

Advances in structural and chemical analysis of catalyst-coated membranes for hydrogen fuel cell applications

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Catalyst-coated membranes are a key element of advanced membrane electrode assembly designs for automotive, hydrogen-based fuel cell systems. The morphology of the catalyst layers of these membranes should provide a structure that is optimised for maximum catalyst utilisation; water management at a wide range of operational temperatures and relative humidity; fuel (hydrogen) and oxidant (oxygen in air) mass-transfer; and optimum electronic conductivity. Because of the multi-component nature of the layers (catalyst, ionomer and catalyst support) and resulting hierarchy in the layered structure at different spatial scales, new tools for their characterisation are required. Such a development should lead to an improved understanding of the links between fuel cell performance and structure of the catalyst layers under various operating conditions. This feature article presents soft X-ray spectromicroscopy as a tool for such studies and shows how it can probe the structural and chemical properties of the membrane and the catalyst layers of membrane electrode assemblies.

A typical state-of-the-art catalyst-coated membrane (CCM) consists of a proton-exchange membrane (PEM) with cathode and anode catalysts coated on opposite surfaces.

Figure 1 shows a schematic diagram of a typical automotive CCM superimposed on a secondary electron microscopy (SEM) image

of a cross-section of the CCM. A function of a PEM is to transport proton charge carriers from the anode to the cathode. The PEM used in a hydrogen fuel cell should also act as a non-permeable, electronically insulating, gas barrier between the cathode and anode of the fuel cell.^[1]

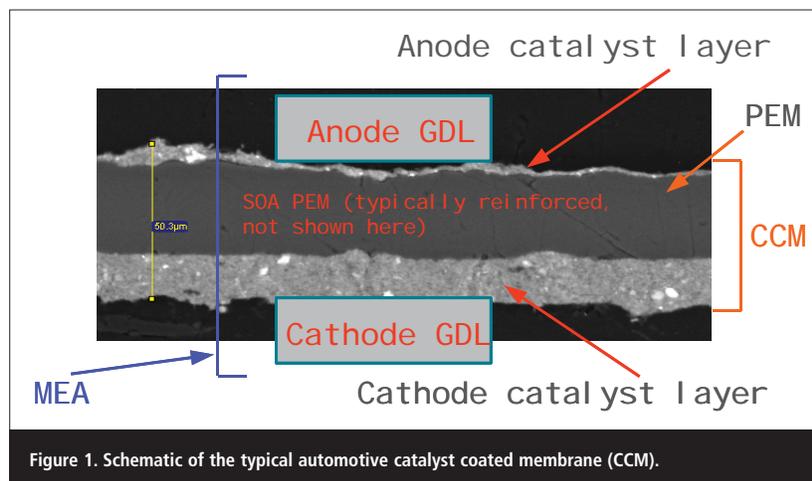


Figure 1. Schematic of the typical automotive catalyst coated membrane (CCM).

Catalyst layers

Requirements for the anode catalyst of the CCM include high hydrogen oxidation reaction mass activity in order to produce anode catalyst layers (CL) with a minimum of expensive catalyst, resistance to carbon monoxide poisoning and corrosion electrochemical resistance.

Requirements for the cathode catalyst of the CCM include high oxygen reduction reaction activity, low costs and durability.^[2]

In the CCM the catalyst layers typically employ a mixture of platinum group metal supported electro-catalysts and ionomers to form a thin layer (from ~2 μm to ~25 μm). The resulting cathode CL must adhere well to the PEM, provide sufficient electrical conductivity (in plane and through plane), provide reactant gas access to the electro-catalyst, have adequate water handling capability and also provide adequate corrosion resistance under oxidising conditions that occur at the cathode of a fuel cell.

Other important requirements of the cathode CL structures include optimised tortuosity in order to provide adequate rates of proton diffusion via the ionomer network, and reactant gas permeability in the transport pores of the bulk of the cathode catalyst layer and microporous layer, which can become limiting as the current density increases.^[3]

One of the common challenges that the fuel cell automotive industry is facing is the lack of adequate characterisation tools that would allow unlocking structure–performance relationships in the CL.

Degradation of the cathode catalyst layer

Fundamental understanding of the cathode CL structure–performance and durability relationships can be achieved if a number of selective *ex-situ* and *in-situ* methods are used to

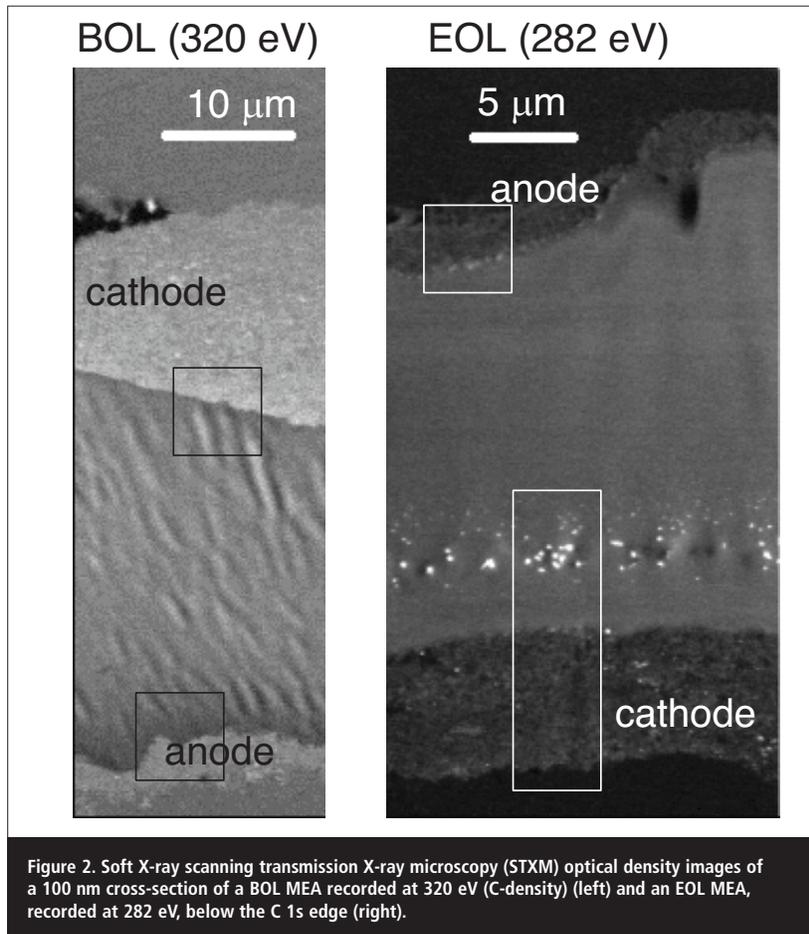


Figure 2. Soft X-ray scanning transmission X-ray microscopy (STXM) optical density images of a 100 nm cross-section of a BOL MEA recorded at 320 eV (C-density) (left) and an EOL MEA, recorded at 282 eV, below the C 1s edge (right).

characterise structures of the CL after CCMs are exposed to real automotive stressors.

Experiments investigating modifications after exposure to stressors have revealed a number of degradation pathways.^[2] It is important to understand not only the morphological changes in CL, but also the chemical changes that take place in all components of the CL.

Pt particle band in proton-exchange membranes

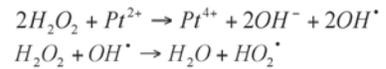
An example of an area that continues to challenge the fuel cell community is the detailed mechanism of Pt particle formation in the CCM as a result of cathode degradation,^[2] as well as the effect of the resulting Pt band on ionomer degradation and CCM durability.^[4]

Three main trends describe research activities aimed at understanding the effect of the Pt particle band on ionomer degradation. **Table 1** provides a summary of different viewpoints which include the following opinions:

- (I) Radicals are generated on the Pt-band

and membrane degradation is initiated there.^[4–7] For example, IR transmission micro-spectroscopy was used to measure degradation finger prints of the Pt-band under OCV durability testing.^[4] Raman micro-spectroscopy results^[5,7] suggest that the Pt-band loses R-SO₃⁻ and R-O-C groups relative to C-F groups. X-ray photoelectron spectroscopy was used^[6] to provide evidence

that both Pt(II) and Pt(IV) cations can be formed during Pt dissolution in the CL. Mixed potentials at the Pt(0) particles in the membrane enable the formation of H₂O₂.^[8] The following reactions^[6] can lead to the generation of peroxide radicals within the membrane:



Peroxide radicals can degrade Nafion both at the chain ends and at the pendant functional groups.

- (II) Pt-band decomposes radicals and suppresses membrane degradation.^[9] According to H. Uchida *et al.*, Pt particles improve membrane durability.

Structural and physical parameters of the cathode catalyst layer

The list of such parameters is too long to discuss fully here. We group these parameters in a few categories and provide brief comments in **Table 2** (see page 8), which also provides basic categories of structural and physical parameters of the cathode catalyst layers that require new or improved characterisation tools.

Important cathode CL characterisations, such as visualisation of its nano-structure, Pt particle distribution, ionomer coverage (thickness distribution) and pore distribution, can be carried out with some limited success by various microscopy techniques (for example, TEM and SEM). However chemical information as well as better imaging is also required.

Results obtained for CCM characterisation by soft X-ray spectromicroscopy are the subject of the remainder of this paper. More specifically, some results of chemical

Test conditions	Conclusions	References
Open-circuit voltage (OCV) hold test. No Pt-band in the membrane at the beginning-of-life (BOL).	Formation of Pt band during OCV tests. Direct evidence that Pt-band promotes ionomer degradation.	4–7
Membrane electrode assemblies (MEAs) were subjected to automotive driving cycle or cathode potential cycling experiments. No Pt-band in the membrane at the beginning-of-life (BOL).	Formation of Pt-band during automotive tests. Indirect evidence of the ionomer degradation or modification.	2,10–12, 18,19, this paper
Membranes were subjected to degradation experiments with mixed H ₂ /air feed simulating gas cross-over effects in MEA. Pt particles were introduced into the membrane prior to the tests.	Pt-band decomposes radicals and suppresses the degradation.	9

Table 1. Summary of selected research on Pt-band formation in proton-exchange membranes.

Category	Structural/physical property	Challenges
Water management	Porosity and pore size distribution, tortuosity, and amount of hydrophobic and hydrophilic pores in the catalyst layers (CL).	Well-established mercury-based method (MIP) for porosity measurements may not be adequate because of the nature of the CL materials. A relatively novel method of standard porosimetry (MSP) may need additional validation for CL. ^[3] Microscopy methods could be used but these could result in limited contrast and radiation damage.
Gas and vapour transport	Effective diffusion coefficients of oxygen and water vapour in the CL. Oxygen solubility in ionomers.	Difficult to measure for small concentration differences. In many cases two-phase flow has to be considered.
Proton transport	Through-plane proton diffusivity in the ionomer phase.	Proton conductivity depends on the distribution of ionomer in the bulk of the CL. In general, through-plane proton conductivity is very difficult to measure. Visualisation of ionomers in the CL is also difficult.

Table 2. Selected structural and physical parameters of the cathode catalyst layer that require the development of novel characterisation methods.

mapping of CCMs and structural analysis of CL with up to 30 nm spatial resolution are presented.

Brief presentations of these results have been given elsewhere.^[10–12] This study provided information on: (I) morphology and chemistry of platinum particles in the membrane; (II) chemical differences between the beginning-of-life (BOL) and end-of-life (EOL) samples; (III) evaluating soft X-ray scanning transmission X-ray microscopy (STXM) versus EDX in TEM and SEM as a probe of the distribution of Co across the CCM; and (IV) evaluating porosity of the CCM.

Soft X-ray spectromicroscopy

STXM is a synchrotron-based technique that provides speciation through near-edge X-ray absorption spectroscopy, and quantitative chemical and orientation mapping at 30 nm spatial resolution.^[13]

All data were collected at the Advanced Light Source using the STXM on beamline 5.3.2.^[14] Soft X-rays from the bend magnet are ‘monochromated’ and focused by a zone plate (Centre for X-ray Optics, 25 nm outer zone, 240 μm diameter) to a spot size of 30 nm.

The sample is (x, y) raster scanned through the zone plate focus while synchronously recording the transmitted X-rays using a phosphor (P31) to convert them to visible light pulses then to an electrical pulse by a photomultiplier tube (Hamamatsu) and counted, typically using a 1 ms count period per image pixel.

Spectra can be collected from individual points, along lines, over areas or even in three dimensions, through angle-scan spectromicroscopy.^[15,16]

High quality images recorded at photon energies where specific components strongly absorb are also used to map individual

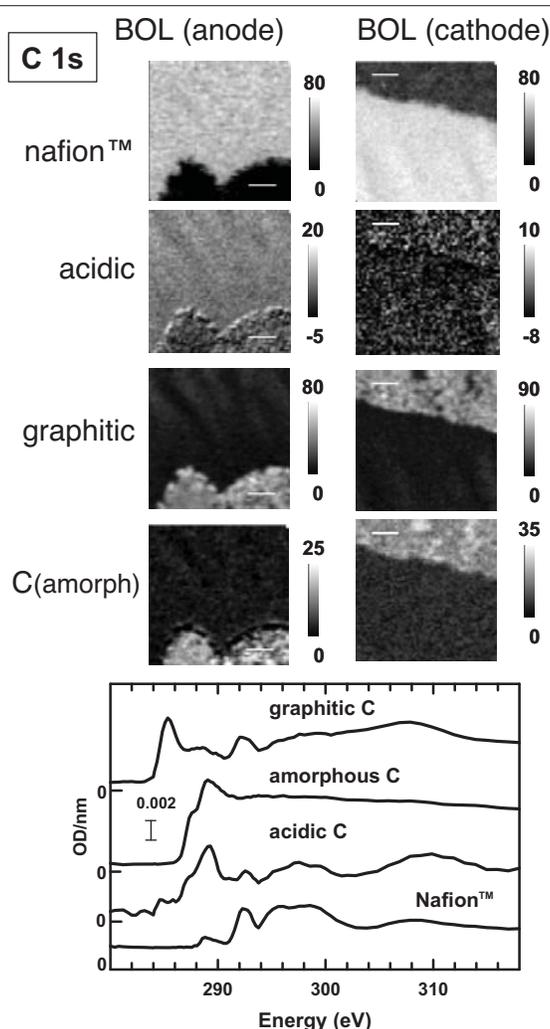


Figure 3. Component maps for Nafion, acidic carbon, graphitic carbon and amorphous carbon derived from C 1s image sequences recorded from (left) anode-membrane and (right) cathode-membrane boundaries of a BOL MEA sample (regions indicated in Figure 2a). The reference spectra used in the fits are on an absolute response scale (OD/nm thickness) and thus the fit coefficients used to construct the component maps have semi-quantitative grey-scale bars (nm thickness/pixel); scale bar = 1 μm.

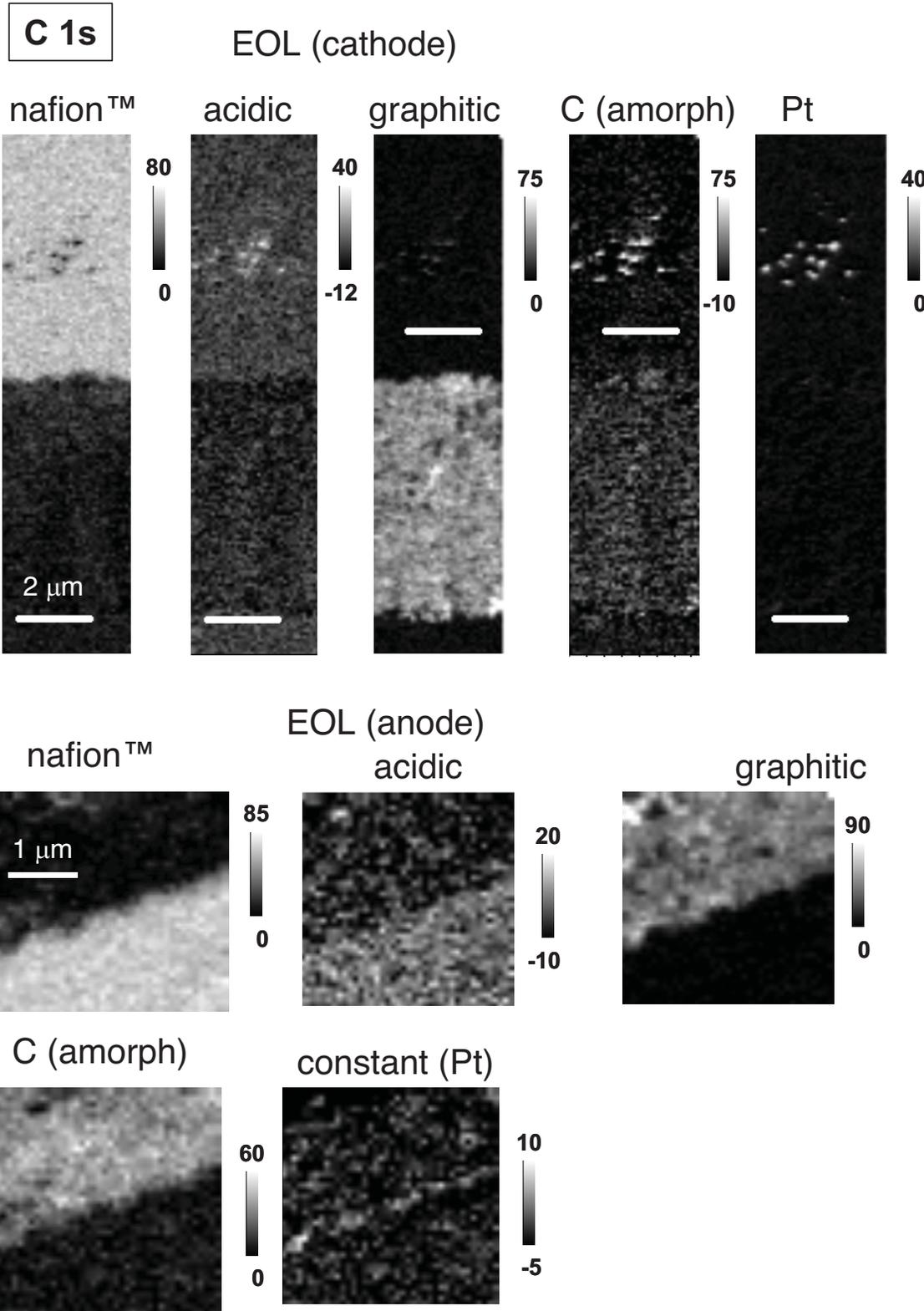


Figure 4. Component maps for Nafion, acidic carbon, graphitic carbon, amorphous carbon and Pt derived from C 1s image sequences recorded from the (upper) cathode-membrane and (lower) anode-membrane boundary of an EOL MEA sample. These regions are indicated in Figure 2b. The grey-scales indicated by the scale bars give nm thickness/pixel.

elements or functional groups. The most detailed information is obtained by recording sequences of 25–100 images (stacks), which are aligned post-acquisition (if needed) and converted from transmission to optical density scale using the incident flux spectrum (I_0) recorded quasi-simultaneously from a region off the sample. Although not used so far in this programme of studies, fully wet samples (that is, ones with up to 2 μm of water) can be examined by sandwiching a fully hydrated sample between two Si_3N_4 (Norcada Inc, Edmonton, Alberta) or polyimide (Luxfilm, Ted Pella) windows, sealed by epoxy or silicone. Samples also can be studied under controlled humidity.^[17]

CCM samples

Membrane electrode assemblies (MEAs) containing PtCo-based carbon-supported cathode catalyst were subjected to a specific drive cycle, simulating the operation of a fuel cell vehicle (FCV).^[18] A drop in performance in the fuel cell stack measured at 1.2 A/cm² was used as a criterion for MEA degradation.

CCMs were extracted from MEAs and CCM cross-sections of 100 nm and/or 300 nm thick were prepared. Post-mortem studies of CCM samples were carried out to determine the degree of Pt dissolution in the membrane. STXM results were complemented

by SEM, TEM imaging and EDX. Using high-resolution TEM, we were able to observe single particles of Pt as well as Pt agglomerates in the membranes subjected to the testing conditions.^[18]

Results

In this work, STXM was applied at the C 1s, N 1s, O 1s, Co 2p and F 1s edges to study MEAs before and after they were subjected to a specific drive cycle, simulating the operation of a FCV.

Chemical differences between the BOL and EOL

F 1s, C 1s and O 1s image sequences from the BOL and several regions of the EOL MEAs were recorded by STXM and analysed in detail by pixel-by-pixel curve fits to suitable reference spectra.

The latter were typically isolated from the image stacks themselves, guided by knowledge of the expected chemical structure and comparison with spectra of pure materials of similar composition.

Figure 2 (see page 7) presents STXM optical density (OD) images of typical samples on a scale sufficient to image the whole MEA cross-section. **Figure 2a** is a BOL sample, measured at 320 eV which emphasises carbon density/thickness.

Figure 2b is an EOL sample measured at 282 eV below the onset of the C 1s absorption, which shows very clearly the Pt particles that have appeared in the membrane 4–8 μm in from the CCL, and also the stronger absorption by the denser carbonaceous cathode and anode layers, as well as the fluorine rich Nafion membrane.

Figure 3 (see page 8) presents the results of a C 1s image sequence analysis of the BOL in the regions of the anode-membrane and cathode-membrane boundaries that are indicated by rectangles in **Figure 2a**. In addition to the expected components (Nafion, graphitic and amorphous carbon) the spectral-spatial data could only be fit adequately if an additional component was introduced, which is labelled 'acidic C', since it is characterised by strong sharp contribution around 289 eV – the energy for C 1s $\rightarrow (\pi^*_{\text{C=O}}$ transitions into carboxylic acids and carboxylates.

The component maps derived from fitting the C 1s image sequences to the indicated reference spectra are on semi-quantitative thickness scales (nm/pixel), indicated by the scale bar for the image grey scales.

In this case there is considerable uncertainty (50% or more) in these numbers because the exact chemical nature and density are not known. However, when those quantities are known, compositional quantitation with a precision of 10% and similar accuracy can be achieved.^[13]

Figure 4 (see page 9) presents the results of a C 1s image sequence analysis of the EOL in the regions of the anode-membrane and cathode-membrane boundaries that are indicated by rectangles in **Figure 2b**.

In addition to the four components whose chemical spectra are indicated in **Figure 3**, the signal from Pt migrated into the membrane is displayed (constant of the fit). Studies were also carried out at the O 1s and F 1s edges, which provided complementary information about the modifications to the membrane in the region of the Pt-band in the EOL sample. In particular, the F 1s study showed that there is a build up of F-rich components in the Pt-band.

More detailed C 1s and O 1s STXM studies were carried out in the region of the platinum particles formed in the platinum-in-the-membrane band in the EOL sample.

Figure 5a presents results from the C 1s analysis, while **Figure 5b** presents the results from O 1s analysis on a different sample. While a detailed interpretation is under development, this is the type of novel spectral results that may help understand the mechanisms involved in particle formation and their effects on the MEAs.

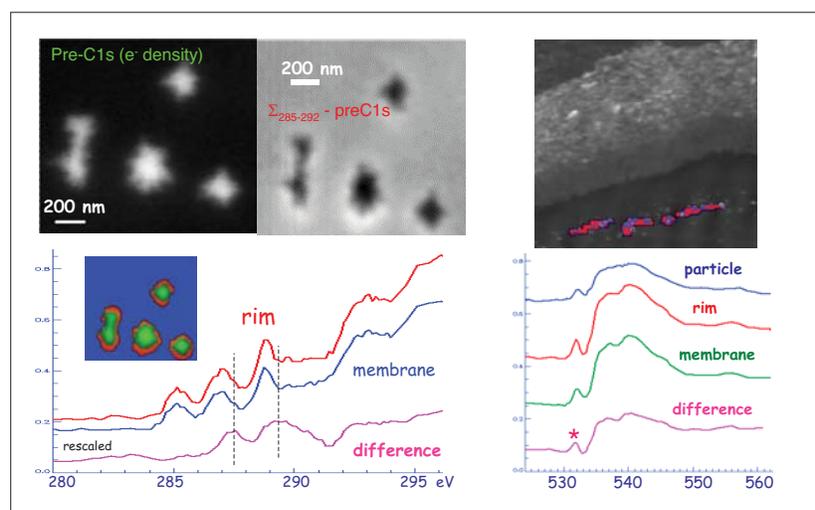
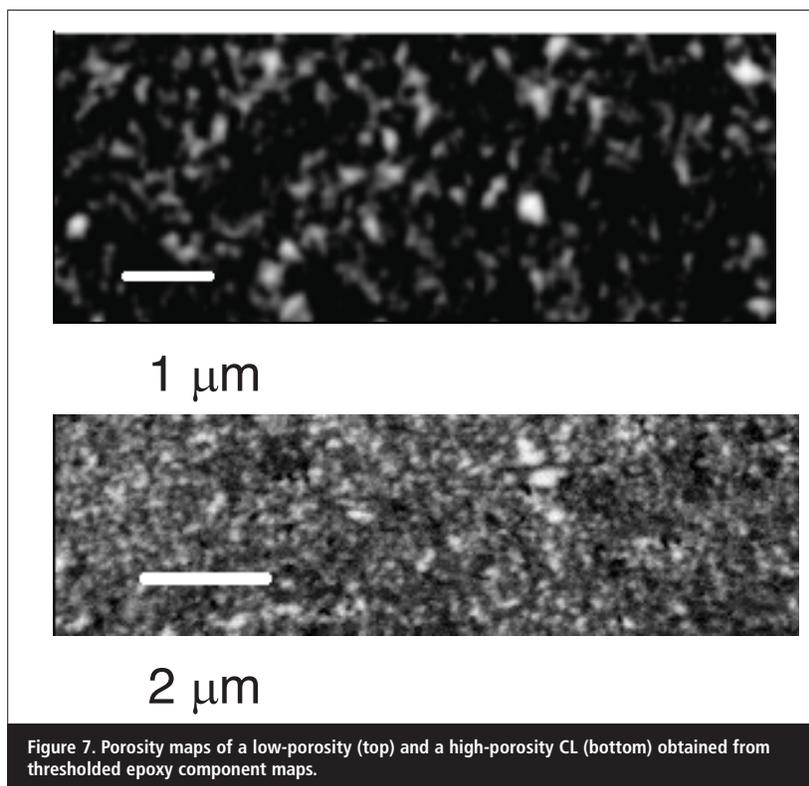
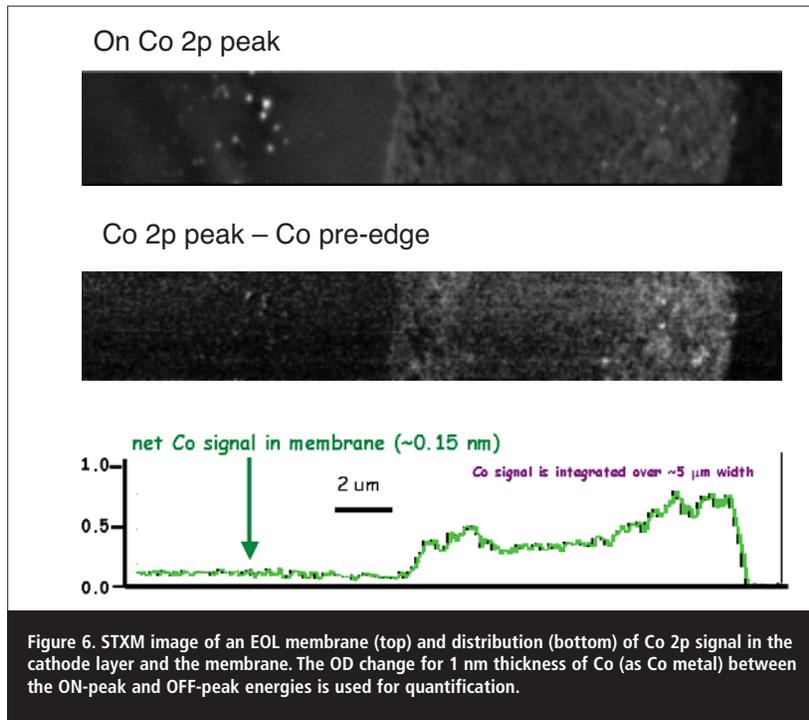


Figure 5(a). (left) Pre-C1s and sum of images in (285–292 eV) region of an EOL MEA. C 1s spectra (shown beneath) from the areas indicated in the inset, along with their difference, indicating the C 1s spectrum in the region of the Pt particles is different from that of the Nafion membrane far from the Pt-band.

Figure 5(b). (right) Soft X-ray scanning transmission X-ray microscopy (STXM) OD image (520 eV) with regions on and adjacent to the Pt band indicated from which spectra were obtained. O 1s spectra (shown beneath) of the particle – rim in the region of the Pt band in the EOL MEA; membrane far from the Pt band; and the difference. This shows a significant shift in the low-lying peak, to an energy typical for carboxylic or carboxylic oxygen sites.



Evaluating STXM for analysis of the distribution of Co across the CCM

The development of a more active oxygen reduction electro-catalyst than Pt has been the

subject of extensive research for many years within the fuel cell community.

It is well known that the kinetic performance of a range of Pt alloy cathode catalysts is significantly higher than the corresponding

pure Pt catalysts. It is also known that under automotive conditions Pt alloy catalysts are not stable.

A commercially available PtCo alloy cathode catalyst was used in our tests. STXM images on the Co 2p_{3/2} peak (778.8 2V) and below the onset of Co 2p absorption (772 eV) were used to map Co quantitatively across the MEA. Co was readily detected in the CCMs from the EOL samples (Figure 6).

Co was not detected in the membranes of the BOL samples (or the level of Co in the membrane was below the STXM detection limit). The Co level detected in the EOL membrane was ~300 ppm v/v, in agreement with bulk measurements of the Co concentration from the membrane isolated from the MEA.

Porosity of the CCM

Figure 7 illustrates the ability of STXM to use its chemical mapping capabilities to map the porosity in MEA components, such as the cathode, the micro-porous layer and the gas diffusion layer.

Here the sample was embedded in a relatively penetrating epoxy, and the component map of the epoxy was used to visualise the porosity. A clear distinction in pore area between the two samples is observed.

Techniques are being developed that will enable image analysis to be applied to such results in order to derive quantitative pore size and ultimately pore-connectivity information. Ultimately, with appropriate sample preparation and measurement it should be possible to quantify porosity, pore size distribution, connectivity and tortuosity from STXM spectrometry,^[15,16] in the dry and wet states.

Conclusions

These results demonstrate that STXM is a useful technique for studying fuel cell MEAs.

Studies at multiple core level edges – C 1s, O 1s and F 1s, and at different spatial scales – can be used to gain an insight into the chemical changes that may occur in association with fuel cell component degradation through automotive operation.

The evaluation study has clearly shown the ability to measure and map Co in the cathode and membrane to low levels (~100 ppm) by STXM. The use of STXM for mapping porosity was also explored.

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