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Size and composition distribution dynamics of alloy nanoparticle electrocatalysts probed by anomalous small angle X-ray scattering (ASAXS)†

Chengfei Yu,† Shirlaine Koh, Jennifer E. Leisch, Michael F. Toney and Peter Strasser*

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Anomalous small angle X-ray scattering (ASAXS) is shown to be an ideal technique to investigate the particle size and particle composition dynamics of carbon-supported alloy nanoparticle electrocatalysts at the atomic scale. In this technique, SAXS data are obtained at different X-ray energies close to a metal absorption edge, where the metal scattering strength changes, providing element specificity. ASAXS is used to, first, establish relationships between annealing temperature and the resulting particle size distribution for Pt$_{25}$Cu$_{75}$ alloy nanoparticle electrocatalyst precursors. The Pt specific ASAXS profiles were fitted with log-normal distributions. High annealing temperatures during alloy synthesis caused a significant shift in the alloy particle size distribution towards larger particle diameters.

Second, ASAXS was used to characterize electrochemical Cu dissolution and dealloying processes of a carbon-supported Pt$_{25}$Cu$_{75}$ electrocatalyst precursor in acidic electrolytes. By performing ASAXS at both the Pt and Cu absorption edges, the unique power of this technique is demonstrated for probing composition dynamics at the atomic scale. These ASAXS measurements provided detailed information on the changes in the size distribution function of the Pt atoms and Cu atoms. A shift in the Cu scattering profile towards larger scattering vectors indicated the removal of Cu atoms from the alloy particle surface suggesting the formation of a Pt enriched Pt shell surrounding a Pt–Cu core.

Together with XRD and TEM, ASAXS is proposed to play an increasingly important role in the mechanistic study of degradation phenomena of alloy nanoparticle electrocatalysts at the atomic scale.

Introduction

Metal nanoparticles are of fundamental scientific and technological interest. Their nanoscale dimensions give rise to fundamentally new optical, electronic, magnetic or catalytic properties, which, for the most part, are sensitively dependent on their

† The HTML version of this article has been enhanced with colour images.
structural characteristics on the nanoscale, such as their particle size and shape.\textsuperscript{1–3} Metal nanoparticle ensembles rarely have well defined monodisperse size or shape, but instead, are generally characterized by a particle size distribution.

In the field of surface catalysis, metal nanoparticle ensembles play a tremendously important role as active catalysts. Their nanoscale dimensions result in a very high reactive surface area per unit mass, which can significantly improve the product yield of nanoparticle catalysts on a per mass basis.\textsuperscript{4} For instance, in fuel cell electrocatalysis, a significant improvement in Pt-mass based current density can be achieved by the use of Pt nanoparticles supported on highly porous carbons compared to unsupported Pt black catalysts.\textsuperscript{5} Furthermore, nanoscale metal nanoparticles exhibit a large fraction of low-coordinated atoms on surface edges and kinks. These atoms often exhibit different chemisorption energies of reaction intermediates compared to higher-coordinated atoms on smooth metal surfaces. Particle size and shape, together with the metal crystal structure, also determine which single crystal facets are exposed and the ratio of these exposed faces.\textsuperscript{6} As a result of this, particle size may become strongly correlated with the observed catalytic surface reaction rate (particle size effect).\textsuperscript{6–10}

Just like with smooth (e.g. single crystal) metal surfaces, surface catalytic reactivity of metal nanoparticles can be tuned by alloying two or more metals. Alloying results in electronic (ligand), geometric, or ensemble effects which modify the surface catalytic activity. Pt nanoparticle electrocatalysts show improved reactivity for the electrooxidation of CO when alloyed with Ru due to a bifunctional mechanism.\textsuperscript{11–13} Similarly, when alloyed with transition metals, Pt nanoparticles exhibit more favorable electrocatalytic rates for the electroreduction of molecular oxygen (ORR), likely due to a combination of geometric and ligand effects.\textsuperscript{14–18} Due to synthetic imperfections, the particle molar composition of alloy nanoparticle ensembles, just like their size, is characterized by a distribution rather than by a single value. Knowledge of this size–composition distribution is important for characterizing and understanding the function of the nanoparticle catalysts.

Metal alloy nanoparticle electrocatalysts, with all their advantages with respect to surface reactivity, come with serious challenges: they are often unstable under catalytic reaction conditions and tend to change their size and composition distributions.\textsuperscript{19–22} Particle size distribution changes are caused by a number of factors. Metal nanoparticles show a reduced melting point compared to the bulk, show pronounced surface diffusion, and suffer from thermodynamic instabilities in the presence of larger particles (Ostwald ripening). Ostwald ripening is the dissolution of the smaller particles to become even smaller and the growth of the larger particles, while diffusion leads to particle coalescence. In addition, in an electrocatalytic system, metal dissolution occurs at high electrode potentials resulting in the loss of active metal surface atoms. As a consequence of these three mechanisms, the mean particle size changes during the course of an electrocatalytic reaction, typically resulting in a reduced specific surface area. All three particle instability mechanisms have been experimentally observed for Pt and Pt alloy electrocatalysts using voltammetric and microscopic techniques,\textsuperscript{19,20,22–24} and simple models have been developed to capture the dynamics of particle size changes.\textsuperscript{25,26} Much research is currently being dedicated to mitigation strategies to stabilize the size and composition of alloy nanoparticle ensembles.\textsuperscript{27–32}

Very little work to date has been dedicated to the understanding of the dynamics of composition distributions of alloy nanoparticle electrocatalysts. In principle, one is looking at time-resolved measurements of alloy particle composition and alloy particle size. Another way to approach this question is through metal-specific particle size distributions. Fig. 1 schematically illustrates atom-specific size distributions for a binary Pt–M alloy nanoparticle ensemble. The solid distribution curve represents the number fraction of Pt atoms as function of particle radius. Small particles consist entirely of Pt atoms. The dashed curve represents the number fraction of a base metal M. Large particles are enriched in M, hence the distribution
curve of M lies above that of Pt. If both curves coincide, this would indicate a perfectly alloyed particle ensemble where small and large particles have identical composition. The distribution curves in Fig. 1 represent the compositional picture at some given time. Probing composition dynamics requires repeated measurement of metal atom specific distribution curves at different times.

The most common experimental methods to probe nanometre scale particle size and composition distributions are transmission electron microscopy (TEM) and X-ray scattering techniques. While the former can provide real space images, the latter are reciprocal-space techniques and measure the Fourier transform of the electron densities. Suitable scattering techniques comprise the wide angle scattering (X-ray diffraction, XRD) as well as the small angle X-ray scattering (SAXS).

Each technique has its advantages and limitations. TEM offers the appeal of images of nanoparticles and (under favorable conditions) individual atoms, yet based on the relatively small particle population analyzed (at best in the thousands) TEM often yields unreliable statistics. TEM particle histograms often suffer from subjective choices that the experimenter makes during the analysis process; for instance, overlooking very small particles and therefore skewing distribution functions towards larger sizes. Based on the interaction of X-ray radiation with atom electron densities, X-ray diffraction offers excellent statistics based on a larger sampling volume (typically more than billions of particles). Mean size estimates are available from analysis of the diffraction peak full width at half maximum (FWHM). However, the mean size estimate refers to crystallite size, which is not necessarily the same as the particle size; this can result in discrepancies between TEM and XRD. Also, being a volume based sampling method, XRD provides volume-averaged sizes, not number averaged sizes as for TEM. SAXS has been used in the past to follow the growth dynamics during the synthesis of Pt nanoparticles. It has also been applied to study the surface oxidation processes of pure Pt electrocatalyst during voltammetric studies. Virtually no work exists on the use of SAXS to study the structural dynamics of alloy nanoparticles.

In this contribution, we aim to highlight the power of SAXS techniques for an ex situ and in situ probing of the structural and compositional dynamics of Pt alloy nanoparticle electrocatalysts. SAXS is ideally suited for scattering objects in the 1–100 nm range. Performed in the “anomalous” scattering mode (ASAXS), it combines the advantages of diffraction in terms of statistical quality with the power of atom-specific size distributions, according to Fig. 1. In the anomalous scattering mode, the SAXS is measured at several energies near a metal absorption edge where the scattering strength of the metal changes.
We will illustrate the power of SAXS for probing particle structure and composition using a class of Cu-rich Pt–Cu alloy electrocatalysts which were recently reported to offer unprecedented catalytic activity for the electroreduction of oxygen in acidic media. We investigated two aspects about this catalyst class. In a first series of experiments, we correlate alloy particle size with the synthesis conditions of the alloy catalysts.

In a second set of experiments, we probe changes in the alloy particle size and composition during an electrochemical dealloying procedure. The active phase of this particular catalyst system is believed to be formed during electrochemical dealloying of Cu atoms prior to catalytic testing: selective Cu atom dissolution from the particle surfaces is assumed to form a nanoparticle with a Pt rich surface region surrounding a Cu rich alloy particle core (core-shell particle). We demonstrate that ASAXS can help clarify the formation dynamics of such structures.

Continued base metal dissolution from Pt alloy particle electrocatalysts under operating conditions has also often been linked to activity degradation. The present work, therefore, also aims to showcase ASAXS as a suitable experimental technique for a fundamental characterization of alloy particle electrocatalyst degradation behavior during reaction conditions. An atomic-scale understanding of the dynamics of particle size and composition distributions of alloy electrocatalyst degradation would be of tremendous importance for progress in the design and development of corrosion stable electrocatalyst systems.

**Experimental**

**Catalyst synthesis**

Pt_{25}Cu_{75} alloy nanoparticle electrocatalyst precursors were synthesized via the liquid salt precursor impregnation method. Measured amounts of a Cu nitrate (Cu(NO_3)_2·3H_2O, Aldrich) were dissolved in de-ionized water (>18.2 MΩ, Milli-Q® gradient system, Millipore Inc.). The precursor solutions were then added to a weighted amount of commercial carbon-supported Pt nanoparticle electrocatalyst (Tanaka Kikinzoku Inc.) with a Pt weight loading of about 30 wt%. The mixtures were then ultrasonicated with a sonifier horn (Branson) for 1 min and then frozen in liquid nitrogen for 5 min. Subsequently, the frozen samples were freeze-dried (Labconco) for 24 h and annealed in flowing hydrogen/argon mixtures in a flow furnace (Lindberg Blue) to a temperature between 600 °C and 950 °C.

**Catalyst film electrode preparation**

Alloy nanoparticle electrocatalyst precursor electrode films were prepared by depositing a dilute suspension of the catalyst powder synthesized as described above onto inch long carbon tape (3M). The catalyst suspension was made by mixing catalyst powder (2.5 mg) with 100 μL de-ionized water (>18.2 MΩ, Millipore Gradient system) containing 5 wt% Nafion® solution (Sigma, #274704). The suspension was ultrasonicated for 1 minute before being deposited onto the carbon tape and then air dried for 3 hours.

**Electrochemical leaching**

Size and compositional changes of the catalytic particles were probed ex situ after voltammetric protocols using anomalous SAXS. The measurements were carried out on the catalyst film electrodes before and after the following electrochemical protocol: the catalyst films were employed as working electrode in a three electrode half cell set up. A Pt wire served as counter, and a Ag/AgCl microelectrode as reference electrode. Potentials are referenced to the reversible hydrogen electrode (RHE). A constant electrode potential of +1.2 V vs. RHE was applied for 5 hours.
**ASAXS**

SAXS is a technique to probe structural features of colloidal size. In a SAXS experiment, the X-ray scattering intensity is measured in the small angle regime; here the scattering arises from electron density inhomogeneities over length scales of 1–100 nm \(^{33,46}\) (see Fig. 2). SAXS, in combination with model-based data analysis, enables the study of size distributions of nanoparticle ensembles as well as temporal changes thereof. If scattering profiles are collected at different X-ray energies, the method is referred to as anomalous small angle X-ray scattering (ASAXS). ASAXS measurements were performed in transmission at the Stanford Synchrotron Radiation Laboratory (SSRL) beam line 4–2 using a MAR165 CCD detector. To obtain information on the platinum in the catalyst samples, SAXS measurements were conducted at two energies, one that is close to the Pt L\(_{3}\) absorption edge \((E_{L3} = 11564 \text{ eV})\) at \(E_1 = 11551 \text{ eV}\) (wavelength \((\lambda)\) of 0.1074 nm) and a second energy far from this absorption edge at \(E_2 = 11450 \text{ eV}\) \((\lambda = 0.1083 \text{nm})\). Similarly, for copper, SAXS measurements were conducted near Cu K absorption edge \((E_{K} = 8979 \text{ eV})\) at \(E_1 = 8975 \text{ eV}\) \((\lambda = 0.1382 \text{nm})\) and far away at \(E_2 = 8880 \text{ eV}\) \((\lambda = 0.1397 \text{nm})\).

"Fit2D" software\(^{47,48}\) was used to reduce the raw scattering data. TIFF images obtained from the ASAXS measurements were integrated in azimuthal angle, resulting in intensity-scattering vector \((I(Q))\), with \(Q = (4\pi/\lambda) \sin \theta\), see Fig. 2) plots. Thereafter, the dark signal was subtracted from these and the data corrected for sample thickness and incident photon flux changes during the measurements.

**XRD**

X-ray measurements are performed on a Siemens D5000 (\(\theta/2\theta\)) Diffractometer equipped with a Cu target and a Braun position sensitive detector (PSD) with an angular range of 8°. The X-ray generator operated at a potential of 35 kV and a current of 30 mA. The data were collected from 21° to 70° 2\(\theta\), using step scans of 0.02° per step and a holding time of 10 s per step.

**Results and discussion**

The ASAXS experiments described here focused on the class of Cu-rich Pt\(_{25}\)Cu\(_{75}\) alloy nanoparticle electrocatalysts, which were recently reported to be highly efficient catalysts for the electroreduction of molecular oxygen in acidic environments.\(^{39–42,49–53}\) The active phase of the catalysts is formed by means of a voltammetric surface dealloying process during which a large fraction of the Cu surface atoms are dissolved leaving a multi-layer Pt enriched particle shell behind that surrounds an Pt–Cu alloy particle core.\(^{40}\)

**Synthesis–structure relationships of Pt alloy nanoparticle ensembles**

In a first series of scattering experiments, the dependence of the particle size distribution on the synthesis conditions was investigated. In particular, the effect of the annealing temperature on the resulting particle size and structure was studied. Fig. 3 shows X-ray diffraction profiles of the three Pt\(_{25}\)Cu\(_{75}\) catalysts considered here. Annealing at 600 °C resulted in incomplete alloying of Cu and Pt atoms. An excess pure face-centered cubic (fcc) Cu phase with sharp reflections is discernible...
in Fig. 3 at 2θ = 43.3°. The Pt–Cu alloy phase formed in this synthesis process has an estimated composition of Pt$_{55}$Cu$_{45}$ (see Table 1) as evaluated from the alloy (111) reflection position using Vegard’s relation.\textsuperscript{54,55} Increased annealing temperatures result in more complete alloying, as shown in Fig. 3, with the 950 °C sample showing no signs of a pure Cu phase. Accordingly, the (111) fundamental reflection of the alloy phase is shifted to larger 2θ, indicating a smaller fcc unit cell parameter (Table 1).

In the ASAXS measurements the scattering intensity, $I_{Pt}(Q,E)$, of a monodisperse ensemble of randomly oriented spherical Pt particles of radius $R$ in vacuum at an incident X-ray energy $E$ is given as\textsuperscript{33,35,36,46,56–58}

$$I_{Pt}(Q,E) = N_p (n_{Pt} f_{Pt}(E))^2 V(R) F^2(Q,R)$$ (1)

With $Q$, $N_p$, $n_{Pt}$, $f_{Pt}(E)$, $V(R)$, and $F(Q,R)$ denoting the modulus of the scattering vector, the particle density in the sample, the Pt atomic density in the particles, the atomic form factor (scattering factor) of Pt atoms, the volume of any one particle, and the particle form factor given as

$$F(Q,R) = \frac{3|\sin QR - QR\cos QR|}{[QR]^3}$$ (2)

If the Pt particles are embedded in a matrix, for instance a solid polymer, the scattering signal is a result of the difference in the atomic form factor of Pt atoms and the

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Nanoparticle catalyst compositions, synthesis conditions, alloy phase composition estimates, mean crystallite and mean particle diameter data of Pt$<em>{25}$Cu$</em>{75}$ alloy particles as well as the $R^2$ factors of the fitting in Fig. 4a</th>
</tr>
</thead>
<tbody>
<tr>
<td>Overall catalyst composition (%)</td>
<td>Annealing temperature/°C</td>
</tr>
<tr>
<td>Pt 25 Cu 75</td>
<td>600</td>
</tr>
<tr>
<td>Pt 25 Cu 75</td>
<td>800</td>
</tr>
<tr>
<td>Pt 25 Cu 75</td>
<td>950</td>
</tr>
</tbody>
</table>

Fig. 3 X-ray diffraction patterns of three Pt$_{25}$Cu$_{75}$ nanoparticle electrocatalyst precursors. Annealing temperatures of each catalyst are given in the graph.
surrounding matrix atoms. The term \((n_{\text{Pt}} f_{\text{Pt}}(E) - n_{\text{m}} f_{\text{m}}(E))^2\) replaces the term \((n_{\text{Pt}} f_{\text{Pt}})^2\) as the source of the scattering contrast in eqn (1), with \(n_{\text{m}}\) and \(f_{\text{m}}\) denoting the average atomic density and atomic form factor of the matrix atoms. As long as the scattering power of Pt atoms is different from those of the matrix, the contrast is non-vanishing and a scattering signal will be obtained. Fortunately, the scattering atomic form factor of Pt is many times larger compared to those of lighter elements, such as carbon, oxygen or hydrogen, and so SAXS is strong.

If the Pt particles are supported on a porous material, the SAXS from the pores \(I_{\text{pores}}(Q)\) contributes to the overall scattering as

\[
I_{\text{total}}(Q,E) = I_{\text{Pt}}(Q,E) + I_{\text{pores}}(Q)
\]  

The interpretation of SAXS \(I(Q)\) curves becomes non-trivial as the unknown scattering contribution of the support is hard to separate from that of the particles.

ASAXS was used to extract the signal of the Pt particles. Near an absorption edge, the Pt scattering intensity is a strong function of the X-ray energy, and the atomic form factor of Pt \(f_{\text{Pt}}(E)\) changes by up to 20% in magnitude\(^{35}\) while the scattering factors of the matrix atoms, and hence the scattering signal from the pores, are unchanged. This is how element specificity is achieved. We chose \(E_1 = 11.551\) keV and \(E_2 = 11.450\) keV in our measurements. Subtracting the scattering profiles \((I(Q,E_2) - I(Q,E_1))\) results in a “net” scattering profile \(I_{\text{Pt}}(Q)\) which represents only the SAXS of the Pt particles.

Similar measurements were carried out near the Cu absorption edge \((E_1 = 8.975\) keV, \(E_2 = 8.880\) keV) to obtain \(I_{\text{Cu}}(Q)\) associated with the Cu only. The ASAXS method cannot distinguish whether or not the Cu atoms are alloyed. If a non-monodisperse particle ensemble is considered as characterized by a particle size distribution, \(P(R)\), the scattering intensity for spherical particles becomes

\[
I_{\text{Pt}}(Q,E) = N_p (n_{\text{Pt}} f_{\text{Pt}}(E))^2 \int P(R) V^2(R) F^2(Q,R) \, dR
\]  

Under these assumptions, we can then extract an element-specific particle size distribution for the Pt atoms and Cu atoms according to the discussion in the Introduction (see Fig. 1). Since the particle loading is small in our samples, there is no inter-particle scattering.

Fig. 4a reports the Pt-specific SAXS of the three carbon-supported Pt\(_{25}\)Cu\(_{75}\) alloy nanoparticle electrocatalyst precursors measured at the Pt edge. To obtain these measured curves, the scattering \((I-\bar{I})\) profiles for the two separate energies were subtracted from each other. For a direct comparison, the three resulting subtracted profiles are shifted in the \(y\)-direction in order to normalize their intensity at low \(Q\). Using the relation

\[
Q = \frac{2\pi}{d}
\]  

the \(Q\) range reported in Fig. 4a is estimated to span particle diameters \(d\) in the 1.5–10 nm range. Larger or smaller objects do not have significant scattering in the chosen \(Q\) range.

Fig. 4a reveals that all three scattering profiles start out with a flat portion at low \(Q\), and show a gradual drop in scattering intensity for larger \(Q\). The Pt\(_{25}\)Cu\(_{75}\) nanoparticle ensemble annealed at 600 °C exhibits larger scattering intensity than the other two nanocatalysts over the entire \(Q\) range. Scattering intensity at large \(Q\) is seen to drop in the order 600 °C > 800 °C > 950 °C annealing temperatures. The trends in scattering intensities as a function of scattering vector indicate that the particle ensemble annealed at 600 °C consists of smaller particles compared to the other two particle ensembles. Thus, annealing temperature is correlated with the alloy particle diameter.
To more quantitatively determine the nanoparticle size distribution and to determine the mean particle diameter, the scattering profiles of Fig. 4a (dashed lines) were fitted with log-normal distribution function

\[
P(R) = \exp \left[ -\frac{1}{2} \left( \frac{\ln \frac{R}{R_0}}{\sigma^2} \right)^2 \right] \frac{\exp[-\frac{1}{2}\sigma^2]}{R\sigma\sqrt{2\pi}}
\]

where \(R_0\) denotes the mean particle radius of the distribution and \(\sigma\) is the log-normal dispersion or width in size. Fig. 4a compared the measured intensities with the fitted intensities (dashed and solid lines, respectively). With this choice of distribution, the FWHM depends on both \(R_0\) and \(\sigma\). While there is no a priori argument why a log-normal distribution should fit experimental SAXS results better than, say, a Gaussian distribution, for many cases they often empirically provide good fits.

The dispersion of the function \(P(R)\) was set to a constant value of \(\sigma = 0.25\) during the fitting of the mean radius \(R_0\) in order to increase the accuracy of the fit over the chosen \(Q\) range. Typical correlation factors \(R^2\) of the curve fittings were in the range 0.95 to 0.99.

Fig. 4  (a) Measured subtracted ASAXS intensities \((E_2 - E_1)\) (“Meas”) and intensity fits using log-normal distribution functions (“Fittings”) of a Pt25Cu75 alloy nanoparticle electrocatalyst precursor prepared at the three different annealing temperatures indicated in the legend. (b) Particle size distribution functions \(P(R)\) for each of the Pt–Cu nanoparticle electrocatalyst precursors in (a) in comparison to the pure Pt nanoparticle catalyst used as a precursor in the preparation of the three alloys. The temperatures indicate the annealing conditions of each catalyst.
of 0.98–1.0 (see Table 1 last column for fittings in Fig. 4a), and thus indicated a very good fit to the experimental data. Table 1 (second column from right) summarizes the fitted mean particle diameters, and Fig. 4b shows the resulting distribution functions \( P(R) \) for the three nanoparticle catalysts. Fig. 4b also includes ASAXS measurements of the carbon supported pure Pt precursor catalyst which was used as starting material in the synthesis of the alloy catalysts. One can see that increasing the annealing temperatures results in a significant shift of the size distribution toward larger diameters. Thus, alloy preparation at higher temperatures resulted in an increase in the resulting mean particle size. The drop in intensity of the distribution maximum is a consequence of the chosen form for \( P(R) \) and does not reflect any absolute particle number information. The chosen expression for \( P(R) \) causes the distribution FWHM to increase with increasing average size, even though the dispersion \( \sigma \) remained constant for all three fits. \( P(R) \) is the number fraction of particles of a given radius \( R \).

This is one of the first reports where ASAXS has been applied to study size distributions of bimetallic Pt alloy nanoparticle electrocatalysts. Dahn et al.\textsuperscript{60,61} and Haubold et al.\textsuperscript{36,62} reported SAXS studies on carbon-supported pure Pt nanoparticles, and found that the metal loading had significant impact on the mean particle size. Benedetti et al.\textsuperscript{63} investigated carbon-supported Au and Pd particles using ASAXS, yet did not report detailed results on their resulting size distribution functions.

Our experimental and fitting results are in excellent agreement with earlier X-ray diffraction reports on the relationship between mean particle size and thermal annealing.\textsuperscript{40,41,43–45,64} Higher annealing temperatures generally cause increased mobility of carbon-supported metal atoms leading to a higher rate of particle coalescence and Ostwald ripening. Given a constant total amount of metal atoms at the beginning of thethermal process, one would expect fewer, but larger, particles for the sample annealed at 950 °C. Previous reports on an exponential size growth with annealing temperatures are not supported by our present data.\textsuperscript{64} Increased heat treatment during alloy synthesis resulted in more complete alloying, as shown in Fig. 3. Also, for Pt alloys with first row transition metals, higher annealing temperature resulted in a alloy lattice contraction and a shift of the alloy (111) peak towards larger 2\( \theta \) values,\textsuperscript{64} in agreement with our present results.

A comparison of the mean crystallite sizes obtained from a Debye–Scherrer analysis with the mean particle sizes obtained from ASAXS is given in Table 1. The data suggests that the XRD based crystallite size values are slightly larger than those from ASAXS, especially for higher temperatures. This is consistent with the notion that diffraction data yields volume-weighted size values, while the ASAXS analysis, just like microscopy methods, results in number averages for the particle size. As a result of this, large particles receive increased relative weight in the ensemble average of diffraction data increasing the average slightly.

It should be noted, however, that a number of additional factors may affect the XRD based crystallite size measurements; for instance, strain effects in small particles. Non-uniform strain results in peak broadening of XRD peaks, and therefore may cause an increase in the diffraction peak widths, which, in turn, reduces the mean size estimate.\textsuperscript{34}

Another complicating factor in the evaluation of mean crystallite sizes of alloy particles using the Scherrer equation is related to the possible presence of an unknown number of alloy phases with distinct composition. Since diffraction peak positions are sensitive to alloy composition, multiple phases in incompletely alloyed samples result in relatively broad peaks and in an underestimate of the true particle size. This could be the reason why the XRD based crystallite size is smaller than the ASAXS value for the incompletely alloyed 600 °C sample in Table 1.

The present ASAXS experiment highlights the complementary nature of X-ray diffraction and SAXS as well as the advantage of applying SAXS in an anomalous mode. While both techniques result from an interaction of X-rays with atom electron
densities, ASAXS provided an accurate correction for background scattering and yielded detailed size distribution information for particles up to about 12 nm (limited by our choice of Q range). In the present study we focused on the scattering contribution from Pt atoms (Pt edge data), yet we will show in the following section that for a uniform bimetallic alloy either metal edge could have been used to determine particle size information.

Electrochemical dealloying of Pt alloy nanoparticle ensembles

In a second series of ASAXS experiments, we investigated the impact of an applied electrode potential and the application of an electrochemical protocol on the size and composition distribution of our Pt–Cu bimetallic catalysts. The nanoparticle size and composition distribution dynamics is of considerable importance for understanding particle degradation phenomena in electrocatalysis. To the best of our knowledge, this is the first time that the changes in the scattering intensity of both Cu atoms and Pt atoms have been investigated for an as-prepared and electrochemically treated (dealloyed) bimetallic Pt alloy nanoparticle electrocatalyst.

We specifically have investigated the size distribution dynamics of Pt25Cu75 nanoparticle catalysts annealed at 950 °C. The high annealing temperature ensured that the as-prepared catalyst attains a uniform alloy composition (compare results from previous section). Fig. 5 reports the subtracted Cu and Pt edge ASAXS of the as-prepared pristine alloy nanoparticle catalyst (before electrochemical treatment) and of the dealloyed electrocatalyst (after application of an electrochemical protocol). The electrochemical protocol consisted of a constant potential hold at 1.2 V vs. RHE in 0.1M perchloric acid for 5 hours at room temperature. The scattering data in Fig. 5 reveal that the scattering profiles of both the Cu and Pt ("Cu edge" and "Pt edge") almost completely overlap over the entire Q range, suggesting that the Pt and Cu specific size distribution functions are nearly the same. From our earlier discussion of Fig. 1, this indicates that the alloy nanoparticles possess a uniform composition regardless of their size. This result does not suggest that the alloy composition is Pt50Cu50, as the distribution functions are normalized.

Fig. 5 ASAXS scattering profile of a Pt25Cu75 alloy nanoparticle electrocatalyst prepared at 950 °C before and after electrochemical treatment at 1.2 V vs. RHE for 5 hours in oxygen saturated 0.1 M HClO4 electrolyte. "Cu edge" and "Pt edge" denote atom specific scattering profiles of the as prepared catalyst particles. "Cu edge dealloyed" and "Pt edge dealloyed" label the profiles after electrochemical treatment.
After application of the electrochemical protocol (profiles marked “Pt edge dealloyed” and “Cu edge dealloyed”), the Pt profile is slightly shifted towards larger values of $Q$, that is, towards smaller particle sizes, while the Cu atomic scattering profile significantly shifted toward smaller particle diameters (larger $Q$). Table 2 reports the detailed mean particle diameters of the fit distribution curves for each metal. The difference in size between the Pt and Cu edge for the as prepared catalyst are below the estimated 5–10% experimental error (4.77 nm and 4.81 nm for Cu and Pt, respectively). Their difference is therefore considered to be insignificant.

Similarly, the difference between the Pt particle size before and after application of the electrochemical protocol is in the order of magnitude of the experimental error and is therefore insignificant (4.81 nm to 4.67 nm). Hence, the size of the scattering particles consisting of contiguous Pt atomic density, regardless of the interspersed presence co-alloyed Cu atoms, does not change during the applied potential. The particle size distribution associated with the Cu atoms, however, drops from 4.77 nm to 4.02 nm and represents a statistically significant change in size during the applied potential protocol. These data show that the mean size of scattering particles consisting of contiguous Cu atoms is reduced after electrochemical leaching. The scattering results cannot distinguish between pure Cu particles or Cu atoms co-alloyed with other metals, such as Pt. Since no pure unalloyed Cu particles were present at the beginning of the experiments, the experimental results suggest that a portion of the alloyed Cu atoms were leached out of the initially uniformly alloyed Pt–Cu alloy particles. Fig. 6a schematically illustrates the case before electrochemical dealloying where the Cu and Pt specific particle sizes are identical, while Fig. 6b illustrates the proposed situation after electrochemical leaching of some portion of the Cu atoms from the surface of the alloy particles. Selective dissolution of Cu atoms created a Pt enriched shell surrounding a Pt–Cu alloy core (core-shell nanoparticle structure). In the core-shell structure, the effective particle size of Cu-specific scattering decreased, because only the core of the particles is participating in the scattering profile.

Our present results represent the first report where ASAXS was used to investigate atom-specific size distribution dynamics of alloy nanoparticle electrocatalysts.

![Fig. 6](https://example.com/fig6.png)

**Fig. 6** (a) Schematics of a uniformly alloyed Pt–Cu alloy nanoparticle giving rise to overlapping scattering profiles for the Cu and the Pt edge. (b) Dealloyed Pt–Cu with a Pt enriched shell surrounding a Pt–Cu core giving rise to a Cu specific scattering profile shifted towards smaller mean diameter.
Our findings indicate that ASAXS techniques can resolve structural transformations, such as metal enrichment or metal depletion during electrochemical treatment of alloy nanoparticles. Such subtle intraparticle structural features are usually difficult to detect using regular XRD techniques. Estimates of the resolution of our techniques based on our experimental error give a minimum thickness of the resulting Pt enriched shells of 0.5 nm. Previous XPS studies of dealloyed Pt–Cu nanoparticles, in fact, estimated the resulting Pt enriched shell thickness to be on the order of 1–2 nm.40 Our results further indicate that ASAXS is insensitive to the degree of alloying of the metal atoms. Hence, the SAXS of unalloyed Cu particles and of Cu atoms inside alloy particles cannot be easily distinguished. This fact underlines the complementary nature of XRD and SAXS, with the former being able to resolve the presence of distinct alloy particle phases, and the latter yielding the detailed atom specific size distribution.

Conclusions

The dynamics of particle size and composition changes is a poorly understood issue of great importance in the area of nanoparticle electrocatalysis. The ability to probe the structural and compositional particle dynamics is pivotal to understanding catalyst degradation behavior, for instance inside fuel cell electrodes, where small alloy particle are exposed to prolonged Faradaic surface electrocatalytic processes, which are known to result in severe decreases in particle surface area.19,20,22 Monitoring metal dissolution phenomena is also of importance to better understand the activation of alloy catalysts by electrochemical surface dealloying, which was shown to be an effective means to modify surface catalytic activity.40

We have demonstrated how ASAXS measurements can be used to obtain atomic-level insight in the size and composition distribution dynamics of Pt–Cu alloy nanoparticle ensembles during alloy particle synthesis and during electrocatalytic treatment of alloy nanoparticles. We found a direct relationship between the resulting mean alloy particle size and the annealing temperature, and have evidenced the loss of Cu atoms from uniform alloy nanoparticles during a constant potential leaching protocol. ASAXS can resolve shifts in the particle size distribution function for many elements, as long as the X-ray absorption edges are accessible. Hence, it will be of great value for the study of degradation mechanisms of pure Pt alloy catalysts in low temperature fuel cells. Tuning the incident X-ray energy over wider ranges, ASAXS is also capable of providing multiple atom-specific size distribution functions. Scattering contributions from distinct metal atoms in alloy particles can thus be separated. Applied to a series of electrochemically treated samples, ASAXS can resolve the composition dynamics of alloy nanoparticle ensembles, and thus can contribute critical information to the compositional stability of alloy particles.

Outlook

Future efforts in the area of ASAXS applied to the study of degradation studies of alloy nanoparticle ensembles will focus on improved time resolution of ASAXS measurements using in situ techniques. In situ ASAXS will be able to provide the onset and the details of particle size and composition dynamics under electrochemical conditions. Combined with theoretical models for particle growth,22,25,26 such in situ ASAXS data will be able to test models and provide insight into the molecular mechanisms of nanoparticle transformation and degradation, such as surface area loss. It is expected that ASAXS will play an increasingly important role in the science of electrocatalytic nanoparticle ensembles.

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