

1 Direct quantification of ion composition and mobility in organic mixed ionic- 2 electronic conductors

3 Direct quantification of ion transport in OMIECs

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12

13 **Abstract**

14 Ion transport in organic mixed ionic-electronic conductors (OMIECs) is crucial due to its direct
15 impact on device response time and operating mechanisms but are often assessed indirectly or
16 necessitate extra assumptions. Operando X-ray fluorescence (XRF) is a powerful, direct probe for
17 elemental characterization of bulk OMIECs, and was employed to directly quantify ion
18 composition and mobility in a model OMIEC, PEDOT:PSS, during device operation. The first
19 cycle revealed slow electrowetting and cation-proton exchange. Subsequent cycles showed rapid
20 response with minor cation fluctuation (~5%). Comparison with optical-tracked electrochromic
21 fronts revealed mesoscale structure dependent proton transport. The calculated effective ion
22 mobility demonstrated thickness-dependent behavior, emphasizing an interfacial ion transport
23 pathway with a higher mobile ion density. The decoupling of interfacial effects on bulk ion
24 mobility, and the decoupling of cation and proton migration elucidates ion transport in
25 conventional and emerging OMIEC-based devices, and has broader implications for other ionic
26 conductors writ large.

27

28 **Teaser**

29 Progression of dopant ion motion in a model mixed ionic-electronic conductor was directly
30 tracked by operando X-ray fluorescence.

31

32 **MAIN TEXT**

33 **Introduction**

34 Organic mixed ionic-electronic conductors (OMIECs) are materials that transport both ions and
35 electrons (1), making them highly versatile for a wide range of applications such as energy storage
36 (2), neuromorphics (3, 4), and bioelectronics (5-9). In order to guide the development of energy-
37 efficient, high-performance sensors and circuits for these applications, understanding the
38 fundamental operating mechanisms of OMIEC-based devices, particularly the complex mixed
39 ion/electron transport and coupling within OMIECs, is critical. Electronic or coupled
40 electronic/ionic properties such as electronic mobility μ and volumetric capacitance C^* and the
41 related material figure of merit μC^* (10, 11) have been extensively investigated (1, 12, 13).
42 However, directly determining ion composition and mobility in device relevant conditions is
43 challenging due to the presence of an electrolyte background and the relatively limited availability
44 of operando elemental analysis techniques.

45 Efforts have been made in previous studies to quantify the ion composition in OMIECs (14-16),
46 although most of these works are based on indirect approaches such as electrochemical quartz
47 crystal microbalance (EQCM) (14, 15). More recently, operando NMR has been used as a direct
48 approach to study the ion composition in poly(3,4-ethylenedioxythiophene)-poly(styrene
49 sulfonate) (PEDOT:PSS) (16), while the generalizability of this study has been limited owing to
50 the usage of millimeter-thick films and non-standard electrolytes. This technique is also unable to
51 effectively distinguish between free cations in the film and those in the electrolyte due to the
52 presence of residual electrolyte within the NMR coil.

53 Similarly, research on ion transport in OMIECs has predominantly relied on indirect evidence. The
54 signals detected by microprobe-based techniques, such as scanning electrochemical microscopy
55 (SECM) (17) and electrochemical strain microscopy (ESM) (18), might inaccurately depict the
56 behavior of the targeted ionic dopants owing to the solvent-related effects. SECM requires the
57 presence of electroactive species to generate measurable currents, making it unsuitable for non-
58 electroactive cations (ex. Na^+ , Rb^+ , Ca^{2+}); while ESM conflates the ion transport with water
59 transport, as the observed swelling is related to the hydration shell (15). Optical methods like the
60 electrochromic moving front (Fig. 1A) have also been applied to indirectly track ion transport in
61 OMIECs, and derive information on the rate of ion transport through the polymer matrix (19-21).
62 However, these indirect optical studies involve assumptions, such as single ion transport within
63 the polymer and that the progressing electrochromic moving front is rate limited by ion transport
64 instead of hole transport (22). A recent report suggests that on longer time scales, ion transport is
65 primarily driven by the internal electrostatic fields within OMIECs, generated by hole

66 displacement currents (23). These assumptions limit the accuracy and reliability of previously
67 reported moving front experiments, highlighting the need for direct measurement of both ion
68 composition and mobility in OMIECs.

69 Different geometries in OMIEC-based devices introduce additional complexity as the direction of
70 ion transport with respect to film texture and interface can be variable. Due to their processability,
71 chemical tunability, and compatibility with aqueous electrolytes, OMIECs are widely used in
72 organic electrochemical transistors (OECTs) (10). Conventional OECTs (cOECTs) employ a
73 planar source-drain electrode structure (**Fig. 1B**), where the dominant ion transport occurs
74 vertically between the thin film and the electrolyte, while electronic transport occurs laterally
75 within the OMIEC channel (1). Vertical ion migration is limited by the ion mobility in bulk
76 OMIECs. Recently, a new vertical OECT (vOECT) architecture has been reported (**Fig. 1C**) (24),
77 featuring a vertically scalable structure and narrow channel lengths controlled by the film
78 thickness, which effectively improve device integration density and sensitivity. In contrast to
79 cOECTs, vOECTs involve lateral ion transport within the encapsulated OMIEC channel,
80 highlighting the interfacial ion transport; despite the anticipated longer ion migration distances
81 required for complete channel doping in vOECTs, their response times have been observed to be
82 comparable to those of cOECTs in operation (24). To further elucidate ion transport in OECTs
83 with different geometries, it is important to decouple ion transport within the bulk from transport
84 at the interfaces.

85 In this study, we introduce a direct approach to quantify ion composition and mobility in OMIECs
86 using operando X-ray fluorescence (XRF). Ex situ XRF has been employed to quantify ion
87 composition in OMIECs under different doping states, but potential errors arise due to sample
88 post-washing used to remove residual electrolyte, and from sample-to-sample variability(25). In
89 contrast, operando XRF measurements separate the incident X-ray pathway from the electrolyte,
90 allowing for real-time measurement of ion composition during electrochemical cycling. This non-
91 invasive technique directly tracks ion mobility from the corresponding elemental peak changes,
92 eliminating the need for additional assumptions on indirect evidence.

93 This study focuses on a model OMIEC system, PEDOT:PSS, prepared from an aqueous dispersion
94 with ethylene glycol (EG) as a co-solvent additive. This system is known for its high electronic
95 conductivity, facile processability, commercial availability, and wide applicability, and has been
96 extensively studied (20, 25-27). The addition of EG to PEDOT:PSS enhances its electronic
97 conductivity by forming locally ordered mesoscale domains (20), thus overcoming hole transport
98 limitations (22, 28). The degree of phase separation and purity can be tuned by adjusting the EG
99 content (20), making it an excellent system for investigating ionic composition and transport

100 during operation. The combination of elemental analysis with thorough thickness-dependent
101 studies reported here have upended the previously understood relationship between bulk cation
102 mobility, EG content, and film morphology (20), revealing that interfacial effects had previously
103 masked bulk cation transport behavior. Specifically, operando XRF has revealed that proton
104 transport cannot be disregarded in low EG content samples with reduced phase purity, and anion
105 transport cannot be disregarded in the interfacial dominated thin film limit, especially in vOECT
106 architecture, such that Donnan exclusion (25) cannot always be presumed.

107 Our findings offer valuable insights into ion transport in OMIECs and the behavior of related
108 devices and circuits. This direct approach for quantifying ion composition and mobility will serve
109 as a basis for molecular design, materials processing, and charge/ion migration modeling, with
110 implications for device performance. Not solely confined to OMIECs, this method can also be
111 applied to investigate complex ion transport mechanisms in various mixed conductors, spanning
112 fields including batteries and solar cells.

113

114 **Results**

115 To directly measure ion composition during electrochemical cycling of films, we developed an
116 operando XRF setup that featured a 3D-printed cell, an Ag/AgCl reference/counter electrode and
117 a fixed PEDOT:PSS coated glass slide. We note that the crosslinker (3-glycidyloxypropyl)-
118 trimethoxysilane (GOPS) was excluded in the film formulation to be in line with previous
119 electrochromic moving front study (20). We anticipate a slower moving front and lower ion
120 concentration in the PEDOT:PSS films with GOPS. A parylene layer was introduced between the
121 PEDOT:PSS and the glass substrate to prevent material delamination. The coated glass slide was
122 further covered by a hydrophobic encapsulation layer (SU-8) on top (**Fig. 2A**, XRF background in
123 **Fig. S1**). Appropriate thickness of encapsulation layer was chosen for accurate determination of
124 ionic composition and mobility (see **method**, operando XRF cell description). A $23000\text{ }\mu\text{m} \times$
125 $20\text{ }\mu\text{m}$ opening was patterned on the lower end of the encapsulation layer to expose the sealed
126 OMIEC film to the aqueous electrolyte. An external voltage was applied to induce ion migration
127 laterally (upward) from the opening, to counterbalance the electronic charges removed/injected.
128 As a result, an electrochromic front was observed to move upward through the dedoped polymer.
129 Notably, we employed heavier ions (Rb^+ and Br^-) as substitutes for Na^+/K^+ and Cl^- , building upon
130 prior studies (25, 29), due to their strong fluorescence that is readily monitored in ambient within
131 the electrochromic front. To further investigate the kinetics of composition modulation, across the
132 measurement the incident X-ray beam was held at fixed distances from the opening and the
133 changes of corresponding elemental fluorescence peak intensity were measured with the XRF

134 detector. The collected XRF spectra (**Fig. 2B** and **Fig. S2**) were analyzed to calculate the actual
135 elemental ratios of Rb (transported from the RbBr electrolyte) and S (inherent from thiophene
136 and/or sulfonate) in the PEDOT:PSS films (**Fig. 2C**) based on calibration curves (detail and error
137 analysis in **SI Part I, Fig. S3-5**). The As fluorescence peaks (at 10.5 and 11.7 keV) from the glass
138 background were used for spectrum normalization.

139

140 **Electrowetting of dry OMIEC film**

141 During the first dedoping process (-1V vs Ag/AgCl in 0.1M RbBr), PEDOT:PSS films experienced
142 substantial proton-cation exchange driven by external dedoping potential. This exchange is
143 expected to take place during the initial operation in top-encapsulated vOECTs, differing from
144 passive ion-exchange in non-encapsulated cOECTs exposed to an aqueous electrolyte. Balancing
145 film homogeneity and signal-to-noise ratio, drop-casted 20% EG mixed PEDOT:PSS (20% EG-
146 PEDOT:PSS) films were first used for quantitative ion composition analysis. Under a dedoping
147 voltage of -1 V vs Ag/AgCl, the ion moving front advanced by ~7 mm in 10h, spatially below the
148 position the electrochromic equilibrium reached (**Fig. S6** and **Fig. 2 (D and E)**). In the region
149 showing a color change, only a gradual increase in the Rb fluorescence was observed (owing to the
150 Rb⁺ cation), but no Br fluorescence was observed (from the Br⁻ anion) (**Fig. 2C**), confirming the
151 Donnan exclusion reported in ex situ characterization of PEDOT:PSS/EG films (25). At the end
152 of the dedoping process, the ratio of Rb to S in the bulk phase was 0.7-0.8 (error analysis in **SI**).
153 Assuming a sulfonate S (S on PSS⁻) to total S ratio of 0.75 (**Fig. S7**, 0.71 in (30)), most of the fixed
154 anions on PSS polyelectrolyte in the dedoped bulk film were balanced by the external cations,
155 which exchanged protons in the original pristine film.

156 The Rb⁺ cation accumulation in the first dedoping process can be divided into two stages (**Fig.**
157 **2C**): a faster ion transport equilibrated in the first 250 minutes, followed by a subsequent slower
158 quasi-linear Rb⁺ accumulation. By extrapolating this tail, a Rb/S ratio of 0.52 is obtained from the
159 intercept, representing the equilibrated Rb⁺ concentration of the first stage. This number matches
160 our previous report through ex situ XRF in thin PEDOT:PSS films (25) and bounded cation
161 concentration measured by operando NMR in millimeter thick films (16). The equilibrated Rb/S
162 ratio (0.52) is notably lower than the sulfonate content (0.75 of the total S), implying a substantial
163 minority proton population still trapped in the film after the first-stage of proton-cation exchange.
164 At the end of the first stage, the spectroscopic signature of neutral absorption (650 nm) stabilized
165 (**Fig. 2E**), which implies a constant hole density in the second stage. Thus, the further Rb⁺
166 concentration increase in the second stage does not reflect a further increase in hole concentration
167 (i.e. doping), but instead indicates additional cation-proton exchange, which will be discussed

168 later. Compositionally, in this first stage, external Rb^+ cations compensate for the holes leaving
169 the film and replace the weakly trapped protons inside the film.
170 The fast initial stage in these samples reflects the ion moving front caused by the electrowetting.
171 Electrowetting occurs due to the interplay of surface energy reduction and the Maxwell stress
172 generated by the electric field near the dry-wet interface (thus attracting free charges and polarized
173 dipoles), resulting in the decrease of contact angle and a hydrophilic interface (31). The speed of
174 the electrowetting process extracted from the samples with a thick encapsulation layer (25 μm) is
175 20 $\mu\text{m}/\text{min}$ (Fig. S8) and 37 $\mu\text{m}/\text{min}$ (Fig. S9) for drop-casted 5% EG- and 20% EG-PEDOT:PSS,
176 respectively. OMIECs undergo film swelling during the wetting process which is, in part,
177 mechanically countered by the encapsulation layer. Thus, the electrowetting speed depends on
178 various complex factors including the thickness and mechanical properties of both the
179 encapsulation layer and the OMIEC film, as well as the device geometry. Specifically, the top gold
180 electrode and polymeric encapsulation layer in vOECT is expected to cause a potential slowdown
181 in electrowetting speed during the initial electrochemical cycles. Consequently, vOECTs may
182 require an extended precycling period to effectively utilize the entire channel area compared to
183 cOECTs.

184 The subsequent linear increase of cations is attributed to an electronic field induced ion exchange
185 between the Rb^+ and the residual strongly trapped protons in the OMIEC film. This exchange
186 process does not occur effectively when the film is passively exposed to salt or undergoes short-
187 term electrochemical cycling without an extended “break-in”. EG-mixed PEDOT:PSS consists of
188 purified PEDOT-rich cores and PSS-rich matrixes. The PEDOT-rich cores function as electronic
189 conducting pathways, while the PSS-rich matrixes serve as ion transport pathways. Initially,
190 external ions are expected to exchange the protons in the more hydrophilic PSS-rich matrixes as
191 they traverse through this matrix. Continuing to apply reductive voltages leads to the gradual
192 displacement by Rb^+ of deeply trapped protons, which may be residing in the less hydrophilic
193 PEDOT-rich domains. Taken together, these data indicate the presence of two populations of
194 protons in PEDOT:PSS and underscore the interdependence of weakly trapped proton exchange
195 and hole transport, especially in the lateral ion transport scenario.

196

197 **Direct measurement of ion composition and mobility in electrochemical cycling**

198 After the first dedoping process (stepping to -1V vs Ag/AgCl), the modulation of ion composition
199 in 20% EG-PEDOT:PSS films decreased in the following electrochemical cycles. The first
200 redoping (stepping to 0V vs Ag/AgCl, Fig. S10) resulted in approximately 7% of Rb^+ cations
201 migrating out the film. Subsequently, we conducted multiple electrochemical cycles (between

dedoped and doped states) on the sample, and analyzed the ionic composition in different doped states, **Fig. 3 (A and B)**. When the polymer is fully dedoped (-0.6 V or -1 V vs Ag/AgCl, above the reductive onset of 20% EG-PEDOT:PSS), the modulation of the Rb⁺ concentration between dedoped and doped states remained stabilized (~5%, **Fig. 3B**). The decreased Rb⁺ concentration modulation from the initial redoping process (**Fig. 3C**) indicates some ion trapping after multiple electrochemical cycles. Nonetheless, the compositional findings emphasize an internal ion reservoir of mobile cations and fixed PSS anions (32), possibly distributed heterogeneously in a mesoscale morphology within PEDOT:PSS (32, 33).

In order to obtain the ion mobility in sufficiently swelled OMIECs, we performed several electrochemical cycles on the samples with thick encapsulation layers (detail in **methods**). This is akin to the pre-cycling or ‘break-in’ often performed, especially in moving front experiments (19-22). After 5-6 cycles, the response curves for the ion concentration at the same position stabilized (**Fig. S11**). The modulation of cations in different samples under the doped and dedoped states was in the range of 5%-10%. A sigmoid fit to these corresponding curves gave the time required for Rb⁺ to migrate a specific distance (**Fig. 3D**), thus obtaining the ion mobility through the model developed by Stavrinidou et al. (19). Specifically, this method gave a Rb⁺ mobility of $3.8 \times 10^{-3} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$ for drop-casted 20% EG-PEDOT:PSS. The reliability of this model was also supported by the kinetic curves when the samples were dedoping under -0.6V vs Ag/AgCl (**Fig. S12**). Notably, this model did not capture the kinetics of the redoping process (0V vs Ag/AgCl). Instead, we observed a spontaneous ion outflux following exponential decay kinetics (**Fig. S13** and **SI part II**).

223

224 **Proton transport across mesoscale domain boundaries**

225 The moving front was also measured optically immediately after the operando XRF experiments
226 to compare the electrochromic and elemental fronts in the same sample. Influenced by the EG
227 content during the sample preparation process, the progression of these two moving fronts (ionic
228 and electrochromic) matched in 20% EG-PEDOT:PSS but diverged in 5% EG-PEDOT:PSS. The
229 evolution of the electrochromic moving front is shown in **Fig. 4A** and **S14B**, for drop-casted 20%
230 EG- and 5% EG-PEDOT:PSS, respectively. The propagation rate of the electrochromic moving
231 front can be extracted from the kinetic curves measured at different distances from the
232 encapsulation opening. For 20% EG-PEDOT:PSS, the cation mobility from both electrochromic-
233 based measurements (19, 20) and operando XRF was comparable (**Fig. 4B**). However, for 5% EG-
234 PEDOT:PSS, the cation mobility obtained by XRF measurements was remarkably lower than that
235 obtained from optical methods (**Fig. 4B**). To assess the reliability of the optical moving front on

236 drop-casted samples, we conducted optical measurements on drop-casted EG-PEDOT:PSS
237 samples with different EG content. In line with the report by Rivnay et al. for spin-coated samples
238 (20), these drop-casted samples also exhibit a decelerated optical moving front with increased EG
239 content (**Fig. S14-15**). The disparity between the optical and XRF moving fronts in low EG content
240 PEDOT:PSS film indicated the presence of other ions in the system that affected the
241 electrochromic moving front.

242 Since no mobile anions were present in drop-casted 5% EG-PEDOT:PSS, we hypothesized that
243 the inconsistency between the optical moving front and the Rb^+ moving front arose from proton
244 transport. To simulate the observed faster optical moving front in the 5% EG-PEDOT:PSS, we
245 conducted optical measurements on drop-casted 20% EG-PEDOT:PSS films after cycled and
246 stabilized in a mixed solution of 50 mM RbBr and HBr, as well as a pure 100 mM HBr solution.
247 The electrochromic moving front in the pure HBr solution was faster than that in the mixed
248 solution, and both were substantially faster than the pH neutral 100 mM RbBr electrolyte
249 previously measured optically and with operando XRF (**Fig. S16A-B**). After the samples cycled
250 in HBr underwent multiple electrochemical cycles in pure RbBr, the speed of the optical moving
251 front slowed again (**Fig. S16C**). The results in 20% EG-PEDOT:PSS (with Rb^+) align with a
252 previous report suggesting that protons exhibit higher mobility in PEDOT:PSS compared to other
253 alkali metal cations (with Na^+ , K^+) (19). This indicates that the faster optical moving front than
254 Rb^+ moving front in 5% EG-PEDOT:PSS is very likely due to a minority population of
255 unexchanged protons.

256 In order to provide additional evidence for this finding, we employed a cation exchange resin to
257 replace the protons in the 5% EG-PEDOT:PSS solution with alkali metal cations. The resulting
258 film, cast from the cation-exchanged solution, exhibited a notably slower (~2/3) optical moving
259 front compared to the film produced from the unexchanged solution (**Fig. S17**).

260 The difference in proton transport between films cast from dispersions with 20% and 5% EG
261 content may stem not solely from a difference in residual proton concentration, but also from a
262 difference in mesoscale structure. The ion composition of drop-casted 5% EG- and 20% EG-
263 PEDOT:PSS used in electrochemical cycling were similar (**Fig. S8B** and **S9A**). Increasing the EG
264 content can substantially enhance the phase separation of PSS-rich and PEDOT-rich domains (20).
265 The phase boundary of 5% EG-PEDOT:PSS is not as clear as that of 20% EG-PEDOT:PSS. As
266 mentioned in the electrowetting process, PSS-rich matrixes have a low concentration of protons
267 and are hypothetically saturated by Rb^+ . In 20% EG-PEDOT:PSS, a decrease in proton
268 concentration leads to a diminished proton flux through the PSS-rich matrixes, resulting in a
269 reduced contribution to the overall flux driving the electrochromic front (**Fig. 4C**). In 5% EG-

270 PEDOT:PSS, less clear phase boundary may lead to a better connected PEDOT network that can
271 facilitate proton transport (**Fig. 4D**). Furthermore, the PEDOT-rich core in 20% EG-PEDOT:PSS
272 is likely less hydrophilic compared to that in 5% EG-PEDOT:PSS, primarily attributable to its
273 reduced PSS content (20). This decreased hydrophilicity in 20% EG-PEDOT:PSS results in
274 reduced swelling of the PEDOT-rich core, akin to the previous observation of limited PEDOT
275 crystallite lattice swelling despite the more pronounced overall swelling in PEDOT:PSS films (25).
276 Consequently, the proton mobility within the less hydrophilic, less swollen PEDOT-rich cores is
277 expected to decrease, as it is less conducive to the Grotthuss mechanism (34). Conversely, faster
278 proton transport in 5% EG-PEDOT likely screens the electric field sensed by Rb^+ , making the
279 difference between Rb^+ and proton moving fronts more pronounced.
280 These results demonstrate that operando XRF can track elemental-specific moving fronts and can
281 distinguish ion transport behaviors among different ions within OMIECs. By combining
282 information from optical observations, XRF data, and previous X-ray scattering research, a
283 multimodal approach was employed to better understand ion transport behaviors and accurately
284 determine ion mobility during operation.

285

286 **Thickness dependent ion mobility**

287 To further investigate the influence of the interface on ion composition and transport, we
288 performed operando XRF on spin-coated films with reduced thickness. The resulting XRF spectra
289 revealed a thickness-dependent anion injection, challenging the previously reported bulk Donnan
290 exclusion in these interface dominated systems (25). In particular, when employing a thin single-
291 layer spin-coated film (20% EG-PEDOT:PSS, ~100nm), anions could enter the film under a
292 dedoping voltage of -1V vs Ag/AgCl. During the dedoping process, the XRF peak at 11.7 keV
293 increased in intensity and progressively shifted to 11.9 keV (**Fig. S18A**), indicating the presence
294 of Br^- ions in the film (also in **Fig. S19**). The Br and Rb compositions were deconvoluted and
295 shown in **Fig. S18B**. X-ray photoelectron spectroscopy (XPS) confirmed the existence of both Rb^+
296 and Br^- ions in the bulk, with Rb^+ ions exhibiting higher concentration at the SU-8/OMIEC
297 interface, while Br^- ions were more concentrated at the parylene/OMIEC interface (**Fig. S20**). In
298 the limit of very thin films (~100 nm), stress concentration during initial electrowetting (OMIEC
299 swelling with electrolyte) may introduce microscopic voids that lack fixed polyanionic charges,
300 allowing the infiltration of liquid electrolyte, and ultimately leading to the breakdown of Donnan
301 exclusion. Subsequent electrochemical cycling revealed that the doping process of the material
302 was dominated by mobile Br^- rather than Rb^+ (**Fig. S18C**). Br^- peaks were observed in the thicker
303 three- and five-layer spin-coated films (300-500 nm), but the anion concentration remained

304 constant, indicating that anions were trapped (or not participating in the doping/dedoping) during
305 the electrochemical cycling process (**Fig. S21 and 22**). Thickness dependent anion injection was
306 also observed in 5% EG-PEDOT:PSS (**Fig. S23-26 and SI Part IV**). Remarkably, the thin samples
307 that contained mobile anions demonstrated an exceptionally high ion mobility, resulting in a rapid
308 moving front that covers a larger distance (>1.5 cm after the first applied voltage for 10 hours, **Fig.**
309 **S27**), indicating that the presence of mobile anions facilitates ion transport within the OMIEC film.
310 The magnitude of the interfacial contribution to overall ion transport and an estimate of bulk cation
311 mobility in OMIECs were ascertained by studying samples of different thickness. The temporal
312 response fit for different thicknesses of 20% EG- and 5% EG-PEDOT:PSS films were plotted in
313 **Fig. 5A** and **5B**, respectively, from which the mobility of cations in the film decreases with
314 increasing film thickness. Plots of the ion mobility versus inverse sample thickness (discussion of
315 sample thickness can be found in SI) showed a linear relationship (**Fig. 5C**). The extrapolation of
316 these two curves gave an estimated bulk mobility from the limit of thickness approaching infinity.
317 Compared to 5% EG-PEDOT:PSS ($1.0 \times 10^{-3} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$), 20% EG-PEDOT:PSS showed a smaller
318 linear slope but a higher bulk cation mobility ($3.1 \times 10^{-3} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$). This implied a more
319 homogenous ion mobility distribution in 20% EG-PEDOT:PSS samples across different thickness,
320 while the ion mobility of 5% EG-PEDOT:PSS shown more thickness-dependency, apparently due
321 to enhanced interfacial ion transport (**Fig. 5D**). The interfacial transport related to a hydrophilic
322 PSS⁻ layer has been reported (35), giving a similar estimated bulk mobility of $2 \times 10^{-3} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$.
323 These calculations yielded a much faster bulk migration rate of Rb⁺ than the electrowetting rate,
324 and represented the ion mobility in hydrated/swelled polymer. As noted above, during
325 electrochemical cycling, a dominant majority of ions (>90%) are retained within the film, allowing
326 cations to migrate between sites instead of traversing the entire electrochromic region from
327 external electrolyte.

328 Determining the bulk mobility and isolating interfacial effects holds practical importance for
329 different OECT architectures (and more broadly, OMIEC devices). In cOECTs, ions migrate into
330 the film primarily via the bulk and orthogonally to the interfacial ion transport directions, and thus
331 are minimally affected by interfacial effects. However, in vOECTs, the top and bottom
332 encapsulation of the OMIEC thin film create interfaces that are parallel to ion transport directions,
333 and the pronounced interfacial effects accelerate ion drift-diffusion. These findings have the
334 potential to advance the optimization of OECT materials choice and fabrication schemes. For
335 instance, implementing suitable surface treatments and decreasing the film thickness in vOECTs
336 has the potential to further improve the device's response time.

337

338 **Mobile ion density**

339 In addition to the electrochromic moving front, we can also obtain the mobile ion density and
340 electronic-ionic coupling efficiency through operando XRF (**SI Part V** and **Fig. 6A**). Based on the
341 reported model which presumes a linear electronic field decay in the dedoped region (19), the
342 mobile cation density P can be extracted from the slope of current density j and inverse square
343 root of time $t^{-1/2}$. Ideally, this mobile cation density should be equal to the injected ion
344 concentration. The linear fitting yields mobile cation density of $3.0 \times 10^{20} \text{ cm}^{-3}$ and $2.2 \times 10^{20} \text{ cm}^{-3}$
345 for drop-casted 20% EG- and 5% EG-PEDOT:PSS (grey box in **Fig. 6B**, thickness dependence
346 also in **Fig. S28**), respectively. These numbers are in line with a previous report (19), and are
347 slightly higher than the concentration of injected Rb^+ . Taking drop-casted 20% EG-PEDOT:PSS
348 as an example, assuming that the Rb to S ratio in the dedoped state is 0.7, and the modulation
349 between the dedoped and doped states is less than 10%, we can conclude that the Rb^+ concentration
350 involved in the electrochemical cycling process is less than $2.6 \times 10^{20} \text{ cm}^{-3}$ (**SI part VI**, 87% of
351 mobile cation density P). This discrepancy between the Rb^+ concentration change, and mobile
352 cation density also results in a slightly lower than 100% electronic-ionic coupling efficiency (e.g.
353 Faradaic side reactions consuming some electronic charge). Given an electronic charge transfer of
354 $0.058 \text{ } \mu\text{mol}$ (or $29.4 \text{ F} \cdot \text{cm}^{-3}$, from measured currents shown in **Fig. S29**), the electronic-ionic
355 coupling efficiency is 93% (**SI Part VI**), close to the result from a previous operando NMR report
356 (16). In summary, the combination of the measured currents and operando XRF demonstrates that
357 Rb^+ remains the primary cation being transported. Additionally, the minor discrepancies between
358 the XRF results and the measured currents could be attributed to proton transport or Faradaic
359 reactions occurring at the encapsulation opening.

360

361 **Discussion**

362 **Ionic mean drift-diffusion length**

363 By analyzing the measured currents in samples with different thicknesses, a relationship was
364 established between the mobile cation density P , XRF cation mobility μ , and sample thickness d .
365 For PEDOT:PSS samples with the same EG content, the XRF-determined cation mobility μ was
366 found to be proportional to the mobile cation density P (**Fig. 6B**). Given the relatively low
367 population of protons and anions that participate in ion transport, the calculated P primarily
368 reflects the mobile Rb^+ density in the sample. As the film thickness increased, both mobile Rb^+
369 density and mobility decreased notably, indicating a higher mobile cation density at the OMIEC-
370 encapsulation interface, compared to the bulk. This result is particularly noteworthy as the
371 migration of ions in OMIECs is relayed by the reorganization of mobile cations rather than a single

372 cation directly migrating from external electrolyte to the optical moving front. Thus, a higher
373 density of cations at the OMIEC-encapsulation interface implies a shorter mean drift-diffusion
374 length for individual cations. This is analogous to shorter hops occurring at a higher rate than
375 longer hops, leading to an accelerated migration rate of cations near the interface (**Fig. 6C**). This
376 also explains the previously reported slight increase of the mobility with external salt concentration
377 (19), and the temperature dependent ion mobility in ionomers (36).

378 Mesoscale phase separation also influences the mobile cation density-mobility relationship. The
379 slope of P - μ plot was inversely proportional to the heterogeneity of ion distribution caused by
380 phase separation. This heterogeneity reflected the ion transport pathway distortion from ideal one-
381 dimensional transport (**SI Part VII**). In 20% EG-PEDOT:PSS, due to larger PEDOT-rich domain
382 size and more distinct phase boundaries, the Rb^+ transport pathway was likely more tortuous
383 compared to that of 5% EG-PEDOT:PSS. This likely led to an increased mean drift-diffusion
384 length compared to the 5% EG-PEDOT:PSS sample with the same mobile cation density. This
385 observation underscores the additional complexity imparted by phase separation on cation
386 transport behavior.

387

388 **Electric field corrected ion mobility**

389 Accurately determining the ion mobility within OMIECs also requires understanding the field
390 distribution in the system. The presence of different ions and ion drift-diffusion behavior can
391 potentially lead to differences in the calculated ion mobility.

392 In the presence of other ions, the optical moving front actually reflects the proton migration rate
393 in 5% EG-PEDOT:PSS, which leads to a systematic error in the migration rate of Rb^+ measured
394 by operando XRF. Due to the proton dedoping of the OMIEC, the electric field sensed by Rb^+ is
395 smaller than that in the previously mentioned model. The time dependent electric field in the
396 OMIEC can be calculated through the optical moving front, and thus modifying the ion migration
397 rate model (**SI PartV**). This gives:

$$398 \mu_{\text{Rb}^+} = \sqrt{\mu_{\text{optical},H} + \mu_{\text{XRF},\text{Rb}^+}} \quad (1)$$

399 The proton decoupled Rb^+ mobility in 5% EG-PEDOT:PSS ($2.1\text{--}2.6 \times 10^{-3} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$) is larger than
400 the mobility directly calculated from XRF moving front. This result suggests a slightly lower bulk
401 Rb^+ mobility in 5% EG-PEDOT:PSS compared to 20% EG-PEDOT:PSS. Despite this correction
402 not altering the main conclusions, it underscores the necessity of a multimodal approach to
403 accurately measure ion mobility within OMIECs.

404 A recent study introduced a quasi-field drift-diffusion model (23), revealing that hole diffusion
405 induces a broadening of the electric field, which plays a more important role in ion transport than

406 initially expected. The ion mobility can be calculated using an extra correction scaling parameter
407 from the ratio of maximum moving front length L_{max}^2 and t in **Fig. 5 (A and B)** (detail in **SI Part**
408 **VIII**). This result ($4.5 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$ for drop-casted 20% EG-PEDOT:PSS) suggests a lower
409 quasi-field ion mobility than the classical ion diffusion model, leading to a cation mobility slightly
410 lower than that in water. However, this raises questions about the applicability of the quasi-field
411 drift-diffusion model to the specific device geometry used in operando XRF measurements,
412 potentially due to the variable length that the moving front traverses.

413
414 **Summary and outlook**

415 We developed a new operando XRF technique to detect ion composition and mobility in bulk
416 OMIEC thin films in real-time. External salt cations migrate into OMIEC in the first
417 electrochemical cycle through electrowetting, followed by a weak relative modulation (5-10% of
418 the cation concentration, compared to initial dedoped state) in subsequent cycles. Notably, this
419 weak relative modulation is smaller than the systematic error in previously reported ex situ
420 measurements (~7%) (25) and emphasizes the importance of operando ion composition studies. In
421 addition, we compared the ion mobility obtained from the compositional modulation with the
422 standard optical moving front experiment. Our findings indicate that the optical method accurately
423 reflects ion migration rates in thick films with obvious phase separation. However, in most other
424 cases, the assumptions underlying the optical method may lead to deviations from the actual ion
425 mobility due to transport contributions of a minority proton population and interfacial
426 enhancements of ion transport. This XRF method based on elemental moving fronts can be used
427 for all polymers that exhibit ion migration regardless of color changes, and is not limited to
428 electrochromic OMIEC systems. To our knowledge, this is the first direct, non-invasive
429 quantification of ion transport in organic polymer materials under operando electrochemical
430 conditions.

431 In the future, this setup can also be used for X-ray absorption fine structure (XAFS) measurements
432 of the ion coordination environment within OMIECs, and mid-infrared spectroscopy for the
433 detection of bipolarons or other higher charged species in different charged states, as the optical
434 path of this setup does not pass through the aqueous electrolyte. Certainly, this method is subject
435 to some limitations. Selecting appropriate ions is crucial to prevent attenuation of the fluoresced
436 X-ray signal, and extrapolations from Rb to other metal cations should be rigorously validated in
437 the future. The challenge of achieving sub-second temporal resolution and sub-millimeter spatial
438 resolution is amplified by the weak ion fluorescence signal. Specifically, for accumulation mode
439 OMIECs with shorter moving fronts, better spatial resolution (i.e. smaller beam size) is necessary

440 to map the concentration differences across smaller length scales. Employing an appropriate
441 voltage range is also important to prevent hole-limited charge transport constraints (22).
442 The unique insights into interfacial effects on ion transport in OMIECs are instrumental in guiding
443 the molecular and device design. To enhance the ion transport performance and thus improve the
444 device response speed, it is crucial to increase mobile ion density within the material. This can be
445 achieved by increasing the ion concentration in the electrolyte or by disrupting the Donnan
446 exclusion of the material. Particularly, in vOECTs, interface engineering between OMIEC and
447 encapsulation may be an effective route to speed up ion lateral transport, as pronounced interfacial
448 effects demonstrate increased participation of mobile ions during electrochemical cycling.
449 Furthermore, in the case of PEDOT:PSS, the presence of residual protons from incomplete proton-
450 cation exchange substantially enhances ion migration speed, particularly in samples with
451 inadequate phase separation, thereby facilitating faster ionic-electronic coupling during
452 electrochemical cycling. The comprehensive information gleaned from this method is not readily
453 accessible or straightforward using existing characterization techniques. This work points to the
454 importance of compositional probes when characterizing such complex systems, especially
455 considering the multiple charged species participating in electrostatic and electrochemical
456 processes.

457

458 **Materials and Methods**

459 **Sample preparation and device fabrication**

460 The EG mixed PEDOT:PSS was prepared by mixing PEDOT:PSS dispersion (1%, Clevios
461 PH1000, Heraeus) with ethylene glycol (5%, 20% and 50% v/v) and 0.2% v/v 4-
462 dodecylbenzenesulfonic acid (DBSA). The mixture was then filtered through a 0.45 μ m PES
463 syringe filter (Whatman Uniflo) to get a homogenous dispersion. Sodium-exchanged
464 PEDOT:PSSNa was synthesized via ion exchange with Amberlite® IR120 Na^+ form cation
465 exchange resin (Sigma-Aldrich). PEDOT:PSS (20 mL) was loaded onto a column packed with
466 resin (2 g); the dispersion was passed through the resin bed under pressure for 30 min.
467 PEDOT:PSSNa was subsequently used without further treatment.

468 To fabricate the device for operando XRF characterization, the glass slide was first coated with 2
469 μ m parylene C, and UV-Ozone for 30 minutes. The mixture was then cast on the parylene-coated
470 glass. For each layer in the spin-coated samples, the mixtures were spined at 1000 rpm for 1
471 minute, following a 2-minute soft bake at 80 °C. For the drop-casted samples, the glass was tilted
472 on a small block. The mixtures were then dropped from the higher end of the glass to flow through
473 the whole surface. The slide was then put on a hot plate horizontally to achieve homogeneous

474 surface coverage. The drop-casted sample was then dry at 80 °C. The dry spin-coated and drop-
475 casted samples were all hard baked at 140°C for 30 minutes, and then immersed in the DI water
476 to remove the residue small molecules. A 2.5 μ m AZ nLOF photoresist or 25 μ m SU-8 photoresist
477 with small opening were patterned through photolithography and used as encapsulation layer. The
478 samples were finally hard bake at 140°C for 30 minutes again to remove the possible cracks on
479 the encapsulation layer.

480 **Operando XRF cell description**

481 The XRF cell was 3D-printed and assembled with an Ag/AgCl counter electrode and a
482 PEDOT:PSS coated glass slide (**Fig. 1a**). The glass slide was fixed on the cell to avoid small
483 displacement during the long-time operando XRF measurements. To prevent any external pressure
484 that might influence the ion mobility within the OMIEC films (37), the electrolyte chamber was
485 left unsealed, and extra electrolyte was introduced by a syringe pump to compensate the
486 evaporation effect thus maintaining the water level. Additionally, the upper surface of the cell was
487 covered with lead tape to block the ion signal from the electrolyte.

488 Due to the sulfur peak attenuation in the encapsulation layer, the accurate determination of ionic
489 composition and mobility in OMIECs requires different encapsulation thickness. A thin
490 encapsulation layer (2.5 μ m) minimized the attenuation of sulfur peaks and thus offered a high-
491 fidelity signal for ion composition measurement. However, the thin encapsulation layer under the
492 electrolyte level proved to be susceptible to deformation over electrochemical cycles due to the
493 film swelling fluctuations. Consequently, this led to inaccuracies in determining ion mobility. To
494 address the aforementioned issues, samples were prepared with a 25 μ m SU-8 encapsulation layer
495 to precisely measure the ion mobility. This thicker encapsulation layer ensured a stable and
496 intimate contact with the OMIEC sample during multiple electrochemical cycling, enabling
497 precise control over the ion migration distance (between the opening gap and the X-ray footprint).
498 As a result, it facilitated a more reliable and consistent determination of ion mobility through a
499 time-resolved electrochromic moving front.

500 **Operando XRF and optical measurement**

501 Operando XRF measurements were conducted in fluorescence mode using spectroscopy-grade
502 ionization chambers (FMB-Oxford). The X-ray beam size on the sample was 1.0 \times 8.0 (vertical \times
503 horizontal) mm. Spectra were collected with excitation energies before (15000 eV) and after
504 (15250 eV) the Rb K-edge to deconvolute the overlapping Br K β and Rb K α peaks. The cell height
505 was controlled by a vertical direction motor, while the other motors remained fixed throughout the
506 entire measurement. The XRF detector (SDD) was placed 65-70 mm away from the sample surface

507 to maximize the sulfur (S) signal. The intensity of the incident X-ray was calibrated using the As
508 K_α peak from the glass background, and all other peaks were normalized accordingly.
509 The potential control during the operando measurement was carried out using a potentiostat
510 (Ivium) with a Ag/AgCl electrode as the reference electrode (CE/RE). To prepare the samples for
511 the kinetic measurements, they were first dedoped at -1 V vs Ag/AgCl for 12 hours, followed by
512 a 100-minute redoping step at 0 V vs Ag/AgCl. To ensure stabilized ion transport, all samples for
513 kinetic measurements were pre-cycled between -1 V and 0 V vs Ag/AgCl for at least 5 cycles.
514 For 5% EG- and 20% EG- drop-casted samples, optical moving front was recorded immediately
515 after the XRF measurement using a spatially resolved camera. The optical moving front for the
516 remaining samples was measured on the benchtop using the same method. Data analysis was
517 performed using Python scripts and ImageJ software.

518 **UV-Vis spectroscopy**

519 To prepare UV-Vis spectroscopy samples, 20% EG-PEDOT:PSS was drop-casted on pieces of 1
520 cm × 2 cm parylene coated glass cleaned with UV-ozone exposure. The SU-8 encapsulation layer
521 was prepared as the operando XRF samples. The beam height relative to the opening was tuned
522 by adjusting the PMMA cuvette height, and the beam size was determined as 2 mm. The UV-Vis
523 spectroscopy was collected in 100 mM aqueous RbBr with an Ag/AgCl pellet (Warner
524 Instruments) reference/counter electrode. Potential control and current measurement were carried
525 out with a potentiostat (Ivium). Simultaneous absorption spectroscopy was recorded with a
526 halogen white light source (Ocean Optics, DH-2000-BAL) and an optical fiber to UV-visible
527 (Ocean Optics, FLAME-S) spectrometers with 200 ms integration times. Electrochemical and
528 spectroscopic data were recorded with Iviumsoft and OceanView software, respectively. Data
529 analysis was performed using Python scripts.

530 **Ex situ XPS measurement and depth profile**

531 The XPS spectra were taken using a Thermo Scientific ESCALAB 250Xi equipped with a
532 monochromatic KR Al X-ray source (spot size of 500 μm) at the Northwestern University Atomic
533 and Nanoscale Characterization Experimental Center (NUANCE). Before data collection, a flood
534 gun was used for charge compensation. The S peak was measured without ionic etching to avoid
535 the reduction of sulfonate. For depth profile, the sample was peeled from the substrate and
536 transferred onto a silicon wafer (**Fig. S20b**). The ionic beam (area: 3 mm × 3 mm) etching time
537 for each data point was set at 30 s (~10 nm). The curve fitting was performed with Avantage
538 (Thermo Scientific) software.

539

540 **Figure Legends**

541 **Fig. 1. Different device geometries.** Ion and electron transport in (A) moving front device, (B)
542 cOEET and (C) vOEET. The cartoons are adapted from (1).

543 **Fig. 2. Electrowetting and proton-cation exchange in the first electrochemical cycle.** (A)
544 side, front and 3D view of operando XRF setup; (B) XRF spectra for drop-casted 20% EG-
545 PEDOT:PSS in the first dedoping (-1V vs Ag/AgCl) process. The distance between the opening
546 gap and X-ray beam footprint X is 6 mm. (C) Ion transport curve during the first dedoping
547 process at X = 6 mm, with Rb in violet squares and Br in brown diamonds; (D) UV-Vis
548 absorbance data of a 20% EG-PEDOT:PSS film as the dedoping electrowetting front moves past
549 the optical fiber. The distance between the opening gap and light spot X is 6 mm. (E) The neutral
550 peak absorbance (at 650 nm) as a function of dedoping time at X = 6 mm. In (B) and (D), the
551 curve changing from red to blue represents the gradual increase in dedoping time.

552 **Fig. 3. Quantifying ion composition and transport kinetics in following electrochemical
553 cycling.** (A) XRF spectra for drop-casted 20% EG-PEDOT:PSS in dedoped (blue) and doped state
554 (magenta) after multiple electrochemical cycles; the baseline is plotted in grey; (B) Rb⁺ transport
555 curve during the later electrochemical cycling process (dedoped at -1V, -0.6V and -0.2V vs
556 Ag/AgCl); (C) extracted elemental ratio between Rb/Br and S of drop-casted 20% EG-
557 PEDOT:PSS after first dedoping/redoping and multiple dedoping/redoping processes; (D) cation
558 kinetic curves during the first dedoping process of different heights, with Rb⁺ in violet.

559 **Fig. 4. The comparison between optical and XRF moving front.** (A) optical moving front in a
560 dedoping process after multiple electrochemical cycles at different probing heights, X; (B)
561 temporal evolution of the ion drift length L in optical (solid square and line) and XRF elemental
562 moving front (hollow square and dash line). Diagram for the Rb⁺ cation (violet) and residue
563 protons (red) transport between mesoscale domains (grey dash lines) in (C) 20% EG- (orange) and
564 (D) 5% EG- (red) PEDOT:PSS.

565 **Fig. 5. Thickness-dependent ion mobility in EG-PEDOT:PSS.** Temporal evolution of the ion
566 drift-diffusion length L of Rb⁺ in (A) 20% EG-PEDOT:PSS and in (B) 5% EG-PEDOT:PSS; (C)
567 thickness dependent Rb⁺ mobility in 20% EG- (orange) and 5% EG-PEDOT:PSS (red),
568 highlighting the bulk mobility extrapolated using colored hollow circles; (D) diagram for interface
569 (between SU-8 encapsulation and PEDOT:PSS) and bulk ion mobility in 20% EG- (orange) and
570 5% EG-PEDOT:PSS (red), highlighting how increased EG content suppresses the interfacial
571 enhancement of ion mobility.

572 **Fig. 6. The relationship between mobile ion density and ion mobility.** (A) temporal evolution
573 of recorded current density of 20% EG-PEDOT:PSS of different thickness; (B) Rb mobility from
574 XRF as a function of the extracted mobile cation density P; the drop-casted samples that reflect

575 majorly bulk mobility were highlighted with grey box; (C) diagram for interface and bulk mobile
576 charge density and the related ion transport pathway.

577

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685

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703 Resource: RW, XJ and JT.

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