

# Disentangling water, ion and polymer dynamics in an anion exchange membrane

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**Semi-permeable polymeric anion-exchange membranes (AEM) are essential for separation, filtration and energy conversion technologies ranging from reverse electrodialysis (RED) systems that produce energy from salinity gradients [1], fuel cells (FC) to generate electrical power from the electrochemical reaction between hydrogen and oxygen [2-3], and water electrolyzer systems (WE) that provide H<sub>2</sub> fuel [4-5]. Anion exchange AEMFCs and AEMWEs rely on the membrane to transport OH<sup>-</sup> ions between the cathode and anode in a process that involves cooperative interactions with H<sub>2</sub>O molecules and the polymer dynamics. Understanding and controlling the interactions between the relaxation and diffusional processes pose a main scientific and critical membrane design challenge. Here, quasi-elastic neutron scattering (QENS) is applied over a wide range of timescales (10<sup>0</sup> - 10<sup>3</sup> ps) to disentangle the water, polymer relaxation and OH<sup>-</sup> diffusional dynamics in commercially available AEM (Fumatech FAD-55) designed for selective anion transport across different technology platforms, using the concept of serial decoupling of relaxation and diffusional processes to analyse the data. Preliminary data are also reported for a laboratory-prepared AEM especially designed for fuel cell applications.**

There is a growing need to develop efficient energy conversion devices using sustainable fuel sources. Polymer electrolyte membrane (PEM) fuel cells that rely on a hydrophobic backbone decorated with ionic side groups to allow selective transport of H<sup>+</sup> or OH<sup>-</sup> are one promising technology. The transport mechanisms involve cooperative interactions between the ions, H<sub>2</sub>O molecules in the surrounding environment, and relaxation dynamics of the polymer backbone and side groups. Established FCs employ electrocatalytic reduction of H<sub>2</sub> to generate H<sup>+</sup> ions that are transported through the PEM, but they rely on Pt-group-metal-based catalytic nanoparticles to effect the kinetically hindered cathodic oxygen reduction reaction as well as H<sub>2</sub> oxidation. Efforts are under way to develop anion-exchange membrane (AEM) systems that employ more sustainable non-noble metal electrocatalysts [6]. These require efficient OH<sup>-</sup> conducting membranes that can withstand highly alkaline

operating environments.

Proton-conducting PEMs derived from Nafion (sulfonated tetrafluoroethylene-based fluoropolymer-copolymers) are widely implemented in present FCs and WEs. Anion-conducting membranes are less well developed but available as specialty products from companies such as FuMA-Tech GmbH [7]. New AEMs incorporating polymer backbones functionalised with quaternary ammonium (QA), imidazolium or guanidinium cations are under development [3,8-11]. The number of water molecules per ionic head group ( $\lambda$ ) [12] is critical in determining the anion conduction mechanism. Simulation studies indicate that ionic current flow in AEMs occurs by a combination of vehicular  $\text{OH}^-$  diffusion and Grotthuss hopping through the H-bonded water network solvated by ionomer side groups (Figs. 1b-d) [13-19]. Changes in water content under operational conditions affect both  $\text{H}_2\text{O}$  and  $\text{OH}^-$  mobility, and these are both affected by the molecular architecture of membrane ion-conducting channels [16-18,20-22]. The water, ion and polymer dynamics are strongly coupled on picosecond to nanosecond timescales over spatial correlations up to several nm. It is essential to determine the molecular-to-mesoscale transport mechanisms of  $\text{OH}^-$  in relation to membrane hydration and polymer relaxation dynamics to build the understanding needed for next-generation AEM design.

Quasi-elastic neutron scattering (QENS) provides a powerful technique to study these processes, with its capacity to combine selective chemical and isotopic substitutions using data obtained from instruments with different energy exchange to disentangle various dynamical contributions across ps–ns timescales. Nafion membranes and related model systems have been probed extensively using QENS [23-26]. The Fumasep FA series of membranes is marketed for anion conduction [27-31]. Fumasep FAD-55 studied here is a non-reinforced AEM with high electronic and low ionic resistance stable in alkaline environments up to pH 9 [27]. Previous QENS investigations on related FAA-3 membranes could not establish the  $\text{OH}^-$  hopping process nor its correlation with water content and polymer dynamics [32-33]. We present a detailed analysis of QENS data for FAD-55 [27-30] in its as-supplied Br- as well as OH/OD- and Cl-substituted forms, over a range of temperatures and hydration levels, using different neutron spectrometers to probe the relaxation and transport dynamics over a wide range of timescales, and disentangle details of the correlated polymer-water interactions and  $\text{OH}^-$ -conductivity mechanism (Figs. 1e-g). The QENS studies are complemented by investigation of polymer degradation occurring when handling OH-forms of the membrane, along with determination of the anionic conductivity correlated with the QENS results. Complementary QENS data were also obtained for a new laboratory-prepared membrane specifically targeted at AEMFC applications (Fig. S8) [34].

### **Samples and measurement conditions**

To evaluate the effects of membrane swelling and water content on the ion mobility, membranes were examined in partially to fully hydrated states expressed in terms of  $\lambda$  to highlight and interpret effects occurring at the molecular to nanoscale, while compensating for ionic exchange capacity (IEC) effects and differences in macroscopic water uptake by different membrane formulations and treatments (Supplementary).

AEMs are susceptible to degradation of the functional groups attached to the polymer backbone in high pH environments especially at low  $\lambda$  values and high temperatures [10,22]. We tested the membrane stability of FAD samples handled under different hydration and thermal conditions in the OH-form by examining the IEC and vibrational (Raman and IR) spectra (Figs. 1h-i). The data were collected on the samples after re-conversion back to the Cl-form after initial handling in the OH-form, and comparing to a Cl-sample that was not

treated with any alkali. We combined our H<sub>2</sub>O content determined by thermogravimetric analysis (TGA) constrained by the degradation studies and the IEC results to determine the  $\lambda$  values of different hydrated membranes, showing no significant degradation (<20%; Fig. S2) when FAD was handled in its OH-form at  $\lambda > 3$  at room temperature, as indicated by the relative intensities of the Raman peaks at 1018 and 1412 cm<sup>-1</sup> due to *N*-methylimidazolium side-groups [35]. These  $\lambda$  values correspond to operational hydration levels achieved within AEMFCs that are not operating at high current densities (Figs. 1h-i; Supplementary text 1) [36]. We did not observe any significant carbonation occurring during sample preparation for QENS studies (Fig. S4), nor any modification of QENS profiles before T-scans in the range 2-325 K (Figs. S16a-e).

Significant degradation (>70%; Supplementary text 1) only occurs after prolonged ( $\geq 10$  hrs) treatment under harsh alkaline conditions for dehydrated membranes at  $\geq 40^\circ\text{C}$ . After treatment under these conditions ( $\lambda = 2$ ) TGA results for the degraded membrane indicated a  $\sim 2$  wt% weight loss below 400 K corresponding to two water molecules that remained strongly H-bonded to the OH<sup>-</sup> group in the nominally dried sample, providing insight into understanding the OH<sup>-</sup> transport mechanism in intact OH-membranes at higher  $\lambda$  values, discussed below (Fig. S1). Weight losses observed at higher T are associated with thermal degradation of the QA groups and polymer backbone [37].

Chemically and isotopically substituted versions of FAD-55 and its hydrating medium were examined: i) the sample in its as-supplied Br-form hydrated in either D<sub>2</sub>O or H<sub>2</sub>O; ii) the membrane in OH-form hydrated in H<sub>2</sub>O; iii) the AEM sample in OD-form hydrated in D<sub>2</sub>O (Figs. 1j-m). The fully deuterated contrast (OD/D<sub>2</sub>O) was designed to focus on polymer backbone relaxation, including QA methyl side group rotation (Fig. 1c). The fully hydrogenated (OH/H<sub>2</sub>O) sample targeted water (at  $\lambda = 13$ ) and OH<sup>-</sup> facilitated hopping dynamics that were revealed at high-energy resolution. Comparisons with the Br/D<sub>2</sub>O and Br/H<sub>2</sub>O data allowed us to evaluate potential effects of OH<sup>-</sup> nucleophilic attack on the QA side groups, that are considered to be a primary cause of degradation in AEM performance especially at low hydration [3,10,21,38]. A newly-prepared membrane (HDPE-VBC-TMA) [34] was also examined at  $\lambda = 4$  in OH-H<sub>2</sub>O (Fig. S8), focusing on high-resolution experiments (IN16B) to directly show the facilitated OH<sup>-</sup> hopping mechanism observed for FAD. Samples had been previously tested for water uptake as well as for alkaline resistance, with IEC decreases <10% when the membrane is dehydrated to  $\lambda = 4$  in OH-form [34]<sup>1</sup>. Neutron scattering experiments were performed at different instruments with complementary resolution to disentangle the interacting contributions to the polymer, H<sub>2</sub>O and OH<sup>-</sup> dynamics<sup>2</sup>.

### **Different dynamic regimes and relaxation processes revealed by EFWS/IFWS**

Elastic and Inelastic scattering intensities were analysed using Fixed Window Scans (EFWS/IFWS) by increasing (IN16B, HFBS, IN6-Sharp) or lowering (IRIS) temperature (T) between 2-325 K. EFWS data and mean square atomic displacements (*msd*) extracted by

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<sup>1</sup> Preliminary results are presented here for comparison with the FAD-55 data: a detailed analysis of the dynamical properties of this new membrane will be reported elsewhere (F. Foglia, A. P. Periasamy et al., in prep.).

<sup>2</sup> Instruments and facilities: the ISIS Neutron and Muon Spallation Source (Harwell, UK), the Institut Laue Langevin (ILL, Grenoble, France), and the NIST Center for Neutron Research (Gaithersburg, USA) using i) high-resolution backscattering (BS) spectrometers IN16B (ILL) and HFBS (NIST) ( $E_{res} = 0.75, 1 \mu\text{eV}$ :  $\sim 0.07\text{-}3$  ns); ii) the time-of-flight (TOF) near-BS spectrometer IRIS (ISIS) ( $E_{res} = 17.5 \mu\text{eV}$ :  $\sim 5\text{-}100$  ps); iii) the IN6-Sharp (operated by the Laboratoire Léon Brillouin at ILL) TOF spectrometer ( $E_{res} = 70 \mu\text{eV}$   $\sim 0.5\text{-}20$  ps) (Figs. 1e-g).

Debye-Waller analysis are shown in Figure 2, with complementary IFWS data provided in Supplementary Information, giving insight into the sequential activation of different dynamical processes as a function of  $T$ . As each process ( $i$ ) becomes activated at  $T_i$ , the elastic intensity drops accompanied by a corresponding increase in inelastic intensity so that the onset of different dynamic processes is revealed by slope changes in the EFWS and IFWS intensity profiles. These EFWS/IFWS variations are modulated by the finite energy or timescale resolution available to each spectrometer, with the dynamics becoming either too fast or too slow compared with the observational window. Analysis of the datasets obtained across the different instruments thus permits recognition of different dynamic regimes and relaxation behaviours as a function of temperature across all AEM samples and hydration states (Fig. 2).

Region 1 (<200 K) is characterized by a regular loss in EFWS intensity accompanied by an msd increase up to ~200 K, with average slope  $d\langle u^2 \rangle/dT \sim 7.4 \pm 0.8 \cdot 10^{-4} \text{ \AA}^2 \text{ K}^{-1}$  for  $\lambda=4$  (IN16B, HFBS, IRIS), increasing to  $13.4 \pm 0.2 \cdot 10^{-4} \text{ \AA}^2 \text{ K}^{-1}$  when examined within the fast (0.5-20 ps) timescale window of IN6-Sharp. We assign these effects excited at low temperature to fast rotations of  $-\text{CH}_3$  groups attached to the polymer [39]. The larger msd change recorded at IN6-Sharp occurs as additional large-amplitude and acoustic-type motions of the polymer backbone contribute to the excitation profile.

In region 2 (>200 K) we observe a rapid EFWS decrease accompanied by a sharp msd rise for  $\text{H}_2\text{O}$ -hydrated samples ( $\lambda=4$ ; Fig. 2a), along with an IFWS intensity maximum recorded at IN16B (Fig. S5). This apparent maximum arises as the probed dynamics enter the backscattering window at ~200 K, to reach an energy-dependent maximum at ~260 K, and then vanish at higher  $T$  as the motional timescales became faster than the observational window. The relaxation time ( $\tau$ ) for this feature is independent of the scattering correlation length ( $Q$ ) indicating a spatially localized process, as is found for the  $-\text{CH}_3$  rotational excitations discussed above, but on a slower timescale. Because analogous behaviour is observed for different AEM hydration levels as well as for  $\text{OH}/\text{H}_2\text{O}$  and  $\text{Br}/\text{D}_2\text{O}$  samples, we can assign these additional features to activation of fast polymer side-chain dynamics occurring on a few ps timescale.

Region 3 is recognised by a sudden drop in EFWS intensity beginning at 250 K, clearly visible across the entire range of slower (IN16B/HFBS, Figs. 2a,c), intermediate (IRIS, Fig. 2b) to fast (IN6-Sharp, Fig. 2d) timescale measurements. The activated process shows a  $Q$ -dependency at low- $Q$  indicating a contribution from centre-of-mass ( $c-o-m$ ) mobility of the species involved. The EFWS changes are more pronounced for  $\text{H}_2\text{O}$ - than  $\text{D}_2\text{O}$ -hydrated samples (Fig. 2b), with the number of mobile species proportional to the hydration state. An accompanying increase in IFWS intensity above 250 K is likewise dependent on the hydration state and isotopic composition (Supplementary Information). We assign this additional  $Q$ -dependent process to rotational-translational water dynamics activated within hydrated AEM samples.

Region 4 is first observed as a moderate but regular decrease in EFWS intensity for the  $\lambda=4$  sample measured on IN16B above  $T \sim 270$  K, accompanied by a continued msd increase with reduced slope (Fig. 2a). Similar changes are observed for  $\lambda=13$  at HFBS (Fig. 2c). These observations indicate activation of a further dynamic process occurring on a much slower timescale than those described above. The IFWS signal is  $Q$ -invariant (Fig. S5) indicating localized dynamics. We assign this additional process to ion hopping facilitated by the remaining  $\text{H}_2\text{O}$  molecule bridging two  $\text{OH}^-$  groups revealed by TGA. It is only clearly detectable on high-resolution spectrometers, where although both polymer motions and

roto-translational water dynamics remain active, these have become too fast to be observed as discrete contributions to the EFWS and IFWS within the resolution window available to lower-resolution instruments.

### Relaxation processes revealed by QENS analysis in the energy exchange domain

We analyzed QENS contributions to datasets plotted in the energy domain between 230-325 K and  $4 \leq \lambda \leq 13$  by fitting Lorentzian functions guided by the EFWS, msd and IFWS results described above (Fig. 3; analysis details in Supplementary Information). We first describe the fast (1-4 ps)  $Q$ -independent polymer backbone and side-chain dynamics for samples containing no mobile protons in the ionic phase ( $D_2O$ -hydrated samples on IRIS and IN6-Sharp) [40] (Figs. 3a-d). These localised dynamics present above 230 K with an activation energy  $E_{A,polymer} \sim 6.3 \text{ kJ mol}^{-1}$  display a decrease in  $\tau_{polymer}$  with increasing temperature with enhanced slope for higher hydration levels (Fig. 3c,d). Because these dynamics are present for all samples this contribution was constrained to be a common component for all the analyses.

In high-resolution (e.g. IN16B:  $E_{res}=0.75 \text{ } \mu\text{eV}$ ) datasets this contributes to a broad underlying QENS background (i.e. polymer dynamics as detected at IRIS and IN6-Sharp and present at all  $\lambda$  and  $T$  values ; Supplementary text 2.2). Water relaxations also contribute to this broad signal. However, the most important feature is the presence of a  $Q$ -independent Lorentzian signal of much smaller width (a few  $\mu\text{eV}$ , equivalent to  $\sim 270 \text{ ps}$ ). The origin of this component was identified by comparing  $OH^-$  and  $Br^-$  datasets (Supplementary text 2.2) and assigned to slow  $OH^-$  hopping dynamics assisted by  $H_2O$  molecules bridging two  $OH^-$  (Figs. 3e-i) [17]. This latter contribution was first detected for  $\lambda=4$  samples at lower temperature (230 K; Fig. 3f), and was maintained at higher hydration levels where the broad background contained contributions from both polymer and  $H_2O$  relaxations (Figs. 3f,g). The  $OH^-$  residence time ( $\tau_{hopping}$ ) and mean hopping distance ( $2\sigma$ ) were determined from the  $Q$ -independent QENS half-width at half-maximum ( $\tau_{hopping} = \hbar/\Gamma$ ) and intensity ( $I = (1 - \exp(-Q^2\sigma^2))$ ) (Figs. 3h,i) [24]).

Analysis of the data indicated a pronounced  $T$ -dependency between 230-325 K with an average activation energy  $E_A = 4.0 \pm 0.2 \text{ kJ mol}^{-1}$  (depending on the hydration state) accompanied by an increase of the hopping distance  $2\sigma$  between 1.8-2.8  $\text{\AA}$  (Figs. 3h,i). Increasing hydration from  $\lambda=4$ -13 led to a reduction in  $\tau_{hopping}$  between 270-200 ps associated with longer (2.6 vs 3  $\text{\AA}$ ) jump distances (Figs. 3h,i). These results agree with simulations indicating a combination of ballistic, sub-diffusive/rattling and diffusive components of  $OH^-$  transport dynamics operating in different but overlapping time regimes [15,19]. The determined values of  $\tau_{hopping}$  and  $2\sigma$ , especially at  $\lambda=4$ . They indicate that on the IN16B timescale mainly  $OH^-$  ‘rattle and hop’ events are being probed, with minimal coupling to longer-range molecular/anionic mobility mechanisms [41]. When probed with a faster time window (e.g. IRIS/IN6-Sharp) the facilitated  $OH^-$  hopping becomes undetectable, as this component becomes incorporated into the elastic line, while the polymer fast-relaxation component is complemented by a further Lorentzian signal. This new feature is associated with dynamics of included water molecules (Fig. 3j), and its behaviour evolves as a function of hydration levels. At  $\lambda=4$  (Fig. 3k) it shows  $Q$ -independent behaviour, compatible with localized (i.e. confined) dynamics ( $\tau \sim 10 \text{ ps}$  and  $E_A \sim 8.4 \text{ kJ mol}^{-1}$ ; Fig. 3m). By  $\lambda=13$  (Fig. 3j) the water dynamics have become  $Q$ -dependent, indicating translationally mobile  $H_2O$  (Fig. 3n). We note that in all these cases an additional approximately linear or extremely broad Lorentzian background was needed to account for very fast (sub-ps) relaxations extending from the vibrational regime.

Our QENS analyses correspond to the interpretation of the EFWS/msd/IFWS datasets above

by describing separate but coupled dynamical regimes and relaxation phenomena, that enter the relaxation profile probed by QENS for isotopically- and chemically-substituted AEM samples, exposed to H<sub>2</sub>O/D<sub>2</sub>O solvents, as a function of hydration levels and temperature. These include i) polymer side-chain and backbone dynamics that operate for all samples throughout the temperature range; ii) localized water motions associated with hydrating H<sub>2</sub>O molecules facilitating release of OH<sup>-</sup> ions from active polymer sites [15] combined with iii) bulk-like diffusion and rotovibrational dynamics of H<sub>2</sub>O molecules with a threshold around  $\lambda \sim 8$ . This progression of water dynamics is rationalized in terms of activation of diffusive motions as mobility channels increase in size and connectivity. Our data agree with simulations predicting large water clusters that could support confined molecular diffusion above  $\lambda = 8$  [10]. Calculated changes in OH<sup>-</sup> diffusivity between  $\lambda = 2.5-4$  reflect a transition between aqueous clusters where lack of network connectivity limits long-range diffusion to an enhanced diffusivity regime following formation of an extended H-bonded network [42]. Previous QENS analyses of Fumasep FAA showed bulk H<sub>2</sub>O diffusion occurring above  $\lambda \sim 5$  [32-33].

### Analyzing the intermediate scattering function to disentangle different relaxation timescales

The measured scattering datasets  $S(Q, \omega)$  were Fourier-transformed to obtain the full intermediate scattering function  $I(Q, t)$  extending between  $\sim 0.5-3000$  ps (Fig. 4; Supplementary text 2.5). This allows an overall view of the sequential processes occurring with different onset temperatures and relaxation dynamics and reveals the coupling between them. This analysis parallels that applied to "serial decoupling" of relaxational and diffusive modes for glass-forming liquids and ion-conducting polymers [43-44]. The combined  $I(Q, t)$  profiles from different instruments reveal clear changes in slope at  $\sim 20$  and  $100$  ps, as the dynamic signatures from fast-relaxing polymer motions are followed by H<sub>2</sub>O translational and then slower facilitated OH<sup>-</sup> hopping processes enter the relaxation profile (Fig. 4a; Fig. S20). The data for different  $Q$  values are shown for the instruments probing different timescale ranges in Figs. 4b-d.

Focusing on the  $\lambda = 4$  sample studied at 230 K, it first develops a plateau at  $\sim 100$  ps followed by a shallower  $I(Q, t)$  reduction to longer timescales (Figs. 4e,f). This sample exhibits a change in  $Q$ -dependency at slow timescales with an inflection at  $\sim 2000$  ps ( $0.6-1.3 \text{ \AA}^{-1}$ ; Fig. 4g), revealing 'rattling' motions over nearest neighbour ( $\sim 3 \text{ \AA}$ ) distances. The results indicate species localized within cage sites, that could have the ability to diffuse over longer (i.e., exceeding the probed window) timescales [45]. Above 280 K, the plateau almost disappears (Fig. 4f) and the entire curve shifts towards shorter timescales (Fig. 4e). The transition between the two behaviours (278 K) sets a limit between facilitated hopping vs diffusion processes controlling the transport and thus dominating the scattering profile, as found for supercooled liquids [46].

The data also highlight an additional underlying component that enhances the facilitated hopping mechanism and eventually dominates the scattering profile above 280 K. This component, visible on the IRIS timescale (Fig. S12), could be responsible for the IFWS  $Q$ -dependence at very low- $Q$  (Figs. S5-6). It might well result from interconnectivity developed between water domains [47] and formation of a hydrogen-bonded network, that are both essential for efficient FC operation [42]. Under fully hydrated conditions, diffusive transport begins to dominate the coupled process, as evidenced by the  $Q$ -dependence of  $I(Q, t)$  at faster timescales (Fig. S20). The implementation of the timescale decoupling approach further permits the identification of a long-range component around one order of

magnitude slower that leads to the  $I(Q,t)$  decay observed into the ns regime, as well as to the quantification of fast vs slow mobile fractions. The “slow” population includes counting two protons per dynamic event, due to one water molecule bridging between QA polymer side-groups and facilitating the OH<sup>-</sup> hopping mechanism (Fig. 5a).

### **Relationships of nanoscale dynamics to OH<sup>-</sup> conductivity**

We measured ionic conductance for FAD in different ionic forms to compare with our QENS analysis (Fig. 5; Fig. S3). A main factor determining anionic mobility concerns the structural integrity of the polymer backbone and ionomeric side groups under the highly alkaline conditions and elevated temperatures during operation. Our degradation studies indicate that FAD-55 maintains its polymeric and side-chain structure at  $T < 40^{\circ}\text{C}$  under alkaline conditions for  $\lambda = 4$  and above. AEMFCs are expected to function at higher temperature ( $> 60^{\circ}\text{C}$  and up to  $80\text{--}95^{\circ}\text{C}$ ), for which more pH- and T-resistant membranes are now being designed and tested [48]. FAD-55 exhibited a noticeable loss in conductivity when operated under low-hydration ( $\lambda = 4$ ) and high-T ( $> 40^{\circ}\text{C}$ ) conditions as expected from the degradation results.

The anionic conductivity is also known to be affected by potential reaction of the OH<sup>-</sup> groups with atmospheric or dissolved CO<sub>2</sub> causing the formation of (bi)carbonate species especially under low-hydration conditions [49-50]. We carefully excluded CO<sub>2</sub> from the sample chambers for our QENS experiments, and FTIR data taken for samples following similar preparation and analysis protocols showed no evidence for these species (Fig. S4). Our conductivity results found the OH<sup>-</sup> mobility to be approximately twice that of Cl<sup>-</sup> (Fig. S3).

The degree of water uptake controls the delicate balance between vehicular vs hopping transport mechanisms as discussed above [17,47]. Computational studies show that as a consequence of electro-osmotic drag, water is partitioned unevenly within the cell along the trajectory between cathode and anode (Fig. 5a) [51]. Under fully hydrated conditions, the coupled process is dominated by vehicular transport with  $D_{tr}$  comparable to the total diffusion coefficient for membranes similar to FAD [15-18]. The simulations further indicate a long-range component comparable to the value computed for OH<sup>-</sup> diffusion [15-16], suggesting that the Grotthuss mechanism contributes ~15% to the total process.

The activation energy  $E_A = 24.5 \pm 4.5 \text{ kJ mol}^{-1}$  for coupled OH<sup>-</sup>/H<sub>2</sub>O diffusion determined by QENS is comparable with that from conductance ( $17.3 \pm 0.1 \text{ kJ mol}^{-1}$ ; Fig. 5b). The higher conductivity is related to the different effect of the hydration shell around the anions, with H-bonding between OH<sup>-</sup> and H<sub>2</sub>O facilitating diffusion and proton hopping. As the hydration level is lowered to  $\lambda = 8$ , representing a typical overall water content within an AEM polymer matrix under normal operating conditions [51], the self-diffusion coefficient becomes ~50% slower than at  $\lambda = 13$  (Fig. 5c). A smaller (~10%) conductivity variation is found when comparing with operation at similar temperatures (Fig. 5c). This result suggests that vehicular transport provides the main contribution to the anion conductivity at high hydration levels. Above  $\lambda = 8$  we expect that channels with bulk water facilitate vehicular diffusion of the anions. At  $\lambda = 4$  and below, water mediated OH<sup>-</sup> hopping becomes the primary component of the coupled transport mechanism, with a limited contribution from vehicular transport activated above 280 K, as demonstrated by the IRIS QENS datasets and  $I(Q,t)$  observed at fast timescales (Figs. 4e-f), as well as by the remarkable reduction in conductivity by around one order of magnitude (Fig. 5c). This reduction cannot be ascribed to membrane degradation as complete recovery of the conductivity is observed at 303 K (Fig. S3b); it is, therefore, due to suppression of ion structural diffusion as well as a lower degree of dissociation (as observed in proton conducting materials).

Our results indicate that OH<sup>-</sup> transport *via* Grotthuss H<sup>+</sup> hopping is enabled within a dynamic complex with three “fast” and one “slow” H<sub>2</sub>O molecules bridging two OH<sup>-</sup> groups, corresponding to the structural configuration suggested for the strongly bound remnant water found by TGA for our fully dried "reference" sample. These three H-containing species must be doubled in number to activate the complementary mass transport process. Our diffusion results at low hydration, where OH<sup>-</sup> has only its first hydration shell completed, are consistent with the model proposed by Zelovich et al. [19].

## Conclusions

Our results provide new insights into OH<sup>-</sup> transport dynamics relevant to the operation of AEMFCs and other devices. They support previous simulations indicating that charge transport occurs by a combination of vehicular OH<sup>-</sup> diffusion and Grotthuss H<sup>+</sup>-exchange with the two mechanisms balanced according to the hydration level [13-18,52]. The reduced efficiency of anion transport at low-hydration is due to the absence of coupling with H<sub>2</sub>O diffusional dynamics enabled at higher hydration, rather than degradation of ionomer functionality. The fact that the dynamics are associated with two slow protons indicating the need for one H<sub>2</sub>O molecule to mediate the OH<sup>-</sup> transport explains why the slower vehicular mechanism dominates at low-hydration. At medium-hydration the conductivity is determined by water mobility slowdown through interactions with the polymer matrix, whereas at high-hydration the diffusivity is dominated by bulk water dynamics. The insights provided by these data provide a guide for the design of new devices, where tuning the membrane nanostructure would result in activation of the anionic hopping mechanism, providing improved performance over a wide range of operational conditions.

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**Author contributions:** The study was initiated as a collaboration between CEA and UCL at a meeting between PRS, FF, PFM, SL, GG, QB and JMZ, following discussions with DJLB and TSM. Neutron scattering experiments were initiated and directed by FF and SL in collaborations with VGS, QB, JMZ, MA and MT at neutron beamline facilities. AJC and KS also participated in neutron scattering experiments, KS carried out ionic conductivity

experiments under supervision from TSM, DJLB and PRS, AJC provided FTIR and TGA data and NM obtained essential SAXS/WAXS and SANS data. FF and PFM worked closely with SL and QB to interpret the neutron scattering results. Sample degradation, IEC determinations and Raman spectroscopy experiments were initiated and carried out by JRV and AP. All authors read, edited, commented on, and fully contributed to developing the study and this manuscript.

**Competing interests:** The authors declare that they have no competing interests.

## Figure legends/captions

**Fig. 1 | Schematic illustration of AEMFC and the FAD-55 AEM in relation to measurement protocol.** **a**, Schematic illustration of an AEMFC and its mode of operation. **b-d**, Sketches illustrating the polymeric membrane, the facilitated  $\text{OH}^-$  hopping mechanism, and water translational dynamics and interactions between these dynamic processes. The cartoon at right shows rapidly relaxing  $-\text{CH}_3$  species attached to the polymer backbone [9] and functional groups [8-10,35]. Note that here we have presumed a structural model for the side group functional groups based on our Raman spectroscopic analyses [35]. **e-g**, Timescales probed in neutron scattering experiments at instruments with different energy resolution characteristics. **h**, Raman spectra recorded on a sample of FAD in its Cl-form (red spectrum, where the FAD sample had not been exposed to any high pH or low hydration conditions) and a sample in the Cl-form after it had been dehydrated at  $\lambda=4$  in the OH-form (green spectrum); spectral intensities normalized to the \* peak to aid visual comparison. **i**, Ion-Exchange Capacities (IEC) for Cl-form FAD samples after they had been treated to different hydration states in the OH-form (green and grey bars; dehydrated at room temperature and  $40^\circ\text{C}$ , respectively) compared to its Cl-form (brown dotted range). **j-m**, chemically/isotopically substituted AEM/hydration medium combinations used to investigate different aspects of the dynamics.

**Fig. 2 | EFWS Intensity and Mean Squared Displacement (msd) data for FAD-55 Membrane.** Profiles were been recorded for FAD-55 at different hydration levels ( $\lambda=4,13$ ) and isotopic compositions (OH/ $\text{H}_2\text{O}$  and Br/ $\text{D}_2\text{O}$ ) at instruments with different  $E_{res}$ . The datasets are separated according to hydration level. **a-b**, low-hydrated samples ( $\lambda=4$ ). **c-d**, fully-hydrated samples ( $\lambda=13$ ). Data obtained at each instrument are designated by different panel outlines: i)  $0.75 \mu\text{eV}$  (high resolution - IN16B; solid light blue); ii)  $1.0 \mu\text{eV}$  (high resolution - HFBS; dashed light blue); iii)  $17.5 \mu\text{eV}$  (intermediate resolution - IRIS; solid blue) and iv)  $70 \mu\text{eV}$  (broad resolution - IN6-Sharp; dark blue). OH/ $\text{H}_2\text{O}$ -hydrated samples (e.g. OH-form) are reported as blue ( $\lambda=13$ ) and green ( $\lambda=4$ ) symbols; Br/ $\text{D}_2\text{O}$ -hydrated samples (e.g. Br-form) are designated by red ( $\lambda=13$ ) and orange ( $\lambda=4$ ) symbols. Information extracted on mean square displacements (*msd*) are provided at right in each panel. The *msd* slope extrapolated from data at low- $T$  is shown as a black line. The plots are used to highlight four dynamic ranges of interest: 1)  $-\text{CH}_3$  polymer dynamics; 2) side-chain polymer dynamics; 3) water dynamics and 4) facilitated ion hopping. Corresponding IFWS data and analysis details are provided in Supplementary Information.

**Fig. 3 | Analysis of QENS associated with different dynamical processes; data for FAD-55 Membrane.** **a**, 424 Schematic illustration of polymer dynamics incorporating methyl group pseudorotation and other fast (1-4 ps depending on hydration state) side chain and backbone dynamics activated above  $T \sim 230 \text{ K}$ . **b**, Analysis of the signal obtained at  $T=300 \text{ K}$  for a  $\lambda=4$  OD/ $\text{D}_2\text{O}$  sample using  $E_{res}=17.5 \mu\text{eV}$  (intermediate resolution - IRIS). The instrument resolution function is shown as a solid blue line underneath the data points (open squares). The fast polymer relaxation gives rise to an extremely broad Lorentzian contribution (grey shaded area) underlying the data. The convolution of the two is shown as the red line fitting through the data points. **c**, relaxation times ( $\tau_{polymer}$ ) for the polymer dynamics extracted from the QENS linewidths for OD/ $\text{D}_2\text{O}$  samples with different hydration levels ( $\lambda=4-13$ ) between  $T=230 \leq T \leq 335 \text{ K}$ . **d**,  $\tau_{polymer}$  values determined for Br/ $\text{D}_2\text{O}$  samples at  $300 \text{ K}$  as a function of hydration level ( $\lambda=0-13$ ). **e**, Schematic illustration of slow (200-500 ps) facilitated  $\text{OH}^-$  ion hopping dynamics that can either be mediated by vehicular transport of  $\text{OH}^-$  ions or Grotthuss  $\text{H}^+$  transport involving depending on the hydration level of the AEM. **f,g**, Scattering profiles at  $\lambda=4$  for OH/ $\text{H}_2\text{O}$  samples at  $230$  and  $300 \text{ K}$ , respectively, measured at IN16B (high resolution). The narrow Lorentzian signal (mauve shaded area) represents the facilitated  $\text{OH}^-$  hopping dynamics superimposed on a very broad background (light blue)

corresponding to underlying polymer + H<sub>2</sub>O dynamics, that occurs on too rapid timescales to contribute to the narrower Lorentzian function within the instrumental  $E_{res}$  (0.75  $\mu$ eV). Symbols and lines for the experimental data (squares), instrumental resolution function (blue) and global fit (red) are as before. **h**, Facilitated hopping dynamics timescale ( $\tau_{hopping}$ ) extracted from QENS linewidths as a function of temperature (230 $\leq$ T $\leq$ 335 K) for OH/H<sub>2</sub>O samples with  $4\leq\lambda\leq 13$ . **i**, OH<sup>-</sup> hopping distance ( $2\sigma$ ) modelled from QENS data for  $4\leq\lambda\leq 13$  OH/H<sub>2</sub>O samples between 230 $\leq$ T $\leq$ 335 K. **j**, Schematic illustration indicating pseudorotational, diffusional and sometimes nanoconfined dynamics of H<sub>2</sub>O molecules occurring within hydrated membrane samples over intermediate (6-14 ps) timescales. **k,l**, Scattering profiles for OH/H<sub>2</sub>O samples with  $\lambda=4$  and 13 recorded at 300 K with  $E_{res}=17.5$  (intermediate resolution - IRIS) and 70 (broad resolution - IN6-Sharp)  $\mu$ eV, respectively. The H<sub>2</sub>O dynamics give rise to the main Lorentzian contribution with narrower linewidth (light blue shaded) with a significantly broader "background" signal due to polymer relaxations (grey shaded component). **m**, H<sub>2</sub>O relaxation timescale determined from QENS linewidths for  $\lambda=4$  at T=230 $\leq$ T $\leq$ 335 K. **n**, Diffusion constants ( $\text{cm}^2 \text{s}^{-1}$ ) determined from fitting QENS profiles for mobile H<sub>2</sub>O molecules within AEM samples with  $\lambda=8-13$  plotted as a function of  $1000/T$ .

**Fig. 4 | Intermediate scattering function to investigate relaxation dynamics as a function of their timescale; data for FAD-55 Membrane.** **a**, Scattering profile in the time domain for H<sub>2</sub>O-hydrated ( $\lambda=4$ ) OH-samples, at 300 K and  $Q=1.4 \text{ \AA}^{-1}$ . The global fit (red continuous curve) is overlaid across all datasets on the data points (black). **b-d**,  $Q$ -dependency of the  $I(Q,t)$  over the investigated timescales (broad resolution: IN6-Sharp -  $E_{res}=70 \text{ \mu eV}$ - panel **d**; intermediate resolution: IRIS -  $E_{res}=7.5 \text{ \mu eV}$ - panel **e**; high resolution: IN16B -  $E_{res}=0.75 \text{ \mu eV}$ - panel **d**). **e-g**, In panel **e** is presented the temperature dependence for OH-samples H<sub>2</sub>O-hydrated ( $\lambda=4$ ) between at 230 (red line) and 325 K (purple line);  $Q=1.4 \text{ \AA}^{-1}$ . Note here that profiles at 280 and 325 K have been obtained only at two energy resolutions (e.g. IRIS and IN16B). Panel **f** represents a highlight of the slow-dynamics process; panel **g** is included to show the deviation from the quadratic dependence of the intermediate scattering function for OH/H<sub>2</sub>O sample at  $\lambda=4$  and  $T=230 \text{ K}$  in the nanosecond timescale. Full details of the analysis are provided in Supplementary text 2.5.

**Fig. 5 | From dynamics parameters to AEM performance; data for FAD-55 Membrane.** **a**, Schematic illustration of an alkaline fuel cell and its mode of operation. We illustrate key areas of different water uptake with sketches indicating the main modes of OH<sup>-</sup>/H<sub>2</sub>O transport. At the anode with higher hydration levels (e.g.  $\lambda=13$ ) the transport dynamics are determined by bulk-like water diffusion, whereas lower hydration (e.g.  $\lambda=4$ , that can drop to  $\lambda=1$  at high current densities) at the cathode involve OH<sup>-</sup> hopping facilitated by the presence of H<sub>2</sub>O molecules hydrogen-bonded to the OH<sup>-</sup> groups attached to ionomer QA side groups. Within the membrane the faster anionic diffusion within the aqueous component at intermediate hydration (e.g.  $\lambda=8$ ) is slowed down by interaction with the polymer. **b,c**, Comparison between diffusion coefficient of anionic species, determined from QENS results (black symbols, left axis), and measured ionic conductance (blue symbols, right axis). Data are shown for  $\lambda=13$  (square symbols in panels **b** and **c**), as well as for  $\lambda=10, 8$  and  $4$  (circle, diamond, and crossed diamond, respectively; panel **c**). In panels **b** and **c** black (left) labels refer to diffusion coefficient ( $D$  in  $\text{cm}^2 \text{s}^{-1}$ ; black symbols); blue (right) labels refer to OH<sup>-</sup> conductivity ( $\sigma$  in  $\text{mS cm}^{-1}$ ; blue symbols).

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## Materials and Methods

### Membrane materials and sample preparation

Fumasep FAD-55 Anion Exchange Membranes (AEM) were purchased as 10×10 cm sheets with 50-60  $\mu\text{m}$  thickness from FuMA-Tech GmbH (Bietigheim, Germany). These polymer materials are designed to have high ionic conductance combined with mechanical and chemical stability at  $\text{pH}<9$ . The membrane package was kept sealed until ready for use. The as-received membranes were treated in aqueous NaCl (1 wt%) at 25°C for 24 h and subsequently washed repeatedly in ultrapure water to remove the salt, demonstrated by testing the conductivity of the washing water.

Samples were examined in Br<sup>-</sup> (to minimise the signal from Br<sup>-</sup> during the neutron experiments) and Cl<sup>-</sup> forms (to best directly compare the QENS and conductivity results) as well as substituted with OH<sup>-</sup>. The ionic forms (OH<sup>-</sup>, Br<sup>-</sup> and/or Cl<sup>-</sup>) were produced by immersing in 1 M NaOH, NaBr (aq), or NaCl (aq) at room temperature for 1h, changing the solution three times to ensure the complete ion-exchange. Each sample was washed repetitively in ultrapure water to remove excess NaOH (NaBr or NaCl), as established by testing the conductivity of the washing water.

Experiments were carried out on three H/D isotopically substituted compositions at water contents ranging between high ( $\lambda=13$ ) and low ( $\lambda=4$ ) hydration levels expressed as the number of water molecules per functional group. The highest  $\lambda$  was obtained by first immersing the membrane in liquid water followed by gentle pad-drying to remove excess liquid; lower hydration was obtained by removing the appropriate amount of water using a vacuum oven (Room Temperature) and heating for specified times followed by weighing. Further low-hydrated samples ( $\lambda\leq 2$ ) were obtained by heating overnight ( $\geq 10$  h) in a vacuum oven at  $T=40^\circ\text{C}$ .

HDPE-VBC-TMA membranes with high alkaline stability and OH<sup>-</sup> conductivity designed for AEMFC technology were produced at the University of Surrey [34]. These samples were tested in OH-form in H<sub>2</sub>O (following the ion-exchange procedure described above) at  $\lambda=4$ .

### Quasi-elastic neutron scattering (QENS) experiments

Four QENS spectrometers at three instrument facilities were used: i) IN6-Sharp (ILL, France), to investigate relaxation dynamics on a ps time scale; ii) IRIS (ISIS, UK), to study dynamics on the tens to hundred ps-time scale; and iii-iv) IN16B (ILL, France) as well as the High Flux Backscattering Spectrometer (HFBS; NIST, USA) to investigate ns timescales. Employing spectrometers that access different timescales was necessary to carry out a full characterization of the sample dynamics.

TOF experiments were performed at 300 K using an incident wavelength of  $\lambda=5.12$  Å (covering a  $Q$ -range between 0.3-2.1 Å<sup>-1</sup>) and an instrument energy resolution of 70  $\mu\text{eV}$  ( $E_{res}$ ; obtained by measuring the reference sample at 2 K); this configuration allows probing motions in the ps time scale of  $0.5<\tau<20$  ps. Complementary experiments were performed from 230-325 K on IRIS, using the PG002 analyser crystal set-up ( $0.56\leq Q\leq 1.84$  Å<sup>-1</sup>) and  $E_{res}$  of 17.5  $\mu\text{eV}$ , probing motions in the in the range  $5<\tau<100$  ps. IN16B experiments were performed using the standard unpolished strained Si(111) monochromator and analyser

corresponding to an incident wavelength of  $\lambda=6.271 \text{ \AA}$  (covering a  $Q$ -range between 0.56 and  $1.79 \text{ \AA}^{-1}$ ), an instrument energy resolution of  $0.75 \text{ \mu eV}$ , and a dynamic range of  $\pm 30 \text{ \mu eV}$ ; HFBS experiments were performed over a  $Q$  range of 0.25 to  $1.75 \text{ \AA}^{-1}$ , with  $E_{res}=1.0 \text{ \mu eV}$  and a dynamic range of  $\pm 15 \text{ \mu eV}$ . These two spectrometers probe motions in the ns time scale ( $0.07 < \tau < 3 \text{ ns}$ ). Any dynamical process with longer characteristic timescale will appear as 'elastic' scattering (i.e., contained within the  $E_{res}$  profile) in the QENS profile, while faster processes that are accessible to the instrument contribute to a background in the QENS dataset.

Elastic fixed window scans (EFWS) were recorded while heating ( $0.13 \text{ K min}^{-1}$ ; from 2 to 300/325 K; IN6-Sharp and IN16B, respectively) or cooling (IRIS) the sample. Inelastic fixed window scans (IFWSs) were recorded either by adjusting the Doppler speed on IN16B to achieve  $\Delta E=3$  and  $6 \text{ \mu eV}$  energy offsets, or integrating an arbitrarily chosen energy range (having integration width equivalent to  $E_{res}$ ; IRIS and IN6-Sharp).

AEM samples were wrapped in Al foil and then loaded into In sealed either in Au-coated flat cell ( $4 \times 5 \text{ cm}$ ) or Al annular cells. In both cases the cells had an inner thickness of  $\sim 0.5 \text{ mm}$  to achieve a neutron transmission of  $\sim 90\%$ , minimising multiple scattering. Vanadium reference and empty can measurements were carried out for data normalization (e.g. detector efficiency corrections and/or data normalisation to absolute units).

#### **Ionic conductivity measurements ( $\text{OH}^-$ and $\text{Cl}^-$ anions, partially to fully hydrated)**

The ionic conductivity for FAD-55 membrane was tested for both ionic forms ( $\text{OH}^-$  and  $\text{Cl}^-$ ) under fully (100% RH) and partially ( $80 \leq \text{RH} \leq 65$ ) hydrated conditions in the temperature range from 303 to 353 K, using a BekaTech four-point probe conductivity cell.

#### **Sample characterisation**

FTIR spectra were recorded on a Bruker Alpha FTIR instrument between  $400\text{-}4000 \text{ cm}^{-1}$  for 16 averaged scans at  $0.25 \text{ cm}^{-1}$  resolution with autosubtracted background. AFM images were recorded using Bruker Dimension Icon with SNL-10A and Scanasyt fluid+ probe. Sample imaging in water was carried out in PeakForce tapping mode. Thermogravimetric analysis (TGA) was performed on a Mettler Toledo TGA/DSC 1. Samples ( $\sim 5 \text{ mg}$ ) in a ceramic pan were heated from  $50\text{-}600^\circ\text{C}$  at  $10 \text{ }^\circ\text{C min}^{-1}$  under  $60 \text{ mL min}^{-1}$  flowing  $\text{N}_2$ , taking measurements at 1s intervals. The raw TGA thermograms were corrected by subtraction of an empty pan measurement, and normalised to their weight at  $50^\circ\text{C}$ . Prior to IEC analysis, samples in Cl-form were vacuum dried at  $50^\circ\text{C}$  for 4 h and the dry mass ( $m_d$ ; g) recorded using a Mettler Toledo Model MS204S analytical balance. Individual samples were separately immersed in aqueous  $\text{NaNO}_3$  ( $20 \text{ cm}^3$ ,  $1.2 \text{ mol dm}^{-3}$ , large excess of  $\text{NO}_3^-$  anions) and the solutions were stirred overnight at 200 rpm to exchange the  $\text{Cl}^-$  with  $\text{NO}_3^-$ . Before titration  $\text{HNO}_3$  ( $1 \text{ cm}^3$ ,  $2 \text{ mol dm}^{-3}$ ) was added to the  $\text{NaNO}_3$  solutions. Each solution was titrated with  $\text{AgNO}_3$  ( $20.00 \pm 0.06 \text{ mmol dm}^{-3}$ ) using the Metrohm 848 Titirino plus auto titrator equipped with Ag-Titrode. The IEC of each sample ( $\text{mmol g}^{-1}$ ) was calculated from end-point volume (EP;  $\text{cm}^3$ ) and  $\text{AgNO}_3$  concentration using:  $IEC = (EP \times 0.02) / m_d$  [34]. Raman spectra (for samples treated as described for IEC determination) were recorded using an InVia Reflex Raman Microscope (Renishaw, UK). Spectra were recorded on five random spots on each sample surface using 785 nm excitation (100 % laser power with pin in to create a spot), a  $20 \times$  objective lens ( $NA = 0.40$ ) and 0.5 s exposure time. To reduce background fluorescence and improve the signal-to-noise ratio, each spectrum was acquired with a minimum photobleach of 120 s and an accumulation time of 500 s. The five spectra recorded for each sample were baseline corrected, normalized to the intensity of  $1300 \text{ cm}^{-1}$  peak (PPO polymer backbone) and averaged to produced a single spectrum per sample.

### **Small and Wide Angle X-ray (SAXS/WAXS) and Neutron Scattering (SANS)**

SAXS/WAXS profiles were acquired on a Nano-inXider instrument (Xenocs, Sassenage, France) using a micro-focus sealed-tube Cu 30 W/30  $\mu\text{m}$  X-ray source (Cu K- $\alpha$ ,  $\lambda=1.54$   $\text{\AA}$ ). The SAXS/WAXS scattering patterns (covering  $Q$ -ranges 0.0045-0.37  $\text{\AA}^{-1}$  and 0.3-4.1  $\text{\AA}^{-1}$ , respectively) were detected simultaneously using two Dectris Pilatus 3 hybrid pixel detectors. Scattering was collected on the same samples measured with SANS and loaded in sealed capsules with kapton windows, at room temperature and humidity. The WAXS profiles were de-convoluted using Origin2019b. SANS measurements were performed on the SANS2d beamline at the ISIS Pulsed Neutron & Muon Source (STFC Rutherford Appleton Laboratory, UK), using neutrons with wavelengths of  $1.65 \leq \lambda \leq 14$   $\text{\AA}$ . Scattering profiles were simultaneously recorded on 2 two-dimensional detectors positioned at 4 and 8 m from the sample; providing a wide scattering vector ( $Q=(4\pi/\lambda)\sin\vartheta$ ) range  $0.0025 \leq Q \leq 0.8$   $\text{\AA}^{-1}$ . FAD membranes were investigated after overnight treatment either (i) in vacuum oven at 40°C ( $\lambda=2$ ) or ii) immersed in liquid H<sub>2</sub>O and removing the excess of surface water pad drying the membrane surface (e.g. hydrated samples). All measurements were performed in sealed 1 mm thick fused quartz Hellma cells at 25°C and room humidity.

**Data and materials availability:** All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials. Source data are available at DOI: 10.5286/ISIS.E.RB1920608, 10.5286/ISIS.E.RB2090038-1 and 10.5291/ILL-DATA.9-11-1916, and provided as a Source Data file. Additional data related to this paper may be requested from the authors.