteresis are found to depend on the sample electrochemical cycling history under both adiabatic and non-adiabatic cycling conditions. Additionally, we detail the unexpected equilibrium and non-equilibrium self-dynamics of different charged states and charge carriers. The observed mesoscale self-dynamics are hypothesized to be the consequence of moving structural distortions of coupled electronic/ionic motions (e.g. polarons) diffusing in equilibrium. Under non-equilibrium conditions, the rapid generation of multicharged species (e.g. bipolarons) upon fast doping significantly modifies the time dynamics, resulting in a long-lived non-equilibrium process of domain coarsening[28]. These observations reveal new insights into the role of the mesoscale for mixed conduction and address a key knowledge gap regarding the role of structure-dynamics-function relationships of OMIEC materials and devices. Specifically, the results here provide a new understanding into the interaction and evolution of charge carrier species and the coupling of these features to the underlying mesoscale materials structure, solvation and device function both near and far from equilibrium. Furthermore, this understanding suggests new materials design rules and functionality through holistic control and engineering of non-equilibrium states during device operation.

Operando XPCS of OMIECs

XPCS is the X-ray analogue of dynamic light scattering and is traditionally used to investigate thermally-driven, time-dependent fluctuations of a system around an equilibrium state. By using a coherent X-ray incident beam, the resulting scattering patterns have an added fine structure resulting from the coherent interference of the scattered wavefronts known as speckles. These speckles are not visible with conventional incoherent X-ray sources and they encode additional information regarding the specific microstate of the system. The subsequent changes of these speckles are often quantified as a series of autocorrelation functions that estimate the characteristic time for the configurational change of a system at a particular length-scale[27,29-32]. These methods have been increasingly applied to study out-of-equilibrium process such as domain growth[33,34] and crosslinking[35-37]. Moreover, the development of analysis and experimental methods are enabling new measurement modalities. For example, recent advances have involved combining XPCS with *in situ* study of mechanical deformation in complex fluids to measure tiny strains under macroscopic stress relaxation[38,39].

For the operando XPCS study of thin-film OMIECs, we used a grazing incidence geometry that increased path-length through the sample and provided access to mesoscale structural information through the small angle scattering. A schematic of the "cone cell" adapted for grazing incidence XPCS (GIXPCS) is shown in **Fig. 1a**. This electrochemical cell features a cylindrical body with a tapered knife edge seal and re-designs to meet the rigidity and stability requirements essential for internal strain measurements. A representative GIXPCS scattering frame is shown in **Fig. 1b.** Beam damage is a serious concern during these measurements and additional discussion is presented in the **Methods section**.

Chemical potential induced strain

During operation, the device thickness varies with the applied chemical potential due to changes in the polymer configuration and the associated solvent/ion uptake. As detailed in Sutton et. al., XPCS data are well suited to estimating sample expansion and contraction through a detailed analysis (**Supplementary Note 1**) of the speckle displacements[40]. Requiring few assumptions, this strain analysis is applicable to many disordered, thick, rough, and heterogenous samples and offers advantages over more widely known methods including quartz crystal microbalance (QCM)[19], ellipsometry, and electrochemical strain microscopy (ESM)[41]. For example, the potential driven thickness change in OMIECs is commonly deduced from electrochemical quartz crystal microbalance (EQCM); however, this method relies on assumptions of the viscoelastic properties and mass transport rather than a direct thickness change. While the observed strains are quite subtle for the materials studied herein, the movement of the speckles is important for all subsequent analysis in this work. Furthermore, we note the estimated strains for all samples correspond to changes in sample thickness only (i.e. uniaxial strain normal to the substrate), as expected for rigidly adhered thin-films (**Supplementary Fig. 2**).

The operando strain and scattering intensity is shown in **Fig. 1c-j** & **2a-d** (and **Supplementary Fig. 4-5**) for acid treated PEDOT:PSS using both 100 mM NaCl and 100 mM RbBr electrolytes and two different electrochemical cycling profiles. Both potential ranges extended across the partly-dedoped (-0.6 V vs. Ag/AgCl), doped (0 V vs. Ag/AgCl), and overdoped (0.6 V vs. Ag/AgCl) states. These electrolytes have similar electrochemical behavior[19]; however, the increased electron density of Rb^+ and Br^- ions provides additional X-ray contrast that aids in the study of these systems. Generally, we observed minimal electrochemically induced strain when using a series of 0.1 V steps designed to approximate a CV shape (**Fig. 1i**) and similar results were observed for extended 0.1 V step experiments (**Supplementary Fig. 6**). However, the larger potential steps of 0.6 V appear to produce more complex behavior (**Fig. 1d-f**) on both short and long timescales. We will refer to the 0.1 V and 0.6 V step cycles hereafter as the adiabatic and non-adiabatic pathways, respectively. The difference in step magnitude behavior suggests the underlying processes depend on the magnitude of the excess chemical potential and not solely on the applied chemical potential, a perspective that will be useful throughout this work.

For the non-adiabatic transient experiments, the short timescale (i.e., on the order of the current transient) XPCS strain and intensity data appear closely associated with the optical spectroscopy and the expected ionic redistribution between crystalline and amorphous regions. The XPCS data were normalized by the device RC time constant and compared to our previously reported operando measurements as shown in **Fig. 2e-f** & **Supplementary Fig. 7**. From our previous EQCM report[19], the mass of the acid treated PEDOT:PSS film increased during the dedoping process with a net cation influx, while the film mass decreased during the redoping process with a net cation outflux. Surprisingly, the estimated strain and intensity from XPCS were not matched to these mass transients[19]. Instead, the estimated strain showed a short, immediate contraction of the film for both dedoping and redoping process. Detailed analysis suggests this is not due to a distribution of strain or a salt gradient through the film thickness (**Supplementary Fig. 8**). This strain feature instead followed the polaron absorption trends[13], implying that the initial strain was associated with changes in the polymer conformation and solvation of the charge carriers generated during fast polarization (**Fig. 2g-h**) and the subsequent crystalline lamella spacing change. The increase in scattered intensity was believed to follow the ions migrating into the crystalline fibers. In the dedoping process, the film strain reflected conformational changes facilitating the hole transfer at the same rate as ion migration into the crystalline fibers (**Fig. 2h-i**, **Table S1** & **Supplementary Note 2**). In the redoping process, the cations migrated out of the crystalline fibers and directly into the electrolyte as inferred by the bulk mass change. This migration led to a similar intermediate state as dedoping process (as discussed in **Supplementary Note 2**) and was then followed by a moderately slower hole transfer (**Supplementary Fig. 9**). These structural insights from the transient XPCS strain data combined with this complementary characterization highlight the complex interplay of electronic, ionic, and mass transport even at relatively short timescales.

Selected control experiments from ethylene glycol (EG) mixed PEDOT:PSS (**Supplementary Fig. 11**) and poly(benzimidazobenzo-phenanthroline) (BBL, **Supplementary Fig. 12**) have been included and illustrate how morphology modifies this strain behavior. Short timescale strain transients were not observed in either material. After an extended period, EG mixed PEDOT:PSS showed a gradual strain develop although BBL remained unchanged. These results suggest that high-performance homopolymers, such as poly(2-(3,3'-bis(2-(2-(2-methoxyethoxy)-ethoxy)ethoxy)ethoxy)-[2,2'-bithiophen]-5-yl)thieno[3,2-b]thiophene) (pg2T-TT), may similarly lack the initial strain spike during the fast polarization, but the details may depend on the system properties. In the case of aqueous NaCl, operando studies of pg2T-TT have shown small changes of the lamellar spacing and some degree of structural hysteresis between the doping and redoping process likely analogous to acid-crystallized PEDOT[15]. However, in an ionic liquid, the structural hysteresis of pg2T-TT is largely absent and may be attributed to a redistribution of the ionic species within the ordered structures[17].

Quantifying state reversibility at the mesoscale

The reversibility of the mesoscale structure can be assessed through relative changes of the speckles. Here, we calculate a correlation matrix C as a metric that estimates the degree of **similarity of the system to itself** at two different points in time. For the purposes herein, a suitable definition of the correlation matrix C is:

$$C(\boldsymbol{q}, t_1, t_2) = \frac{\langle I(\boldsymbol{q}, t_1) I(\boldsymbol{q}, t_2)\rangle_{\boldsymbol{q}}}{\langle I(\boldsymbol{q}, t_1)\rangle_{\boldsymbol{q}} \langle I(\boldsymbol{q}, t_2)\rangle_{\boldsymbol{q}}} \tag{1}$$

Where $\boldsymbol{q}$ is the scattering wave vector of a pixel in the scattering pattern, and I is the scattering intensity. The bracket $\langle \cdots \rangle_{\boldsymbol{q}}$ describes an average of correlations within a narrow $\boldsymbol{q}$ range with similar statistical properties. The correlation matrix C can be plotted as a 2D map - denoted as a "C map" - and is particularly useful for understanding equilibrium and non-equilibrium processes. Values of C greater than 1 imply that states are positively correlated, i.e. morphologically similar in detail at different times and a value equal to 1 indicates that the states are uncorrelated. These C maps can be influenced by strain[40], which tends to lower the degree of correlation. We further modified the C map definition to create "strain-corrected" C maps through shifting of relevant detector pixels where applicable, numerically correcting for the film expansion and contraction. For comparison, uncorrected C maps have been included in **Supplementary Fig. 13**, and a comparison of alignment methods have been included in **Supplementary Fig. 14**.

The strain-corrected C maps and electrochemical profiles demonstrate both applied electrochemical potential and history couple to structural self-similarity at the mesoscale (**Fig. 3**). The strain-corrected C map for adiabatic steps (**Fig. 3a**) appears coarsely divided into two regions and we labelled these states q and p for convenience. Correlations were highest within subregions qQ and pP of the C map and suggest a series of small changes of chemical potential within each state result in morphologies with a higher degree of self-similarity. Crossing the state transition boundary from q→p or p→q appears to introduce a measurable and reversible change in the structural self-similarity as indicated by the reduced C values in subregion qP. In contrast, the non-adiabatic process (**Fig. 3b & Supplementary Fig. 15)** showed a path dependent structural hysteresis. Here, we use o, r and h to represent the doped (or oxidized), partly dedoped (or reduced) and high doped states, respectively. Within each state of fixed chemical potential (subregions oO, rR, o`O`, hH, o``O``), we observed the highest degree of self-similarity; however, this similarity decreased between states, e.g. for o→r, subregion oR is reduced. Remarkably, the structural similarity of the system after going through the full electrochemical hysteresis cycle, pathway o→r→o`→h→o`` (subregion oO``), was higher than both partial cycles, pathway o→r→o` (subregion oO`) and o`→h→o`` (subregion o`O``). Thus, while the starting and ending chemical potentials are the same, the reversibility of the system state depends on its history.

Self-dynamics in equilibrium and non-equilibrium conditions

The enhanced contrast from the 100 mM RbBr electrolyte reveals both the equilibrium and non-equilibrium self-dynamics and their unexpected dependence on electrochemical potential changes. Strain corrected C maps from doped-to-partly-dedoped (o→r) and partly-dedoped-to-redoped (r →o`) voltage steps are shown in **Fig. 4a&d**. The behavior of these voltage steps revealed significant differences in the underlying physical processes.

The r→o` state transition showed the evolution of a long-lived and complex non-equilibrium state (**Fig. 4a**) that is well described by a coarsening process following phase separation of a mixture. After the voltage step and current transient, a small induction subregion with fast dynamics was observed. This induction subregion was followed by a fan-like subregion of progressively slowing fluctuations where the correlation functions are well described by a theoretical model[42-44] for time evolution of phase separating mixtures (**Fig. 4b&c)**. Physically, this model gives a method of scaling the dynamic evolution of domain sizes $R(t)$ (with an initial domain size kC) in non-equilibrium based on the time t from the initial state change:

$$R(t) = k\left(t^{\frac{1}{n}} + C\right) \tag{2}$$

Additional details of the model derivation and fitting methods are provided in the **Supplementary Note 3**. The fan-like subregion showed power-law scaling of the correlation times with an extracted order parameter of $n = 3$ (**Fig. 4f**). This value of the order parameter corresponds to the "Langevin Model B" system which describes phase separating mixtures with a conserved order parameter[28]. In the context of this OMIEC, this model suggests mesoscale dynamics are driven by the interaction of two distinct types of (potentially) mobile domains. The total volume of each domain type is fixed, and the average domain volume increases linearly with time.

In the case of an o→r transition, the system dynamics within the partly-dedoped state appeared to reach an equilibrium behavior on the timescale of the current transient (**Fig. 4d**). This equilibrium is characterized by the correlation time within the rR subregion being a function only of the time difference $\delta t = t_2 - t_1$. The strain corrected C map within the partly-dedoped region were fit to the previous model for comparison (simulated C map shown in **Fig. 4e)**, giving a time constant of ~500s (**Fig. 4f**, details in **Supplementary Note 4**).

The origin of the long-term equilibrium and non-equilibrium evolution

The origin of the scattering appears connected to several aspects of the mixed conduction processes at the mesoscale. At the simplest level, the mesoscale structure is a dynamic mixture of quasi-permanent paracrystalline and amorphous material. The material undergoes large structural changes that appear to be mostly reversible under electrochemical cycling as charges move through and transform the internal structure. These results are themselves remarkable; however, the additional observations of path dependent, and long-lived non-equilibrium states begin to suggest a more profound and critical connection to the underlying charge carrier species existence. Beginning with the fluctuations of the partly-dedoped state shown in the previous section, we hypothesize that these dynamics relate to the moving structural distortions of diffusing charge carrier species. The doped state is known to contain both polaron and bipolaron species while the partly-dedoped state primarily consists of neutral and polaron species. This assignment of the dynamics to the charge carriers - primarily polarons in the partly-dedoped state - implies coordinated motion of solvation shells, ions, and electrons occurring in equilibrium.

We anticipate that the equilibrium motion of charge carriers will rely on the local ionic mobility, the relative energetic barriers for both ionic and electronic species' motion, and the requisite solvation shells. These coordinated motions may have origins in local free volume fluctuations activating transport and we believe such fluctuations may be inferred through temperature-dependent measurements. These measurements are beyond the scope of this initial work, but the results here suggest this is likely to be a productive future research direction.

The asymmetry in the dedoping transition (o→r) and the exceptionally long non-equilibrium period after redoping (r→o’) suggests bipolaron dynamics are far from trivial. Bipolarons may require significant local rearrangements of the counterion structure and solvation environment to accommodate the local charge. We note the colloquial use of the term bipolarons here to simply denote a multiply charged species - the identity and structures are unknown. Moreover, the underlying interactions between charge carrier species is entirely unknown. The fast equilibration upon dedoping (o→r) suggests the bipolaron species are easy to convert to evenly distributed polarons and neutral species.[13] On redoping (r→o') with a large potential step, the overall concentrations of both species also reach a steady state quickly;[13] however, both polarons and bipolarons are likely created at a wide distribution of sites within the heterogenous film due to the applied overpotential. A schematic of the slow migration and coarsening of the bipolaron domains is shown in **Fig. 5**, which explains the ubiquitous slower turn-on (redoping) speed of devices compared to their turn-off (dedoping) speed and is important for understanding transient device behavior in circuits[19,45,46]. This final uneven bipolaron aggregation might originate from a higher preference of bipolarons towards either the more crystalline or amorphous subdomains[47]. To the authors' knowledge, Bazant et. al., describes the most relevant electrochemical theory under these non-equilibrium conditions[48]. Essentially, the spatial distribution of carriers does not necessarily reflect regions with the lowest activation energies or where they may be generated under adiabatic operation observed in the stepped CV experiments. The observed bipolaron spatial distribution may also be present in homopolymers (such as BBL and pg2T-TT) despite the current results where small-angle scattering signals of these materials are too weak for quantitative analysis.

Consequently, harnessing these long-lived non-equilibrium states to create novel devices and functionality remains an intriguing and open question. For example, one may envision electrochemical pulsing schemes that leverage the spatial heterogeneities for temporary memory, logical operations, and state machines in macroscopic devices. If the scale and degree of spatial fluctuations can be tuned, these local modulations in conductance may also be useful for modulating weights in neuromorphic crossbar devices. Moreover, non-equilibrium functionality may be significantly enhanced by adding greater diversity to the number and character of interacting charge carrier species, opening new synthetic design space for multifunctional materials along with the use of multivalent ions, ionic mixtures, and ionic liquids.

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Contributions

R.W., D.M. and C.J.T. designed, tested the operando cell, and conducted the experiments. J.S., S.N. and Q.Z. supported the operando GIXPCS measurements in APS. C.J.T., J.R. and B.D.P conceived and directed the study. R.W. analyzed the data and conducted the model simulation under the supervision of C.J.T. R.W., J.R., and C.J.T. wrote the manuscript with discussion and input from all authors.

Competing interests

The authors declare no competing interests.

Figure Legends

Fig. 1 Operando GIXPCS to monitor chemical potential induced strain in adiabatic and non-adiabatic processes. a, operando grazing incidence small angle XPCS setup; **b,** example XPCS pattern of acid treated PEDOT:PSS exposed in 100 mM RbBr. **c,** Application of 0.6 V potential steps (non-adiabatic) with operando GIXPCS in 100 mM NaCl and the resulting **d,** charging current, **e,** strain in z direction, where the positive value corresponds to increasing film thickness, and **f,** the overall scattering intensity change. **g,** Application of 0.1 V potential steps (adiabatic) with operando GIXPCS and the resulting **h,** charging current, **i,** strain in z direction, **j,** the overall scattering intensity change.

Fig. 2 Sequence of strain, phase contrast and charge kinetics. 0.6 V potential step with operando GIXPCS of acid treated PEDOT:PSS cycled in 100 mM RbBr: **a,** the voltage profile (black); **b,** charging current (grey); **c,** strain in z direction (orange), where the positive value is the vertical upward strain (away from substrate); **d,** the overall scattering intensity change (navy blue); RC-normalized curves between $0\tau_{RC}$ and $3\tau_{RC}$ for **e,** dedoping process and **f,** redoping process to show the order of polaron population kinetics (red), and mesoscale domain strain (orange), phase contrast (navy blue) and charge transport (grey) transients; the cartoon for vertical strain in dedoping process: **g,** the initial state; **h,** the first negative strain spike; **i,** the strain relaxation in the opposite direction. The vertical strain is marked with orange arrows.

Fig. 3 Mesoscale state reversibility in adiabatic and non-adiabatic processes. Strain-corrected C maps for **a,** small and **b,** large potential steps in 100 mM NaCl electrolyte. The voltage profiles along with labels have been added along with dotted lines to demark regions and transitions of interest. For the large potential steps, the first potential step was applied at 30 sec.

Fig. 4 Mesoscale domain self-dynamics. a, the strain corrected C map of the r→o` transition (redoping process); the fan-like subregion is marked with black dashed lines and the fitting area is inside the purple box. For illustrative purposes, a dashed white line denotes a diagonal line cut used in the model fitting process ($\bar{t} = 200s$). Note that the voltage step happens at $t = 0s$. **b,** Simulated C map from the theoretical model of the r→o` transition; **c,** model fitting of diagonal line cuts with experimental data (hollow points) and the least-square fitting results (solid lines) of the r→o` transition for $\bar{t} = \frac{t_1+t_2}{2}$ of 75s, 100s, 125s, 150s, 175s and 200s; **d,** the strain corrected C map of the o→r transition (dedoping process); the invariant-time decorrelation is marked with black dash lines. **e,** Simulated C map from the theoretical model of the o→r transition; **f,** the predicted time extracted from the line cut fitting, assuming the order parameter of $n = 3$ (in **Formula 2**). Data are presented as fitting values with error bars representing the 95% confidence interval.

Fig. 5 Domain coarsening of the "Langevin Model B" system and an associated schematic of the polymer morphology undergoing this process. Polymer backbones (middle schematics) are represented as colored lines on a black background. Bipolaron domains (together with the counter ions and their solvation shell) are denoted by dark orange and polaron domains are colored yellow. The voltage and current profiles are plotted on the right. A simulated C map of this system is shown in **Supplementary Fig. 25**.

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Method

Sample preparation: PEDOT/PSS (Clevios PH-1000) from Heraeus Holding GmbH was filtered through 0.45 μm poly(ether sulfone) (PES) filters to remove large particles. The filtrate was drop-casted on a 100nm gold deposited p-type Boron-doped Si wafer (0-100 ohm cm^{-1}) (University

Wafer) at 70 °C. The wafer had been successively sonicated in acetone and isopropyl alcohol and exposed to UV-ozone prior to drop-casting. The drop-casted films were dried at 120 °C for 20 min to remove excess water inside. After cooling down, the samples were treated with 95% H_2SO_4 for 3h. After rinsing in DI water, the samples were first heated at 60 °C for 30 min and then at 120 °C for 30 min in ambient to form homogeneous metallic purple films. The substrate before OMIEC drop cast was characterized with atomic force microscopy (AFM, **Supplementary Fig. 23**), giving a vertical roughness of 1.2-1.4 nm with a horizontal grain size of ~60nm. The AFM images were collected at the NUANCE center in Northwestern University in tapping mode. The images were subject to standard image processing (image flatting and contrast enhancement) using the NanoScope software.

Operando GIXPCS: Grazing-incidence XPCS experiments were performed at beamline 8-ID-I (Advanced Photon Source, Argonne National Laboratory) with an X-ray energy of 10.92 keV and 2 μm×20 μm beam size. The coherent X-rays in grazing incidence were directed through knife-edge seal of the cone cell as shown in **Fig. 1a**, passing through the electrolyte and OMIEC film. In the experiments, x-ray flux was empirically determined to minimize damage: a low attenuation for short transients (denoted ‘att1’) and a higher attenuation (denoted as 'att4' and equivalent to 1/12 of att1) for the longer experiments. All the measurements were performed after several electrochemical cycles for reversible state changes. The incident beam was aligned in the middle of the cone cell to minimize the external strain. The scattering patterns were collected with a detector reading frequency of 10Hz. The data analysis was performed using a series of Python and Matlab scripts with detailed method and theory presented in the **Supplementary Information**. To maximize the scattering signal strength, acid-treated PEDOT:PSS was selected as the model OMIEC system, including its well-textured structure and clear mesoscale domain boundary. While NaCl was initially chosen as the electrolyte due to its relevance in typical OMIEC applications, the weak scattering limited quantitative analysis. Consequently, we also employed RbBr (high electron density) as the electrolyte to increase the scattering of mesoscale features for our quantitative kinetic analysis and model fitting.

Cell description: As previously reported for complementary GIWAXS measurements,[13] the cone cell uses a cylindrical body with a tapered, knife edge pressed against the supported thin film. The knife edge deforms slightly to seal, providing a rigid, X-ray transparent window for both the incident and scattered beams to interact with the electrolyte and sample. The substrate is fully supported using a combination of a flattened, polished screw and a thin epoxy film; this support provides the mechanical stability during electrochemical cycling and minimizes deformation of the silicon due to the pressure of the knife edge seal. We note that the electrochemical cell has minimal parasitic currents and satisfies the strict requirements for rigidity and stability required for GIXPCS.

Data Availability

The original data underlying the figures in the main text are publicly available from the Northwestern University respository (Dryad) at DOI: 10.5061/dryad.4b8gthtkq. The datasets generated and/or analysed during this current study are available from the corresponding author upon request.

Code availability

Both Python and Matlab code is available publicly from the Northwestern University respository (Dryad) at DOI: 10.5061/dryad.4b8gthtkq.