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# Probing platinum degradation in polymer electrolyte membrane fuel cells by synchrotron X-ray microscopy<sup>†</sup>

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Synchrotron-based scanning transmission X-ray spectromicroscopy (STXM) was used to characterize the local chemical environment at and around the platinum particles in the membrane (PTIM) which form in operationally tested (end-of-life, EOL) catalyst coated membranes (CCMs) of polymer electrolyte membrane fuel cells (PEM-FC). The band of metallic Pt particles in operationally tested CCM membranes was imaged using transmission electron microscopy (TEM). The cathode catalyst layer in the beginning-of-life (BOL) CCMs was fabricated using commercially available catalysts created from Pt precursors with and without nitrogen containing ligands. The surface composition of these catalyst powders was measured by X-ray Photoelectron Spectroscopy (XPS). The local chemical environment of the PTIM in EOL CCMs was found to be directly related to the Pt precursor used in CCM fabrication. STXM chemical mapping at the N 1s edge revealed a characteristic spectrum at and around the dendritic Pt particles in CCMs fabricated with nitrogen containing Pt-precursors. This N 1s spectrum was identical to that of the cathode and different from the membrane. For CCM samples fabricated without nitrogen containing Pt-precursors the N 1s spectrum at the Pt particles was indistinguishable from that of the adjacent membrane. We interpret these observations to indicate that nitrogenous ligands in the nitrogen containing precursors, or decomposition product(s) from that source, are transported together with the dissolved Pt from the cathode into the membrane as a result of the catalyst degradation process. This places constraints on possible mechanisms for the PTIM band formation process.

# 1. Introduction

The mechanisms of degradation of the catalyst and catalyst support in proton-exchange membrane (PEM) fuel cell electrodes are under intensive investigation<sup>1-12</sup> since PEM fuel cells are on the verge of commercial use in automotive applications. The PEM fuel cell catalyst, commonly platinum (Pt) or one of its alloys, consists of highly dispersed and chemically active nanoparticles (2–4 nm) which are distributed over a high-surface-area carbon (C-support).<sup>1</sup> This support is a dense network of carbon nanoparticles (20–50 nm) that form the conductive and porous

body (10–50 nm pore diameter) of the fuel cell electrodes.<sup>1</sup> A significant mode of degradation during operation is dissolution of the platinum catalyst in the cathode and its re-appearance as Pt metal nanoparticles (2–200 nm) located in a specific region of the proton-exchange membrane<sup>8,9</sup> called in this work (and elsewhere) a Pt-in-membrane (PTIM) band. Control and retardation of the dissolution of the Pt nanoparticles will improve the lifetime of PEM fuel cells. Although much progress has been made in the last few years in understanding the Pt dissolution mechanisms<sup>1,4–6,12</sup> there is still no clear picture of the sequence of chemical processes occurring in the 1–2 µm reaction zone close to the cathode–membrane interface which leads to loss of an electrochemically active catalyst surface area and ultimately PEM fuel cell failure.

One challenge to understanding the dissolution and re-deposition of the catalyst in the fuel cell membrane is a lack of analytical methods that can directly measure chemical and material properties in fabricated fuel cells over a size scale of 50  $\mu$ m and with a spatial resolution better than 50 nm. Scanning and transmission electron microscopy (SEM, TEM) have been used for characterizing PEM fuel cell materials, often with sub-nm spatial resolution,<sup>13</sup> and for routine electrode-membrane analysis.<sup>3,5,8–10</sup> Despite the initial

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success in visualizing the PTIM band, these tools are limited to morphological characterization and are unable to provide detailed chemical information. X-Ray diffraction (XRD), X-ray photoelectron (XPS) and energy dispersive X-ray spectroscopies (EDX) are powerful analytical methods that are complementary to SEM and TEM. However, the ability of these techniques to deliver chemical details of fuel cell components is limited mainly to analysis of raw materials (not the fabricated CCMs) or (in the case of EDX in SEM and TEM) analytical measurements are associated with reduced spatial resolution, long acquisition times and complications with radiation damage. In addition, EDX only provides an elemental picture, without any insights into detailed molecular structural information and speciation.

Scanning transmission soft X-ray microscopy (STXM),<sup>14</sup> a relatively new analytical tool able to provide detailed molecular structural information and full speciation (i.e. bonding as well as elemental) at high spatial resolution ( $\sim 30$  nm), is now being applied to PEM fuel cells.<sup>15-18</sup> Here we use STXM to investigate the chemical environment at and near the Pt particles that form in the PEM membrane (i.e. the PTIM band) in the course of fuel cell operation protocols designed to accelerate Pt dissolution. In particular, we map a nitrogensignature in close proximity to the Pt-particles and track the source of this spectroscopic signature back to the electrode fabrication by analyzing CCM samples prepared using Pt catalyst precursors with and without nitrogenous ligands. Although both beginning-of-life (BOL) and end-of-life (EOL) CCM samples were measured, the detailed mechanism of degradation is outside of the scope of this paper. Instead, our focus is on characterizing the changes in the chemical character of the PTIM band in EOL samples, and correlating those observations with changes in the Pt catalyst precursor, thereby providing constraints on proposed mechanisms as well as exemplifying the value added of applying STXM to PEM-FC research. The impact of different Pt precursors on the localized chemistry of the PTIM band in EOL samples is revealed in detail. Comparisons between N 1s spectra for BOL and EOL CCMs are presented as ESI.<sup>†</sup>

Two different commercial PEM catalyst coated membrane samples were used and subjected to accelerated testing protocols that simulated "in field" operation conditions. Besides having dissimilar membranes (reinforced vs. non reinforced), these CCMs had cathode catalyst layers prepared by different technologies that involved different Pt based precursors. In one, the catalyst was generated from a Pt-precursor containing nitrogenous ligands, while in the other the catalyst was generated from hexachloroplatinate. The CCMs were assembled into fuel cells and tested using customized voltage cycling protocols designed to accelerate Pt dissolution in that particular CCM. The ultra-thin (100-200 nm) cross-sections of BOL and EOL samples were examined with both TEM and STXM. Near edge X-ray absorption fine structure (NEXAFS) spectra<sup>19</sup> recorded at the N 1s edge with STXM were used to differentiate and spatially map different regions of the BOL and EOL CCMs: specifically, the carbon supported Pt-catalyst, the perfluorosulfonate (PFSA) membrane, and, for the EOL sample, the PTIM band. In addition, this analysis provided spectra and chemical maps at and around the Pt particles in the PTIM band of the EOL samples. In those samples with cathodes fabricated with the

nitrogen precursor, the N 1s spectral signature at and around the reduced metal Pt particles was found to be the same as that of the cathode, and distinctly different from the N 1s spectrum of the PFSA membrane. In those samples with cathodes fabricated *without* the nitrogen precursor, the N 1s spectral signature was similar in all parts of the sample. STXM was used to visualize the spatial distribution of the cathode-derived nitrogen signal around the Pt particles.

# 2. Experimental

## 2.1 Materials

Two catalyst coated membrane samples were examined in this work. The nitrogen containing CCMs for *sample A* consisted of a 25.4 µm thick Nafion NR-211 (DuPont) membrane coated with proprietary Pt/C anode and cathode catalysts with loadings of 0.05 mg cm<sup>-2</sup> and 0.25 mg cm<sup>-2</sup>, respectively. The tested membrane electrode assembly (MEA) had an active area of 45 cm<sup>-2</sup>. The CCM of *sample B* was proprietary fabricated using a catalyst specifically manufactured *without* nitrogen containing Pt precursors. The sample B CCMs consisted of an 18 µm thick Gore-Select membrane coated with Gore proprietary catalysts with a 0.1 and 0.4 mg cm<sup>-2</sup> loading on the anode and cathode, respectively. The cathode in this sample was made from a cathode catalyst that used hexachloroplatinic acid as a precursor. The MEA for sample B had an active area of 48.4 cm<sup>-2</sup>.

MEAs were tested using AFCC's subscale test hardware with parallel flow channels and operated on a test station with control over the gas flow, pressure, RH, cell temperature, and load. Both samples were subjected to test cycles under  $H_2/air$ operation designed to accelerate the Pt dissolution degradation mechanism by using voltage–load cycling. An electronic load was used to bring the cell potential to a specific lower value while a power supply was used to increase the potential to a value above the open circuit voltage. Lab View software was used to control the load bank and the power supply system. The testing conditions were adjusted with respect to the particular A and B CCM specification in order to initiate and amplify the Pt dissolution–reduction processes.

Sample A was cycled between 0.6 V and 1.2 V (IR-corrected) using a square wave cycle (30 s low potential, 30 s high potential). The cell temperature was held at 68 °C. Anode and cathode gas flows were 6.5 slpm for hydrogen and 12 slpm for air streams, respectively, and both streams were hydrated at 100% RH. High flows were used to minimize temperature and RH gradients in the cell. Anode and cathode pressures were 24.7 and 21.8 psig respectively. 5000 cycles were completed on sample A. Potential cycling of sample B used a square wave cycle over the potential range between 0.6 and 1.0 V (IR-corrected) (2 s at low potential and 10 s at high potential). The cell temperature was 80 °C. The gas flows and humidity were 2 slpm and 100% RH on the anode and 12 slpm and 100% RH on the cathode, respectively. 20000 cycles were completed on sample B. Though both potential cycling experiments used here accelerate the Pt dissolution failure mechanism to a similar degree, the advantage of using the second voltage cycle is that it better represents vehicle operation and avoids voltages > 1.0 V which may cause carbon corrosion with some carbon types.

#### 2.2 CCM sampling

Samples of the catalyst coated membranes  $(1 \times 1 \text{ cm})$  were extracted from the BOL and EOL membrane electrode assemblies. Small rectangular  $(1 \text{ mm} \times 3 \text{ mm})$  pieces of the CCM samples were cut, and either sandwiched between two polystyrene (PS) beads or embedded in a custom epoxy<sup>20</sup> optimized for STXM, and then ultra-microtomed at room temperature using a Leica Ultracut UCT ultramicrotome (Leica Mikrosystem, Wien, Austria). The nominal (target) thickness of the CCM sections was 100 nm in order to have a peak optical density between 0.5 and 1.5 at the C 1s edge. Several ultramicrotomed sections of CCM were deposited on a 100-mesh formvar-coated Cu TEM grid (~30 nm thickness of a formvar film).<sup>21</sup>

#### 2.3 X-Ray photoelectron spectroscopy

The surface chemical composition of commercial catalysts A and B used in the preparation of CCM samples A and B was investigated by X-ray photoelectron spectroscopy (XPS). The analysis was performed using a Kratos Axis Ultra DLD system with a monochromatic Al X-ray source and a hemispherical energy analyzer. Low resolution survey scans were recorded using 160 eV pass energy, while high resolution spectra with an energy resolution of 25 meV were obtained using 20 eV pass energy. The binding energy scale for all spectra was calibrated with respect to C 1s at 284.6 eV. Curve fitting was performed with XPSPEAK 4.1 software.

#### 2.4 Transmission electron microscopy

A TEM JEOL JEM1200 TEMSCAN electron microscope (Peabody, MA, USA) equipped with a 4 megapixel digital camera (Advanced Microscopy Techniques Corp. (AMT) Danvers, MA, USA) was used to study the same microtomed CCM cross section samples prepared for STXM. The microscope was operated at an accelerating voltage of 80 kV. The exposure time was kept as short as possible to minimise radiation damage to the perfluorosulfonate membrane which is the most radiation sensitive component.

## 2.5 Scanning transmission X-ray microscopy

STXM measurements were conducted at the Advanced Light Source (ALS, Lawrence Berkeley National Laboratory (LBNL), USA) using the STXM microscope<sup>22</sup> on beamline  $5.3.2.2^{23}$  which is a bending magnet beamline producing monochromated soft X-rays from 250 to 700 eV with better than 1500 resolving power ( $E/\Delta E$ ) covering the C, N, F, and O absorption edges. The details of the STXM instrument and its operation are described elsewhere.<sup>14,22</sup> A sketch of the STXM is presented in Fig. 1a. Monochromatic X-rays from the beamline illuminate a Fresnel zone plate (ZP) lens which focuses the X-rays to a  $\sim 25$  nm spot. An order sorting aperture (OSA) is used to block the zeroth order light. The sample (S) is positioned at the focal point of the ZP and those X-rays that pass through the sample are detected in a single photon counting mode using a detector (D) consisting of a phosphor to convert soft X-rays to visible light and a high performance photomultiplier to detect the visible photons. Images at a single X-ray energy are measured by recording



**Fig. 1** Scanning Transmission X-ray Microscopy (STXM) and image processing principles. (a) Sketch of the STXM which consists of a zone plate (ZP), order selecting aperture (OSA), sample (S), sample holder (H), and detector (D), (b) an example of STXM data processing for a N 1s image sequence measured for a microtomed cross-section of a catalyst coated membrane (CCM) (sample B). The zones are (top to bottom): polystyrene support (1), cathode (2), continuous (3 and 5) and porous (4) parts of the polymer electrolyte membrane (PEM), respectively. For the image taken at 390 eV, the boundaries between the zones are highlighted.

the transmitted X-ray intensity, I(X, Y, E) at each pixel in a user-selected area of the sample which is raster scanned with a fine piezo stage (H).

Detailed chemical mapping at a specific inner shell edge is obtained by measuring images over a range of energies (50–100 energy points), as outlined in Fig. 1b. For the present measurements the STXM chamber was filled with He (1/3 atm), the zone plate (manufactured by the Center for X-ray Optics, LBNL) had 25 nm outer zone width, 240  $\mu$ m diameter and a 90  $\mu$ m central stop. The OSA was 50  $\mu$ m in diameter. Images were measured with a dwell time of 1 ms per pixel over the N 1s energy interval (390–430 eV).

## 2.6 Near edge X-ray absorption fine structure spectroscopy

For a given image sequence, the transmitted intensity at each pixel  $I(X_i, Y_j)$  as a function of energy is converted to the NEXAFS spectrum of that point of the sample by applying the Beer–Lambert law, OD =  $-\ln(I/I_o) = \mu\rho d$ , where I is the light through the sample,  $I_o$  is the transmitted light through a region off of the sample (in this case, on the formvar support), OD is the optical density,  $\mu$  is the mass absorption coefficient,  $\rho$  is the density of the material, and d is the sample thickness. Peaks in NEXAFS spectra originate from transitions from the ground to core excited states, which in turn, are related to chemical bonding around the core excited atom. NEXAFS spectra are unique and characteristic for each chemical species.<sup>19</sup> Thus they can be used for chemical characterization and, with suitably intensity-calibrated reference spectra,<sup>14</sup> for quantitative analysis. In general, the C 1s, O 1s and F 1s NEXAFS are of most interest for fuel cell research because these are the majority elements in the components of the CCM and the embedding medium. However, in this article we focus on results measured at the N 1s edge since it was found to be particularly sensitive to aspects of the dissolution of the catalyst and its re-deposition to form the PTIM band inside the PFSA membrane during accelerated testing.

#### 2.7 STXM data processing

Chemical maps were derived from the measured image sequences (stacks<sup>24</sup>) using the aXis2000 software package.<sup>25</sup> The analysis consists of six major steps: (i) alignment of the images in the stack, (ii) converting transmitted intensities into optical densities, (iii) obtaining reference spectra for chemical components in the region examined; (iv) chemical mapping by fitting the OD stack to a set of suitable reference spectra; (v) confirming the validity of the fit by examination in spectral space; and (vi) preparing displays of the component and composite maps.

Image alignment is performed using a cross-correlation algorithm implemented in aXis2000. The reference spectra of the material components are obtained from selected regions of the sample where the presence of a pure component of interest is certain. For example, the CCM samples have a distinct, layered structure: cathode-membrane-anode, from which the component spectra for the PFSA membrane and the carbon support can be obtained. In some cases reference spectra from other samples with a composition identical to that of the sample are used. For chemical mapping (Fig. 1b) singular value decomposition (SVD),<sup>26</sup> which is an efficient matrix inversion procedure equivalent to an optimized least squares fit (linear regression) in over-determined data sets, was used to fit the OD spectrum at each pixel to a linear combination of reference spectra.<sup>14</sup> Maps of multiple chemical components are combined into a single color-coded map which displays the distribution of up to three components in the scanned region of the sample (e.g. Fig. 1b). One can select a mapping in which the intensity of each color is independently scaled to the signals of the individual components ('rescaled'), or a common intensity scale over all components may be used ('absolute'). For quantitative analysis the intensity scales of the reference spectra are placed on an absolute scale by matching to the X-ray absorption response outside the structured near edge region, computed for the elemental composition of the chemical component at its standard density. When spectra with such absolute intensity scales (optical density per nm thickness) are used as the reference spectra in the image sequence analysis, the intensities of the component maps correspond to the absolute thickness (in nm) of that component at its standard density.

# 3. Results

## 3.1 STXM characterization

Depending on the hydrogen crossover properties of the membrane, operational pressure and overpotential, the PTIM band can be intentionally developed within the polymer electrolyte membrane.<sup>4,8,9,27</sup> Fig. 2(a)–(d) shows TEM images of the cathode catalyst–membrane interfaces including the



**Fig. 2** TEM images of end-of-life (EOL) CCMs. (a) Sample A, CCM EOL embedded in polystyrene, the scale bar is 2  $\mu$ m. The zones are: the polystyrene support (1), the depletion layer (~2  $\mu$ m) in the cathode from which the platinum is dissolved (2), the Nafion membrane (3), and the Pt in the membrane (PTIM) band (4). (b) Image of the Pt-particles in the Pt band of the EOL CCM sample A, the bar is 0.5 um. (c) Sample B, CCM EOL embedded in polystyrene, the bar is 2  $\mu$ m. The zones are: the polystyrene support (1), the cathode (2), the Gore membrane (3), and the Pt band (4). (d) Image of the PTIM particles in sample B, EOL CCM, the scale bar is 0.5  $\mu$ m.

Pt-band from the two EOL PEM fuel cell samples A and B after the Pt dissolution stress test. Because of the high spatial resolution ( $\sim 1$  nm) TEM is able to visualize the particle shape in detail. For example, the Pt-particles formed in the membrane of the EOL sample A are dendritic with a highly ramified shape consisting of approximately three orders of branching scale, while those from the EOL sample B are more regular, and faceted. However, TEM without electron energy loss spectromicroscopy (which would be very challenging for this sample due the high radiation sensitivity of the PFSA membrane) cannot distinguish differences in chemical speciation of regions of interest (ROI) such as the Pt particle core, the region near the Pt particles, and in the membrane far from the particles. Nevertheless, we sought knowledge of the local chemistry for EOL CCMs in the Pt-band region for samples A and B (with cathodes fabricated through different procedures involving different precursors) since it may provide interesting insights into the Pt dissolution, transport, and deposition processes occurring during the stress test.

STXM spectromicroscopy was used to study the chemical environment in the Pt-band, especially in the membrane close to, and at the Pt particles. The spatial resolution of STXM is  $\sim$  30 nm, much coarser than that of TEM. Therefore the Pt particles appear as rather smooth objects in STXM images (see Fig. 3). This paper focuses on measurements at the N 1s absorption edge with an ultimate goal to explore the effect of the composition of the cathode catalyst layer on the chemistry around the Pt particles in the membrane. Spectra of three particular local regions were extracted from the N 1s stack of the EOL sample A in the region of the Pt band (Fig. 3): (1) the center of Pt particles, (2) the membrane at the edge of the Pt particles (which may contain spatially unresolved Pt and associated compounds), and (3) the membrane far away from the particles (polymer electrolyte membrane area). Fig. 4a shows the NEXAFS spectra extracted from the N 1s stack for these three regions of sample A, for which the catalyst was fabricated with the nitrogen Pt precursor along with the N 1s



**Fig. 3** Average of 70 images of a N 1s STXM image sequence for EOL CCM of sample A in the region of the Pt band.

spectrum of the cathode catalyst layer (the spectra of the cathode for the BOL CCM of sample A as well as for the carbon support and for the different embedding materials are



**Fig. 4** (a) N ls spectra of the EOL CCM of sample A extracted from the Pt core (first from top, red), the edge of Pt particles (third, green) and the membrane (fourth, blue). The inset plots are the masks for each region (same region as Fig 3). The white part indicates the area from which these spectra were extracted. The N ls spectrum of the cathode of the same section of the EOL sample A is also shown (second, black). (b) N ls spectra of the membrane, Pt-edge, Pt-core and cathode after subtraction of a curved background extrapolated from the pre-N ls region and unit normalization in the continuum. The spectrum of the cathode is offset by 1 unit. Extended data presentations of the BOL CCM and individual components of sample A are presented in the ESI. $\dagger$ 

shown in the ESI<sup>†</sup>). The regions of interest (ROI) from which these spectra were extracted are indicated in the insets to Fig. 4. The optical density in the N 1s signal is  $\sim 0.1-0.2$  OD units, sitting on a much larger underlying C 1s continuum. Fig. 4b displays the spectra of the Pt-core, Pt-edge, and the membrane of sample A after subtracting a curved background and normalizing the difference to 1 in the continuum above 425 eV. The spectrum of the core of the Pt particles in the PTIM band is guite different from the other two and very similar to that of the cathode. The spectra for the edge of the particles and the main parts of the PFSA membrane are similar but slightly different, especially between 400-404 eV. All three spectra have a well defined broad peak at 405.8 eV. The spectrum of the Pt-core has three additional features: shoulders on the main peak at 402 and 410 eV and a broad peak at 418 eV. These same spectral features are also detected in the N 1s spectrum of the cathode (see Fig. 4). The Pt-edge spectrum (from the area close to the Pt particles) has a weak shoulder at 402 eV, which is a reduced intensity version of the corresponding shoulder at the same energy observed in the spectrum of the core of the Pt particles and the cathode. The magnitude of this shoulder relative to the rest of the N 1s spectrum is strongly dependent on the width and placement of the zone selected around the Pt particles, indicating that this signature is associated with the Pt particles.

The N 1s spectra of the Pt-core, Pt-edge and membrane were used as reference signals for the SVD analysis of the N 1s stack for the EOL CCM of sample A. Fig. 5 presents the derived component maps for the Pt-core (Fig. 5a), the Pt-edge (Fig. 5b), and the PFSA membrane (Fig. 5c), respectively. A rescaled color composite of the three components is presented in Fig. 5d. For sample A the N 1s spectrum of the core of the Pt particle is very distinct from that of the membrane far from the PTIM band, while the spectrum of the region adjacent to the Pt particles is intermediate in character. The N 1s spectra of the Pt core and the cathode are nearly identical. These spectral signatures are very reproducible and thus provide a means to investigate the Pt degradation and the Pt band formation mechanism. Although a detailed spectral dissection is outside the scope of this paper, comparison to the N 1s spectra of a range of molecular species suggests that the main 406 eV peak is associated with amine functional groups while the shoulder at lower energy (402 eV) is likely associated with amide functional groups.<sup>28,29</sup> In summary, the N 1s STXM analysis of sample A shows the presence of a characteristic N 1s amide signature in and around the Pt particles in the PTIM band which is *similar* to that of the cathode for both BOL and EOL samples.

In contrast the EOL CCM of sample B, for which the CCM was fabricated *without* the nitrogen containing Pt precursor, showed no differences between the N 1s spectra of the membrane, and the core, or edge of Pt particles in the PTIM band. Fig. 6a plots the N 1s spectra for these three regions, taken from the Pt band shown in the inset image. Fig. 6b plots the spectra of the Pt-core, Pt-edge, and the membrane after subtracting a curved background and normalizing the difference to 1 in the continuum above 425 eV. There is no difference among the spectra of the Pt-core, Pt-edge or membrane, although these spectra are somewhat different from that of the cathode of sample B.

We explored various possible choices of reference spectra for singular value decomposition (SVD) analysis of the N 1s stack for the EOL CCM of sample B. When we tried to include



**Fig. 5** STXM spectromicroscopy: mapping the EOL CCM of sample A in the region of the Pt band from the N ls edge. (a) Component map of the Pt core, (b) component map of the signal at the edge of the particles, (c) component map of the membrane, (d) color coded composite of the three component maps.

signals extracted separately from the Pt-edge and Pt-core, an unsatisfactory fit was observed as a result of instability of the fit due to the lack of any significant difference in the Pt-edge, Pt-core and the membrane spectra. The best fit was obtained using just the spectra of the Pt-core and the membrane, with the major difference of those two spectra being the fact that there is a much larger non-N 1s signal at the Pt particles due to the high electron density of the Pt. Fig. 7 presents the component maps for the Pt-core and the membrane, along with a color coded composite of these component maps.

## 3.2 XPS characterization of cathode catalyst powders

The nature and surface composition of the two catalyst powders used for fabrication of the CCMs were studied by XPS.



**Fig. 6** (a) N 1s spectra of the EOL CCM of sample B in the regions of the Pt core (second from top, red), edge of Pt particles (third, green) and the membrane (fourth, blue). The inset is the average of 53 images of the N 1s STXM image sequence in the region of the Pt band. The N 1s spectrum of the cathode of the same section of the EOL sample A is also shown (first, black). (b) N 1s spectra of the membrane, Pt-edge, Pt-core and cathode after subtraction of a curved background extrapolated from the pre-N 1s region and unit normalization in the continuum. The spectrum of the cathode is offset by 1 unit. The N 1s spectrum of the BOL CCM of sample B is presented in the ESI. $\dagger$ 

Fig. 8 shows low-resolution survey XPS spectra for catalyst A and catalyst B. Both catalysts show similar predominant peaks for O Is (binding energy 532 eV), Pt 4d (295–334 eV), C Is (284.6 eV) and Pt 4f (72 eV). The smaller intensity signals include the O Auger transition at 970.0 eV, Pt 4s (722 eV) and Pt 4p (607 eV and 520 eV) XPS lines, and Pt 5p and Pt 5d peaks below 60 eV. However, only in catalyst A, an additional small peak for N Is (~2 atomic %) is observed at a binding energy of 398 eV. The N Is high-resolution XPS spectrum (inset to Fig. 8) shows that there are three components contributing to the overall N Is signal. The first component at 398.9 eV is consistent with NH<sub>x</sub> species, while the peaks at higher binding energies are due to contributions from NO<sub>2</sub><sup>-</sup> (403.3 eV) and NO<sub>3</sub><sup>-</sup> species (406.4 eV).<sup>30</sup>

Pt 4f high resolution XPS spectra were measured (Fig. 9a and b) to investigate if the N signature in catalyst A is related to the nature of the Pt species in two catalyst powders. The individual components related to different Pt oxidation states



**Fig. 7** STXM spectromicroscopy: mapping the EOL CCM of sample B in the region of the Pt band from the N 1s edge. (a) Component map of the Pt core, (b) component map of the membrane, (c) color coded composite of the two component maps.



**Fig. 8** XPS survey spectrum of commercial cathode catalyst powders A and B. The inset figure shows the high resolution N 1s spectrum, with curve fit results.



**Fig. 9** High resolution Pt 4f spectrum from (a) catalyst A and (b) catalyst B, with curve fit results. For peak areas and other information, see Table 1.

are fitted as Pt  $4f_{7/2}$  and Pt  $4f_{5/2}$  doublets separated by 3.3 eV and the derived binding energies of Pt  $4f_{7/2}$  peaks were compared to the literature.<sup>31</sup> The component at the lowest binding energy of 71.3 eV is characteristic of metallic Pt<sup>0</sup>, while the components at higher binding energies (72.3 eV and 74.0 eV) are consistent with Pt<sup>2+</sup> from Pt(OH)<sub>2</sub> and PtO respectively.<sup>31</sup> However, according to tabulated binding energies,<sup>31</sup> the binding energy of Pt<sup>2+</sup> from the Pt-N precursor that is commonly used to prepare catalysts,  $Pt(NH_3)_2(NO_2)_2$ , is similar to that of PtO. The peak at the highest binding energy of 75.4 eV is characteristic for  $Pt^{4+}$  indicating the possible presence of PtO<sub>2</sub>.<sup>31</sup> The relative atomic percentages for the individual components as well as the  $Pt^{n+}/Pt^0$  ratios are reported in Table 1. It is apparent that catalyst A has a smaller contribution from metallic Pt as compared to catalyst B. In addition, catalyst A has a significantly larger  $Pt^{n+}/Pt^0$  ratio, and especially a larger  $Pt^{2+}/Pt^{0}$  ratio with respect to catalyst B.

The N signature found in catalyst A and the differences in the amount of metallic and oxidized Pt between the two catalysts can be explained in the following way. Preparation of the commercial Pt based catalysts involves impregnation of a carbon support by a suitable Pt precursor solution, a process followed by reduction with hydrogen at high temperature.<sup>32,33</sup> Often, amino-based Pt precursors, such as  $Pt(NH_3)_2(NO_2)_2$ , are used for the impregnation process. From the NIST XPS data base<sup>31</sup> the binding energy of  $Pt^{2+}$  of this compound is very close to that of PtO. Therefore, the existence of N in catalyst A with a mixed amino–nitro nature and a larger amount of  $Pt^{2+}$  (especially the increased contribution of the component at a binding energy of 74.0 eV) are consistent with residual Pt–N complex species remaining in the commercial catalyst A, possibly due to an incomplete reduction step.

Table 1 XPS results for the commercial cathode catalysts A and B

	Pt species, relative intensities (%)				Ratios	
Property	Pt <sup>0</sup>	Pt <sup>2+</sup> from Pt(OH) <sub>2</sub>	Pt <sup>2+</sup> from PtO and Pt–N precursor	Pt <sup>4+</sup>	$\frac{\mathrm{Pt}^{n+}}{\mathrm{Pt}^{0}}$	Pt <sup>2+</sup> /Pt <sup>0</sup>
BE of Pt	71.3	72.3	73.9	75.3	—	
Catalyst	43.4	38.1	14.1	4.4	1.3	1.2
Catalyst B	75.0	12.2	8.5	4.3	0.3	0.3

#### 4. Discussion

The STXM results indicate that, although both samples A and B contain nitrogen, the same, amine-dominated N 1s spectrum is observed everywhere in sample B, whereas there are two distinct types of N 1s spectra in sample A, one observed in the membrane, and the other observed in the cathode and the PTIM band. This difference is due to the fact that N containing catalyst precursors were used in sample A but not in sample B. The similarity of the N 1s spectra of the cathode and PTIM band in sample A suggests a common chemical origin, which is most likely residues of amine and amide based catalyst precursor species used in fabrication of the catalyst for sample A. One possible source of the amine and amide groups in the cathode of sample A is Pt(NH<sub>3</sub>)<sub>2</sub>(NO<sub>2</sub>), diamine dinitritoplatinum (II), which is a common precursor for fabrication of the Pt-catalyst. This is supported by the XPS measurements on the catalyst powders.

Additional STXM experiments were performed on two samples: a pure PFSA membrane, and a thin film cast from a pure ionomer solution (see ESI<sup>†</sup>). In both cases a N ls signal was detected which was rather similar to the N ls spectra of the CCM of sample B. This amine dominated spectrum could originate from the ionomer membrane. The nitrogen species of sample B do not seem to be involved in the Pt degradation and transport and are distributed homogeneously all over the membrane, in the cathode, and around Pt particles of EOL sample B, Fig 7c.

The difference in the N 1s spectra of the Pt particles and the membrane of sample A indicates that there are amide containing species characteristic of the cathode at and around the Pt particles. Why do these species concentrate in close proximity to the Pt nanoparticles? We suggest that ionic forms of the nitrogen containing species originating from the Pt–N-precursor migrate from the cathode into the membrane during voltage cycling. Although these observations provide intriguing evidence for a possible involvement of amide species in Pt dissolution–migration, removal of N-containing precursors did not stop the Pt dissolution process. This can be interpreted to indicate that either the N-chemistry is not a driver for the PTIM band formation, or that there may be a number of different paths for platinum dissolution and redeposition.

#### 5. Summary

To date there is only limited information about how different stress tests and sample fabrication methods affect the Pt degradation–redeposition process in the cathode–membrane assembly. This study introduces STXM spectromicroscopy as

a new technique for characterization of fuel cell samples with high spatial resolution. Using this method we were able to provide novel chemical information from the local environment at and around Pt particles formed within the membrane in EOL samples. It has been shown that the local chemistry at the Pt particles in PTIM can be traced back to the nature of the catalyst precursor used for the cathode preparation. While this result does not directly inform the mechanism of Pt dissolution, transport and deposition in PTIM bands, this evidence (that there is co-transport of N-species with the Pt) needs to be considered when evaluating different possible mechanisms. It would seem to exclude certain scenarios, such as mechanisms involving solely a water and/or hydroxyl complex of individual Pt ions as the transporting species. These results also illustrate the ability of STXM to provide a wealth of structural and chemical information that can be used in the future to study other details of degradation mechanisms in CCMs.

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