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Structural dynamics and activity of nanocatalysts inside fuel cells by *in operando* atomic pair distribution studies[†]

Valeri Petkov,*^a Binay Prasai,^a Shiyao Shan,^b Yang Ren,^c Jinfang Wu,^b Hannah Cronk,^b Jin Luo^b and Chuan-Jian Zhong*^b

Here we present the results from a study aimed at clarifying the relationship between the atomic structure and activity of nanocatalysts for chemical reactions driving fuel cells, such as the oxygen reduction reaction (ORR). In particular, using in operando high-energy X-ray diffraction (HE-XRD) we tracked the evolution of the atomic structure and activity of noble metal-transition metal (NM-TM) nanocatalysts for ORR as they function at the cathode of a fully operational proton exchange membrane fuel cell (PEMFC). Experimental HE-XRD data were analysed in terms of atomic pair distribution functions (PDFs) and compared to the current output of the PEMFC, which was also recorded during the experiments. The comparison revealed that under actual operating conditions, NM-TM nanocatalysts can undergo structural changes that differ significantly in both length-scale and dynamics and so can suffer losses in their ORR activity that differ significantly in both character and magnitude. Therefore we argue that strategies for reducing ORR activity losses should implement steps for achieving control not only over the length but also over the time-scale of the structural changes of NM-TM NPs that indeed occur during PEMFC operation. Moreover, we demonstrate how such a control can be achieved and thereby the performance of PEMFCs improved considerably. Last but not least, we argue that the unique capabilities of in operando HE-XRD coupled to atomic PDF analysis to characterize active nanocatalysts inside operating fuel cells both in a time-resolved manner and with atomic level resolution, *i.e.* in 4D, can serve well the ongoing search for nanocatalysts that deliver more with less platinum.

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Introduction

Devices for clean energy conversion such as fuel cells are a very plausible alternative to mankind's dependence on fossil fuels.¹ The fuel cell technology, however, may not become commercially viable unless affordable and sufficiently active nanocatalysts for speeding up the sluggish chemical reactions driving cells' operation, such as the oxygen reduction reaction (ORR) taking place at the cathode of virtually all fuel cells, are developed.^{1,2} Indeed, a number of excellent nanocatalysts for ORR, for the most part multi-metallic nanoparticles (NPs),

have been developed over the last decade.^{3–7} Despite real progress, fuel cells are not yet on the market, mostly because the superb ORR activity of multi-metallic NPs would decay during cells' operation, thereby limiting the cells' performance.

The problem triggered off numerous studies on the impact of the highly corrosive environment inside fuel cells on the catalytic activity of multi-metallic NPs for ORR. Studies indicated that under operating conditions, multi-metallic NPs can undergo large-scale structural changes, ranging from orderdisorder transitions to complete phase segregation and so suffer a substantial loss in ORR activity. Hence, strategies for limiting the latter through inhibiting the former are being considered, and some adopted, typically resorting to tests conducted in a lab, *i.e. ex situ*.^{2–9}

We assembled a fully functional proton exchange membrane fuel cell (PEMFC) optimized for high-energy X-ray diffraction (HE-XRD) and carried out *in operando* atomic pair distribution studies^{10–14} on the evolution of the atomic structure and ORR activity of pertinent noble metal-transition metal (NM–TM) nanocatalysts^{15–20} as they function inside the PEMFC. Studies showed that highly dynamic structural

^aDepartment of Physics, Central Michigan University, Mt. Pleasant, Michigan 48858, USA. E-mail: petko1vg@cmich.edu

^bDepartment of Chemistry, State University of New York at Binghamton,

New York 13902, USA. E-mail: cjzhong@binghamton.edu

^cX-ray Science Division, Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois 60439, USA

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fluctuations occurring at the Ångstrom length-scale and irreversible large-scale structural changes, such as a gradual growth of the order of a few nm, can indeed be equally responsible for the decay of the ORR activity of NM–TM nanocatalysts during cells' operation.

We argue that, to be fully successful, efforts to limit that decay should strive to achieve control not only over the lengthscale but also over the dynamics of the structural changes that multi-metallic NPs indeed undergo inside operating fuel cells. Moreover, we demonstrate how such a control can be achieved. Also, we argue that *in operando* HE-XRD coupled to atomic PDF analysis is a technique worthy of employing on a more regular basis than now because it can provide a sound atomiclevel foundation for the effort to develop efficient nanocatalysts for fuel cell related applications.

PEMFCs are typical devices for efficient and clean energy conversion. In particular, PEMFCs convert the chemical energy released during an electrochemical reaction between hydrogen and oxygen into electrical energy. The conversion involves a catalyst-assisted splitting of hydrogen (H₂) molecules at the PEMFC anode into protons and electrons, known as the hydrogen oxidation reaction (HOR). The resulting protons (H⁺) permeate through a membrane electrode assembly (MEA) to the PEMFC cathode while electrons (e⁻) reach it *via* an external circuit, thus generating current output. Oxygen (O₂) molecules reduced at the PEMFC cathode react with the protons arriving at it, forming water. The reaction, known as ORR, is six orders of magnitude slower than HOR, necessitating a very efficient catalyst for speeding it up.^{21,22}

It has been shown that, barring losses due to an inefficient supply of oxygen and hydrogen gases to the PEMFC electrodes and Ohmic-type resistance of the PEMFC's components, the current output of an operating PEMFC, *i*, can be evaluated through the so-called Butler–Volmer equation²³ as follows:

$$i = i_{\rm o} \exp\left(-\frac{\alpha F \Delta V_{\rm act}}{RT}\right) \tag{1}$$

where i_0 is the so-called exchange current density, α is the socalled charge transfer coefficient assuming values between 0 and 1, F and R are the Faraday and ideal gas constants, respectively, T is the temperature at which the PEMFC operates and $\Delta V_{\rm act}$ is the so-called ORR activation overpotential. Largely, quantities i_0 and ΔV_{act} reflect the number of catalytically active sites at the PEMFC cathode and the fraction of the electrical energy generated by the PEMFC lost in activating the sluggish ORR, respectively. As eqn (1) shows, the current output of an operating PEMFC, and so the PEMFC performance, would be high when i_0 is high and ΔV_{act} is low. Evidently, an efficient PEMFC cathode catalyst should both provide high i_0 , usually referred to as the electrochemical active surface area (ECSA) of that catalysts, and have the innate ability to speed up ORR through keeping ΔV_{act} low. Usually, the latter is referred to as the specific activity (SA) of that catalyst for ORR.

Pure Pt NPs are the best monometallic catalysts for ORR due to, among others, their intrinsically high SA for

ORR.^{15,21,22} Pure Pt NPs however are not quite suitable for large scale applications because Pt is one of the world's rarest metals. Besides, ORR over Pt NPs proceeds via a number of elementary steps involving reaction intermediates such as Pt-O and Pt-OH. The intermediates would bind strongly to the surface of Pt NPs and so substantially reduce their SA for ORR.²⁴ Nanoparticles of the NM-TM family, where NM = Pt, Pd and Au and TM = Ni, Co, Fe, Cu, V and Mo, are more affordable and active catalysts for ORR as compared to pure Pt NPs.^{3,4,6,19,25-28} The improved SA of NM-TM NPs for ORR is attributed to the so-called ligand,^{5,15,18,21,27,29} strain^{6,15,16,30-33} and geometric effects. The first one arises from charge exchange between particular NM and TM species (e.g. between Pt and Ni) in the NPs. The second one arises from shortening (compressing) of NM-NM bond lengths in the NPs, usually occurring when larger in size NM species, such as Pt (2.77 Å) and Pd (2.75 Å), are intermixed with smaller in size TM species, such as Ni (2.49 Å) and Co (2.52 Å). Both effects lead to a downshift of the d electron states of NM species in the respective NM-TM NPs, thus reducing the so-called "poisoning" effect of ORR intermediates. According to Pauling's theory of chemical bonding,³⁴⁻³⁶ and as shown by independent experimental³⁷ and DFT studies,³⁸ the length and strength of bonds between metal atoms and the charge transfer between the metal atoms involved are intimately coupled and so difficult to tell apart. Therefore, here we consider that the ligand and strain effects in NM-TM NPs largely act together and refer to them as bonding effects. On the other hand, the geometric effect envisages that particular configurations of NM and TM species at the surface of NM-TM NPs are behind their improved SA for ORR.³⁸⁻⁴⁶

Though proven superb as catalysts for ORR, NM-TM NPs are not quite able to perform as desired inside operating fuel cells. This is because under the highly corrosive environment in fuel cells, NM-TM NPs undergo specific structural changes that inflict losses in their ORR activity. The changes are largely caused by leaching of atomic species from the NPs. The leaching may result in a complete disintegration of smaller NM-TM NPs (<4 nm) and re-deposition of leached-off atomic species onto the surface of larger NM-TM NPs. Transition metal species are much more likely than NM species to leach from NM-TM NPs during cells' operation. This is because the reduction potential of the former is much lower than that of the latter (e.g. -0.28 V and -0.24 V for Co and Ni vs. 0.92 V and 1.19 V for Pd and Pt, respectively). On the other hand, leached-off NM species are much more likely than leached-off TM species to re-deposit onto the surface of larger NM-TM NPs. The re-deposition occurs via a process known as Ostwald ripening and, typically, results in a substantial further growth and phase segregation of larger NM-TM NPs into NM-TM cores and sizable NM shells. It has also been found that NM-TM NPs can end up segregated into TM-rich cores and NMrich shells merely because TM species leach from the NP surface alone.^{9,19,47-50} Furthermore, studies have shown that NM-TM NPs can grow in size through coalescing involving displacement and collision of neighbouring NPs.51-53 The

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currently prevailing understanding is that gradually evolving, large-scale structural changes of NM–TM NPs, such as nanometer-sized growth, severe depletion of near-surface TM species, phase segregation and complete disintegration, would contribute the most to the losses in ORR activity these NPs suffer during cells' operation.^{2,5,9,54–58} This is not necessarily the case as our *in operando* atomic pair distribution studies show.

Results and discussion

2.1 Sample synthesis and characterization

For completeness, we studied the members of two families of NM–TM NPs currently pursued as catalysts for ORR, in particular binary Pd–Ni and ternary Pt–Ni–Co metal NPs (both <10 nm). Binary Pd–Ni NPs represent ORR catalysts not containing Pt. Ternary Pt–Ni–Co NPs represent ORR catalysts containing Pt intermixed with two distinct TM species, hereafter referred to as TM' and TM" species, respectively. The NPs were synthesized by the wet chemical routes described in the Methods section of the ESI.† We targeted Pd–Ni NPs with chemical composition close to Pd₁Ni₄. In the case of the ternary Pt–Ni–Co system, we targeted NPs with chemical composition close to Pt₅₀(Ni+ Co)₅₀ wherein the relative amount of Ni and Co species is approximately the same. This is because such types of NM–TM NPs have been found very promising as ORR catalysts.^{13,14,59}

The exact chemical composition of as-synthesized NPs was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES), described in the Methods section of the ESI,† and was found to be Pd₃₀Ni₇₀ and Pt₄₅Ni₃₃Co₂₂, respectively. The size and shape of as-synthesized NPs were determined by transmission electron microscopy (TEM). The distribution of NM (Pd and Pt) and TM (Ni and Co) species across the respective NPs was determined by high-angle annular dark-field (HAADF) scanning TEM (STEM) imaging. Details of the TEM and HAADF-STEM experiments can be found in the Methods section of the ESI.[†] Exemplary TEM and HR-TEM images are shown in Fig. 1. HAADF-STEM images are shown in Fig. 2. As the respective images indicate, assynthesized Pd₃₀Ni₇₀ and Pt₄₅Ni₃₃Co₂₂ NPs are spherical in shape, near random alloys and approximately 7.1 \pm 0.6 nm and 7.3 \pm 0.6 nm in size, respectively.

X-ray photoelectron spectroscopy experiments, described in the Methods section of the ESI[†] (*e.g.* see Fig. S1[†] and the associated text), show that the chemical composition at the surface of as-synthesized $Pd_{30}Ni_{70}$ and $Pt_{45}Ni_{33}Co_{22}$ NPs is nearly identical to their average chemical composition, as determined by ICP-AES, thus confirming that as-synthesized NPs are single phase nanoalloys.

2.2 Ex situ catalytic and structure studies

At first, structural changes and the related losses in the ORR activity of Pd–Ni and Pt–Ni–Co NPs were studied *ex situ*. The goal was to provide a point of reference for the *in operando*



Fig. 1 Representative TEM (left column) and HR-TEM (right column) images of as-synthesized (first row) Pd–Ni and (second row) Pt–Ni–Co NPs on carbon. The NPs appear spherical in shape and with an average size of approximately 7.1 ± 0.6 nm and 7.3 ± 0.6 nm, respectively. Note that the " \pm " deviation from the average NP size is the half width at full maximum of a Gaussian-like distribution of sizes extracted from populations of several hundred NPs sampled by different TEM images.



Fig. 2 Representative HAADF-STEM images and elemental maps for assynthesized (first row) Pd-Ni ($Pd_{30}Ni_{70}$) and (second row) Pt-Ni-Co ($Pt_{45}Ni_{33}Co_{22}$) NPs.

studies. In particular, the ECSA and mass activity (MA) of assynthesized Pd–Ni and Pt–Ni–Co NPs for ORR were determined on a laboratory electrochemical (3-electrode) cell through standard voltammetry (CV) and rotating disk electrode (RDE) experiments.⁸ Losses in the MA and ECSA were evaluated on the same cell following a protocol suggested by the US DOE hydrogen fuel programme.⁵² To be more specific, the cell was cycled between 0.4 V and 1.0 V *vs.* RHE (Reference Hydrogen Electrode) and the ECSA and ORR (MA) activities of Pd–Ni and Pt–Ni–Co NPs that have undergone a given number of cell cycles were determined again through standard CV and RDE experiments. Details of CV and RDE experiments are given in the Methods section of the ESI.[†] Exemplary CV and RDE curves are shown in Fig. S2.[†] The MA and ECSA of assynthesized and electrochemically cycled (400, 1000 and 3000 times) Pd–Ni and Pt–Ni–Co NPs are summarized in Table S1.[†] The SA of the respective NPs for ORR, as determined from MA and ECSA data, is also given in that table. Inspection of the data in Table S1[†] shows that as-synthesized Pd–Ni and Pt–Ni–Co NPs are excellent catalysts for ORR. Also, it shows that the ORR (both MA and SA) activity of Pd–Ni and Pt–Ni–Co NPs decreased during the electrochemical cycling. The rate of decrease in the MA of Pd–Ni and Pt–Ni–Co NPs with the number of cell cycles is shown in Fig. 3.

The chemical composition, size and shape of Pd–Ni and Pt–Ni–Co NPs that have undergone 400, 1000 and 3000 cell cycles were determined by ICP–AES and TEM experiments, as described in the Methods section of the ESI[†]. In line with the results of prior studies on the catalytic activity of NM–TM NPs,^{3,4,49,60} the results of ICP–AES experiments conducted here show that TM species leached from both Pd–Ni and Pt–Ni–Co NPs during the electrochemical cycling. In particular, the chemical composition of Pd–Ni NPs that have undergone 400, 1000 and 3000 cell cycles changed from the initial one of $Pd_{30}Ni_{70}$ to $Pd_{39}Ni_{61}$, $Pd_{46}Ni_{54}$ and $Pd_{69}Ni_{31}$, respectively. That



Fig. 3 Catalytic and structure data of Pd–Ni (a) and Pt–Ni–Co (b) NPs electrochemically cycled between 0.4 V and 1.0 V inside a standard 3-electrode cell. Data suggest a gradual decrease in the ORR (MA) activity (green triangles), GSA (magenta squares), relative TM content (orange circles) and bonding effects in the NPs (blue rhombi) with the number of cell cycles. Note that bonding effects are estimated from PDF-derived fcc-lattice parameters reflecting the characteristic atomic-pair distances in the respective NPs. Broken lines through the data points are a guide to the eye.

of Pt-Ni-Co NPs that have undergone 400, 1000 and 3000 cell cycles changed from the initial one of Pt45Ni33Co22 to Pt₅₆Ni₂₅Co₁₉, Pt₅₇Ni₂₄Co₁₉ and Pt₅₉Ni₂₃Co₁₈, respectively. Losses in TM species suffered by Pd-Ni and Pt-Ni-Co NPs that have undergone 400, 1000 and 3000 electrochemical cycles are summarized in Fig. 3a and b, respectively. Results of TEM experiments showed that Pd-Ni and Pt-Ni-Co NPs not only suffered significant losses in TM species but also significantly increased in size during the electrochemical cycling. In particular, as TEM and HR-TEM images summarized in Fig. 4 and 5 show, the average size of Pd–Ni NPs that have undergone 400, 1000 and 3000 cell cycles increased from the initial one of $7.1 \pm 0.6 \text{ nm}$ to $7.5 \pm 0.6 \text{ nm}$, $8.2 \pm 0.7 \text{ nm}$ and $8.9 \pm 0.8 \text{ nm}$, respectively. That of Pt-Ni-Co NPs that have undergone 400, 1000 and 3000 cell cycles increased from the initial one of 7.3 ± 0.6 nm to 7.7 ± 0.6 nm, 8.4 ± 0.7 nm and 9.1 ± 0.8 nm, respectively.



Fig. 4 Representative TEM (left column) and HR-TEM (right column) images of Pd–Ni NPs on carbon that have undergone (first row) 400, (second row) 1000 and (third row) 3000 cycles between 0.4 V and 1.0 V inside a standard electrochemical cell. The NPs appear spherical in shape and with an average size of approximately 7.5 \pm 0.6 nm, 8.2 \pm 0.7 nm and 8.9 \pm 0.8 nm, respectively. Note that the " \pm " deviation from the average NP size is the half width at full maximum of a Gaussian-like distribution of sizes extracted from populations of several hundred NPs sampled by different TEM images.



Fig. 5 Representative TEM (left column) and HR-TEM (right column) images of Pt-Ni-Co NPs on carbon that have undergone (first row) 400, (second row) 1000 and (third row) 3000 cycles between 0.4 V and 1.0 V inside a standard electrochemical cell. The NPs appear spherical in shape and with an average size of 7.7 \pm 0.6 nm, 8.4 \pm 0.7 nm and 9.1 \pm 0.8 nm, respectively. Note that the " \pm " deviation from the average NP size is the half width at full maximum of a Gaussian-like distribution of sizes extracted from populations of several hundred NPs sampled by different TEM images.

The distribution of NM and TM species across Pd–Ni and Pt–Ni–Co NPs that have undergone 3000 cell cycles was determined by HAADF-STEM experiments described in the Methods section of the ESI.[†] At odds with the findings of several prior studies,^{20,47,49,54,60} HAADF-STEM images (see Fig. 6) indicate that, despite having suffered significant losses in TM species and undergone a significant increase in size, Pd–Ni and Pd–Ni–Co NPs did not segregate into NM–TM cores and NM shells during the *ex situ* electrocatalytic studies.

Structural changes of the electrochemically cycled Pd–Ni and Pt–Co–Ni NPs were assessed by *ex situ* HE-XRD coupled to atomic pair distribution function (PDF) analysis. Details of HE-XRD experiments and the derivation of atomic PDFs, G(r), are given in the Methods section of the ESI.† Exemplary HE-XRD patterns and atomic PDFs are shown in Fig. S5† and 7, respectively. The average size of as-synthesized and electrochemically cycled Pd–Ni and Pt–Co–Ni NPs was also determined by analysis of the width of Bragg-like peaks in the



Fig. 6 Representative elemental maps of (first row) Pd-Ni and (second row) Pt-Ni-Co NPs used as an ORR catalyst at the working electrode of a standard electrochemical cell cycled 3000 times between 0.4 V and 1.0 V. Note that the chemical composition of electrochemically cycled Pd-Ni and Pt-Ni-Co NPs has changed from the initial one of Pd₃₀Ni₇₀ and Pt₄₅Ni₃₃Co₂₂ to Pd₆₉Ni₃₁ and Pt₅₉Ni₂₃Co₁₈, respectively, as determined by ICP-AES. Ni species are in red, Co species are in green and Pt species are in blue.

Fig. 7 Experimental *ex situ* (symbols) and model (red lines) atomic PDFs of Pd–Ni NPs and Pt–Ni–Co NPs. Data for as-synthesized NPs and NPs that have undergone 400, 1000 and 3000 cycles between 0.4 V and 1.0 V inside a standard electrochemical cell are shown. The refined fcc-lattice parameters and the model's quality indicators, R_{w} , are shown for each data set.

respective *ex situ* HE-XRD patterns using the widely applied Scherrer formalism.⁶¹ Results, listed in the Methods section of the ESI,† appeared consistent with the NP sizes determined by

TEM experiments, thus testifying to the ability of HE-XRD to provide accurate data for the average size of multi-metallic NPs that have undergone electrochemical cycling.

For a given amount of atomic species in a spherical NP, the surface area that can be associated with the species, usually referred to as a geometric surface area (GSA), is inversely proportional to the diameter, *i.e.* the size of the NP. Therefore, the observed gradual growth of Pd-Ni and Pt-Ni-Co NPs with the number of cell cycles can be looked at as a gradual decrease in their GSA and, hence, ECSA during the electrochemical cycling. Indeed, this is exactly what occurred as the results from our independent CV experiments show (see Table S1[†]). Since the surface of NM-TM NPs is partly occupied by TM species, which facilitate but do not participate directly in ORR, the ECSA of NM-TM NPs determined by CV experiments would be smaller than their GSA determined by XRD or TEM. Nevertheless, as studies have shown,^{62,63} the GSA and ECSA of multi-metallic NPs used as ORR catalysts are strongly related to each other and, hence, changes in the former can be used as a relative measure of changes in the latter. The rate of decrease in the GSA of Pd-Ni and Pt-Ni-Co NPs with the number of cell cycles, reflecting the rate of decrease in their ECSA, is shown in Fig. 3.

To assess changes in the overall arrangement of atomic species in Pd-Ni and Pt-Ni-Co NPs that have undergone 400, 1000 and 3000 electro-chemical cycles, we approached the respective atomic PDFs with a simplistic model constrained to the fcc-type crystal structure exhibited by bulk Ni, Co, Pd and Pt metals as well as by their alloys.⁶⁴ Note, by definition, that $G(r) = 4\pi r(\rho(r) - \rho_0)$, where $\rho(r)$ and ρ_0 are the local and average atomic number densities, respectively. Accordingly, the PDF G(r) peaks at distances where the local atomic density is larger than the average one, *i.e.* at distances between pairs of atoms, immediate and all farther neighbours, within the NPs studied. In this respect, G(r) is similar to the so-called Patterson function that is widely used in traditional crystallography.^{11-13,61} Crystal structure-constrained modeling was done as described in ref. 65 and exemplified in Fig. 7. Inspection of the data in the figure shows that the atomic arrangement in both Pd-Ni and Pt-Ni-Co NPs, as-synthesized and electrochemically cycled, is fcc-like. Also, it shows that the fcc-lattice parameters for as-synthesized Pd-Ni (3.762 Å) and Pt-Ni-Co NPs (3.784 Å) are smaller than those for pure Pd (3.891 Å) and Pt (3.924 Å) metals, respectively. The fcc-lattice parameters for the electrochemically cycled Pd-Ni and Pt-Ni-Co NPs, i.e. the characteristic atomic-pair distances in the NPs, however, are seen to increase toward those for pure Pd and Pt metals, respectively. The increase indicates that bonding effects in Pd-Ni and Pt-Ni-Co NPs, such as contraction of metal-to-metal atom bond lengths, diminish as the NPs are functioning as an ORR catalyst inside a 3-electrode cell. The evolution of bonding effects in Pd-Ni and Pt-Ni-Co NPs, as measured by PDF-derived changes in the characteristic atomic-pair distances in the NPs, are shown in Fig. 3.

To cross-check the results of HAADF-STEM experiments indicating that both as-synthesized and 3000 times cycled

Pd-Ni and Pt-Ni-Co NPs are single phase nanoalloys, we built and tested several 3D models featuring plausible phase states of the NPs. The models were built by Molecular Dynamics (MD) simulations based on the quantum-corrected Sutton-Chen method.^{12,66,67} Initial models consisted of atomic configurations with the size (7-9 nm), shape (spherical) and chemical composition, as determined by ICP-AES, of the actual NPs modeled. The configurations included phase-segregated Janus, TM-NM-TM sandwich, NM core-TM shell and TM core-NM shell type NPs. A configuration featuring a single phase NM-TM nanoalloy was also tested. All configurations were optimized in terms of energy, *i.e.* stabilized at the atomic level, by MD carried out under non-periodic boundary conditions as described in the Methods section of the ESI.† Atomic PDFs derived from the MD optimized models were compared with the respective experimental PDFs, as obtained by independent ex situ HE-XRD experiments, and the phase state of assynthesized and electrochemically cycled Pd-Ni and Pt-Ni-Co NPs was ascertained. As an example, results of the MD simulations of as-synthesized Pd-Ni NPs are shown in Fig. 8. The respective MD models are shown in Fig. S11.[†] As the data in Fig. 8 and S11[†] show, a model featuring a single phase Pd₃₀Ni₇₀ nanoalloy reproduces the experimental PDF for assynthesized Pd-Ni NPs much better than models featuring phase-segregated Pd₃₀Ni₇₀ NPs. Models featuring nanoalloys were also found to reproduce the experimental PDFs for as-synthesized Pt-Ni-Co (Pt45Ni33Co22) NPs, electrochemically cycled Pd-Ni (Pd₆₉Ni₃₁) NPs and electrochemically cycled Pt-Co-Ni (Pt₅₉Ni₂₃Co₁₈) NPs much better than models featuring phase segregated NPs. Thus, the results of MD simulations corroborated the findings of HAADF-STEM imaging, namely, that under conditions relevant to operating fuel cells, NM-TM NPs may both suffer big losses in TM species and significantly increase in size and yet remain single nanophase.

To assess structural changes specific to the surface of NM-TM NPs whereat chemical reactions indeed take place, we refined their nanoalloy-type MD models further by hybrid reverse Monte Carlo (RMC) simulations.68,69 The refinement was necessary since, more often than not, actual metallic NPs exhibit both a specific surface structure, e.g. are not terminated by perfectly flat facets, and non-trivial chemical patterns, which are difficult to capture through MD simulations alone.^{70,71} Note that, as demonstrated in Fig. S10,† HE-XRD, in general, and the higher-r part of atomic PDFs G(r), in particular, are sensitive to the atomic arrangement at the surface of metallic NPs used in catalytic applications (typically <15 nm). Indeed, this may not come as a surprise since atoms at the surface of these NPs occupy a substantial fraction of their volume and HE-XRD is known to be a volume sensitive (down to a few %) technique.^{11,61} To be more precise, atoms forming the top two surface layers of the 7-10 nm in size Pd-Ni and Pt-Ni-Co NPs studied here are about 25% of all atoms in the NPs. The simulations were carried out under non-periodic boundary conditions and guided by the respective atomic PDFs as described in the Methods section of the ESI.† The best RMC fits to the experimental PDF data are shown in Fig. 9. The

Fig. 8 Experimental (symbols) and MD model-derived (red lines) atomic PDFs of as-synthesized Pd–Ni (Pd₃₀Ni₇₀) NPs. The difference (blue lines) between the experimental and model-derived PDF data is given (shifted by a constant factor for clarity) for each data set. Snapshots of the respective MD models, shown in Fig. S11,† and the model's quality factors, R_{we} , are also given for each data set.

respective RMC-refined 3D models are shown in Fig. 10. The models were analysed in terms of bonding distances between surface NM atoms, first coordination numbers (CNs) involving surface NM atoms and first total CNs for all surface atoms since, as prior studies have repeatedly shown,^{30–33,38–46} these

structural characteristics of NM–TM NPs are of prime importance to their catalytic activity for ORR. Results of the analysis, in particular the surface CNs obtained, are summarized in Fig. 11.

As the data in Fig. 11 show, NM and TM species at the surface of as-synthesized Pd-Ni and Pt-Ni-Co NPs are well intermixed together and so have a plenty of unlike first neighbours to interact with, including exchanging charge and adjusting the size so as to minimize local stresses arising from the mismatch between their atomic radii. Not surprisingly, Pd-Pd and Pt-Pt bonding distances at the surface of assynthesized Pd-Ni and Pt-Ni-Co NPs, as extracted from the respective RMC-refined models, were found to be 2.68 Å and 2.69 Å, respectively, *i.e.* to be considerably "compressed" as compared to NM-NM distances in the respective NM metals. This, by virtue of the bonding effects discussed above, should have rendered as-synthesized Pd-Ni and Pt-Ni-Co NPs excellent catalysts for ORR in terms of SA. On the other hand, the first NM-NM neighbours at the surface of Pd-Ni and Pt-Ni-Co NPs that have undergone 3000 electrochemical cycles, as extracted from the respective RMC-refined models, appeared separated by 2.73 Å. Evidently, during the electrochemical cycling, NM-NM bonding distances at the surface of Pd-Ni and Pt-Ni-Co NPs expanded toward NM-NM distances in the respective metals. This, by virtue of the bonding effects discussed above, should have inflicted significant losses in the SA activity of Pd-Ni and Pt-Ni-Co NPs for ORR. Furthermore, the concurrent significant losses in SA and GSA/(ECSA) suffered by Pd-Ni and Pt-Ni-Co NPs that have undergone 3000 electrochemical cycles should have resulted in significant losses in their MA for ORR. Indeed, this is what experimental data for MA, ECSA and SA of Pd-Ni and Pt-Ni-Co NPs summarized in Table S1[†] show.

Altogether, results of our *ex situ* studies on the structural changes and concurrent losses in the ORR activity of NM–TM NPs show that, under conditions relevant to operating fuel cells, both Pd–Ni and Pt–Ni–Co NPs suffer substantial losses in TM species. The former however are losing TM species at a higher rate as compared to the latter. Furthermore, both Pd–Ni and Pt–Ni–Co NPs suffer substantial losses in their GSA, SA and, hence, MA for ORR. The loss of ORR (MA) activity however is much more pronounced with the former as compared to the latter. Evidently, Pt–Ni–Co NPs appear more stable as a catalyst for ORR as compared to Pd–Ni NPs. Typically, this very useful conclusion is what standard *ex situ* studies would deliver.

Results of the *ex situ* studies, however, provide little clue as to why the rate with which Pd–Ni and Pt–Ni–Co NPs incur ORR (MA) activity losses does not scale well with the rates with which they lose TM species and increase in size. In particular, Pd–Ni NPs incur about 60% loss in ORR (MA) activity, 9% loss in GSA/ECSA and 30% loss in TM species during the first 400 electrochemical cycles. Ternary Pt–Ni–Co NPs that have undergone 400 cell cycles also incur about 30% loss in TM species. At the same time they incur a 4% loss in GSA/ECSA and a 19% loss in ORR activity only. Furthermore, results of the *ex situ*

Fig. 9 Experimental (symbols) and RMC model-derived (red lines) atomic PDFs of Pd–Ni NPs (left) and Pt–Ni–Co NPs (right) studied by *ex situ* and *in operando* experiments as described in the text. The model's quality factors, R_{w} , and the difference (blue lines) between the experimental and RMC model-derived PDFs are given for each data set. Snapshots of the respective RMC models are also given. Note that, in the active state, both Pd–Ni and Pt–Ni–Co NPs suffer significant losses in TM species.

Nearly Random alloys

Fig. 10 Full-scale models of Pd–Ni (left) and Pt–Ni–Co (right) NPs. Models in the first row represent as-synthesized NPs. Models in the third row represent *in operando* and *ex situ* studied NPs. Note that, in the active state, both Pd–Ni and Pt–Ni–Co NPs significantly increase in size, enrich in NM species and yet do not phase segregate. Models in the middle row emphasize the presence of highly dynamic structural changes in the respective NPs that occur in the course of PEMFC operation (full arrows). Such changes may not be revealed by *ex situ* studies (hollow arrows). Noble metals (Pd and Pt) are in red. Transition metals Ni and Co are in gray and green, respectively.

Fig. 11 First NM–NM (upper panel), NM–TM (middle panel) and total (lower panel) CNs of surface atoms in Pd–Ni and Pt–Ni–Co NPs, as-synthesized (black bars) and then subjected to 3000 electrochemical cycles inside either a 3-electrode cell (blue bars) or an operating PEMFC (red bars).

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studies provide little clue as to why, though nanoalloys, the rate with which Pd-Ni and Pt-Ni-Co NPs lose TM species does not scale well with the rate with which the fcc-lattice parameters for the NPs expand toward the lattice parameters for the respective pure NMs. That should have been the case according to the so-called Vegard's law.^{36,37} In particular, both Pd-Ni and Pt-Ni-Co NPs that have undergone 400 cell cycles incur about 30% loss in TM species whereas their fcc-lattice parameters expand by 56% and 18%, respectively. Moreover, results of the *ex situ* studies provide little clue as to why Pd-Ni and Pt-Ni-Co NPs both incur big losses in TM species (80% and 30%, respectively) and significantly increase in size (by ~2 nm each) while undergoing 3000 cycles between 0.4 V and 1.0 V and yet remain single phase. Missing knowledge prevents addressing the problem with the excessive ORR activity losses suffered by the NPs (90% and 50%, respectively) on a sound structural basis. That knowledge can be provided by in operando atomic pair distribution studies as demonstrated below.

2.3 In operando catalytic and structure studies

A fully functional PEMFC optimized for HE-XRD experiments was assembled and used to study the evolution of the atomic structure and ORR activity of Pd-Ni and Pt-Ni-Co NPs under conditions typical for operating PEMFCs. A schematic of the PEMFC is shown in Fig. S3.[†] MEAs for the PEMFC were prepared using either Pd-Ni (Pd₃₀Ni₇₀) or Pt-Ni-Co (Pt₄₅Ni₃₃Co₂₂) NPs as the PEMFC cathode catalyst. Commercial Pt NPs were used as a catalyst for HOR at the PEMFC anode. Studies involved collecting HE-XRD and ORR (MA) activity sensitive data while cycling the PEMFC between 0.6 V and 1.2 V as suggested by the US DOE hydrogen fuel programme.⁵² During the cycling, high-purity hydrogen and nitrogen gases were fed to the PEMFC anode and cathode compartments, respectively, and the current output of the PEMFC was recorded aroundthe-clock. More details of the PEMFC hardware, MEA preparation and PEMFC cycling can be found in the Methods section of the ESI.† Exemplary polarization curves showing the current output of the PEMFC resulting from the repetitive application of external voltages in the range of 0.6 V to 1.2 V are shown in Fig. S4.† Inspection of the data in Fig. S4† shows that the current output of the PEMFC decreases with the number of voltage cycles. That decrease however is much more pronounced when Pd-Ni NPs are used as the PEMFC cathode catalyst as compared to the case when Pt-Ni-Co NPs are used instead. Evidently, in a fuel cell environment, the ORR activity of Pd-Ni NPs decays over time faster as compared to that of Pt-Ni-Co NPs. The observation is fully in line with the conclusion of ex situ catalytic studies, namely, that Pd-Ni NPs are less stable as an ORR catalyst as compared to Pt-Ni-Co NPs. Following the protocol of *ex situ* catalytic studies (see the Methods section of the ESI[†]) we designated the current output of the PEMFC at 0.9 V on the polarization curves as a measure of the MA of Pd-Ni and Pt-Ni-Co NPs for ORR. The evolution of the ORR (MA) activity of Pd-Ni and Pt-Ni-Co NPs with the number of voltage cycles undergone inside the PEMFC, as

extracted from the respective polarization curves, is shown in Fig. 12.

The chemical composition of Pd–Ni and Pt–Ni–Co NPs that have undergone 3000 voltage cycles inside the PEMFC was determined by ICP–AES experiments and found to be $Pd_{82}Ni_{18}$ and $Pt_{60}Ni_{22}Co_{18}$, respectively. Evidently, Pd–Ni and Pt–Co–Ni NPs suffer substantial losses in TM species both when studied inside an electrochemical cell, *i.e. ex situ*, and inside an operating PEMFC, *i.e. in operando*. The amounts of TM species lost by the NPs during the *ex situ* and *in operando* studies however are not quite the same, in particular in the case of Pd–Ni NPs.

HE-XRD patterns for Pd–Ni and Pt–Ni–Co NPs were collected while the NPs were undergoing voltage cycling inside the PEMFC in intervals of 3 min, for 1 min each. In total, HE-XRD patterns were collected over a period of 12 h, necessary to reach the preset number of 3000 PEMFC cycles. Exemplary *in operando* HE-XRD patterns for Pd–Ni and Pt–Ni–Co NPs, as corrected for the PEMFC hardware and other backgroundtype (air *etc.*) scattering, are shown in Fig. S6 and S7,† respectively. Exemplary atomic PDFs derived from the *in operando* XRD patterns for Pd–Ni and Pt–Ni–Co are shown in Fig. S8 and S9,† respectively.

Fig. 12 Catalytic and structure data of Pd–Ni (a) and Pt–Ni–Co (b) NPs exposed to the gas-phase environment inside an operating PEMFC. Data reveal an irregular evolution of the ORR (MA) activity (green triangles), GSA (magenta squares) and bonding effects (red circles) in the NPs with the number of PEMFC cycles. Note that the bonding effects are estimated from PDF-derived fcc-lattice parameters reflecting the characteristic atomic-pair distances in the respective NPs. Full lines (in green) are best fits to the MA data obtained during the first 500 (exponential decay of MA; $R^2 = 0.95$) and subsequent 2500 (linear decay of MA; $R^2 = 0.98$) PEMFC cycles. Attempts to approximate the MA with a single exponential function resulted in an inferior overall fit ($R^2 = 0.81$).

The average size of Pd–Ni and Pt–Ni–Co NPs that have undergone voltage cycling inside the PEMFC was determined by analysis of the width of Bragg-like peaks in the respective *in operando* HE-XRD patterns using Scherrer's formalism.⁶¹ The size was used to assess the evolution of GSA and, hence, ECSA of Pd–Ni and Pt–Ni–Co NPs during the PEMFC operation. The rate of change of the GSA of Pd–Ni and Pt–Ni–Co NPs with the number of PEMFC cycles, representing the rate of change of their ECSA, is shown in Fig. 12. Inspection of the data in the figure shows that under conditions typical for operating PEMFCs, both Pd–Ni and Pt–Ni–Co NPs continuously increase in size and so suffer irreversible losses in their ECSA.

To assess the changes in the atomic arrangement in Pd–Ni and Pt–Ni–Co NPs occurring while the NPs function as the PEMFC cathode catalysts, we approached the respective *in operando* atomic PDFs with a simplistic model constrained to an fcc-type crystal structure. The merits of such a modeling are discussed above. Exemplary fits to *in operando* PDFs for Pd–Ni and Pt–Ni–Co NPs are shown in Fig. 13. As the data in the figure show, the fcc-lattice parameters for Pd–Ni and Pt–Ni–Co NPs increase toward those for the respective bulk metals with the number of voltage cycles. The increase indicates that the bonding effects in Pd–Ni and Pt–Ni–Co NPs, such as contraction of first neighbour (*i.e.* bonding) distances, diminish while the NPs function as the PEMFC cathode catalysts. Fcc-lattice

Fig. 13 Experimental *in operando* (symbols) and model (red lines) atomic PDFs of Pd–Ni NPs and Pt–Ni–Co NPs. Data of as-synthesized NPs and NPs that have undergone 400, 1000 and 3000 PEMC cycles are shown. The refined fcc-lattice parameters and model quality indicators, R_{wr} , are shown for each data set.

parameters for Pd–Ni and Pt–Ni–Co NPs resulting from fits to the full sets of the respective *in operando* PDFs are summarized in Fig. 14. As can be seen in the figure, atomic-pair distances in Pd–Ni and Pt–Co–Ni NPs that have undergone the same number of PEMFC cycles increase, *i.e.* approach the bulk values, to a rather different extent. The evolution of the atomic-pair distances and, hence, bonding effects in Pd–Ni and Pt–Ni–Co NPs with the number of PRMFC cycles is shown in Fig. 12.

To ascertain the phase state of Pd-Ni and Pt-Ni-Co NPs that have undergone 3000 PEMFC cycles, we built and tested several 3D models featuring plausible phase states of the NPs. Initial models consisted of atomic configurations with the size (~9 nm), shape (spherical) and chemical composition of the actual NPs modeled as determined by ICP-AES. The configurations featured phase segregated Janus, NM-TM-NM sandwich, NM core-TM shell, TM core-NM shell and NM-TM core-NM shell type NPs. A model featuring single phase NM-TM nanoalloy was also considered (see Fig. S12[†]). The initial atomic configurations were optimized in terms of energy, i.e. stabilized at the atomic level, by MD carried out under nonperiodic boundary conditions as described in the Methods section of the ESI.† Atomic PDFs derived from the MD optimized models were compared with the respective in operando atomic PDFs and the phase state of the NPs modeled was ascertained, as exemplified in Fig. 15. Results from MD simu-

Fig. 14 Fcc-lattice parameters of (a) Pd–Ni and (b) Pt–Ni–Co NPs that have undergone electrochemical cycling inside an operating PEMFC (red circles) and a standard 3-electrode cell (blue squares). Data are obtained from fits to *ex situ* and *in operando* atomic PDFs as demonstrated in Fig. 7 and 13, respectively. The fcc-lattice parameters of bulk Pd and Pt metals are also shown for comparison. Solid lines in blue are a guide to the eye.

Fig. 15 Experimental (symbols) and MD model-derived (red lines) atomic PDFs of Pd–Ni NPs that have undergone 3000 PEMFC cycles. The NPs suffered big losses in TM (Ni) species and so their chemical composition changed from the initial one of $Pd_{30}Ni_{70}$ to $Pd_{82}Ni_{18}$. The difference (blue lines) between the experimental and model-derived PDF data is given (shifted by a constant factor for clarity) for each data set. Snapshots of the respective MD models, shown in Fig. S12,† and model's quality factors, R_{w} , are also given for each data set.

lations showed that *in operando* studied Pd–Ni and Pt–Ni–Co NPs are single phase nanoalloys.

To assess the structural changes specific to the surface of Pd-Ni and Pt-Ni-Co NPs that have undergone 3000 voltage

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cycles at the cathode of an operating PEMFC, the respective nanoalloy-type MD models were refined further by hybrid RMC simulations as described in the Methods section of the ESI.† The refinement is essential as discussed above. The best RMC fits to the *in operando* atomic PDFs for the NPs modeled are shown in Fig. 9. The respective RMC-refined models are shown in Fig. 10. The models were analysed in terms of bonding distances between surface NM atoms, first CNs involving surface NM atoms and first total CNs for all surface atoms. Results from the analysis, in particular the CNs, are summarized in Fig. 11.

The first neighbour Pd-Pd and Pt-Pt distances at the surface of Pd-Ni and Pt-Ni-Co NPs that have undergone 3000 PEMFC cycles, as extracted from the respective RMC-refined models, were found to be 2.74 Å and 2.72 Å, respectively, *i.e.* considerably longer than the distances between nearby NM atoms at the surface of as-synthesized NPs. The observed "decompression" of NM-NM bonding distances would diminish the SA of surface NM species for ORR and, hence, render Pd-Ni and Pt-Ni-Co NPs less active as catalysts for ORR. As a result, the current output of the PEMFC would diminish. This is indeed what the experimental polarization curves show (see data in Fig. S4[†]). Inspection of the data in Fig. 11 shows that about half the NM (Pd) atoms at the surface of Pd-Ni NPs that have undergone 3000 PEMFC cycles have 1 to 2 TM (Ni) atoms as first neighbours while the rest have no unlike (Ni) neighbours at all. For comparison, most surface Pd atoms in the assynthesized Pd-Ni NPs are coordinated with 3 to 5 Ni atoms. Besides, the surface of cycled Pd-Ni NPs appears rather rough, *i.e.* populated with a significant number of 3-, 4- and 5-fold coordinated atoms. By contrast, surface NM (Pt) atoms in Pt-Ni-Co NPs that have undergone 3000 PEMFC cycles have 3 to 5 unlike (Ni + Co) neighbours, *i.e.* have not experienced much of a change in their coordination environment. The surface landscape in cycled Pt-Ni-Co NPs does not appear much changed either (compare the data for the total CNs shown in Fig. 11). The observation indicates that, though counterintuitive, the surface of NM-TM NPs may not get any smoother as they lose TM species and increase in size while inside an operating PEMFC.

The observed drastic decrease in the number of surface TM species in the electrochemically cycled Pd-Ni NPs however posed the question: are indeed these NPs uniform NM-TM nanoalloys or nanoalloys exhibiting some surface segregation of NM (Pd) species? To answer it and so verify the findings of MD modeling, we computed the so-called Cowley's short-range order parameter⁷² for Pd species in the *ex situ* and *in operando* studied Pd-Ni NPs. For the purpose, we used the respective CNs shown in Fig. 11. Computation details can be found in the Methods section of the ESI.[†] Values of Cowley's parameter showed that Pd species in Pd-Ni NPs that have undergone 3000 electrochemical cycles, either in the 3-electrode cell or the PEMFC, hardly exhibit any tendency to segregate toward the NP surface. For completeness, Cowley's parameter for Pt species in the ex situ and in operando studied Pt-Ni-Co NPs was also computed. Its values showed that Pt species in the electrochemically cycled Pt–Ni–Co NPs do not tend to segregate toward the NP surface either. Analysis of the full sets of *in operando* atomic PDFs for Pd–Ni and Pt–Ni–Co NPs, shown in Fig. 16, reveals why indeed NM–TM NPs exposed to an environment typical for operating PEMFCs can remain single phase nanoalloys.

In particular, as colour maps in Fig. 16 show, peaks in the in operando PDFs for Pd-Ni and Pt-Ni-Co NPs oscillate in both position and intensity while the NPs are used as the PEMFC cathode catalysts. The oscillations of the individual PDF peaks are, at the sub-Ångstrom length-scale, largely out-of-phase, start as soon as the PEMFC starts operating and last with the same vigour until it stops. The observation indicates that the individual atomic coordination spheres in Pd-Ni and Pt-Ni-Co NPs experience continuous fluctuations in terms of coordination radii and coordination numbers, i.e. that NM and TM species in Pd-Ni and Pt-Ni-Co NPs continuously re-arrange with respect to each over the time period of the PEMFC operation. This re-arrangement may not come as a big surprise given the fact that the interdiffusion of atomic species in multi-metallic NPs can be several orders of magnitude faster than that of atomic species in the respective bulk metallic materials.^{73–75} Therefore, it may be concluded that as soon as atomic species, presumably TM ones, start leaching from NM-TM NPs, thereby generating atomic vacancies, NM and TM species remaining in the NPs start seeking and forming energetically more favorable local configurations through interdiffusion across the NPs. The interdiffusion carries on until its major driving force, that is, the leaching of TM species, lasts, *i.e.* until the PEMFC operates. Moreover, the fast interdiffusion of NM and TM species in NM-TM NPs inside an operating PEMFC does not seem to be influenced much by their continuous growth (see the data for the evolution of the GSA of Pd-Ni and Pt-Ni-Co NPs with the number of PEMFC cycles shown in Fig. 12).

The inherent ability of atomic species in NM-TM NPs to rearrange fast in response to local changes in the chemical composition can result in substantial ORR activity losses. In particular, as the data in Fig. 12 show, the current output of the PEMFC, i.e. the MA of Pd-Ni and Pt-Ni-Co NP for ORR, drops exponentially during the first few hundred (~500) PEMFC cycles (see the solid line through the respective data points and the associated text in Fig. 12). The drop is highly correlated with the concurrent fast expansion of the initially "compressed" characteristic atomic pair distances in the NPs, including NM-NM bonding distances (correlation coefficient $R^2 = 0.95$ for a plot of the magnitude of ORR activity losses vs. the rate of expansion of the atomic pair distances during the first few hundred PEMFC cycles; see Fig. 12). According to the Butler–Volmer formalism (see eqn (1)) the current output of an operating PEMFC would decrease exponentially when ΔV_{act} jumps, i.e. when the SA of NM-TM NPs for ORR drops. Evidently, the fast "decompression" of the characteristic atomic pair distances in Pd-Ni and Pt-Ni-Co NPs, in particular NM-NM ones, leads to a fast drop in their SA and, hence, to an exponential decay in their MA for ORR. Note that decay may

Fig. 16 (lower panel) *In operando* atomic PDFs of (a) Pd–Ni and (b) Pt–Ni–Co NPs as derived from HE-XRD patterns collected in intervals of 3 min while the NPs are undergoing 3000 voltage cycles (0.6 V–1.2 V) inside the PEMFC shown in Fig. S3.† (middle panel) Color maps of the *in operando* PDFs. (topmost panel) Color maps of the low-*r* peaks in the *in operando* PDF emphasizing the persistent fluctuations in the local atomic ordering in both Pd–Ni and Pt–Ni–Co NPs during the voltage cycling. Note that positions of the individual PDF peaks, *i.e.* of the individual atomic coordination spheres in the NPs, oscillate within ± 1 Å at the most.

not originate from a sharp decrease in the ECSA of Pd–Ni and Pt–Ni–Co NPs since, as the data in Fig. 12 show, their growth during the first few hundred PEMFC cycles is rather limited. Besides, it is not proportionate to the rate with which Pd–Ni and Pt–Ni–Co NPs lose TM species either. Therefore, it may be concluded that, though occurring at the sub-Ångstrom length-scale, the continuous structural fluctuations in Pd–Ni and Pt–Ni–Co NPs are sufficient to disrupt significantly cooperative interactions between TM and NM atoms near the NP surface, in particular the bonding (ligand and strain) effects discussed above. As a result, the ORR activity of these NPs drops soon after the PEMFC is turned on.

As the data in Fig. 12 also show, the MA activity of both Pd–Ni and Pt–Co–Ni NPs keeps deteriorating while the NPs are undergoing further 2500 PEMFC cycles. In particular, after dropping fast during the first few hundred PEMFC cycles, the ORR activity losses incurred by Pd–Ni and Pt–Ni–Co NPs are seen to increase linearly with the number of subsequent PEMFC cycles (see the solid line through the respective data points in Fig. 12). According to the Butler–Volmer formalism (see eqn (1)) the current output of an operating

PEMFC would diminish linearly with losses in the exchange current density, io, i.e. with losses in the ECSA of NM-TM NPs. The highly decelerated expansion of the characteristic atomic-pair distances in Pd-Ni and Pt-Ni-Co NPs and the concurrent steady decrease in their GSA/ECSA, i.e. their steady growth, indicate that the latter increasingly becomes responsible for the observed gradual decrease in the ORR activity occurring after the PEMFC has operated for a while (correlation coefficient $R^2 = 0.95$ for a plot of the magnitude of ORR activity losses vs. the GSA/ECSA losses occurring after the initial few hundred PEMFC cycles; see Fig. 12). Notably, as the data in Fig. 17 and the associated Fig. 12 and 16 show, ORR activity losses due to highly dynamic local structural fluctuations of the order of ± 1 Å and such arising from irreversible nanoscale structural changes involving steady depletion of near-surface TM species and NP growth (of the order of a few nm) can indeed be very much comparable in magnitude and so equally responsible for the decay of the innately superb ORR activity of NM-TM NPs during an extended period (e.g. 3000 cycles taking 12 h to complete) of PEMFC operation.

Fig. 17 Relationship between the structural changes and resulting losses in the ORR (MA) activity of Pd–Ni (left) and Pt–Ni–Co (right) NPs as deciphered through (a) *ex situ* (see data in Fig. 3) and (b) *in operando* (see data in Fig. 12) studies described in the text. When added together, ORR activity losses due to the fast disruption of bonding effects in the NPs (areas in blue) and gradual growth of the NPs (areas in magenta) reduce MA to values (areas in green) that are pretty close to the experimental data (green triangles). The observation indicates that these losses are (i) the major factors behind the decay of the ORR activity of Pd–Ni and Pt–Ni–Co NPs occurred during the respective studies and (ii) largely independent of each other. The latter can be explained by the fact that, contrary to the NP growth, the fast disruption of bonding effects observed here does not involve effective mass transport during the cells' operation. In particular, it is inflicted by highly dynamic local structural fluctuations involving uncorrelated displacements (fast interdiffusion) of atoms within individual NPs and not a correlated exchange of atoms between individual NPs. Note that the broken lines through the few data points in (a) and, hence, the hatched areas they enclose are merely an approximation. On the other hand, results presented in (b) are based on many tens of data points reflecting the evolution of MA (green triangles), GSA/ECSA (magenta squares) and characteristic structural features (open circles), such as atomic-pair (including bonding) distances, of Pd–Ni and Pt–Ni–Co NPs as they function as the PEMFC cathode catalysts. For reference, data points in (b) shown as stars are derived as the difference between 100% and the algebraic sum of the experimental data points shown as open circles and magenta squares.

It is to be underlined that ex situ studies are very much capable of identifying nanoscale structural changes of NM-TM NPs that can inflict substantial losses in their ORR activity such as leaching of TM species, NP growth and phase segregation. Besides, ex situ studies are easier to perform than in operando ones. Therefore, undoubtedly, ex situ studies on the likely impact of cells' operating conditions on the atomic structure and, hence, catalytic activity of multimetallic nanocatalysts for ORR, in particular NM-TM NPs, are very useful. The foregoing structural changes of NM-TM NPs however involve mass transport, in particular the exchange of atomic species between individual NM-TM NPs, and so occur gradually during cells' operation. Thus, structural changes of NM-TM NPs that do not involve effective mass transport during cells' operation and yet inflict ORR activity losses, such as local structural fluctuations enabled by the inherently fast interdiffusion of atomic species in nm-sized metallic materials, may be missed easily when studied ex situ. One of

the reasons is that *ex situ* studies are done within time frames that do not necessarily fit well the dynamics of structural changes of NM-TM NPs occurring during cells' operation. Besides, highly dynamic or not, structural changes of NM-TM NPs exposed to the gas-phase environment inside operating fuel cells do not necessarily follow the trajectory of structural changes observed when the NPs are studied in the liquid-phase environment inside standard electrochemical cells. Therefore, undoubtedly, *in operando* studies on the structure–functionality relationship(s) in multi-metallic nanocatalysts can indeed be a very useful addition to *ex situ* studies.

For example, researchers have noticed that "pre-conditioning" of NM–TM NPs through limited dissolving of TM species may both reduce losses in their catalytic activity for ORR and ease some technical issues such as undesired depositing of leached-off TM species on the MEA of PEMFCs.^{6,18,32,53,76,77} However, as studies have shown, "pre-conditioned" MN–TM NPs do not necessarily perform as expected inside operating PEMFCs, especially when the PEMFCs work in a "start-up & shut down" mode and so their cathode experiences voltage excursions of 1.2 V and even higher (*e.g.* see Fig. 5 in ref. 13, Fig. 6 in ref. 44 and Fig. S5 in ref. 78). We argue that efforts such as "pre-conditioning" of multi-metallic nanocatalysts through limited dissolving of particular atomic species can turn more successful if guided by *in operando* atomic pair distribution studies and not by educated intuition alone.

Also, we argue that, to be fully successful, current efforts to reduce losses in the catalytic (ORR) activity of multi-metallic NPs should aim at achieving control not only over irreversible structural changes of the NPs involving steady mass transport but also over highly dynamic structural fluctuations in the NPs that do not involve effective mass transport during cells' (PEMFCs) operation. In particular, based on the results of our *in operando* studies, we argue that the inherently fast interdiffusion of atomic species in multi-metallic nanocatalysts for ORR should be limited as much as possible. Furthermore, we show that this can be achieved through simple yet effective strategies outlined below. Elements of the strategies have been utilized in some studies^{7,27,79–81} but not pursued in a systematic manner. The strategies may include treating the assynthesized or "pre-conditioned" NM-TM NPs at a moderate temperature so as to anneal out the excess volume typically present in metallic materials lacking a perfectly 3D periodic atomic structure. The inherently increased strength of bonding between distinct metallic species in chemically ordered NM-TM NPs can also be exploited. Furthermore, typically, multimetallic nanocatalysts for ORR exhibit an fcc-type structure. Doping the catalysts with atomic species prone to adopt a structure type different from fcc, such as the fairly affordable bcc V, bcc Mo and hcp Y, can also be very helpful. To demonstrate the potential of these strategies we synthesised Pt-Co NPs doped with V species and then deliberately processed the NPs at 600 °C and 800 °C. Data from in operando studies on the resulting $Pt_{51}VCo_{48}$ NPs are presented in Fig. 18. As can be seen in the figure, Pt₅₁VCo₄₈ NPs processed at 800 °C retain their ORR activity to a greater extent as compared to Pt₅₁VCo₄₈ NPs processed at 600 °C. As a result, the performance of the PEMFC in terms of current output is improved when the former are used as the PEMFC cathode catalyst as compared to the case when the latter are used instead.

Fig. 18 (left) (a) Exemplary polarization curves (out of 260) obtained on the PEMFC shown in Fig. S3† while $Pt_{51}VCo_{48}$ NPs treated at 600 °C, as described in ref. 82, were used as the PEMFC cathode catalyst. Arrows emphasize the diminishing current output of the PEMFC with the number of voltage (0.6 V –1.2 V) cycles. (b) Evolution of the ORR (MA) activity of $Pt_{51}VCo_{48}$ NPs treated at 600 °C (symbols in blue) and 800 °C (symbols in red) during 1500 voltage cycles. (right) Color maps of the *in operando* atomic PDFs of the respective NPs. Local structural fluctuations in the $Pt_{51}VCo_{48}$ NPs treated at 600 °C. Accordingly, the decay of the MA for ORR and, hence, the decay of the current output of the PEMFC are less pronounced when the latter are used as the PEMFC cathode catalyst as compared to the case when the former are used instead.

Conclusions

In summary, in operando HE-XRD and atomic pair distribution studies can assess accurately changes in the atomic structure and (ORR) activity of multi-metallic nanocatalysts, such as NM-TM NPs, as they are used inside operating fuel cells. In particular, the evolution of GSA and, hence, ECSA of the NPs can be assessed by analyzing the FWHM of Bragg-like peaks in the in operando HE-XRD patterns. The Fourier transform of the patterns, that is the in operando PDFs, can be used to assess the structure type and characteristic atomic pair distances in the NPs through simplistic, traditional crystallographyconstrained modeling. Alternatively, atomic pair distances of interest, e.g. bonding distances, can be assessed directly from the positions of peaks in the in operando PDFs. The phase state of the NPs can be determined by a search and match procedure involving comparing the in operando PDFs with PDFs computed from 3D structure models featuring plausible nanophase states. The models can be generated by MD or other computational techniques. Indeed comparing experimental XRD patterns with "standard" XRD patterns is the common approach to assess the phase state of polycrystalline (µm-sized) materials. Note that Fourier transformation is a unitary operation and so atomic structure-relevant information in HE-XRD patterns collected in reciprocal space is not modified in any way when represented in real space in terms of atomic PDFs. Most successful MD models can be refined against the experimental in operando PDFs by RMC-type techniques in a manner mirroring the so-called Rietveld refinement that is a common procedure in structural studies of fine polycrystalline powders.11,61,65 The refined 3D models can be analyzed in terms of structural characteristics of importance to catalysis, including bonding distances and CNs for atoms at the NP surface. The characteristics will be reliable since, as demonstrated in Fig. S10,† atomic PDFs are fairly sensitive to the surface structure of metallic NPs. In operando structure and catalytic data, e.g. the current output of the operating cells (PEMFCs), complemented, any time possible, with pieces of knowledge obtained by other catalysis relevant techniques, such as XPS, EXAFS, SAXS, HR-TEM, HAADF-STEM, 3-electrode cells and others, can be compared side by side and the mechanism(s) through which metallic nanocatalysts change at the atomic level and so suffer activity losses during cells' operation can be deciphered. This can help take control over the former, reduce the latter and so bring fuel cells a step closer to commercialization.

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