



HAL
open science

Imaging Heterogeneous Electrocatalyst Stability and Decoupling Degradation Mechanisms in Operating Hydrogen Fuel Cells

Isaac Martens, Antonis Vamvakeros, Nicolas Martinez, Raphaël Chattot, Janne Pusa, Maria Valeria Blanco, Elizabeth A Fisher, Tristan Asset, Sylvie Escribano, Fabrice Micoud, et al.

► **To cite this version:**

Isaac Martens, Antonis Vamvakeros, Nicolas Martinez, Raphaël Chattot, Janne Pusa, et al.. Imaging Heterogeneous Electrocatalyst Stability and Decoupling Degradation Mechanisms in Operating Hydrogen Fuel Cells. ACS Energy Letters, 2021, pp.2742-2749. 10.1021/acseenergylett.1c00718 . hal-03290343

HAL Id: hal-03290343

<https://hal.science/hal-03290343v1>

Submitted on 19 Jul 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32

Imaging heterogeneous electrocatalyst stability and decoupling degradation mechanisms in operating hydrogen fuel cells

33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

*Isaac Martens,^{†,‡} Antonis Vamvakeros,^{†,§,^} Nicolas Martinez,^{||} Raphaël Chattot,[†] Janne Pusa,[†]
Maria Valeria Blanco,[†] Elizabeth A. Fisher,[‡] Tristan Asset,[∇] Sylvie Escribano,^{||} Fabrice
Micoud,^{||} Tim Starr,[○] Alan Coelho,^h Veijo Honkimäki,[†] Dan Bizzotto,[‡] David P. Wilkinson,ⁱ
Simon D.M. Jacques,[^] Frédéric Maillard,[∇] Laetitia Dubau,[∇] Sandrine Lyonnard,^{*||} Arnaud
Morin,^{*j} Jakub Drnec^{*†}*

[†]European Synchrotron Radiation Facility, Grenoble, France.

[‡]Advanced Materials and Process Engineering Laboratory, Department of Chemistry, University
of British Columbia, Vancouver, Canada.

[§]Department of Chemistry, University College London, London, UK.

[^]Finden Ltd., Oxfordshire, UK.

^{||}Univ. Grenoble Alpes, CEA, CNRS, IRIG, SyMMES, F-38054 Grenoble, France.

[∇]Univ. Grenoble Alpes, Univ. Savoie Mont Blanc, CNRS, Grenoble INP, LEPMI, Grenoble,
France.

^oIndependent researcher, St. Johann im Tirol, Austria.

^hCoelho Software, Brisbane, Australia.

ⁱDepartment of Chemical and Biological Engineering, University of British Columbia,
Vancouver, Canada.

^jUniversité Grenoble Alpes, CEA, 17 Avenue des Martyrs, F-38000 Grenoble.

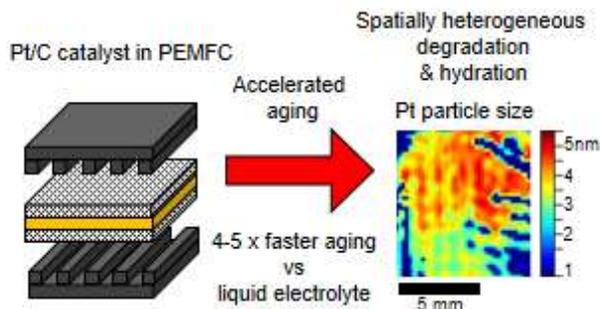
Corresponding Author

*drnec@esrf.fr, sandrine.lyonnard@cea.fr, arnaud.morin@cea.fr

ABSTRACT

Proliferation of hydrogen fuel cell systems is hindered by degradation of the platinum catalyst. Here, we provide a device level assessment of the catalyst degradation phenomena and its coupling to nanoscale hydration gradients, using advanced *operando* X-ray scattering tomography tailored for device-scale imaging. Gradients formed inside the fuel cell produce heterogeneous degradation of the catalyst nanostructure, which can be linked to the flow field design and water distribution in the cell. Striking differences in catalyst degradation are observed between operating fuel cell devices and the liquid cell routinely used for catalyst stability studies, highlighting the crucial impact of the complex operating environment on the catalyst degradation phenomena. This degradation knowledge gap accentuates the necessity of multimodal, *in situ* characterization of real devices when assessing the performance and durability of electrocatalysts, and more generally, electrochemically active phases used in energy conversion and storage technologies.

TOC GRAPHIC



Large scale adoption of hydrogen energy systems requires reliable, cost competitive water electrolyzers and fuel cells, of which the polymer electrolyte membrane (PEM) variants are most popular.¹ The performance and cost are both driven by design of a multi-layered nanocomposite membrane electrode assembly (MEA).² Despite great progress in optimizing individual components of the PEM fuel cell (PEMFC) MEAs in laboratory model systems^{3,4}, these advances have not always translated into improved performance at the device level⁵⁻⁷, because strong interactions between different components and the complex chemical environment of an operating cell hinders the integration of each component into an optimized MEA architecture^{6,8}. These effects apply not only to catalyst activity, where poisoning of the Pt surface by ionomer is increasingly recognized as a limiting factor,⁷ but also to water/thermal transport, electrolyte stability, and myriad other issues related to integrated systems engineering.⁹ Improving the durability of high performance catalysts presents a great challenge and is limited by our understanding of the degradation phenomena.^{10,11} Carefully balancing the performance, durability, and cost of the oxygen reduction reaction (ORR) catalyst is necessary for technological advancement of PEMFC systems.¹²

1
2
3 The degradation processes of Pt-based ORR catalysts have been rigorously investigated under
4 idealized laboratory conditions (i.e. in inert atmosphere, room temperature, and ultrahigh purity
5 liquid electrolyte). The oxidation and reduction of the Pt surface plays a central role¹³ with
6 potential cycles triggering nanoparticle reconstruction and dissolution¹⁴. This leads to corrosion,
7 Ostwald ripening and coalescence of the nanoparticles during operation, lowering the surface area
8 and mass activity of the catalyst.¹⁵ The extent to which catalyst activity and durability
9 measurements under idealized conditions transfer directly to the hot, gas phase polymer electrolyte
10 MEA environment, remains an open question¹⁶, and the answer will guide development of active
11 materials and operating protocols towards more robust performance. While much is known about
12 degradation occurring specifically inside MEAs^{6,8,9,12,15,17–22}, direct cell performance prediction
13 based on rotating disc electrode studies remains challenging, especially for nanostructured
14 catalysts, due to the phenomena discussed above.

15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
Techniques which can simultaneously probe all the components of functional devices at the
nanoscale are urgently required to optimize the MEA architecture and operating conditions.
Spectromicroscopy approaches using electron²³, neutron²⁴, and photon beams^{14,21,25} are powerful,
but generally laborious and/or limited to *ex situ* experiments. Significant advances in spatial and
time resolution with *in situ* X-ray absorption tomography have been recently achieved.^{26,27}
However, spatial resolution is often limited to scales greater than 100 nm and lacks the critical
nanoscale and chemical information about the catalyst and supporting materials. This information
is necessary to connect the catalyst activity, morphology and stability to the overall MEA
performance.²⁸ These properties determine the device's life cycle, with major impact on its
economic feasibility.²²

1
2
3 Here, we study the catalyst degradation phenomena in an operating PEMFC using novel high
4 energy X-ray scattering techniques, simultaneously mapping chemical composition with X-ray
5 diffraction computed tomography (XRD-CT) and nanostructure by small angle X-ray scattering
6 computed tomography (SAXS-CT) across the device scale of several centimeters (Fig. 1A).^{29–31}
7
8 XRD-CT has been previously used to investigate solid oxide fuel cells³², catalytic reactors³³ and
9 batteries³⁴ from hundreds of micrometers up to millimeters in size and provides atomic scale
10 information about the used materials. To understand the degradation phenomena at the device
11 level, we have extended these techniques to samples 10x larger than previously possible, such that
12 entire X-ray transparent 5 cm² PEMFCs³⁵ can be imaged (Fig. 1A). The voxel size (200 μm x 200
13 μm x 50 μm) shown here is currently limited by the beam size and measurement speed, and can
14 be optimized for larger devices down to sub-micrometer resolution using 4th generation X-ray
15 sources. Detailed descriptions of the method are available as supplementary information.

16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31 Major advancements in computed tomography algorithms allow a direct observation of the rapid
32 heterogeneous nanostructural deterioration of the MEA. Catalyst aging was explored under two
33 different degradation conditions: under a potentiostatic hold at 1 V, and through a commonly used
34 cyclic voltammetry accelerated stress test (AST). The catalyst degradation is directly linked to the
35 formation of chemical and/or temperature gradients, correlated to the water distribution in the cell
36 materials, and imprinted by the macroscale geometry of the flow field. Evidence of heterogeneous
37 aging has been previously observed in end-of-life samples using *ex situ* analysis with TEM¹⁸ or
38 X-ray diffraction²⁰. Characterizing and predicting the gradients at different operating conditions
39 and integrating the structural evolution of electrocatalysts with fuel cell design will be increasingly
40 necessary to mitigate degradation and lower the cost of the technology.

41 42 43 44 45 46 47 48 49 50 51 52 53 **3D chemical mapping using X-ray scattering tomography**

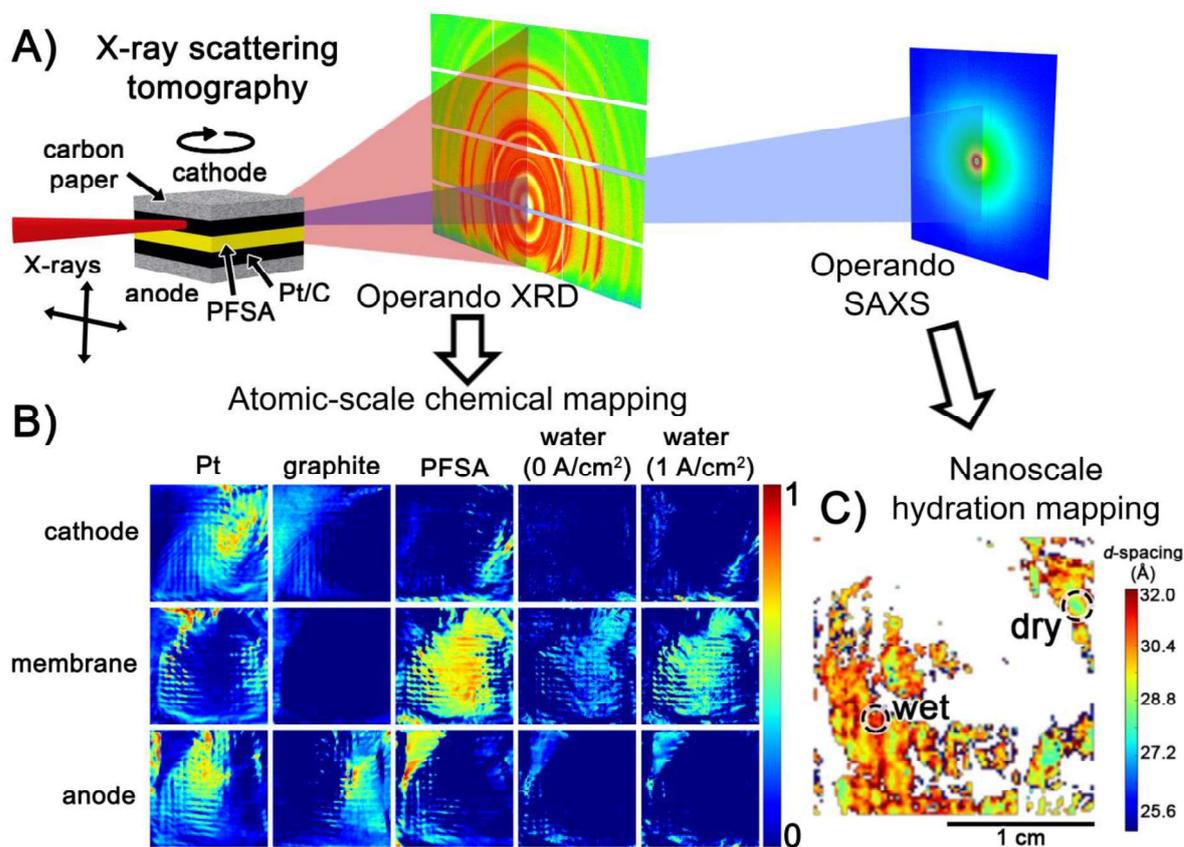


Figure 1. In situ X-ray scattering tomography of a fuel cell membrane electrode assembly. A) Schematic of the grazing incidence diffraction tomography. B) Chemical maps of tomography slices collected through the cathode, PFSA membrane, and anode and obtained by simple deconvolution of reconstructed XRD patterns. Each map in B) is 1.9 cm across, 200 μm resolution, measured over the central region covered by the flow field of the 5 cm^2 cell. The cell was operated at 80°C and 100% relative humidity. The three slices were collected at 1 V, and during operation at 0.6 V, 1 A/cm^2 . C) SAXS tomography of slice through the PFSA membrane in a separate experiment, collected at 0.8 A/cm^2 , 75°C, 80% relative humidity. The color indicates the d-spacing of the ionomer phase segregation, reflecting local hydration.

1
2
3 The main advantage of XRD-CT is its superior chemical contrast in comparison to standard
4 absorption-contrast tomography (Fig. 1B). The chemical maps, which can be merged into 3D
5 images (Fig. S1), reflect the intrinsic heterogeneous nature of the PEMFC largely imprinted by the
6 flow field design. The color mapping is normalized for each phase to the highest intensity detected
7 across all three slices. Compression of the flow field induces wrinkling in the MEA, on the order
8 of a few microns, generating lined patterns in the Pt and ionomer signals (note that the parallel
9 channels of the cathode and anode plates were aligned perpendicular to each other).¹⁹ This
10 heterogeneous pressure field alters mass and thermal transport, as well as the mechanical
11 properties of the electrodes, generating chemical gradients (H_2O , O_2 , pH, $\text{Pt}^{2/4+}$) inside the cell and
12 defining the nanoscopic degradation phenomena in the catalyst layer, which we will show later.
13
14

15 One of the most important aspects of fuel cell operation affected by the flow field is the water
16 transport and distribution inside the catalyst layer, gas diffusion layer, and ionomer membrane,
17 which is critical for obtaining maximum cell performance.^{26,36} XRD-CT allows the spatial
18 distribution of liquid water to be obtained from the amorphous background of the XRD patterns
19 (Fig. 1B, detail in S5). The water distribution obtained in this manner is shown for slices collected
20 at two different conditions: i) at 1 V, $\sim 0 \text{ A/cm}^2$ and, ii) at 0.6 V, where the cell is operating at high
21 current density (1 A/cm^2 , 0.6 W/cm^2). Differences in the quantity and distribution of water are
22 detected throughout the device (Fig. 1B, far right column) and local water accumulation is
23 observed, especially inside the ionomer membrane under the landing areas where the flow field
24 structure touches the MEA. While not rigidly ordered, X-ray scattering from the ionomer produces
25 several features over a very wide angular range, including the well-known nanoscale
26 ionic/hydrophobic phase segregation ($\sim 0.15 \text{ \AA}^{-1}$, Fig. S16), and semicrystalline packing of the
27 backbone matrix ($\sim 2.5 \text{ \AA}^{-1}$, Fig. S5). Unfortunately, the water, ionomer and carbon content in
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3 pixels containing large quantities of Pt (i.e. inside the catalyst layer specifically) is difficult to
4
5 obtain as the weak scattering from the light materials is masked by the high attenuation of Pt.
6
7 These limitations can be addressed by imaging hydration gradients inside the cell with SAXS-CT,
8
9 which is extremely sensitive to ionomer hydration. The phenomena of water collecting underneath
10
11 the fuel cell flow fields has been studied for decades using X-rays³⁷ and neutrons^{17,38}. Quantitative
12
13 measurements of ionomer nanostructure by SAXS add significant value to standard water imaging
14
15 experiments, since hydration inside the polymer electrolyte can be precisely determined.^{39,40}
16
17 SAXS-CT allows the spatial correlation of ionomer nanostructure, with the water content in the
18
19 other cell constituents while using the same X-ray probe. A SAXS-CT slice collected in a separate
20
21 experiment during cell operation (0.8 A/cm², ~0.59 V, 80% relative humidity) reveals the
22
23 heterogeneous hydration of the membrane throughout the MEA with significantly better detail
24
25 than in the XRD measurement (Fig. 1C). The SAXS curves were modelled as a power law
26
27 background with a Gaussian ionomer peak (Fig. S16).⁴¹ The thin membrane was not perfectly
28
29 aligned with the plane of the slice, so we restrict our analysis to the regions where the ionomer
30
31 peak is clearly visible. Comparatively wet and dry regions inside the membrane can be resolved
32
33 through changes in the *d*-spacing of the ionomer peak which indicates the distance between ionic
34
35 nanodomains increases from 3.5 to 3.8 nm in the preferentially hydrated regions. The wet and dry
36
37 regions exhibit a vertically lined pattern correlated with the positions of the flow field. This pattern
38
39 is similar to the water distribution from the XRD-CT measurements, validating the data obtained
40
41 by less precise XRD pattern analysis (note that the cathode and anode flow field ribs were aligned
42
43 parallel to one another for the SAXS imaging). The SAXS shows that the membrane is partially
44
45 hydrated, about 10% by weight (fully hydrated membranes contain up to 25% water^{42,43}). Streaks
46
47 in the SAXS-CT image show the membrane underneath the flow field rib is preferentially hydrated
48
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3 pointing to the same hydration distribution pattern within the membrane as the liquid water in the
4 carbon diffusion layers observed previously.³⁸ SAXS-CT analysis confirms that the nanoscale
5 spatial heterogeneities arising from significant hydration gradients are correlated to the flow field
6 pattern. Heterogeneity in the XRD-CT images is therefore also likely connected to the
7 inhomogeneous distribution of water inside different layers of the device.
8
9

16 **Degradation after a potentiostatic hold at 1 V**

17
18 To correlate the water distribution inside the cell to the nanostructural heterogeneity of the catalyst
19 and aging mechanisms within the MEA^{44,45}, we extract the catalyst's structural parameters from
20 the XRD-CT patterns. The intensity parameter of the Pt diffraction signals corresponds to the
21 quantity of material, while the peak widths are related to the average particle size and defect
22 content of the Pt catalyst. The main complication limiting such analysis on full scale operational
23 devices are peak broadening artefacts known as parallax errors (i.e. peak broadening as a function
24 of $\tan 2\theta$, Figs. S9 & 10). These distortions in XRD-CT images of large samples >1 cm have until
25 now limited the quality and reliability of nanostructural parameters obtained from the diffraction
26 data (e.g. lattice parameter, peak widths).³⁵ Here we disclose a new tomographic algorithm called
27 Direct Least-Squares Reconstruction (DLSR) which provides a generalized solution to this
28 problem, and corrects for parallax distortion in arbitrarily large samples. Therefore, the practical
29 maximum sample size for XRD-CT is limited only by penetration of the X-ray beam. This advance
30 extends the capabilities of scattering-contrast tomography from laboratory specimens to samples
31 normally imaged using hospital-style CT scanners, including practical fuel cell devices. The DLSR
32 algorithm quantitatively recovers the diffraction profile (Figs. S11-S15) and the microstructure of
33 the Pt catalyst in the fuel cell, including the particle size and strain. The computationally expensive
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3 nature of the parallax-corrected reconstruction currently limits the image resolution, although rapid
4
5 advances in software capability are expected. A detailed discussion on parallax artefacts, its
6
7 correction using the DLSR algorithm, and benchmarking versus conventional algorithms can be
8
9 found in the Supplementary Information.

10
11
12 Figure 2 shows images of the Pt nanostructure obtained from Rietveld analysis of a single XRD-
13
14 CT image slice collected through the cathode of a degraded MEA during operation at 1 A/cm².
15
16 The degradation was induced by holding the potential at 1 V for 10 hours at 80°C, which is slightly
17
18 above open circuit voltage (ca. 0.95 V).¹⁵ These high, cell reversing potentials lead to Pt oxidation
19
20 and degradation.⁴⁶ Variations in the Pt intensity map (Fig. 2A), reflect the mechanical distortion
21
22 of the catalyst coated membrane inside the pressurized cell during operation. The region where the
23
24 ionomer membrane protrudes into the measured slice shows particles up to 100 nm in size (yellow
25
26 arrow, in Fig. 2B). While degradation gradients through the cross-section of catalyst layers have
27
28 been previously reported using *ex situ* TEM^{18,47}, the size of the Pt nanoparticles in the region of
29
30 these protrusions are an order of magnitude larger than expected. Nanoparticles of this size are
31
32 typically found in the "Pt band", formed near and inside the membrane of aged MEAs.^{48,49} Even
33
34 though the formation of this Pt band has been identified as a key factor in the stability of field-
35
36 tested MEAs⁵⁰, *in situ* detection of Pt band formation has not been previously reported. Higher
37
38 resolution imaging and aging conditions which emphasize Pt band formation will be necessary to
39
40 confirm the localization of these large Pt particles inside the membrane.
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

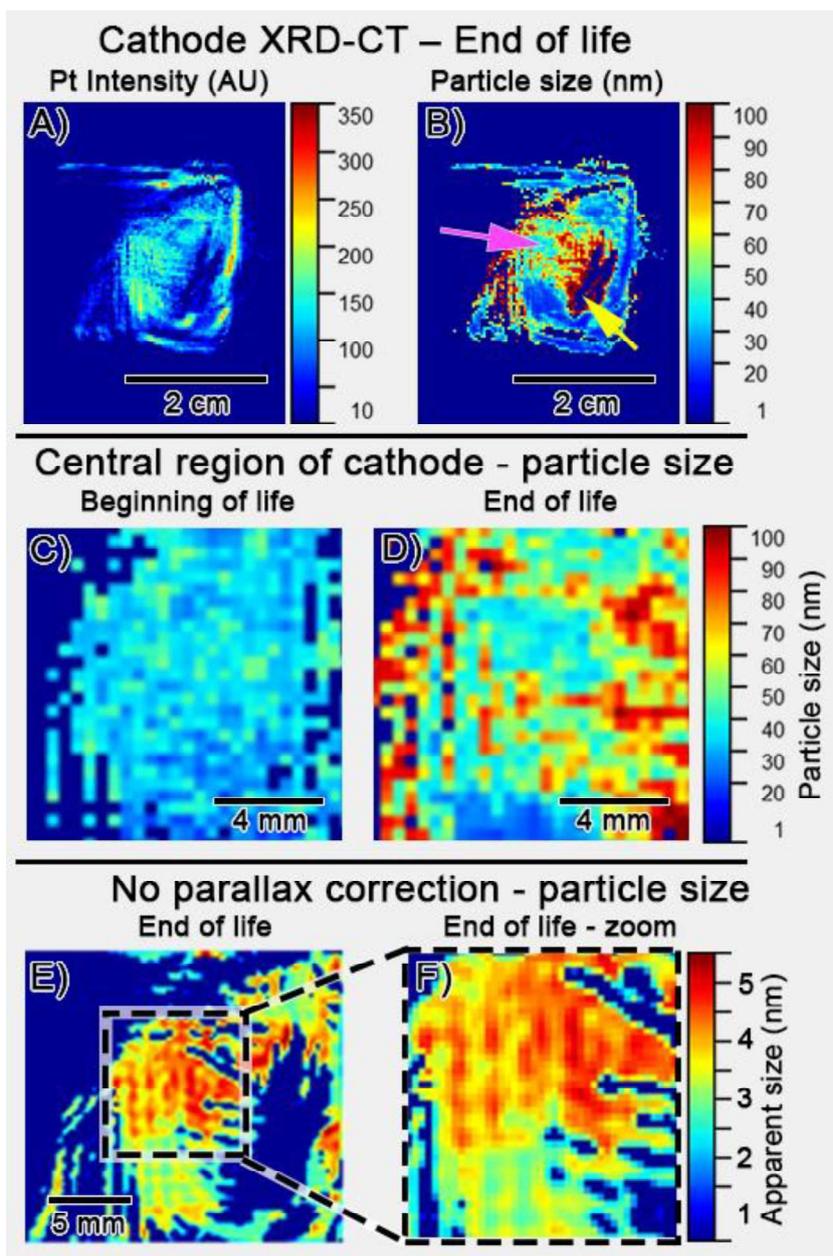


Figure 2. XRD-CT of Pt cathode catalyst. A) Pt intensity distribution over the single CT slice. B) Pt particle size map, parallax corrected. The yellow arrow indicates the region where the ionomer membrane protrudes into the slice. C, D) Particle size maps for identical regions in the central region of the electrode (magenta arrow in B) at the beginning and end of testing, respectively. E) High resolution crystallite size map for central region of the electrode at end of testing, without parallax correction. F) Magnification of E) showing detailed particle size map.

1
2
3 The central region of the sample (Fig. 2B, magenta arrow) can be seen in greater detail in Figs.
4
5 2C & D. Although the spatial resolution of these parallax corrected images is limited (500 μm) the
6
7 particle size in the sample at the beginning of testing (Fig. 2C) is much more spatially
8
9 homogeneous than after testing (Fig. 2D). Higher spatial resolution XRD-CT images can be
10
11 obtained if parallax correction is neglected (Figs. 2E and 2F, 200 μm resolution), with the trade-
12
13 off that the calculated particle sizes are qualitative and only comparative analysis is possible.
14
15 Vertical and horizontal streaks are visible in the uncorrected maps, where the particles are
16
17 systematically larger in regions covered by the flow field plates. Therefore, the morphological
18
19 degradation of catalyst nanoparticles in these regions is more severe, coincident with previously
20
21 observed thinning of the membrane and local Pt corrosion.^{51,52} The specific factors responsible for
22
23 this nanoscale heterogeneity at high potentials are not easily decoupled. However, the link between
24
25 flow field design and water content detected by SAXS-CT, and the correlation to the water
26
27 distribution in the cell with catalyst degradation suggests that locally altered concentration and
28
29 mass transport of dissolved species (O_2 , H^+ , $\text{Pt}^{2/4+}$) underneath the flow field ribs enhances
30
31 degradation. A detailed understanding of how these complex gradients produce heterogeneous
32
33 aging requires further study under well-defined aging conditions, likely guided by input from the
34
35 growing fuel cell modelling community.
36
37
38
39
40
41

42 **Degradation during accelerated stress testing in PEMFC vs conventional cells**

43
44 Given the heterogeneity observed inside the catalyst layer during aging in an operating PEMFC
45
46 device, the relevance of aging data from laboratory model systems deserves scrutiny because
47
48 catalyst durability is principally assessed using cyclic voltammetry in ultrahigh purity liquid
49
50 electrolyte at room temperature on a rotating disc electrode (RDE).^{53,54} To evaluate the differences
51
52 in these environments, the most popular catalyst AST protocol (sweeping between 0.6-1.0 V at 50
53
54
55
56
57
58
59
60

1
2
3 mV/s with Ar atmosphere on the cathode) was employed on the same commercial catalyst (Fig.
4 S21) inside the PEMFC and with a conventional three electrode RDE cell.² X-ray diffraction was
5
6 measured *in situ* at multiple locations in the cathode throughout the AST of the PEMFC sample
7
8 and transmission electron microscopy (TEM) images were collected for both the PEMFC and the
9
10 RDE cell catalyst at the beginning and end of the test.
11
12
13

14
15 Both catalyst particle ripening and dissolution of Pt in the PEMFC sample are directly observed
16 during the AST. The mean crystallite size of the Pt increases from 4.6 nm to 10.3 nm (Fig. 3, top)
17 and approximately 30% of the Pt in the cathode dissolved (Fig. 3, bottom), which is consistent
18
19 with previous work.^{14,46} Neither parameter follows a linear trend with the number of cycles: a large
20
21 fraction of the overall change takes place in the first few cycles and the degradation slowly
22
23 diminishes in effect without reaching a plateau.⁴⁴
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

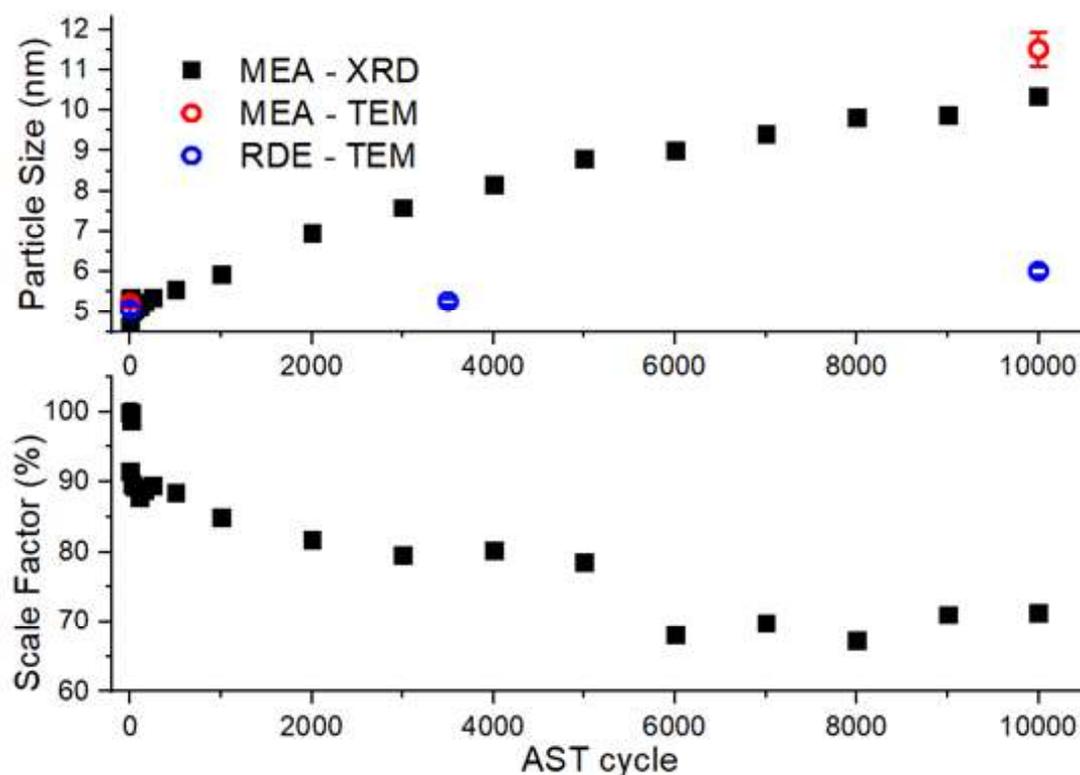


Figure 3. Particle size (top) and percentage of Pt remaining in electrode (bottom) over 10^4 cycles of accelerated stress testing (0.6-1.0 V, 50 mV/s) determined from Rietveld analysis. Mean particle sizes for the full MEA cathode and rotating disc electrode (RDE) determined by electron microscopy are overlaid (red and blue circles, respectively). The temperature of the PEM and RDE cells during ageing was 80°C and 20°C, respectively. The error estimated from the Rietveld covariance matrix is smaller than the plotted XRD markers. The TEM data error bars correspond to the standard error of the log-normal fit.

As anticipated, the catalyst in the PEMFC aged dramatically faster than inside a conventional RDE cell. These differences can be attributed to the PEMFC environment, including higher temperature, lower pH, and enhanced mass transport of dissolved species, all of which promote corrosion of metallic catalysts. Although no tomography was performed, XRF mapping of the

1
2
3 MEA sample after ageing showed that the dissolution was fairly homogeneous and XRD at
4
5 multiple locations, both in the channels and landing areas, yielded similar results (Fig. S26). These
6
7 data indicate that the chemical environment created inside the fuel cell during this AST profile is
8
9 more homogeneous than the cell degraded by potentiostatic hold at 1 V, and questions the utility
10
11 of current ASTs to assess catalyst stability during PEMFC operation. This is because the chemical
12
13 and temperature gradients, which define the degradation dynamics as discussed above, are linked
14
15 to faradaic reactions, and are suppressed during stress testing under inert atmosphere. Therefore,
16
17 the only reliable way to benchmark the catalyst stability, is to study the materials in a PEMFC
18
19 device during operation. Furthermore, the predictions obtained from laboratory model systems are
20
21 substantially and systematically different than catalyst degradation in devices.
22
23
24
25

26 **Distinguishing catalyst degradation mechanisms through XRD**

27
28 Studies which track the dissolution of Pt inside operating PEMFCs are relatively rare. In this
29
30 case, the quantity of Pt observed *in situ* by XRD can be correlated to the electrochemical surface
31
32 area (ECSA) of the catalyst measured throughout the test. The ratio of the ECSA to Pt loading
33
34 throughout the AST is related to the surface-area-to-volume ratio of the catalyst, which can be
35
36 used to probe degradation mechanisms, since different mechanisms produce characteristic trends.
37
38 Processes such as local electrochemical disconnection, surface activation, or partial corrosion or
39
40 larger particles produce increasing ECSA / loading ratios. Aggregation and ripening degradation
41
42 modes produce decreasing ratios, while catalyst detachment from the support followed by
43
44 dissolution would maintain a constant ratio. The observed trend is the sum of all simultaneous
45
46 degradation modes. The shape of the normalized ECSA / Pt loading curve for the MEA is presented
47
48 in Figure 4A. The ECSA is initially unstable and reaches a maximum after the first 100 cycles
49
50 (attributed to surface cleaning), even though 12% of the Pt loading dissolves during this activation
51
52
53
54
55
56
57
58
59
60

1
2
3 phase. The ECSA / Pt loading ratio then decreases smoothly between cycle 100 and 10000. During
4
5 this second phase, only 16% of the catalyst dissolves/detaches, but 63% of the ECSA is lost to
6
7 ripening, aggregation, and other mechanisms altering the morphology, but not the quantity of Pt.
8
9 The large difference between these numbers highlights both the importance of Pt redeposition and
10
11 particle-particle interactions in the degradation mechanism of commercial PEMFC catalysts, and
12
13 how Pt corrosion represents just one (but critical) step. We predict that the aging of shape-
14
15 controlled catalysts under well-defined conditions would benefit even further from direct
16
17 measurements of surface area to volume ratios during *operando* experiments.
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

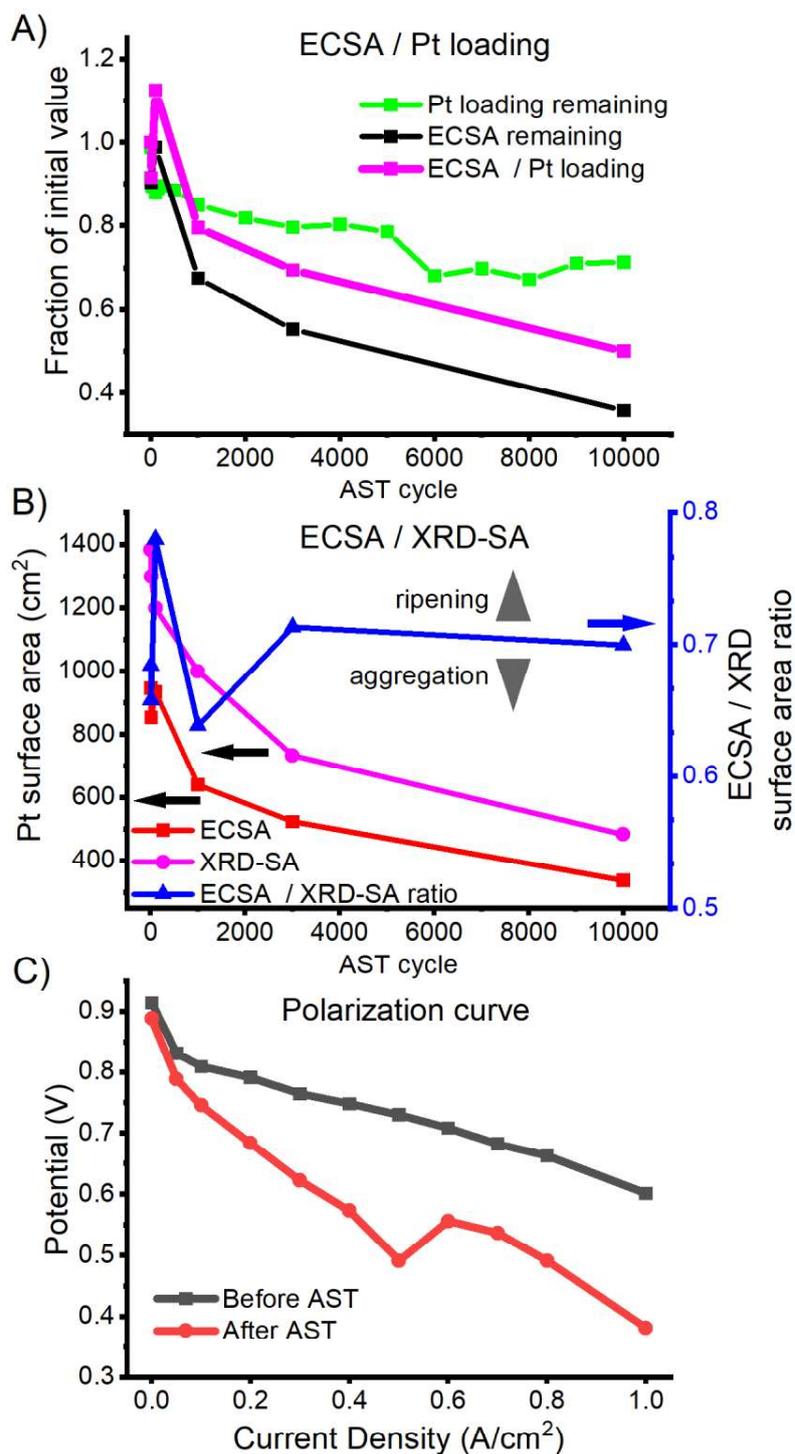


Figure 4. A) Ratio of metallic Pt to ECSA remaining as a function of AST cycle number. Both values have been normalized to the first cycle. B) Pt ECSA and total theoretical surface area calculated from the XRD loading and crystallite size (XRD-SA), and their ratio over the course of

1
2
3 the AST cycling. The Pt catalyst was modelled as monodisperse spheres, using the parameters
4 from Figure 3. C) Polarization curves of MEA before and after AST cycling, extracted from Fig.
5 S28. The cell was operated at 80°C, flowing H₂/air at 100%RH.
6
7
8
9

10
11
12 The ratio of the ECSA to crystallite size by XRD allows ripening and aggregation degradation
13 mechanisms to be decoupled. The observed crystallite size is unaffected by aggregation, but
14 responds to ripening/coalescence processes, while the ECSA is sensitive towards both. The loading
15 and crystallite size measured with XRD allow the “total” Pt surface area of the catalyst to be
16 calculated on an absolute scale. The electrochemically connected fraction, dispersion, or
17 “utilization” of the Pt catalyst can be estimated from the ratio of the ECSA and this XRD calculated
18 surface area (XRD-SA). Aggregation would cause the observed ECSA / XRD-SA ratio to
19 decrease, while coalescence and ripening produce either higher or constant values depending on
20 the catalyst morphology. The total surface area of the catalyst measured by cyclic voltammetry
21 and calculated by XRD in cm², along with the ECSA / XRD-SA ratio of the two are shown in
22 Figure 4B. The catalyst was approximated as monodisperse spheres, with no corrections for
23 surface area blocked by carbon support, electrochemically disconnected particles or aggregation.
24 Following the initial 100 cycles over which the catalyst surface is cleaned and the ECSA increases,
25 the ECSA/XRD-SA ratio decreases to 64% at 1000 cycles, then increases and stabilizes at 70-71%
26 for the remainder of the AST. We attribute these changes to an aggregation phase, followed by
27 coalescence and ripening. The total range of the ECSA/XRD-SA ratio is relatively stable (64-
28 78%), even though the total surface area changes drastically over the course of the AST. This
29 indicates that aggregation processes only account for a few percent of the changes in ECSA, while
30 coalescence and ripening phenomena are responsible for the majority of the decrease in surface
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3 area. The ~70% accessibility of the total Pt surface calculated from XRD is physically reasonable
4
5 considering both the simplicity of this model, and that the carbon support and Pt aggregates block
6
7 the remaining ~30% of a Pt crystallite's surface. The drastic loss of cathode ECSA during the AST
8
9 produces clear performance degradation of the PEMFC device, as shown in the ORR polarization
10
11 curves collected before and after the AST (Fig. 4C). The deep structural insight provided by
12
13 operando XRD greatly enhances the value of even simple AST experiments on standard
14
15 commercial catalysts. Ratios of microstructural parameters allow the contributions of competing
16
17 degradation mechanisms to be decoupled.
18
19
20

21
22 Major advances in XRD-CT reconstruction algorithms allow for simultaneous assessment of
23
24 nanostructural and chemical heterogeneities inside an operational 5 cm². Interactions between
25
26 different phases can be correlated at high current densities with a single probe. The XRD-CT
27
28 images provide nanoscale information and show spatially resolved differences in the aging of
29
30 catalyst particles, which correlate to the flow field geometry and water distribution within the
31
32 device observed by SAXS-CT. Therefore, the macroscopic design of the cell has a decisive role in
33
34 the nanoscopic degradation phenomena of the catalyst, which needs to be taken into account at all
35
36 levels of PEMFC design. Accelerated stress testing tracked by *in situ* X-ray diffraction indicates
37
38 that catalyst aging inside PEMFCs is extremely aggressive when compared to conventional RDE
39
40 testing, even in the absence of faradaic currents which further accelerate the ageing. X-ray
41
42 scattering tomography and *operando* AST measurements are shown to be a powerful platform for
43
44 deconvoluting the degradation mechanisms of electrocatalysts. Stress tests performed in a liquid
45
46 cell should be critically evaluated in order to predict catalyst degradation rates and mechanisms in
47
48 functional systems. The presented strategy for deep, *in situ* and *operando* characterization bridging
49
50 fundamental chemistry and device engineering is generally applicable to the next generation of
51
52
53
54
55
56
57
58
59
60

1
2
3 batteries, solar cells, and other energy conversion and storage systems with few compromises in
4
5 electrochemical performance. These devices are composed of complex materials, where chemical
6
7 reactivity, transport phenomena, and degradation mechanisms are intrinsically coupled, yielding
8
9 heterogeneous distributions of phases. Advanced tools capable of providing real-time, multi-scale
10
11 chemical and structural information are therefore invaluable towards understanding the evolution
12
13 of these systems. We anticipate that such non-intrusive and holistic approaches, which combine
14
15 several X-ray scattering tomography techniques, will enhance understanding of the roles, and
16
17 interactions between different constituents, allowing next-generation materials to be incorporated
18
19 into PEMFCs and other electrochemical devices.
20
21
22

23 **Supporting Information**

24
25 Detailed descriptions of the sample preparation, small angle X-ray scattering, X-ray
26
27 diffraction, computed tomography data analysis algorithms, 3D reconstructions, Rietveld
28
29 refinement, electron microscopy, particle size analysis, X-ray spectroscopic imaging, and
30
31 electrochemical characterization can be found in the Supporting Information.
32
33
34

35 **Notes**

36
37
38 I.M., A.V., R.C., J.P., M.V.B., E.A.F., T.A., T.S., D.B., D.P.W, and J.D. performed the XRD
39
40 experiments. N.M, S.E., F.M., S.L., A.M, and J.D. performed the SAXS experiments. A.V.,
41
42 A.C., and S.J. devised and implemented the DLSR algorithm. I.M. and J.D. wrote the
43
44 manuscript. D.B., D.P.W., S.L., A.M., V.H., S.J., F.M., L.D. and J.D. supervised the work. All
45
46 authors reviewed the manuscript.
47
48

49
50
51 The authors declare no competing financial interest.
52

53 **ACKNOWLEDGMENT**

1
2
3 This work was supported by Automotive Partnership Canada and NSERC. A.V. is supported
4
5 through the European Union Horizon 2020 program under Grant Agreement No. 679933
6
7 (MEMERE). The SAXS-CT was funded by Institut Carnot Energies du Futur under the
8
9 STATUQUEAU project.
10
11
12
13
14

15 REFERENCES

- 16
17 (1) Staffell, I.; Scamman, D.; Velazquez Abad, A.; Balcombe, P.; Dodds, P. E.; Ekins, P.; Shah, N.; Ward, K. R. *Energy Environ.*
18
19 *Sci.* **2019**, *12* (2), 463–491.
20
21
22 (2) Office of Energy Efficiency and Renewable Energy. *2019 Annual Merit Review and Peer Evaluation Report*; 2019.
23
24 (3) Chen, X.; Kang, Y.; Huo, Z.; Zhu, Z.; Huang, W.; Xin, H. L.; Snyder, J. D.; Li, D.; Herron, J. A.; Mavrikakis, M.; Chi, M.; More,
25
26 K. L.; Li, Y.; Markovic, N. M.; Somorjai, G. A.; Yang, P.; Stamenkovic, V. R.; Chen, C.; Kang, Y.; Huo, Z.; Zhu, Z.; Huang, W.;
27
28 Xin, H. L.; Snyder, J. D.; Li, D.; Herron, J. A.; Mavrikakis, M.; Chi, M.; More, K. L.; Li, Y.; Markovic, N. M.; Somorjai, G. A.;
29
30 Yang, P.; Stamenkovic, V. R. *Science* **2014**, *343* (6177), 1339–1343.
31
32 (4) Stephens, I. E. L.; Bondarenko, A. S.; Grønbjerg, U.; Rossmeisl, J.; Chorkendorff, I. *Energy Environ. Sci.* **2012**, *5* (5), 6744.
33
34 (5) Kocha, S. S.; Shinozaki, K.; Zack, J. W.; Myers, D. J.; Kariuki, N. N.; Nowicki, T.; Stamenkovic, V.; Kang, Y.; Li, D.;
35
36 Papageorgopoulos, D. *Electrocatalysis* **2017**, *8* (4), 366–374.
37
38 (6) Kongkanand, A.; Mathias, M. F. *J. Phys. Chem. Lett.* **2016**, *7* (7), 1127–1137.
39
40
41 (7) Ly, A.; Asset, T.; Atanassov, P. *J. Power Sources* **2020**, *478*, 228516.
42
43
44 (8) Banham, D.; Ye, S. *ACS Energy Lett.* **2017**, *2* (3), 629–638.
45
46
47 (9) Kodama, K.; Nagai, T.; Kuwaki, A.; Jinnouchi, R.; Morimoto, Y. *Nat. Nanotechnol.* **2021**, *16* (2), 140–147.
48
49
50 (10) Gocyla, M.; Kuehl, S.; Shviro, M.; Heyen, H.; Selve, S.; Dunin-Borkowski, R. E.; Heggen, M.; Strasser, P. *ACS Nano* **2018**,
51
52 *12* (6), 5306–5311.
53
54 (11) Pizzutilo, E.; Geiger, S.; Grote, J.-P.; Mingers, A.; Mayrhofer, K. J. J.; Arenz, M.; Cherevko, S. *J. Electrochem. Soc.* **2016**, *163*
55
56
57
58
59
60

- 1
2
3 (14), F1510–F1514.
4
5
6 (12) Shao, M.; Chang, Q.; Dodelet, J.-P.; Chenitz, R. *Chem. Rev.* **2016**, *116* (6), 3594–3657.
7
8
9 (13) Alsabet, M.; Grden, M.; Jerkiewicz, G. *J. Electroanal. Chem.* **2006**, *589* (1), 120–127.
10
11 (14) Gilbert, J. A.; Kariuki, N. N.; Subbaraman, R.; Kropf, A. J.; Smith, M. C.; Holby, E. F.; Morgan, D.; Myers, D. J. *J. Am. Chem.*
12
13 *Soc.* **2012**, *134* (36), 14823–14833.
14
15 (15) Guilminot, E.; Corcella, A.; Charlot, F.; Maillard, F.; Chatenet, M. *J. Electrochem. Soc.* **2007**, *154* (1), B96.
16
17 (16) Ahmed, M.; Morgan, D.; Attard, G. A.; Wright, E.; Thompsett, D.; Sharman, J. *J. Phys. Chem. C* **2011**, *115* (34), 17020–
18
19 17027.
20
21 (17) Fairweather, J. D.; Spornjak, D.; Weber, A. Z.; Harvey, D.; Wessel, S.; Hussey, D. S.; Jacobson, D. L.; Artyushkova, K.;
22
23 Mukundan, R.; Borup, R. L. *J. Electrochem. Soc.* **2013**, *160* (9), F980–F993.
24
25 (18) Dubau, L.; Castanheira, L.; Maillard, F.; Chatenet, M.; Lottin, O.; Maranzana, G.; Dillet, J.; Lamibrac, A.; Perrin, J.-C.;
26
27 Moukheiber, E.; Elkaddouri, A.; De Moor, G.; Bas, C.; Flandin, L.; Caqué, N. *Wiley Interdiscip. Rev. Energy Environ.* **2014**,
28
29 *3* (6), 540–560.
30
31 (19) Meyer, Q.; Zeng, Y.; Zhao, C. *Adv. Mater.* **2019**, *31* (40), 1–25.
32
33 (20) Cheng, L.; Khedekar, K.; Rezaei Talarposhti, M.; Perego, A.; Metzger, M.; Kuppan, S.; Stewart, S.; Atanassov, P.; Tamura,
34
35 N.; Craig, N.; Zenyuk, I. V.; Johnston, C. M. *Adv. Energy Mater.* **2020**, *10* (28), 2000623.
36
37 (21) Takao, S.; Sekizawa, O.; Samjeské, G.; Nagamatsu, S.; Kaneko, T.; Yamamoto, T.; Higashi, K.; Nagasawa, K.; Uruga, T.;
38
39 Iwasawa, Y. *J. Phys. Chem. Lett.* **2015**, *6* (11), 2121–2126.
40
41 (22) Shao, Y.; Yin, G.; Gao, Y. *J. Power Sources* **2007**, *171* (2), 558–566.
42
43 (23) Lopez-Haro, M.; Guétaz, L.; Printemps, T.; Morin, A.; Escribano, S.; Jouneau, P.-H.; Bayle-Guillemaud, P.; Chandezon, F.;
44
45 Gebel, G. *Nat. Commun.* **2014**, *5* (1), 5229.
46
47 (24) Mukundan, R.; Borup, R. L. *Fuel Cells* **2009**, *9* (5), 499–505.
48
49 (25) Wu, J.; Zhu, X.; West, M. M.; Tyliszczak, T.; Shiu, H. W.; Shapiro, D.; Berejnov, V.; Susac, D.; Stumper, J.; Hitchcock, A. P.
50
51
52
53
54
55
56
57
58
59
60

- 1
2
3 *J. Phys. Chem. C* **2018**, *122* (22), 11709–11719.
4
5
6 (26) Zenyuk, I. V.; Parkinson, D. Y.; Hwang, G.; Weber, A. Z. *Electrochem. commun.* **2015**, *53*, 24–28.
7
8 (27) Xu, H.; Marone, F.; Nagashima, S.; Nguyen, H.; Kishita, K.; Büchi, F. N.; Eller, J. *ECS Trans.* **2019**, *92* (8), 11–21.
9
10 (28) Tuae, X.; Rudi, S.; Petkov, V.; Hoell, A.; Strasser, P. *ACS Nano* **2013**, *7* (7), 5666–5674.
11
12 (29) Kleuker, U.; Suortti, P.; Weyrich, W.; Spanne, P. *Phys. Med. Biol.* **1998**, *43* (10), 2911–2923.
13
14 (30) Schroer, C. G.; Kuhlmann, M.; Roth, S. V.; Gehrke, R.; Stribeck, N.; Almendarez-Camarillo, A.; Lengeler, B. *Appl. Phys. Lett.*
15
16 **2006**, *88* (16), 164102.
17
18 (31) Jacques, S. D. M.; Di Michiel, M.; Beale, A. M.; Sochi, T.; O'Brien, M. G.; Espinosa-Alonso, L.; Weckhuysen, B. M.; Barnes,
19
20 *P. Angew. Chemie Int. Ed.* **2011**, *50* (43), 10148–10152.
21
22 (32) Li, T.; Heenan, T. M. M.; Rabuni, M. F.; Wang, B.; Farandos, N. M.; Kelsall, G. H.; Matras, D.; Tan, C.; Lu, X.; Jacques, S.
23
24 D. M. M.; Brett, D. J. L.; Shearing, P. R.; Di Michiel, M.; Beale, A. M.; Vamvakeros, A.; Li, K. *Nat. Commun.* **2019**, *10* (1),
25
26 1497.
27
28 (33) Vamvakeros, A.; Jacques, S. D. M.; Di Michiel, M.; Matras, D.; Middelkoop, V.; Ismagilov, I. Z.; Matus, E. V.; Kuznetsov, V.
29
30 V.; Drnec, J.; Senecal, P.; Beale, A. M. *Nat. Commun.* **2018**, *9* (1), 4751.
31
32 (34) Finegan, D. P.; Vamvakeros, A.; Cao, L.; Tan, C.; Heenan, T. M. M.; Daemi, S. R.; Jacques, S. D. M.; Beale, A. M.; Di Michiel,
33
34 M.; Smith, K.; Brett, D. J. L.; Shearing, P. R.; Ban, C. *Nano Lett.* **2019**, *19* (6), 3811–3820.
35
36 (35) Martens, I.; Vamvakeros, A.; Chattot, R.; Blanco, M. V.; Rasola, M.; Pusa, J.; Jacques, S. D. M.; Bizzotto, D.; Wilkinson, D.
37
38 P.; Ruffmann, B.; Heidemann, S.; Honkimäki, V.; Drnec, J. *J. Power Sources* **2019**, *437*, 226906.
39
40 (36) Holdcroft, S. *Chem. Mater.* **2014**, *26* (1), 381–393.
41
42 (37) Oberholzer, P.; Boillat, P. *J. Electrochem. Soc.* **2014**, *161* (1), F139–F152.
43
44 (38) Kulkarni, N.; Cho, J. I. S.; Rasha, L.; Owen, R. E.; Wu, Y.; Ziesche, R.; Hack, J.; Neville, T.; Whiteley, M.; Kardjilov, N.;
45
46 Markötter, H.; Manke, I.; Shearing, P. R.; Brett, D. J. L. *J. Power Sources* **2019**, *439*, 227074.
47
48 (39) Kusoglu, A.; Weber, A. Z. *Chem. Rev.* **2017**, *117* (3), 987–1104.
49
50
51
52
53
54
55
56
57
58
59
60

- 1
2
3 (40) Hussey, D. S.; Spornjak, D.; Weber, A. Z.; Mukundan, R.; Fairweather, J.; Brosha, E. L.; Davey, J.; Spendelow, J. S.; Jacobson,
4 D. L.; Borup, R. L. *J. Appl. Phys.* **2012**, *112* (10), 104906.
5
6
7 (41) Martinez, N.; Gebel, G.; Blanc, N.; Boudet, N.; Micha, J.-S. S.; Lyonnard, S.; Morin, A. *ACS Appl. Energy Mater.* **2019**, *2* (5),
8 3071–3080.
9
10
11 (42) Shi, S.; Weber, A. Z.; Kusoglu, A. *J. Memb. Sci.* **2016**, *516*, 123–134.
12
13
14 (43) Ge, N.; Banerjee, R.; Muirhead, D.; Lee, J.; Liu, H.; Shrestha, P.; Wong, A. K. C.; Jankovic, J.; Tam, M.; Susac, D.; Stumper,
15 J.; Bazylak, A. *J. Power Sources* **2019**, *422*, 163–174.
16
17
18 (44) Asset, T.; Gommès, C. J.; Drnec, J.; Bordet, P.; Chattot, R. R.; Martens, I.; Nelayah, J.; Job, N.; Maillard, F.; Dubau, L. *ACS*
19 *Catal.* **2019**, *9* (1), 160–167.
20
21
22 (45) Chattot, R.; Martens, I.; Scohy, M.; Herranz, J.; Drnec, J.; Maillard, F.; Dubau, L. *ACS Energy Lett.* **2020**, *5* (1), 162–169.
23
24
25 (46) Cherevko, S.; Kulyk, N.; Mayrhofer, K. J. J. *Nano Energy* **2016**, *29*, 275–298.
26
27
28 (47) Chen, S.; Gasteiger, H. A.; Hayakawa, K.; Tada, T.; Shao-Horn, Y. *J. Electrochem. Soc.* **2010**, *157* (1), A82.
29
30
31 (48) Ferreira, P. J.; la O', G. J.; Shao-Horn, Y.; Morgan, D.; Makharia, R.; Kocha, S.; Gasteiger, H. A. *J. Electrochem. Soc.* **2005**,
32 *152* (11), A2256.
33
34
35 (49) Yasuda, K.; Taniguchi, A.; Akita, T.; Ioroi, T.; Siroma, Z. *J. Electrochem. Soc.* **2006**, *153* (8), A1599.
36
37
38 (50) Macauley, N.; Alavijeh, A. S.; Watson, M.; Kolodziej, J.; Lauritzen, M.; Knights, S.; Wang, G.; Kjeang, E. *J. Electrochem. Soc.*
39 **2014**, *162* (1), F98–F107.
40
41
42 (51) Durst, J.; Lamibrac, A.; Charlot, F.; Dillet, J.; Castanheira, L. F.; Maranzana, G.; Dubau, L.; Maillard, F.; Chatenet, M.; Lottin,
43 *O. Appl. Catal. B Environ.* **2013**, *138–139*, 416–426.
44
45
46 (52) White, R. T.; Wu, A.; Najm, M.; Orfino, F. P.; Dutta, M.; Kjeang, E. *J. Power Sources* **2017**, *350*, 94–102.
47
48
49 (53) Nandjou, F.; Poirot-Crouvezier, J.-P.; Chandesris, M.; Blachot, J.-F.; Bonnaud, C.; Bultel, Y. *J. Power Sources* **2016**, *326*,
50 182–192.
51
52
53 (54) Mittermeier, T.; Weiß, A.; Hasché, F.; Gasteiger, H. A. *J. Electrochem. Soc.* **2018**, *165* (16), F1349–F1357.
54
55
56
57
58
59
60

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60