„This is the peer reviewed version of the following article: M. Oezaslan, A.-K. Herrmann, M. Werheid, A. I. Frenkel, M. Nachtegaal, C. Dosche, C. Laugier Bonnaud, H. C. Yilmaz, L. Kühn, E. Rhiel, N. Gaponik, A. Eychmüller, T. J. Schmidt (2017). Structural Analysis and Electrochemical Properties of Bimetallic Pd-Pt Aerogels prepared by a two-step Gelation Process. ChemCatChem, Volume 9, Issue 5, March 8, 2017, Pages 798–808, which has been published in final form at [DOI:10.1002/cctc.201600667](https://doi.org/10.1002/cctc.201600667)
This article may be used for non-commercial purposes in accordance with [Wiley Terms and Conditions for Self-Archiving](#)."

Structural Analysis and Electrochemical Properties of Bimetallic Pd-Pt Aerogels prepared by a two-step Gelation Process

M. Oezaslan^{1,2*}, A.-K. Herrmann³, M. Werheid³, A. I. Frenkel⁴, M. Nachtegaal¹, C. Dosche², C. Laugier Bonnaud^{1,5}, H. C. Yilmaz^{1,6}, L. Kühn³, E. Rhiel⁷, N. Gaponik³, A. Eychmüller³, T. J. Schmidt^{1,8*}

- 1) Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland.
- 2) Physical Chemistry, Carl von Ossietzky University of Oldenburg, 26111 Oldenburg, Germany.
- 3) Physical Chemistry, TU Dresden, 01062 Dresden, Germany.
- 4) Department of Physics, Yeshiva University, 245 Lexington Avenue, New York 10016, USA.
- 5) present address: Laboratoire d'Electrochimie et de Physico-chimie des Matériaux et des Interfaces, 38400 St Martin d'Hères, France.
- 6) present address: Laboratory of Inorganic Chemistry, ETH Zurich, 8093 Zurich, Switzerland.
- 7) Light and electron microscopy service unit of the School of Mathematics and Science, Carl von Ossietzky University of Oldenburg, 26111 Oldenburg, Germany.
- 8) Laboratory of Physical Chemistry, ETH Zurich, 8093 Zurich, Switzerland.

corresponding authors: Mehtap Oezaslan (mehtap.oezaslan@uni-oldenburg.de); Thomas J. Schmidt (thomasjustus.schmidt@psi.ch)

Keywords: self-assembly, bimetallic aerogel, Pd-Pt, two-step gelation process, high-resolution scanning transmission electron microscopy, extended X-ray absorption fine structure spectroscopy, chemical homogeneity.

Abstract.

Multi-metallic aerogels have emerged as a promising unsupported, high surface area-based metal material for different applications in heterogeneous catalysis and electrochemistry. The fabrication of these multi-metallic aerogels is based on a complex gelation process which is characterized by controlled aggregation of metallic nanoparticles to form a macroscopic network structure in aqueous solution. However, achieving structural homogeneity of the multi-metallic aerogels in terms of diameter of the nanochains and chemical composition at the nano- as well as at the macro-scale is still a great challenge.

In this paper, we show the characterization of two Pd-Pt aerogels prepared by the two-step gelation method. The structural homogeneity and chemical distribution of both metals (Pd and Pt) inside the aerogels were analyzed using high-resolution (scanning) transmission microscopy (HR(S)TEM), energy-dispersive X-ray spectroscopy (EDX), extended X-ray absorption fine structure (EXAFS) spectroscopy, and cyclic voltammetry. Based on the microscopic and spectroscopic results, the Pd-Pt aerogels show the presence of Pd/Pt-rich domains inside the long-range framework. It is evident that the initial monometallic features dominate over alloying during the gelation process. Although the same synthetic approach for Pd-Pt aerogels with different atomic ratios was used, we observed that the sizes of these monometallic domains strongly varied between the Pd-rich and Pt-rich aerogels. For instance, the Pd-rich aerogels showed larger clusters with a size range from few nanometers up to several tens of nanometers, while the dimension of the clusters of the Pt-rich aerogels varies from the sub-nanometers to a few nanometers. The presence of the metal clusters strongly influenced the electrochemical robustness of these Pd-Pt aerogels. Electrochemical durability investigations revealed that the aerogels with a high content of Pd are less stable due to the gradual dissolution of the less noble metal in particular inside the Pd-rich domains. A better chemical and structural homogeneity might improve the life-time of the Pd-Pt aerogels under electrochemical conditions.

In this work, we provide a better understanding about the structure and chemical distribution of the bimetallic aerogel framework prepared by the two step gelation process.

1. Introduction.

Recently, multi-metallic aerogels have attracted great attention in different application fields of heterogeneous catalysis and electrochemical reactions.¹⁻¹¹ Unsupported metallic materials like aerogels, nanowires, nanotubes, nanoplates and nanostructured films are of large interest due to their high conductivity, high resistance and improved catalytic performance for (electro)chemical reactions.¹²⁻¹⁸ Metal aerogels are a novel class of unsupported materials with low density, high porosity and large surface area. The three-dimensional metal framework structure is formed by nanoparticles that are well connected and linked with each other. Due to their unique structure, aerogels have the potential to combine physical and chemical properties of nanomaterials and macroscopic materials. The chemical, physical and (electro)catalytic properties of multi-metallic aerogels can be tuned by chemical composition, size and shape of the nanoparticles acting as building units and kind of the linking in order to gain large surface area and high porosity.^{1,4,11,19-23}

In the last few years, a broad range of synthetic methods has been developed to design multi-metallic aerogels with various chemical compositions, structures and morphologies.^{2-6,8,24,25} In particular, two main synthetic approaches for the preparation of multi-metallic aerogels have been developed: (i) a spontaneous one-step gelation process²⁻⁴ and (ii) a two-step gelation process.^{4,5} The gelation process is, generally, described by connecting and linking of nanoparticles to form a long-ordered three-dimensional hydrogel in aqueous solution as primary stage for the preparation of aerogels. During the one-step gelation process the formation of hydrogel takes place spontaneously. In contrast, the two-step gelation process introduces first the synthesis of a stable colloidal sol containing monodisperse nanoparticles by chemical reduction of metal precursor salts and then the formation of the hydrogel by induced destabilization of the colloidal suspension. The drying process or more precisely the exchange of the solvent for the transformation of hydrogels into aerogel monoliths is similar in both synthetic approaches. A mild drying process like the supercritical CO₂ drying can be applied to avoid any shrinkage and even collapse of the metal framework. Altogether, the gelation process is the crucial step for the preparation of multi-metallic aerogels and strongly influences their final morphology and chemical composition and thus their resulting mechanical, chemical and (electro)catalytic properties.

Electrocatalytic properties of multi-metallic materials strongly differ from those of the monometallic counterparts. The alteration of the activities is largely based on electronic^{26,27}, ensemble²⁸ and geometric effects^{27,29} (based on the mismatch of lattice parameters). These effects rarely appear alone and it is often difficult to distinguish between them. In most cases, it is even desired that synergetic effects between ligand and geometric effects appear based on the mixture of dissimilar atoms to further improve the reactivity, selectivity and durability of these multi-metallic materials. Recently, unsupported Pd-Pt aerogels prepared by the one-step gelation process have emerged as one of the promising electrocatalysts for the oxygen reduction reaction (ORR, $\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$, $E^0 = 1.23 \text{ V}$) which takes place at the cathode side of fuel cells.^{2,4} Improvements of the catalytic activity and durability at reduced costs for this reaction may help to spread out the world-wide application of fuel cell systems. Here, we present a distinctly different synthetic route of bimetallic aerogels as previously published. The present bimetallic aerogels in this work were prepared by the two-step gelation process. The BET (Brunauer–Emmett–Teller) surface areas of this class of unsupported metallic aerogels are in the range of 60-80 m²/g and compared to other unsupported metallic materials the aerogels show superior surface areas.^{4,5}

The relationships between reactivity and life-time are strongly correlated with the structure and the chemical composition of these aerogels. High structural homogeneity and defined chemical composition are needed, yet, this can be a great challenge for macroscopic aerogels that form during the gelation process at ambient or low temperatures of 70-90 °C. This challenge, generally, is faced by all self-assembled nanostructured multi-metallic materials like nanowires, nanotubes, nano-porous materials etc. Therefore, a broad range of high-resolution microscopic and spectroscopic techniques is required to characterize these nanostructured materials on different length scales (ranging from the Ångstrom- to the macro-scale). The combination of several techniques is essential to provide information about the structure and chemical composition of these unsupported multi-metallic materials over a broad length scale. In particular, for the Pd-Pt aerogel system XRD analysis appear very difficult because of the similar lattice parameters and small crystallite sizes. A well-known strategy to improve the chemical homogeneity in nanostructured multi-metallic materials is the thermal treatment at high temperatures.^{30,31} However, in most cases, a typical side-effect is the loss of the nanostructure by agglomeration and collapse of the fragile network structure resulting in a drastic decrease of the surface area.

In this work, we investigated the homogeneity and chemical distribution of self-assembled Pd-Pt aerogels prepared by the two-step gelation process. Pure Pd, Pt and Pd-Pt systems show face-centered cubic (fcc) crystal structure with space group of Fm-3m. Since the lattice parameters of pure Pt and Pd metals are very similar (3.8870 Å for Pd and 3.9250 Å for Pt obtained from the Inorganic Crystal Structure Database (ICSD)³²) and the presence of nano-sized domains, crystal phase identification by using Rietveld refinement is not meaningful for these materials. Based on the combined results from HR(S)TEM-EDX and EXAFS, the distributions of Pd and Pt atoms inside the aerogel framework prepared by the two-step gelation process were uncovered. We observed that the initial structure of monometallic domains resisted an alloy formation. More specifically, Pd-rich aerogels showed large monometallic domains consisting of Pd or Pt with sizes of few up to several tens of nanometers. The Pt-rich aerogel showed a more uniform distribution of Pd and Pt atoms at the nano- and macro-scale. Only at the Ångstrom-scale, the arrangement of homo-metallic pairing atoms signifying a tendency to clustering of atoms was identified by EXAFS. In addition, the electrochemical stability of the Pd₈₀Pt₂₀ aerogel was investigated by using in-situ EXAFS. In this work, we provide deeper insights into the structure and chemical distributions of the Pd-Pt aerogels prepared by the two-step gelation process for the first time and discuss the capability of these Pd-Pt aerogels for electrochemical applications.

2. Experimental Part.

2.1 Gelation and formation of various bimetallic Pt-Pd aerogels.

Aqueous colloidal solutions of monometallic Pt and Pd nanoparticles were prepared separately (described in supporting information). We used as precursor salts, $\text{H}_2\text{PtCl}_6 \cdot 6 \text{H}_2\text{O}$ ($\geq 99.95\%$, Sigma Aldrich) and PdCl_2 (99.999% Sigma Aldrich). The atomic ratios of Pd:Pt were varied between 4:1 and 1:4, respectively. The gel formation took place at 348 K and was stopped after 5 and 10 hours, respectively, while the supernatant above the hydrogel became a clear solution. The transformation of hydrogel to solid aerogel without significant loss of porosity was carried out by using a supercritical dryer with liquid CO_2 (13200J-AB, SPI Supplies). After drying, the Pd-Pt aerogels appear as black monoliths and were stored at room temperature in air.

2.2 High-Resolution (Scanning) Transmission Electron Microscopy (HR(S)TEM) and Energy-Dispersive X-Ray Spectroscopy (EDX).

The TEM measurements were performed on a ZEISS LIBRA 200 microscope. The microscope was operated with an acceleration voltage of 200 kV. The TEM micrographs were acquired by the iTEM Software. The samples were prepared by dispersing the aerogels in methanol. The aerogel dispersion was dropped onto a copper grid coated with a thin Formvar-carbon film and dried at room temperature in air. The mean diameters of the nanochains of the Pt-Pd aerogels were established by using Software iTEM 5.2 (Olympus Soft Imaging Solutions GmbH).

The high-resolution (S)TEM-EDX investigations were carried out on a JEOL JEM2100F. The acceleration voltage of the microscope was 200 kV. The EDX maps of Pd and Pt in the aerogels were measured and analyzed by using the Oxford INCA Energy TEM250 Software. For the EDX mapping the characteristic energy intensities of the L_{α} -line for Pd and for Pt were evaluated. EDX spot measurements were carried out with an electron beam spot size of 1.5 nm in the STEM mode and an acquisition time of around 60s.

2.3 Extended X-Ray Absorption Fine Structure (EXAFS) spectroscopy.

EXAFS investigations were performed on the X10DA (SuperXAS) beamline at the Swiss Light Source (SLS). The storage ring was operated at a beam current of 400 mA and at 2.4 GeV. EXAFS spectra were recorded at the Pt L_3 - and Pd K-edges for Pd-Pt aerogels in transmission mode. Incident (I_0) and transmitted (I_1 and I_2) X-rays were detected by ionization chambers filled with Ar for the Pd K-edge measurements. The lengths of the ionization chambers for the

incident and transmitted X-rays were 15 cm and 30 cm, respectively. Similar ionization chambers were used for the Pt L₃-edge measurements, however, the ionization chambers were filled with N₂. EXAFS data reduction and analysis was performed using IFEFFIT³³. Preliminary data processing included the background subtraction and edge-step normalization. The energy axis (eV) was converted to photoelectron wave number k units ($\text{\AA}^{-1}$) by assigning the origin, E_0 , to the first inflection point of the absorption edge. The resulting $\chi(k)$ functions were weighted with k^2 to compensate for the dampening of the XAFS amplitude with increasing k and were subsequently Fourier-transformed to obtain pseudo radial structure functions (RSFs). Fitting of the experimental data was done by a non-linear least square Levenberg-Marquardt method.

Ex-situ EXAFS measurements. Solid aerogel samples were prepared as pellets by using cellulose as binder. The EXAFS spectra of the Pt and Pd absorption edges were then concurrently analyzed by applying several constraints between fitting parameters, as follows. In the fits, the interatomic distances (R) and their mean square disorder parameters (σ^2) of the hetero-metallic bonds Pt-Pd and Pd-Pt (as measured from the Pt and Pd absorber perspectives, respectively) we constrained to be equal to each other. Pure Pt and Pd foils were used as reference to establish the amplitude reduction factors for Pd and Pt. By fitting of the bulk metals that possess face-centered cubic (fcc) structure, the coordination number of the first nearest neighbor (Pt-Pt or Pd-Pd) bonds were fixed at 12 and the amplitude reduction factors (S_0^2) for Pd and Pt were varied. The final S_0^2 values obtained were 0.83 and 0.91 for Pt and Pd, respectively, and were then fixed to these values in the fits of the aerogel EXAFS data. For that, the theoretical scattering paths of all pairs (Pt-Pt, Pt-Pd, Pd-Pt and Pd-Pd) were calculated using the fcc structure where some atoms in the nearest neighbor positions were replaced by an opposite type.

In-situ electrochemical EXAFS measurements. A home-made electrochemical-spectroscopic PEEK cell with Kapton windows and three electrodes was employed to investigate the changes of the aerogel structures in an electrochemical environment. A gold wire and a mercury-mercury sulfate (MMS) electrode were used as counter electrode and reference electrode, respectively. 0.1 M HClO₄ was used as electrolyte solution. For the preparation of the WE, a dispersion consisting of an aerogel – water – iso-propanol – Nafion mixture (described in part 2.4) was dropped onto a carbon paper and dried at around 40°C in air. The calculated metal loading was around 100 $\mu\text{g cm(geometric)}^{-2}$. Before the EXAFS measurements were commenced, an electrochemical pretreatment of the WE was performed to remove any impurities and oxygen-containing surface species from the aerogel film and/or carbon paper. The WE was electrochemically pretreated in a

potential range of 0.35 and 1.20 V/RHE at a scan rate of 50 mV s⁻¹ in 0.1 M HClO₄. Afterwards, the WE was built in the cell. The WE was electrochemically cycled in the range of 0.5 and 1.5 V/RHE at a scan rate of 50 mV s⁻¹. During the run, after 50, 100 and 200 potential cycles, in-situ EXAFS spectra (three scans) were recorded from the aerogel samples at a constant potential of 0.5 V/RHE.

2.4 Electrochemical characterization via thin film rotating disk electrode (RDE) technique.

Preparation of the working electrode (WE). 1 – 2 mg of the aerogel was added to a 5.00 ml solution consisting of water (3.98 ml), iso-propanol (1.00 ml) and Nafion (20 µl of 5 wt.% Nafion solution). After horn-sonication for 30 min (supplied by Hielscher UP200H, Germany), 10 µl of the dispersion was pipetted onto the previously cleaned and mirror-like surface of a glassy carbon (GC) electrode (with outer diameter of 5 mm) embedded in Teflon (supplied by PINE, USA). The coated electrode was dried for 20 – 25 min at 40°C in air resulting in a thin homogenous film. The calculated total metal loading of the working electrode (WE) was between 10 – 20 µg_{metal} cm(geometric)⁻². The GC electrode was previously polished with 0.3 µm and then with 0.05 µm Al₂O₃ suspension on the Microcloth polishing paper (supplied by Prüfmaschine AG, Switzerland).

Electrochemical cyclic voltammetry experiments. All electrochemical measurements were carried out in a home-made three-compartment electrochemical glass cell by using the thin film RDE technique^{34,35} equipped with a rotator (supplied by PINE, USA) and a potentiostat (Biologic, France). The electrochemical glass cell was cleaned in a “piranha” solution (a mixture of 3/4 H₂SO₄ (96-98 %) and 1/4 H₂O₂ (30 %)) overnight and then washed with purified water (18.2 MΩ cm at room temperature) several times. A three-electrode configuration was used consisting of a gold wire as counter electrode, a MMS electrode (supplied by Biologic, France) or Hydroflex (supplied by Gaskatel, Germany), respectively, as reference electrode and the aerogel-coated thin film GC electrode as WE. The reference electrode was held in place by a Luggin-Haber capillary, where the opening of the capillary was positioned below the center of the WE at a distance of around 3 mm. The 0.1 M HClO₄ electrolyte solution was freshly prepared by dilution of a 70 % suprapure HClO₄ (supplied by VWR). The quality of nitrogen and carbon monoxide (supplied by Messer) were 5.0 and 4.5, respectively.

Determination of the electrochemically active surface area (ECSA) by the CO stripping method. The WE was immersed into the electrolyte solution (0.1 M HClO₄) under potential control and with a rotation speed of 1600 rpm (rotations per minute). The potential of the WE was held at 0.1 V/RHE during the saturation with CO and N₂. The CO gas was bubbled through the frits into the electrolyte for 8 min. Then, the electrolyte was saturated with N₂ for 25 min to remove the excess of dissolved CO from the electrolyte. Afterwards, three cyclic voltammogram (CV) profiles were recorded with a scan rate of 50 mV s⁻¹ between 0.35 and 1.2 V/RHE.

For the determination of the ECSA, the first CV profile showing the oxidation peak of the adsorbed CO monolayer was subtracted from the second CV profile to take into account the adsorption of anions (OH⁻, ClO₄⁻) on the aerogel surface between 0.4 and 1.2 V/RHE. The ECSA was estimated by using the CO stripping peak assuming a charge of 415 $\mu\text{C cm}_{\text{real}}^{-2}$ for a Pd₅₀Pt₅₀ system to oxidize one CO monolayer. Based on the pseudo-capacities of pure Pt³⁶ (420 $\mu\text{C cm}^{-2}$) and Pd³⁷ (410 $\mu\text{C cm}^{-2}$) surfaces the values for the other Pd-Pt aerogels are weighted, respectively. Throughout the paper, all potentials are reported with respect to the reversible hydrogen electrode (RHE).

Electrochemical degradation measurements. An accelerated electrochemical degradation experiment was subjected on the aerogels to investigate their electrochemical durability under harsh conditions. The potential cycling between 0.5 and 1.5 V/RHE is often applied to examine the electrochemical resistance of metal nanoparticles and support materials for fuel cell applications.³⁸⁻⁴² The CV profiles were recorded between 0.5 and 1.5 V/RHE at a scan rate of 50 mV s⁻¹ in N₂-saturated 0.1 M HClO₄. During the run-time, after 100 and 200 potential cycles, the ECSA was determined by the CO stripping method. In between, the electrolyte was removed and refilled with a fresh 0.1 M HClO₄ to eliminate any impurities which can be formed during the potential cycling up to 1.5 V/RHE (e.g. decomposition of the electrolyte).

3 Results and Discussion.

3.1 Various architectures of multi-metallic aerogels.

In the case of the self-assembled bimetallic aerogels prepared by the two-step gelation process, three possible architectures can be formed: (i) non-alloyed, (ii) randomly disordered alloyed (solid solution) and (iii) segregated aerogel nanostructure as shown in Figure 1. The initial nanoparticles are the respective building blocks of the nanochain segments inside the aerogel which should result in the (i) non-alloyed structure. If surface diffusion processes take place at the interfaces between the linked nanoparticles, the dissimilar atoms can re-arrange in this region and form (ii) alloyed or (iii) core-shell nanochain motifs. The question arises if the inter-diffusion process occurs at the interfaces between the neighboring monometallic particles during the gelation and how the aerogel structure would change due to the high mobility of these dissimilar atoms.

Figure 1. Possible architectures of bimetallic aerogels prepared by the two-step gelation process.

3.2 Transmission Electron Microscopy (HRTEM).

In Figure 2, representative TEM micrographs at low and high magnifications of the pristine Pd-Pt aerogels illustrate the typical long-range three-dimensional nanochain-like network structure. The results from the TEM investigations at higher magnification (Fig. 2c and 2f) reveal that the diameter of the nanochains slightly varies along its direction. The mean diameter of the nanochains was 5.1 ± 1.3 nm and 3.9 ± 1.1 nm for the as-prepared Pd₈₀Pt₂₀ and Pd₂₀Pt₈₀, respectively. Only at the sections where two or more nanochains cross, a stronger aggregation of the particles was observed.

Figure 2. TEM micrographs with low (a, d) and high magnifications (b, e) of the pristine $\text{Pd}_{80}\text{Pt}_{20}$ and $\text{Pd}_{20}\text{Pt}_{80}$ aerogels. The mean particle size along the nanochain-based structure was established by counting of around 150 – 200 nanoparticles resulting in 5.1 ± 1.3 nm and 3.9 ± 1.1 nm for the pristine $\text{Pd}_{80}\text{Pt}_{20}$ and $\text{Pd}_{20}\text{Pt}_{80}$, respectively.

Figure S1 displays the HRTEM micrographs of representative regions of the Pd-Pt aerogels showing single crystalline domains with their lattice fringes embedded in the nanochains. Various orientations of the crystallites were observed and indicate the polycrystallinity. The grain boundaries of the anchored nanoparticles signify no preferred growth direction which would be expected e.g. for twin growth. We can conclude that the anchoring of nanoparticles was not influenced by the initial orientation of the nanoparticles during the coalescence process.

3.3 Bright-Field Scanning Transmission Electron Microscopy (BF-STEM) equipped with Energy-Dispersive X-Ray Spectroscopy (EDX).

Figure 3 shows the representative BF-STEM images and the corresponding EDX maps of the pristine Pd-Pt aerogels. The average atomic ratios of Pd:Pt established from these broad regions (shown in Fig. 3a and 3d) at low magnification were 17:83 and 82:18 with an error of 1-2

atomic (at.) % for the Pd₂₀Pt₈₀ and Pd₈₀Pt₂₀ aerogels, respectively. These values are in good agreement with the original content of pure single Pd and Pt nanoparticles which were mixed in the gelation process. The XPS analysis shows that the oxidation states of Pd and Pt inside the aerogels are mainly metallic and only a small content of oxidized Pd was found (see Fig. S3 in SI). This suggests that the chemical composition of the Pd-Pt aerogel networks can be easily tuned by the addition of the desired amount of metal nanoparticles during the hydrogel synthesis.

Additional EDX maps and EDX spot analysis with an electron beam spot size of 1.5 nm were performed on both aerogels to clarify the distribution of Pt and Pd atoms inside the nanostructure. In case of the pristine Pd₈₀Pt₂₀ aerogel (see Fig. 3b and 3c), the comparison of the EDX maps of Pd and Pt visualizes that the Pt atoms are arranged in two different motifs. On the one hand, Pt atoms appear as Pt-rich clusters in the nanochains and on the other hand the residual Pt atoms are interfused with Pd atoms to form an alloy. Both motifs (Pt-rich clusters and Pt-alloys) are randomly distributed in this framework. To clarify the difference between Pt-rich clusters and Pt-alloys, we define clusters as areas with a strong enrichment of one metal (the fraction of the other metal is less than a few at. % established by EDX), while Pt-alloys are a mixture of two metals (the fraction of the other metal is larger than 10 at. %). The dimension of the randomly distributed Pt-rich clusters varies strongly from a few up to several tens of nanometers. Also, the regions where a mixture of Pt and Pd was identified ranged from approximately a few up to several tens of nanometers. It is evident, that the Pt atoms are not homogeneously distributed over the entire metallic framework. It seems that Pd atoms are better distributed over large regions of the nanochains. Consequently, due to the strong appearance of Pt clusters, the aerogel framework exhibited regions which consisted of almost pure Pd. In other words, since less Pt atoms are available to form a solid solution with Pd, Pd atoms are also ordered in form of Pd-rich clusters. Finally, based on the appearance of large fraction of unalloyed material, the structure of the as-prepared Pd₈₀Pt₂₀ aerogel looks similar to the postulated structure in Figure 1a.

Representative EDX maps obtained from the pristine Pd₂₀Pt₈₀ aerogel are shown in Figure 3e and 3f. The comparison between the EDX maps for Pt and Pd signifies a more homogeneous distribution of both metals along the nanochains. The appearance of large Pt-rich or Pd-rich clusters was not observed at this magnification. It seems that the observed arrangement of Pt and Pd atoms for this aerogel is a random mixture as postulated in Figure 1b for alloyed

aerogels. It is noted that local heterogeneity inside the single nanoparticles along the nanochains by formation of small clusters of sub-nanometer sizes are very difficult to estimate from EDX maps due to the relatively low lateral resolution of this technique.

Figure 3. BF-STEM micrographs (a, d) combined with EDX maps of the Pd (b, e) and the Pt (c, f) L_{α} -line of the pristine $\text{Pd}_{80}\text{Pt}_{20}$ and $\text{Pd}_{20}\text{Pt}_{80}$ aerogels. The EDX maps of Pd and Pt are displayed in red and green, respectively.

EDX spot measurements were conducted to establish the local chemical composition of the unbranched as well as branched nanochains for the pristine Pd-Pt aerogels shown in Figure S2. The spatial distribution of both metals along the nanochains within the $\text{Pd}_{80}\text{Pt}_{20}$ aerogel showed regions with a very high content of one metal as well as mixed regions with different atomic ratios. Although, the EDX map results for the pristine $\text{Pd}_{20}\text{Pt}_{80}$ aerogel (Fig. 3 e-f) give the strong impression of a well homogenous distribution of both metals along the nanochains, the local EDX spot analysis revealed a significant change of the chemical composition from location-to-location. The variation is not so strong (around 10 %) compared to the EDX results for the pristine $\text{Pd}_{80}\text{Pt}_{20}$ aerogel. Only few small regions showed a high content of only one metal (see position (2) in Fig. S2b). Since both metals are largely dispersed along the nanochains, the

distribution of the Pd₂₀Pt₈₀ aerogel is more homogenous compared to that of the Pd₈₀Pt₂₀ aerogel. The formation of monometallic clusters with different sizes can be likely explained by the different diffusion coefficients of Pd and Pt surface atoms and/or the statistical probability, describing what sort and how frequently initial monometallic nanoparticles collide and fuse to form a nanochain in aqueous media. Further work is in progress to better understand the observed clusters inside the Pd-Pt aerogels.

3.4 Ex-situ Extended X-ray Absorption Fine Structure (EXAFS) Spectroscopy.

EXAFS spectroscopy measurements were performed on the as-prepared Pd-Pt aerogels to provide better insight into the degree of alloying. In Figure 4a, 4c and 4e, the k^2 -weighted EXAFS spectra of the Pd-Pt aerogels are plotted with those of the corresponding metal foils at the respective edges. The comparison shows that the k^2 -weighted EXAFS data of the Pd-Pt aerogels look similar to the data of the pure Pd or Pt foils. This suggests a monometallic characteristic behavior of Pt and Pd atoms inside the Pd-Pt aerogels.

Figure 4b, 4d and 4f show the k^2 -weighted Fourier transformed EXAFS spectra (black solid lines) and their corresponding best fits (red solid lines) of the pristine Pd₈₀Pt₂₀ and Pd₂₀Pt₈₀ aerogels. Table I summarizes the best fit parameters of the nearest coordination numbers (N), atomic distances (R) and mean square disorder parameter (σ^2) for the pristine Pd-Pt aerogels. In the case of the Pd₈₀Pt₂₀ aerogel, both spectra at the Pt L₃-edge and Pd K-edge were used for the multi-edge EXAFS fit analysis (Fig. 4b and 4d). The multi-edge EXAFS fit analysis for the Pd₈₀Pt₂₀ aerogel revealed that the peaks in the Fourier-transformed k^2 -weighted EXAFS spectra at the Pt L₃-edge and Pd K-edge correspond to the scattering pairs of Pt-Pt and Pd-Pd atoms in the first shell, respectively, without a detectable contribution of hetero-metallic Pt-Pd and Pd-Pt bonds. Thus, the Pd₈₀Pt₂₀ aerogel shows a strong monometallic behavior in the local coordination environment, which indicates the formation of Pd-rich and Pt-rich clusters within the aerogel framework. Similar multi-edge EXAFS fit results were obtained for the pristine Pd₅₀Pt₅₀ aerogel.¹¹ In both Pd-Pt aerogels, the Pd- and Pt-rich clusters prevail over the features of Pd-Pt alloys.

As the sum of all partial coordination shells corresponds to the total coordination shell of each metal, it is noted that the values of the total coordination shell for Pd and Pt atoms are lower than that for the macroscopic (bulk) counterparts ($N_{\text{total}}=12$) indicating that the aerogels exhibit nanoparticle-like characteristics. The values of the total coordination shell for Pd and Pt atoms are similar signifying that the particle size of the pure Pt and Pd nanoparticles are almost equal.

This observation is consistent with the results from the TEM analysis (shown in Figure 2, $d_{\text{avg}} = 5.1 \pm 1.3$ nm for $\text{Pd}_{80}\text{Pt}_{20}$ and $d_{\text{avg}} = 3.9 \pm 1.1$ nm for $\text{Pd}_{20}\text{Pt}_{80}$).

Figure 4. k^2 -weighted Pd K-edge and Pt L₃-edge EXAFS data (a, c and e) and their Fourier transformed EXAFS data (b, d and f) for the pristine $\text{Pd}_{80}\text{Pd}_{20}$ and $\text{Pd}_{20}\text{Pt}_{80}$ aerogels. The inserted plots (b, d and f) show the imaginary part of the k^2 -weighted Fourier transformed EXAFS spectra (black lines) and the corresponding fits (red lines).

Figure 4f shows the k^2 -weighted Fourier transformed EXAFS spectra of the pristine $\text{Pd}_{20}\text{Pt}_{80}$ aerogel recorded at the Pt L_3 -edge. The best fit for this aerogel (see Table I) indicates the presence of a homo-metallic bond (Pt-Pt) in the first shell. Although the $\text{Pd}_{20}\text{Pt}_{80}$ aerogel showed a better homogeneity within the nanochains at the few nanometer scale established by STEM-EDX, the EXAFS results clearly revealed homo-metallic pairing features at the Ångstrom-scale. Consequently, we can conclude that Pd atoms are largely neighbored with Pd atoms in the first shell. It is noted that the features of the homo-atomic pairing were only observed by Ångstrom-resolved EXAFS data. At large length scales, both metals, Pd and Pt, show an even distribution over the whole aerogel structure.

Table I. First nearest neighbour coordination shell (N), atomic distance (R), mean square disorder parameter (σ^2), shift of energy (E_0) at the corresponding edges, R_f -factor (closeness of the fit as quality parameter) for the pristine $\text{Pd}_{80}\text{Pt}_{20}$ and $\text{Pd}_{20}\text{Pt}_{80}$ aerogels prepared by the two-step gelation process.

	shell / phase	N	R / Å	$\sigma^2 \times 10^{-4} / \text{Å}^2$	$\Delta E_0 / \text{eV}$	R_f
$\text{Pd}_{80}\text{Pt}_{20}$	Pt – Pt ₁ / Fm-3m	9.4 ± 1.2	2.759 ± 0.004	53 ± 5	7.9 ± 0.9	0.0127
	Pd – Pd ₁ / Fm-3m	9.2 ± 0.8	2.789 ± 0.005	89 ± 7	-8.1 ± 0.6	
$\text{Pd}_{20}\text{Pt}_{80}$	Pt – Pt ₁ / Fm-3m	9.1 ± 0.6	2.756 ± 0.003	55 ± 3	7.7 ± 0.6	0.0043

In summary, different techniques were used in this work to identify the structure, chemical distribution and homogeneity of the self-assembled Pd-Pt aerogels prepared by the two-step gelation process. The Pd-Pt aerogels consisting of finite plurality of connected single nanoparticles showed a highly complex structure in regard to the homogeneity and chemical distribution. With this preparation method, the coalescence of monometallic Pt and Pd nanoparticles lead to a chemically heterogeneous structure, where the original cluster motif fully dominates over the alloying as illustrated in Figure 1a. The presence of monometallic domains inside the aerogel indicates that the diffusion kinetics of the Pd and Pt atoms at ambient and low temperatures are very slow. Further studies are required to better understand the two-step gelation process, its reproducibility and interdiffusion kinetics for the Pd-Pt aerogel system.

3.5 Electrochemically active surface area (ECSA) via the CO stripping method.

We chose for the determination of the ECSA of the Pd-Pt aerogels the CO stripping method, because the typical underpotential hydrogen deposition (H_{upd}) method is inappropriate for Pd-based materials due to the formation of the absorbed hydrogen.⁴³⁻⁴⁵ Figure 5 shows the CO stripping profiles for both aerogels in 0.1 M HClO_4 . The large anodic current peak is associated with the electrochemical oxidation of the adsorbed CO monolayer to water and carbon dioxide. The potentials at the current maxima are around 0.86 V/RHE and 0.96 V/RHE for the $\text{Pd}_{20}\text{Pt}_{80}$ and $\text{Pd}_{80}\text{Pt}_{20}$ aerogels, respectively. We suggest that effects of the size of the nanochains are likely negligible since the average diameter of both aerogels are similar. Therefore, a shift of the CO stripping peak is largely related to the chemical composition of the surface and subsurface. The observed broad and slightly irregular CO stripping peak is affected by the local variation of the surface composition of the bimetallic aerogels.

Figure 5. CO stripping cyclic voltammetry (CV) profiles of the pristine $\text{Pd}_{80}\text{Pt}_{20}$ (red line) and $\text{Pd}_{20}\text{Pt}_{80}$ (black line) aerogels. Experimental parameters: scan rate of 50 mV s^{-1} , metal loading of $12 - 17 \mu\text{g cm}^{-2}_{(\text{geo.})}$ in 0.1 M HClO_4 at room temperature. The arrows indicate the scan direction.

The mean values of the ECSA were $66 \pm 3 \text{ m}^2 \text{ g}_{\text{metal}}^{-1}$ and $52 \pm 8 \text{ m}^2 \text{ g}_{\text{metal}}^{-1}$ for the $\text{Pd}_{20}\text{Pt}_{80}$ and $\text{Pd}_{80}\text{Pt}_{20}$, respectively. The resulting ECSA values are almost comparable to commercially available Pt nanoparticles supported on high surface area carbon.^{38,46,47} Since the ECSA values are similar to the BET values, it appears that a large fraction of the surface of the bimetallic aerogels is free from impurities. In principle, the total surface area should be

catalytically active for the electrochemical activation of small molecules like oxygen. Therefore, we tested these aerogels for the electrocatalytic reduction of oxygen (ORR) in acidic media. Unfortunately, the Pd-Pt aerogels prepared by the two-step gelation process showed insufficient catalytic performance (not shown). The poor reactivity was likely correlated with the structural inhomogeneity of these materials. Possible strategies to improve the distribution and hence the catalytic properties of these aerogels would be the modification of synthesis parameters (e.g. temperature or using smaller nanoparticles) and/or the thermal annealing.

3.6 Electrochemical short-term durability tests of the Pd₈₀Pt₂₀ and Pd₂₀Pt₈₀ aerogels.

An accelerated cyclic voltammetry test protocol was applied to analyze the durability of the Pd-Pt aerogels in the potential range of 0.5 and 1.5 V/RHE with 50 mV s⁻¹ in N₂-saturated 0.1 M HClO₄ at room temperature. During the run, after a certain number of cycles CO stripping profiles were recorded to monitor the changes of the ECSA. Figure 6 shows the course of the ECSA in dependence of the cycle number for the Pd₈₀Pt₂₀ and Pd₂₀Pt₈₀ aerogels after the potential cycling (0.5 - 1.5 V/RHE). It is clear that for the Pd₈₀Pt₂₀ aerogel (Fig. 6a) the CO stripping current peak drastically decreased and concurrently shifted to lower anodic potentials with increasing cycle number. The shift of the CO stripping peak is likely related to the surface enrichment of Pt in the aerogel by electrochemical dissolution of Pd and/or by increase of the particle size (e.g. Ostwald ripening). It is well-known that with increasing particle size the oxophilicity of the Pt particles decreases and results in a shift of the CO stripping current peak to higher anodic potentials.³⁶ The electrochemically active surface area (SA) (not normalized to the used mass of aerogel) were estimated from the CO stripping peak and normalized to the initial SA value (Begin-of-Life). Fig. 6c and 6d show the normalized values of SA in dependence of the cycle number. For the Pd₈₀Pt₂₀ aerogel the SA dropped to below 20 % after 200 cycles between 0.5 and 1.5 V/RHE resulting from the strong depletion of Pd. It is assumed that the drastic decrease of SA for the Pd₈₀Pt₂₀ aerogel is caused by the high content of Pd as well as the strong heterogeneity observed with STEM-EDX and EXAFS (see Figure 3 – 4). In particular regions of the nanochains containing high Pd content became very unstable at high anodic potentials. It seems that during the backward scan most of the Pd ions in the electrolyte were not redeposited on the aerogel surface. The large error bars shown in Figure 6c were established from five independent RDE measurements. The relatively large error bars are likely related to the very

rapid depletion and strong instability of Pd inside the aerogel in this potential range. Altogether, the existence of large Pd-enriched regions mainly destabilized the entire aerogel network structure making it unsuitable for fuel cell application. It is not clear to date how the electrochemical dissolution process of palladium occurs during the potential cycling. Several studies about polycrystalline Pd showed that in the anodic scan the Pd already formed surface oxides at low potentials relative to the standard potential in acidic media.⁴⁸⁻⁵⁰ The thickness of Pd oxide layers increased with increasing upper potential, however, at high upper potentials the electrochemically pre-formed palladium oxide commenced to dissolve in the anodic scan. However, most of the Pd oxide electrochemically dissolved in the backward scan before the Pd oxide can be reduced to metallic Pd. Similar electrochemical dissolution behavior was observed for Pt. The electrochemical dissolution mechanisms for macroscopic metal electrode surfaces were comprehensively studied by many groups.⁵¹⁻⁵³ They showed that the electrochemical dissolution rate of polycrystalline Pt is pronounced at the transition state between oxidation and reduction processes. For instance, if the Pt surface electrochemically oxidizes by increasing the anodic potential (larger than 1.2 V/RHE), the backward (cathodic) scan causes an acceleration of the dissolution process of an oxidized Pt surface. In contrast, during the anodic scan the dissolution rate of metallic Pt is almost negligible. As Pd is less noble and thus exhibits more oxophilic behavior, we suggest that the electrochemical dissolution of Pd occurs much easier compared to Pt.

Figure 6b shows the CO stripping profiles for the Pd₂₀Pt₈₀ aerogel after a certain number of cycles from 0.5 and 1.5 V/RHE with 50 mV s⁻¹. The shift of the CO stripping current peak to lower anodic potentials was very small. Only the comparison of the shape of the CO stripping current peak exhibited a significant change before and after electrochemical cycling. After 100 cycles the CO stripping current peak became clearly narrower indicating an improved distribution of the sizes of the nanochains or of the chemical surface composition inside the treated aerogel. The course of the SA in dependence of the cycle number is shown in Figure 6d. It is noted, that the SA decreased only by 25 %. The unsupported Pd₂₀Pt₈₀ aerogel exhibited a considerable electrochemical durability. Many studies on carbon-supported Pt nanoparticles (Pt/C) showed a loss of ECSA of around 40-50% under similar conditions.^{38,42} The large loss of ECSA for Pt/C is associated with carbon corrosion, dissolution of small nanoparticles and particle detachment. The

experimentally observed improved stability of the Pd₂₀Pt₈₀ aerogel was largely caused by the higher content of Pt and the absence of a carbon support material.

Figure 6. (a – b) CO stripping cyclic voltammetry profiles of Pd-Pt aerogels after a certain number of cycles (0, 100 and 200 cycles) between 0.5 and 1.5 V/RHE at 50 mV s⁻¹ in N₂-saturated 0.1 HClO₄. The calculated loadings were in the range of 10-17 μg cm⁻²(metal). (c – d) Normalized surface area (SA) loss in dependence of the cycle number induced by electrochemical cycling up to 1.5 V/RHE.

3.7 Structural stability of the Pd₈₀Pt₂₀ aerogel probed by in-situ electrochemical EXAFS. As the Pd₈₀Pt₂₀ aerogel showed the largest alteration during the electrochemical cycling, in-situ EXAFS studies were carried out to better understand its aging. During the EXAFS measurements, the aerogel-coated working electrode was under potential control and was held at 0.5 V/RHE. This potential is in the electrochemical double layer regime of both metals and reduces the electrochemical formation of oxygen-containing species on the aerogel surface. In other words, in the double layer regime, the surface of both metals should mainly exist in the metallic state.

Figure 7a shows the in-situ k^2 -weighted Fourier transformed EXAFS spectra (black lines) and the corresponding best fits (red lines) for the Pd₈₀Pt₂₀ aerogel recorded at the Pd K-edge and by holding the potential of 0.5 V/RHE after a certain cycle number (0.5 – 1.5 V/RHE). The best fit parameters for the first shell of the treated Pd₈₀Pt₂₀ aerogel are summarized in Table II. The behavior of the coordination numbers for Pd-Pd, Pd-Pt and Pd-M (M=Pt, Pd) pairs versus the cycle number is plotted in Figure 7c.

After the electrochemical cleaning process (between 0.35 and 1.2 V/RHE with 50 mV s⁻¹, 10 cycles) we observed the presence of a Pd-Pt scattering pair in the Pd₈₀Pt₂₀ aerogel. After 10 potential cycles, the N(Pd-Pt) is in the range of around 2.3 ± 1.0 , while the N(Pd-Pd) decreased from 9.0 ± 0.7 to 7.1 ± 1.0 (a change of around 23%). The evolution of Pd-Pt pairing atoms is largely related to the re-arrangement of the particle surface by electrochemical re-dissolution and re-deposition of Pt and Pd atoms from the electrolyte or by surface diffusion of Pd and Pt atoms to form a Pd-Pt alloy. Generally, low coordination numbers are largely associated with surface atoms, because of the absence of additional atoms compared to their corresponding atoms in the bulk. The comparison of the N(Pd-Pt) and N(Pd-Pd) indicates that Pt atoms exist at the surface of the aerogel or that the Pd atoms preferred to deposit on Pt-rich clusters. Both processes can form an alloy at the surface or at the solid-solid interface. As Pt is more electrochemically stable than Pd, we suggest that the surface of the aerogel is gradually enriched with Pt. The gradual increase of Pt atoms on the surface and subsurface was also indicated by the CO stripping experiments (see Fig. 6a). The gradual accumulation of Pt atoms at the surface may protect the residual Pd atoms for further electrochemical dissolution.

Figure 7c shows the course of the total coordination number which can be estimated from the sum of N(Pd-Pt) and N(Pd-Pd) during the experiment. The N(Pd-M) was almost stable over the potential cycling test protocol (before and after 200 cycles) the total coordination numbers did not change within the experimental uncertainties, 9.3 ± 0.7 and 9.6 ± 1.2 , respectively), indicating that the diameter size of the nanochains seems to be almost unchanged. It is noted that a change of the total coordination number of the adsorbing Pd atom would drastically affect the particle size. Figure 7d illustrates the structural changes of the Pd-rich aerogel induced by electrochemical cycling and visualizes the depletion of Pd and the enrichment of Pt inside the electrochemically treated aerogel to hinder the further electrochemical dissolution of Pd atoms.

We want to emphasize that these in-situ EXAFS results involves only information about the local structural changes of Pd atoms inside the Pd₈₀Pt₂₀ aerogel during the aging process. The observed features for the Pd-rich aerogel constitute only a glimpse on the structural durability induced by electrochemical cycling. Nevertheless, the in-situ EXAFS results provide new insights into the electrochemical aging process of the novel Pd-rich aerogel.

Table II. First nearest neighbour coordination number (N), total Pd-metal coordination number (N_{Pd-M}), atomic distances (R), mean square disorder parameter (σ^2), shift of energy (ΔE_0) at the Pd K-edge, R_f - factor for the electrochemically treated Pd₈₀Pt₂₀ aerogel.

cycle number	shell / phase	N	$R / \text{\AA}$	$\sigma^2 \times 10^{-4} / \text{\AA}^2$	$\Delta E_0 / \text{eV}$	R_f
0 = as prepared	Pd – Pd _I / Fm-3m	9.3 ± 0.7	2.767 ± 0.005	88 ± 5	-7.9 ± 0.5	0.0070
10 = pretreated	Pd – Pd _I / Fm-3m	7.0 ± 0.9	2.748 ± 0.008	70 ± 12	2.0 ± 0.6	0.0015
	Pd – Pt _I / Fm-3m	2.3 ± 1.0	2.710 ± 0.025	66 ± 30		
	Pd – M/ Fm-3m	9.3 ± 1.0				
50	Pd – Pd _I / Fm-3m	7.6 ± 0.8	2.734 ± 0.006	59 ± 8	-5.0 ± 0.6	0.0012
	Pd – Pt _I / Fm-3m	4.2 ± 1.8	2.713 ± 0.023	97 ± 49		
	Pd – M/ Fm-3m	11.8 ± 1.3				
100	Pd – Pd _I / Fm-3m	8.4 ± 2.2	2.744 ± 0.013	60 ± 19	4.1 ± 1.2	0.0098
	Pd – Pt _I / Fm-3m	0.7 ± 1.5	2.723 ± 0.020	11 ± 51		
	Pd – M/ Fm-3m	9.1 ± 1.8				
200	Pd – Pd _I / Fm-3m	7.1 ± 1.0	2.734 ± 0.009	54 ± 10	-7.5 ± 0.9	0.0034
	Pd – Pt _I / Fm-3m	2.5 ± 1.3	2.705 ± 0.023	60 ± 31		
	Pd – M/ Fm-3m	9.6 ± 1.1

Figure 7. (a) In-situ k^2 -weighted Fourier transformed EXAFS spectra (black lines) and the corresponding fits (red lines) for the $\text{Pd}_{80}\text{Pt}_{20}$ aerogel at the Pd K-edge recorded after a certain number of cycles in the potential range of 0.5 and 1.5 V/RHE at 50 mV s^{-1} in N_2 -saturated 0.1 M HClO_4 . (b) Imaginary part of the k^2 -weighted Fourier transformed EXAFS spectra (black lines) and the corresponding fits (red lines). (c) Evolution of the coordination number for the pairing atoms (Pd-Pd, Pd-Pt and Pd-M) in dependence of the number of cycles for the $\text{Pd}_{80}\text{Pt}_{20}$ aerogel. (d) Illustration of the aging process of the $\text{Pd}_{80}\text{Pt}_{20}$ aerogel induced by electrochemical cycling.

4 Conclusions

We comprehensively investigated the structure and chemical composition of Pd₈₀Pt₂₀ and Pd₂₀Pt₈₀ aerogels prepared by a two step-gelation process. By using (S)TEM-EDX and EXAFS, we identified the final structure and chemical distribution for both aerogels at different length scale. It was evident that the Pd/Pt-rich clusters originating from the initial nanoparticles prevail over the alloy formation. The size of the monometallic domains strongly varied between the Pd-Pt aerogels. For instance, the Pd-rich aerogel showed a stronger chemical heterogeneity due to the presence of large Pd/Pt-rich clusters with a size of several tens of nanometers. In contrast, the STEM-EDX analysis revealed a more homogeneous distribution of Pd and Pt atoms inside the Pd₂₀Pt₈₀ aerogel at a larger length scale. The EXAFS investigations showed features of homo-atomic pairing (Pd-Pd and Pt-Pt) in the first coordination shell, indicating clusters at the local-scale. Therefore, the Pd₂₀Pt₈₀ aerogel showed a higher structural and chemical homogeneity compared to the Pd₈₀Pt₂₀ aerogel.

In addition, the CO stripping experiments revealed that the electrochemically active surface areas (ECSA) of the Pd-Pt aerogels are similar to the BET surface areas evaluated by physisorption, signifying that the aerogel surfaces were free from any impurities, organic ligands etc. and showed a high accessibility for the electrocatalytic conversion of small molecules. However, to improve the electrocatalytic performance, a better homogeneity and chemical distribution of the bimetallic aerogel is necessary.

The accelerated degradation test protocol showed that in particular Pd-rich clusters inside the Pd₈₀Pt₂₀ aerogel strongly suffered during the electrochemical cycling. Strong changes of the structure and chemical composition induced by electrochemical cycling were in-situ monitored by using EXAFS and CO stripping experiments. Thereby, Pd-rich aerogels showed a lower electrochemical stability compared to Pt-rich aerogels. The enhanced aging process of the Pd-rich aerogels is strongly based on the successive electrochemical dissolution of Pd, in particular the strong depletion of Pd from the Pd-rich clusters. To increase the robustness of Pd-rich aerogels, the surface and subsurface structure and composition need to be homogeneous and uniform.

Homogeneity of the aerogels is important to stabilize the long-range network structure. In particular regions with higher content of less noble metal can be easily dissolved under electrochemical conditions and hence displays so called “*weak spots*” where the electrochemical degradation process is strongly accelerated in these regions. Therefore, control of the structure and chemical distribution of both dissimilar kinds of metal atoms inside the short-range of the

nanochains as well as inside the long-range of the aerogel framework during the two-step gelation is important.

5 Acknowledgments

Financial supports from the Deutsche Forschungsgemeinschaft (DFG), the Swiss National Science Foundation (SNF) and the European Research Council (ERC-2013-AdG AEROCAT) are gratefully acknowledged. Furthermore, the funding of the JEOL JEM2100F HR-TEM by the DFG (INST 184/106-1 FUGG) is acknowledged. A.I.F. acknowledges funding of his work by the U. S. Department of Energy Grant No. DE-FG02-03ER15476.

Table of Contents:

6 References

- (1) Oezaslan, M.; Liu, W.; Nachttegaal, M.; Frenkel, A. I.; Rutkowski, B.; Werheid, M.; Herrmann, A. K.; Laugier-Bonnaud, C.; Yilmaz, H. C.; Gaponik, N.; Czyrska-Filemonowicz, A.; Eychmüller, A.; Schmidt, T. J. Homogeneity and elemental distribution in self-assembled bimetallic Pd-Pt aerogels prepared by a spontaneous one-step gelation process. *Physical Chemistry Chemical Physics* **2016**, *18*, 20640 - 20650.
- (2) Liu, W.; Rodriguez, P.; Borchardt, L.; Foelske, A.; Yuan, J.; Herrmann, A.-K.; Geiger, D.; Zheng, Z.; Kaskel, S.; Gaponik, N.; Kötz, R.; Schmidt, T. J.; Eychmüller, A. Bimetallic Aerogels: High-Performance Electrocatalysts for the Oxygen Reduction Reaction. *Angewandte Chemie International Edition* **2013**, *52*, 9849-9852.
- (3) Liu, W.; Herrmann, A.-K.; Geiger, D.; Borchardt, L.; Simon, F.; Kaskel, S.; Gaponik, N.; Eychmüller, A. High-Performance Electrocatalysis on Palladium Aerogels. *Angewandte Chemie International Edition* **2012**, *51*, 5743-5747.
- (4) Liu, W.; Herrmann, A.-K.; Bigall, N. C.; Rodriguez, P.; Wen, D.; Oezaslan, M.; Schmidt, T. J.; Gaponik, N.; Eychmüller, A. Noble Metal Aerogels—Synthesis, Characterization, and Application as Electrocatalysts. *Accounts of Chemical Research* **2015**, *48*, 154-162.
- (5) Herrmann, A.-K.; Formanek, P.; Borchardt, L.; Klose, M.; Giebel, L.; Eckert, J.; Kaskel, S.; Gaponik, N.; Eychmüller, A. Multimetallic Aerogels by Template-Free Self-Assembly of Au, Ag, Pt, and Pd Nanoparticles. *Chemistry of Materials* **2014**, *26*, 1074-1083.
- (6) Gaponik, N.; Herrmann, A.-K.; Eychmüller, A. Colloidal Nanocrystal-Based Gels and Aerogels: Material Aspects and Application Perspectives. *The Journal of Physical Chemistry Letters* **2012**, *3*, 8-17.
- (7) Gesser, H. D.; Goswami, P. C. Aerogels and related porous materials. *Chemical Reviews* **1989**, *89*, 765-788.
- (8) Zhu, C.; Du, D.; Eychmüller, A.; Lin, Y. Engineering Ordered and Nonordered Porous Noble Metal Nanostructures: Synthesis, Assembly, and Their Applications in Electrochemistry. *Chemical Reviews* **2015**.
- (9) Zhu, C.; Wen, D.; Leubner, S.; Oschatz, M.; Liu, W.; Holzschuh, M.; Simon, F.; Kaskel, S.; Eychmüller, A. Nickel cobalt oxide hollow nanospheres as advanced electrocatalysts for the oxygen evolution reaction. *Chemical Communications* **2015**, *51*, 7851-7854.
- (10) Zhu, C.; Wen, D.; Oschatz, M.; Holzschuh, M.; Liu, W.; Herrmann, A.-K.; Simon, F.; Kaskel, S.; Eychmüller, A. Kinetically Controlled Synthesis of PdNi Bimetallic Porous Nanostructures with Enhanced Electrocatalytic Activity. *Small* **2015**, *11*, 1430-1434.
- (11) Kühn, L.; Herrmann, A.-K.; Rutkowski, B.; Oezaslan, M.; Nachttegaal, M.; Klose, M.; Giebel, L.; Gaponik, N.; Eckert, J.; Schmidt, T. J.; Czyrska-Filemonowicz, A.; Eychmüller, A. Alloying Behavior of Self-Assembled Noble Metal Nanoparticles. *Chemistry – A European Journal* **2016**, *22*, 13446–13450.
- (12) Bonakdarpour, A.; Wenzel, J.; Stevens, D. A.; Sheng, S.; Monchesky, T. I.; Lobel, R.; Atanasoski, R. T.; Schmoekel, A. K.; Vernstrom, G. D.; Debe, M. K.; Dahn, J. R. Studies of Transition Metal Dissolution from Combinatorially Sputtered, Nanostructured $Pt_{1-x}M_x$ ($M=Fe, Ni; 0 < x < 1$) Electrocatalysts for PEM Fuel Cells. *J. Electrochem. Soc.* **2005**, *152*, A61.
- (13) Debe, M. K.; Schmoekel, A. K.; Vernstrom, G. D.; Atanasoski, R. High voltage stability of nanostructured thin film catalysts for PEM fuel cells. *Journal of Power Sources* **2006**, *161*, 1002-1011.
- (14) Liao, H.; Hou, Y. Liquid-Phase Templateless Synthesis of Pt-on-Pd_{0.85}Bi_{0.15} Nanowires and PtPdBi Porous Nanoparticles with Superior Electrocatalytic Activity. *Chemistry of Materials* **2013**, *25*, 457-465.
- (15) Liao, H.; Zhu, J.; Hou, Y. Synthesis and electrocatalytic properties of PtBi nanoplatelets and PdBi nanowires. *Nanoscale* **2014**, *6*, 1049-1055.

- (16) Muench, F.; Oezaslan, M.; Rauber, M.; Kaserer, S.; Fuchs, A.; Mankel, E.; Brötz, J.; Strasser, P.; Roth, C.; Ensinger, W. Electroless synthesis of nanostructured nickel and nickel–boron tubes and their performance as unsupported ethanol electrooxidation catalysts. *Journal of Power Sources* **2013**, *222*, 243-252.
- (17) Muench, F.; Oezaslan, M.; Seidl, T.; Lauterbach, S.; Strasser, P.; Kleebe, H. J.; Ensinger, W. Multiple activation of ion track etched polycarbonate for the electroless synthesis of metal nanotubes. *Applied Physics A: Materials Science & Processing* **2011**, *105*, 847-854.
- (18) Muench, F.; Oezaslan, M.; Svoboda, I.; Ensinger, W. Electroless plating of ultrathin palladium films: self-initiated deposition and application in microreactor fabrication. *Materials Research Express* **2015**, *2*, 105010.
- (19) Ferrando, R.; Jellinek, J.; Johnston, R. L. Nanoalloys: From Theory to Applications of Alloy Clusters and Nanoparticles. *Chemical Reviews* **2008**, *108*, 845-910.
- (20) Liu, R.; Liu, J.-f.; Jiang, G.-b. Use of Triton X-114 as a weak capping agent for one-pot aqueous phase synthesis of ultrathin noble metal nanowires and a primary study of their electrocatalytic activity. *Chemical Communications* **2010**, *46*, 7010-7012.
- (21) Tang, S.; Vongehr, S.; Wang, Y.; Cui, J.; Wang, X.; Meng, X. Versatile synthesis of high surface area multi-metallic nanosponges allowing control over nanostructure and alloying for catalysis and SERS detection. *Journal of Materials Chemistry A* **2014**, *2*, 3648-3660.
- (22) Zhu, C.; Guo, S.; Dong, S. Rapid, General Synthesis of PdPt Bimetallic Alloy Nanosponges and Their Enhanced Catalytic Performance for Ethanol/Methanol Electrooxidation in an Alkaline Medium. *Chemistry – A European Journal* **2013**, *19*, 1104-1111.
- (23) Zhu, Z.; Zhai, Y.; Zhu, C.; Wang, Z.; Dong, S. Bimetallic alloy nanowires and nanosponges: A comparative study of peroxidase mimetics and as enhanced catalysts for oxygen reduction reaction. *Electrochemistry Communications* **2013**, *36*, 22-25.
- (24) Cai, B.; Wen, D.; Liu, W.; Herrmann, A.-K.; Benad, A.; Eychmüller, A. Function-Led Design of Aerogels: Self-Assembly of Alloyed PdNi Hollow Nanospheres for Efficient Electrocatalysis. *Angewandte Chemie International Edition* **2015**, *54*, 13101-13105.
- (25) Wen, D.; Liu, W.; Haubold, D.; Zhu, C.; Oschatz, M.; Holzschuh, M.; Wolf, A.; Simon, F.; Kaskel, S.; Eychmüller, A. Gold Aerogels: Three-Dimensional Assembly of Nanoparticles and Their Use as Electrocatalytic Interfaces. *ACS Nano* **2016**, DOI: 10.1021/acsnano.5b07505.
- (26) Kitchin, J. R.; Norskov, J. K.; Barteau, M. A.; Chen, J. G. Modification of the surface electronic and chemical properties of Pt(111) by subsurface 3 d transition metals. *Journal of Chemical Physics* **2004**, *120*, 10240-10246.
- (27) Kitchin, J. R.; Norskov, J. K.; Barteau, M. A.; Chen, J. G. Role of Strain and Ligand Effects in the Modification of the Electronic and Chemical Properties of Bimetallic Surfaces. *Physical Review Letters* **2004**, *93*, 156801.
- (28) Slanac, D. A.; Hardin, W. G.; Johnston, K. P.; Stevenson, K. J. Atomic Ensemble and Electronic Effects in Ag-Rich AgPd Nanoalloy Catalysts for Oxygen Reduction in Alkaline Media. *Journal of the American Chemical Society* **2012**, *134*, 9812-9819.
- (29) Hammer, B.; Norskov, J. K. Theoretical surface science and catalysis - calculations and concepts. *Advances in Catalysis* **2000**, *45*, 71-129.
- (30) Oezaslan, M.; Hasché, F.; Strasser, P. In Situ Observation of Bimetallic Alloy Nanoparticle Formation and Growth Using High-Temperature XRD. *Chemistry of Materials* **2011**, *23*, 2159-2165.
- (31) Oezaslan, M.; Hasché, F.; Strasser, P. In-situ High Temperature X-ray Diffraction Study of PtCu₃ Alloy Electrocatalyst for PEMFC. *Zeitschrift für anorganische und allgemeine Chemie* **2010**, *636*, 2111-2111.
- (32) Inorganic Crystal Structure Database (ICSD).
- (33) Newville, M. IFEFFIT : interactive XAFS analysis and FEFF fitting. *J. Synchrot. Radiat.* **2001**, *8*, 322-324.

- (34) Schmidt, T. J.; Gasteiger, H. A.; Stab, G. D.; Urban, P. M.; Kolb, D. M.; Behm, R. J. Characterization of High-Surface-Area Electrocatalysts Using a Rotating Disk Electrode Configuration. *Journal of The Electrochemical Society* **1998**, *145*, 2354-2358.
- (35) Schmidt, T. J.; Gasteiger, H. A.: Rotating thin-film method for supported catalysts. In *Handbook of Fuel Cells*; John Wiley & Sons, Ltd, 2010.
- (36) Maillard, F.; Savinova, E. R.; Stimming, U. CO monolayer oxidation on Pt nanoparticles: Further insights into the particle size effects. *Journal of Electroanalytical Chemistry* **2007**, *599*, 221-232.
- (37) Hara, M.; Linke, U.; Wandlowski, T. Preparation and electrochemical characterization of palladium single crystal electrodes in 0.1 M H₂SO₄ and HClO₄: Part I. Low-index phases. *Electrochimica Acta* **2007**, *52*, 5733-5748.
- (38) Hasché, F.; Oezaslan, M.; Strasser, P. Activity, stability and degradation of multi walled carbon nanotube (MWCNT) supported Pt fuel cell electrocatalysts. *Physical Chemistry Chemical Physics* **2010**, *12*, 15251-15258.
- (39) Hasché, F.; Oezaslan, M.; Strasser, P. Activity, Structure and Degradation of Dealloyed PtNi₃ Nanoparticle Electrocatalyst for the Oxygen Reduction Reaction in PEMFC. *Journal of The Electrochemical Society* **2012**, *159*, B25-B34.
- (40) Hasché, F.; Oezaslan, M.; Strasser, P. Activity, Stability, and Degradation Mechanisms of Dealloyed PtCu₃ and PtCo₃ Nanoparticle Fuel Cell Catalysts. *ChemCatChem* **2011**, *3*, 1805-1813.
- (41) Borup, R. L.; Davey, J. R.; Garzon, F. H.; Wood, D. L.; Inbody, M. A. PEM fuel cell electrocatalyst durability measurements. *J. Pow. Sourc.* **2006**, *163*, 76-81.
- (42) Borup, R.; Meyers, J.; Pivovar, B.; Kim, Y. S.; Mukundan, R.; Garland, N.; Myers, D.; Wilson, M.; Garzon, F.; Wood, D.; Zelenay, P.; More, K.; Stroh, K.; Zawodzinski, T.; Boncella, J.; McGrath, J. E.; Inaba, M.; Miyatake, K.; Hori, M.; Ota, K.; Ogumi, Z.; Miyata, S.; Nishikata, A.; Siroma, Z.; Uchimoto, Y.; Yasuda, K.; Kimijima, K.-i.; Iwashita, N. Scientific Aspects of Polymer Electrolyte Fuel Cell Durability and Degradation. *Chemical Reviews* **2007**, *107*, 3904-3951.
- (43) Montes de Oca, M. G.; Kumarakuru, H.; Cherns, D.; Fermín, D. J. Hydrogen Adsorption at Strained Pd Nanoshells. *The Journal of Physical Chemistry C* **2011**, *115*, 10489-10496.
- (44) Yun, S.; Ted Oyama, S. Correlations in palladium membranes for hydrogen separation: A review. *Journal of Membrane Science* **2011**, *375*, 28-45.
- (45) Gabrielli, C.; Grand, P. P.; Lasia, A.; Perrot, H. Investigation of Hydrogen Adsorption and Absorption in Palladium Thin Films: II. Cyclic Voltammetry. *Journal of The Electrochemical Society* **2004**, *151*, A1937-A1942.
- (46) Gasteiger, H. A.; Kocha, S. S.; Sompalli, B.; Wagner, F. T. Activity benchmarks and requirements for Pt, Pt-alloy, and non-Pt oxygen reduction catalysts for PEMFCs. *Applied Catalysis B: Environmental* **2005**, *56*, 9-35.
- (47) Oezaslan, M.; Strasser, P. Activity of dealloyed PtCo₃ and PtCu₃ nanoparticle electrocatalyst for oxygen reduction reaction in polymer electrolyte membrane fuel cell. *Journal of Power Sources* **2011**, *196*, 5240-5249.
- (48) Shrestha, B. R.; Baimpos, T.; Raman, S.; Valtiner, M. Angstrom-Resolved Real-Time Dissection of Electrochemically Active Noble Metal Interfaces. *ACS Nano* **2014**, *8*, 5979-5987.
- (49) Shrestha, B. R.; Nishikata, A.; Tsuru, T. Channel flow double electrode study on palladium dissolution during potential cycling in sulfuric acid solution. *Electrochimica Acta* **2012**, *70*, 42-49.
- (50) Conway, B. E. Electrochemical Oxide Film Formation at Noble-Metals as a Surface-Chemical Process. *Progress in Surface Science* **1995**, *49*, 331-452.
- (51) Conway, B. E. Electrochemical oxide film formation at noble metals as a surface-chemical process. *Progress in Surface Science* **1995**, *49*, 331-452.
- (52) Topalov, A. A.; Katsounaros, I.; Auinger, M.; Cherevko, S.; Meier, J. C.; Klemm, S. O.; Mayrhofer, K. J. J. Dissolution of Platinum: Limits for the Deployment of Electrochemical Energy Conversion? *Angewandte Chemie International Edition* **2012**, *51*, 12613-12615.

(53) Cherevko, S.; Zeradjanin, A. R.; Keeley, G. P.; Mayrhofer, K. J. J. A Comparative Study on Gold and Platinum Dissolution in Acidic and Alkaline Media. *Journal of The Electrochemical Society* **2014**, *161*, H822-H830.